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**U.S. Department of Energy
Fossil Energy
Advanced Research and Technology Development**

FOSSIL ENERGY MATERIALS PROGRAM

**Quarterly Progress Report for the
Period Ending December 31, 1981**

Fossil Energy Materials Program Office

OAK RIDGE NATIONAL LABORATORY
Operated by Union Carbide Corporation for the U.S. Department of Energy

*Fossil
Energy
Program*

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AR&TD FOSSIL ENERGY MATERIALS PROGRAM
QUARTERLY PROGRESS REPORT FOR THE PERIOD
ENDING DECEMBER 31, 1981

R. A. Bradley, Manager
Fossil Energy Materials Program

Contributions by

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Cornell University
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IIT Research Institute
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and
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By
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PREVIOUS REPORTS IN THIS SERIES

- ORNL/FMP-81/1 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending December 31, 1980
- ORNL/FMP-81/2 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending March 31, 1981
- ORNL/FMP-81/3 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending June 30, 1981
- ORNL/FMP-81/4 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending September 30, 1981

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INTRODUCTION

R. A. Bradley and P. T. Carlson

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Oak Ridge, Tennessee 37830

The objective of the AR&TD Fossil Energy Materials Program is to conduct research and development on materials for fossil energy applications with a focus on the longer-term and generic needs of the various fossil fuel technologies. The program includes research aimed toward a better understanding of materials behavior in fossil energy environments and the development of new materials capable of substantial enhancement of plant operations and reliability.

The management of the Program has been decentralized to DOE Oak Ridge Operations Office (ORO) and the Oak Ridge National Laboratory (ORNL) as technical support contractor. The organizational relationship between DOE Headquarters, ORO, and ORNL is illustrated in Fig. 1. A substantial portion of the work on the AR&TD Fossil Energy Materials Program is performed by participating subcontractor organizations. All subcontractor work is technically monitored by Program staff members at ORNL and Argonne National Laboratory (ANL). The performing institution, principal investigator and technical monitor for each project are shown in Fig. 2.

Fig. 1. Organizational Relationships between DOE-HQ, DOE-ORO, and ORNL for the AR&TD Fossil Energy Materials Program.

The ORNL Fossil Energy Materials Program Office compiles and issues this combined quarterly progress report from camera-ready copies submitted by each of the participating subcontractor organizations. Distribution is as shown on pages 361-67. Future reports will be issued on a quarterly basis to a similar distribution.

This report of activities on the program is organized in accordance with a work breakdown structure defined in the AR&TD Fossil Energy Materials Program Plan for FY 1982-86 (Ref. 1) in which projects are organized according to fossil energy technologies. A graphic summary of this organization is provided in Fig. 3. This report is divided into parts and chapters with each part describing projects related to a particular fossil energy technology. Chapters within a part provide details of the various projects associated with that technology.

At present, no ORO/ORNL-managed projects are directed toward materials research and development for coal mining, cleaning, beneficiation, and handling; fuel cells; magnetohydrodynamics; or oil shale. Thus, these activities are not discussed in this report. As projects are initiated in these areas, the report will be expanded to include those activities.

We hope this series of AR&TD Fossil Energy Materials Program quarterly progress reports will aid in the dissemination of information developed on the program. Plans for the program will be issued annually. A draft of the program plan for FY 1982-86 has been prepared and is in the review process. This program plan (ORNL/TM-7964) will be issued in FY 1982. The implementation of these plans will be reflected by these quarterly progress reports, and this dissemination of information will be augmented by topical or final reports as appropriate. Highlights of projects that are part of this program are provided in the bimonthly DOE newsletter, "Materials and Components in Fossil Energy Applications."

Projects of the AR&TD Fossil Energy Materials Program

Project Work Breakdown Structure Element and Title	Performing Institution	Principal Investigator	Technical Monitor ^a
<u>Program Management and Technology Assessment; Task Leader: P. T. Carlson</u>			
ORNL-1.0(A), Management of the AR&TD Fossil Energy Materials Program	Oak Ridge National Laboratory	P. T. Carlson	R. A. Bradley
ORNL-1.0(B), Critical Materials Requirements for Synthetic Fuel Facilities	Oak Ridge National Laboratory	D. L. Lennon	R. A. Bradley
ANL-1.0, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	W. A. Ellingson	R. A. Bradley
<u>Materials for Coal Liquefaction; Task Leader: R. R. Judkins</u>			
UCB-3.1(A), A New Class of Steels for Thick Wall Pressure Vessels	University of California-Berkeley	E. R. Parker	R. W. Swindeman
UCB-3.1(B), Design of Low Alloy Steels for Thick-Walled Pressure Vessels	University of California-Berkeley	E. R. Parker	R. W. Swindeman
UTN-3.1, Investigation of the Transformational Characteristics and Cold-Cracking Sensitivity of Modified 9 Cr-1 Mo Steel	University of Tennessee	C. D. Lundin	R. W. Swindeman
CSM-3.2, Characterizing and Improving the Toughness of Thick-Sectioned 2 1/4 Cr-1 Mo Electroslag Weldments	Colorado School of Mines	G. R. Edwards	R. W. Swindeman
PNST-3.2, An X-ray Study of Residual Stresses in Narrow-Groove TIG Weldments	The Pennsylvania State University	C. O. Ruud	R. W. Swindeman
CU-3.3, Hydrogen Attack in Cr-Mo Steels at Elevated Temperatures	Cornell University	Che-Yu Li	R. W. Swindeman
ORNL-3.3(B), Effects of Heat Treatment on Microstructure and Mechanical Properties of Cr-Mo Steels	Oak Ridge National Laboratory	R. K. Nanstad	R. R. Judkins
UCSB-3.3, Analysis of Hydrogen Attack on Pressure Vessel Steels	University of California-Santa Barbara	G. R. Odette	R. W. Swindeman
WEC-3.3, Study to Optimize Cr-Mo Steels to Resist Hydrogen and Temper Embrittlement	Westinghouse Electric Corporation	B. J. Shaw	R. W. Swindeman
MPC-3.4, Corrosion in Coal Liquefaction Processes	Metal Properties Council	F. F. Lyle ^c	R. R. Judkins
ORNL-3.4, Corrosion in Coal Derived Liquids	Oak Ridge National Laboratory	R. R. Judkins	R. R. Judkins
BCL-3.5, Evaluation of Advanced Materials for Slurry Erosion Service	Battelle-Columbus Laboratories	I. G. Wright	E. L. Long, Jr.
LBL-3.5, Coal Liquefaction Alloy Test Program	Lawrence Berkeley Laboratory	A. V. Levy	E. L. Long, Jr.
<u>Materials for Coal Gasification; Task Leader: W. A. Ellingson^b</u>			
ANL-4.1, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	K. Natesan	K. Natesan ^b
ANL-4.3, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	K. Natesan	K. Natesan ^b
INEL-4.3, The Effect of Coal Gasification Atmospheres on Axial Creep of Alloys	Idaho National Engineering Laboratory	R. B. Loop	K. Natesan ^b
ANL-4.4(A), Materials Technology for Coal Conversion Processes	Argonne National Laboratory	K. Natesan	K. Natesan ^b
MPC-4.4(A), Corrosion of Metals and Refractories in Coal Gasification Pilot Plants	Metal Properties Council	K. J. Barton ^d	K. Natesan ^b
MPC-4.4(B), Erosion-Corrosion of Materials in Coal Gasification Pilot Plants	Metal Properties Council	K. J. Barton ^d	K. Natesan ^b
ANL-4.5, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	K. J. Reimann	R. W. McClung
ANL-4.8, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	C. R. Kennedy	C. R. Kennedy ^b
ISU-4.8, Creep Behavior of Refractory Concretes	Iowa State University	T. D. McGee	C. R. Kennedy ^b
MIT-4.8, Thermomechanical Model for Refractory Concrete Liner-Anchor Interaction	Massachusetts Institute of Technology	O. Buyukozturk	W. A. Ellingson ^b
ANL-4.9, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	C. R. Kennedy	C. R. Kennedy ^b
IITRI-4.9, Design, Engineering and Evaluation of Refractory Liners for Slagging Gasifiers	IIT Research Institute	S. A. Bortz	C. R. Kennedy ^b
PNST-4.9, Refractories in Slagging Gasifiers	The Pennsylvania State University	A. Muan	C. R. Kennedy ^b
UCCND-4.9, Engineering Evaluation and Review of IITRI Refractory Test Facility	Oak Ridge National Laboratory	D. L. Lennon	D. L. Lennon

Fig. 2. Projects of the AR&TD Fossil Energy Materials Program.

Projects of the AR&TD Fossil Energy Materials Program - Continued

Project Work Breakdown Structure Element and Title	Performing Institution	Principal Investigator	Technical Monitor ^a
<u>Ceramics for Heat Engines and Heat Recovery; Task Leader: D. R. Johnson</u>			
LANL-5.10, Short Fiber Reinforced Structural Ceramics	Los Alamos National Laboratory	F. D. Gac	D. R. Johnson
ORNL-5.10 and -5.11, Ceramics for Heat Engines and Heat Recovery	Oak Ridge National Laboratory	D. R. Johnson	D. R. Johnson
NBS-5.12, High-Temperature Applications of Structural Ceramics	National Bureau of Standards	E. R. Fuller	P. F. Becher
ORNL-5.12, Ceramics for Heat Engines and Heat Recovery	Oak Ridge National Laboratory	D. R. Johnson	D. R. Johnson
<u>Alloys for Combustion Systems and Heat Engines; Task Leader: J. H. DeVan</u>			
ANL-6.4, Materials Technology for Coal Conversion Processes	Argonne National Laboratory	K. Natesan	J. H. DeVan
ORNL-6.4, Heat Exchanger and Internal Structural Materials for AFB ₂	Oak Ridge National Laboratory	J. H. DeVan	J. H. DeVan

^aExcept as noted, affiliation is with Oak Ridge National Laboratory.

^bArgonne National Laboratory.

^cSouthwest Research Institute.

^dITT Research Institute.

Fig. 2. Projects of the AR&TD Fossil Energy Materials Program.

11/1/81

Fig. 3. Work Breakdown Structure for the AR&TD Fossil Energy Materials Program.

REFERENCE

1. Compiled by R. A. Bradley and R. R. Judkins, *AR&TD Fossil Energy Materials Program Plan for FY 1982-86*, ORNL/TM-7964, in review.

PART II -- MATERIALS FOR COAL LIQUEFACTION

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UCB-3.1(A) - A NEW CLASS OF STEELS FOR THICK-
WALL PRESSURE VESSELS

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INTRODUCTION

The objective of this program is to develop a new class of steels that can be field-fabricated into large diameter, thick wall pressure vessels for coal gasification/liquefaction systems. In previous work it was found that in some Fe-C-V-Ni alloys a good combination of strength and toughness could be obtained through an isothermal decomposition into ferrite and vanadium carbide.

The specific objective in the current program is to develop an Fe-C-V-Ni alloy which exhibits strength and toughness comparable to those of commercially available pressure vessel steels, such as A542 (A387) and A533, through a simple continuous cooling process. The program is divided into four tasks as follows:

1. Evaluation of Continuous Cooling Characteristics and Optimization of Composition
2. Vanadium Carbide Dissolution and Coarsening Kinetics
3. Hydrogen Attack Studies
4. Weldability Studies

The continuous cooling characteristics of six different Fe-C-V-Ni alloys will be determined in Task 1. The microstructure-mechanical property relationships in these alloys will be established for various austenitization conditions and cooling rates in order that optimal compositions and heat treatments may be assessed. In Task 2, vanadium carbide coarsening behavior during prolonged tempering at elevated temperatures will be investigated as will be the kinetics of dissolution into austenite when the alloy is heated to the very high temperatures often

encountered during welding. Hydrogen attack susceptibility will be investigated in Task 3 by measuring mechanical property degradation after exposing the alloys to high temperatures and high pressure hydrogen for sustained periods of time. Weldability of the Fe-C-V-Ni alloys will be studied in Task 4. The initial approach in this task is to characterize the microstructure and mechanical properties of the heat affected zone (HAZ) where rapid heating into the austenite range is followed by rapid cooling.

Table 1: Chemical Compositions of Alloys

Alloy	Nominal (wt-pct)					
	C	V	Ni	Mn	Nb	Fe
A-1	0.1	0.5	1.5	0.5	0.025	bal
A-2	0.1	0.5	3.0	0.5	0.025	bal
B-1	0.15	0.75	1.5	0.5		bal
B-2	0.15	0.75	3.0	0.5		bal
C-1	0.2	1.0	1.5	0.5		bal
C-2	0.2	1.0	3.0	0.5		bal

Table 2: Mechanical Properties

Alloy	Aust. Temp. °C	Cooling Rate	Yield ksi	UTS ksi	El. %	RA %	CVN (ft-lb)	
							RT	Upper Shelf
A-1	900	1"	60	74	33	73	205	205
A-1	1000	1"	74	95	22	64	3	135
A-1	1000	slow	60	77	31	71	10	135
A-2	900	1"	76	90	31	70	160	165
A-2	1000	1"	113	131	22	60	3	35
A-2	900	fast	70	89	30	69	150	180
A-2	1000	slow	82	103	29	68	7	125
B-1	900	1"	61	75	37	78	225	225
B-1	1000	1"	93	116	24	64	16	152
B-2	900	1"	78	94	32	74	165	165
B-2	1000	1"	136	153	18	46	3	25
B-2	900	fast	85	97	31	72	185	185
C-1	900	1"	62	80	35	76	240	245
C-1	1000	1"	89	106	28	75	235	245
C-1	900	fast	64	75	34	75	-	-
C-1	1000	slow	73	86	34	75	235	240

Table 3: Chemical Compositions of Alloys -
Second Series

Nominal (wt-pct)								
<u>Alloy</u>	<u>C</u>	<u>V</u>	<u>Ni</u>	<u>Mn</u>	<u>Al</u>	<u>Si</u>	<u>Mo</u>	<u>Fe</u>
D-1	0.2	1.0	3.0	0.5	0.5	--	--	bal
D-2	0.2	1.0	3.0	0.5	--	1.0	--	bal
D-3	0.2	1.0	3.0	0.5	--	--	1.5	bal

RESULTS FROM PRIOR QUARTERS

Evaluation of Continuous Cooling Characteristics
and Optimization of Composition

Continuous cooling transformation (CCT) curves have been presented in previous reports for the six alloys shown in Table 1 that constituted the initial system of alloys investigated. The start and finish temperatures for the decomposition of austenite appear nearly independent of vanadium and carbon content and seem to be fixed by the amount of nickel in the alloy. However, increasing the vanadium and carbon contents in the alloys has been shown to shift the transformation curves toward shorter times.

Mechanical properties evaluated (for the initial system of alloys) are summarized in Table 2. The best combination of tensile and impact properties for any of the alloys is obtained by austenitizing the material at 900°C. The 0.1C and 0.15C series alloys, after austenitization at 1000°C, were brittle at room temperature, but after austenitization at 900°C showed Charpy impact energies in the range of 170-225 ft-lbs at room temperature. The 0.2C alloys showed excellent impact properties at both 900°C and 1000°C austenitization temperatures while the tensile properties compared favorably with those for the 0.1C and 0.15C alloys. In this connection, from results so far, the 0.2C-1.0V-1.5Ni-0.5Mn alloy may be said to be the optimum composition for the initial system of alloys.

A second series of alloys, containing certain compositional modifications, has been obtained (Table 3) and is being investigated with the objectives of: (1) moving the nose of the pearlite and bainite curves further to the left (i.e., toward shorter times); and (2) raising the temperature (during the continuous cooling process) at which the transformation from austenite to vanadium carbide and ferrite takes place. Investigation of this new series of alloys during the previous quarter revealed that additions of Al and Si move the austenite-to-ferrite starting curve to shorter times by more than a factor of 10. The addition

of aluminum had a greater effect on the growth kinetics as the completion curve to ferrite for Alloy D-1 is moved to much shorter times while the completion curve to ferrite for Alloy D-2 is hardly affected. Presently, it appears that the addition of 0.5Al has quickened the nucleation and growth kinetics by approximately a factor of 10.

Transmission Electron Microscopy (TEM)

TEM micrographs submitted in previous reports show the microstructures obtained for different compositions, austenitization temperatures, and cooling rates. For the initial series of alloys, the study of the microstructures in relation to the mechanical properties evaluated has shown that a random dispersion of vanadium carbide particles in a ferrite matrix is ideal while a bainite-like microstructure results in mechanical properties that are unsatisfactory.

DISCUSSION OF CURRENT ACTIVITIES

Evaluation of Continuous Cooling Characteristics
and Optimization of Composition

Optical metallography of samples continuously cooled for Alloys D-1, D-2, and D-3 shows the effect of cooling rates on the resulting microstructures. The metallography was obtained by dilatometry in which specimens were austenitized at 1000°C for 15 minutes prior to cooling at varied cooling rates.

Figures 1 through 4 show the effect of various cooling rates on the microstructure of Alloy D-1. In Figure 1, a cooling rate of 600°C/min gives a grain size of approximately 8 microns with limited areas having a bainitic structure, but with the majority of the grains appearing to be ferritic. A cooling rate of 120°C/min gives a uniform ferritic microstructure (Figure 2) with small carbide-like particles at the interior of the grains. In Figure 3, a 60°C/min cooling rate gives a similar microstructure but the average grain size appears to have increased by a factor of 3. In Figure 4, the cooling rate of 20°C/min results in much the same microstructure and grain size as seen in Figure 3.

Figures 5 through 7 show the effect of cooling rate on the microstructure of Alloy D-2. With a cooling rate of 600°C/min, the microstructure is bainitic with isolated islands of ferrite at the previous austenite grain boundaries (Figure 5). But with the slower cooling rate of 120°C/min (Figure 6), the microstructure is almost uniformly ferritic. Isolated areas of bainitic regions and a small number of carbide-like particles are also present. At the 10°C/min cooling rate (Figure 7), the microstructure is uniformly ferrite with less grain growth than observed in Alloy D-1 with a comparable cooling rate (Figure 4).

The effect of cooling rate on the microstructure of Alloy D-3 is seen in Figures 8 through 10. The martensitic (Figure 8), mixed martensite and lower bainite (Figure 9), and upper bainite (Figure 10)

microstructures correspond to a 600°C/min, 300°C/min and 60°C/min cooling rates, respectively. Ferrite was not detected in this alloy at even the slowest cooling rate.

The effect of austenitizing temperature and amount of vanadium carbide in solution in Alloy D-1 is seen in Figure 11. A continuous cooling transformation (CCT) curve with an austenitizing temperature of 1200°C for 5 minutes was developed because all of the vanadium carbide is expected to be in solution at this temperature. The cooling rate necessary for complete ferrite microstructure has been slowed to less than 120°C/min. But, by step cooling from 1200°C for 5 min to 1000°C for 15 minutes the cooling rate necessary to produce a uniform ferrite microstructure has been increased greatly. The CCT's for both austenitizing treatments are still shifted to longer times than with an austenitizing treatment of 1000°C for 15 minutes as reported earlier.

Fig. 1 Alloy D-1, Cooling Rate of 600°C/min

Fig. 2 Alloy D-1, Cooling Rate of 120°C/min

Fig. 3 Alloy D-1, Cooling Rate of 60°C/min

Fig. 4 Alloy D-1, Cooling Rate of 20°C/min

Fig. 5 Alloy D-2, Cooling Rate of 600°C/min

Fig. 6 Alloy D-2, Cooling Rate of 120°C/min

Fig. 7 Alloy D-2, Cooling Rate of $10^{\circ}\text{C}/\text{min}$

Fig. 8 Alloy D-3, Cooling Rate of $600^{\circ}\text{C}/\text{min}$

Fig. 9 Alloy D-3, Cooling Rate of 300°C/min

Fig. 10 Alloy D-3, Cooling Rate of 60°C/min

Fig. 11 Effect of Higher Austenitizing Temperature

UCB-3.1(B) -- DESIGN OF LOW-ALLOY STEELS FOR
THICK-WALLED PRESSURE VESSELS

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Department of Materials Science
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INTRODUCTION

The objective of this program is to modify existing commercial low-alloy steels or to develop new alloys which can be field-fabricated into large diameter, thick walled pressure vessels for coal gasification and liquefaction systems.

Emphasis will be placed on evaluating the effects of minor additions of Ni and Mn to 2.25Cr-1Mo steel, and Cr, Mn and Si to Mn-Mo-Ni steel.

Five areas of study have been defined:

- (1) Hydrogen Attack
- (2) Temper Embrittlement
- (3) Fracture Mechanics Testing
- (4) Weldability
- (5) Elevated Temperature Properties

The hydrogen attack study will investigate the metallurgical variables which control the attack susceptibility of low-alloy pressure vessel steels. The influence of microstructure, carbide stability, carbide morphology and alloying elements will be studied in detail. Comparisons will be made between commercial 2.25Cr-1Mo steel, SA533B and their alloy modifications, particularly those containing additional Cr which the Nelson curves predict to have improved hydrogen attack resistance.

Temper embrittlement studies will be continued on the modifications of 2.25Cr-1Mo to determine whether the minor additions of Ni and Mn enhance segregation of phosphorus to prior austenite grain boundaries. Both surface (quenched and tempered) and simulated cooled and tempered (12" - 16" 1/4T location) microstructures will be examined. The effects of rare earth elements (mischmetal in reducing the embrittlement

susceptibility of Cr-Mo and Ni-Cr-Mo steels will be assessed. The effects of impurity element segregation on the hydrogen attack susceptibility of these steels will also be studied.

The fracture mechanics program will obtain J_{Ic} and δ_{Ic} critical crack opening displacement values, using the unloading compliance test method, for the alloy modifications which show improved tensile strengths and Charpy impact values. The relationship between these parameters and microstructural variables will be carefully studied.

The weldability study will investigate the nature of heat affected zone microstructures produced in plates of the base steels and their alloy modifications. Bead on plate tests will be used to determine the influence of heat input and preheat temperature on the heat affected zone microstructures. Mechanical property tests will evaluate the welds produced with the different alloy modifications.

Elevated temperature tests will determine whether the minor alloy additions have any major effect on creep rupture properties of these steels.

RESULTS FROM PRIOR QUARTERS

Hydrogen Attack of Model Alloy Systems

Samples of model alloy systems based on Fe-0.15C-0.5Mn with 2 atomic percent Cr, Mo or W have been exposed to hydrogen at 550°C and 1500 psi for 1000 hours. The tensile strength of the base steel was approximately the same as that of the sample exposed 500 hours while ductility in terms of reduction in area showed a 50% decrease in the sample exposed for 1000 hours. The tensile strength and ductility in both the Cr and Mo modifications remained the same for both 500 hour and 1000 hour exposures. The W modification showed a steady decrease in tensile strength, percent strain to fracture, and percent reduction in area as the exposure time increased. Fracture surfaces of all the alloy systems showed typical dimpled rupture failures. It was not possible to distinguish regions of voids attributable to hydrogen attack. However, the W modification showed a small region of intergranular failure with void formation on the grain boundary facets which might have been a product of methane bubble formation. No sign of hydrogen attack could be detected with scanning electron microscopy in the Cr and Mo modifications.

Temper Embrittlement Study of A543

The effects of rare earth elements on the temper embrittlement susceptibility of A543 (3.5Ni-Cr-Mo) steel were investigated in three sample conditions: (1) A543; (2) Remelt A543; and (3) Remelt A543 plus rare earth elements. The results for base A543 steel have shown that 50 ft-lb impact transition energy shifted from -150°C to +15°C (165°C) for the oil quenched sample after embrittlement treatment and from -132°C to -14°C (118°C) for the simulated cooled samples after isothermal aging. Much larger shifts of the 50 ft-lb impact transition temperature resulted after isothermal aging. The remelt of A543 showed a drastic reduction of upper shelf energy probably due to a high inclusion content in the remelt condition. It thus was not possible to compare 50 ft-lb transition temperatures. However, 30 ft-lb impact energies showed a shift from -175°C

to -5°C (180°C) for the oil quenched and tempered material after the isothermal aging treatment. The remelt also showed a comparable shift in transition temperature for the oil quenched and tempered base A543. Data for the remelt plus rare earth addition also showed low values of upper shelf energy when compared to the base steel. However, the 20 ft-lb transition impact energy increased only 20°C (-120°C to -100°C) for the oil quenched and tempered sample and 80°C (-150°C to -70°C) for the simulated cooled and tempered sample after isothermal aging. Although the shifts in 20 ft-lb transition temperatures are significantly lower for the rare earth treated samples, the benefits in terms of reduced susceptibility to temper embrittlement were overshadowed in this case by the high volume fraction of inclusions resulting from poor melting practice.

Elevated Temperature Properties

The creep-rupture properties of the 2.25Cr-1Mo base and its modifications (mainly with Mn, Ni, Cr and their combinations) have been investigated. All test samples were austenitized at 1000°C for 1 hour. This was followed by a 12" 1/4T simulated cool. Tempering was carried out at 650°C for 4 hours and followed by a water quench. Creep-rupture tests were conducted with a 1-inch gauge length specimen (ASTM # 150) at 600°C , 560°C , and 500°C for durations of up to 2000 hours. The increase in minor alloying composition for the 2.25Cr-1Mo steel generally decreased creep strength throughout the temperature range investigated. The 1% Mn modifications, when compared to the base steel, caused a marked reduction in creep strength (15% -30%). The 0.5%Mn + 0.5%Ni modifications, when compared to the base steel, also exhibited a reduction in creep strength but only about half of that observed in the 1%Mn modification. The 0.5% Mn + 1%Ni modification, when compared to the 0.5%Mn + 0.5%Ni modification, did not change the level of creep strength, thus indicating that the addition of extra Ni had not caused any significant change in creep strength. The 0.5% Mn + 0.5%Ni + 0.02%V modification has shown a small improvement in creep strength when compared to the 0.5%Mn + 0.5%Ni modification. The addition of 0.75%Cr to the 0.5%Mn + 1%Ni modification resulted in reduction of creep strength by about 18% to 38%. The

present data on creep-rupture strength have also been compared with the currently published creep data on the same scale of Larson-Miller's parameter. It was clear from the comparison that the rupture strength of the present alloy systems lies within the scatter band on the upper side of slow cooled and tempered, and the lower side of the quenched and tempered, conditions of the reported data. A comparison was made between the present creep-rupture strength of the 2.25Cr-1Mo base and 3Cr-1Mo-1Ni steels (0.75%Cr + 0.5%Mn + 1%Ni modification), and the strength level of 3Cr-1Mo steel developed by Lukens Steel Company⁽¹⁾. It showed that the present 3Cr-1Mo-1Ni steel is comparable to the low strength 2.25Cr-1Mo steel in the quenched and tempered condition while the base steel (2.25Cr-1Mo) exhibits only slightly lower values of rupture strength than high strength quenched and tempered 2.25Cr-1Mo steel. A comparison also has been made with 3Cr-1Mo steel developed by Climax Molybdenum Company. It showed that the creep strength of the present 3Cr-1Mo-1Ni system lies at a much lower level than that for the alloy developed by Wada et al⁽²⁾. It was noted, however, that this 3Cr-1Mo steel (Wada et al) contained much higher levels of Mo and V than the present 3Cr-1Mo-1Ni steel. A comparison of the present results of the 2.25Cr-1Mo base and 3Cr-1Mo-1Ni steels has also been made with the data of a conventional 2.25Cr-1Mo and vanadium modification developed by the Japan Steel Works⁽³⁾. The present 3Cr-1Mo-1Ni steel seemed to be comparable to their conventional 2.25Cr-1Mo steel while the base 2.25Cr-1Mo steel is comparable to their vanadium steel. Notable features of the variations of creep rupture ductility in terms of reduction in area in the 2.25Cr-1Mo base and its modifications were two distinctive curves of the reduced rupture ductility at the longer test times. In both the 1%Mn modification and the 0.5%Mn + 0.5%Ni modifications, there has not been any improvement in creep ductility. In contrast to the Mn modification, the addition of 0.5%Ni to the 0.5%Mn + 0.5%Ni modification has improved the creep rupture ductility without sacrificing creep strength. The modification with Cr has also improved rupture ductility although creep strength has been substantially lost when compared to the 1%Ni + 0.5% Mn modification.

DISCUSSION OF CURRENT ACTIVITIES

Hydrogen Attack of Model Alloy Systems

Further results of hydrogen attack tests on the 2.25Cr-1Mo steel and its modifications (with Mn, Ni, Cr and their combinations) have been obtained this quarter. The specimen preparation procedures, chemical compositions of the alloys, and the heat treatment conditions have been reported previously⁽⁴⁾. Thick section specimens (12" - 1/4T) of the base 2.25Cr-1Mo steel and four modifications [(a) 1%Ni; (b) 0.5%Mn + 0.5%Ni + 0.02%V; (c) 0.5%Mn + 1%Ni; and (d) 0.75%Cr + 0.5%Mn + 1%Ni (3Cr-1Mo-1Ni-1Mn)] steels have been exposed to a hydrogen atmosphere at 550°C and 2000 psi for 1000 hours. The macroscopic surface observation of the exposed samples revealed that no blisters or fissures were observed in all the specimens examined. The tensile and impact properties of the hydrogen-exposed materials have been evaluated only on three modifications. The tensile strength of hydrogen-exposed 3Cr-1Mo-1Ni steel has decreased slightly from that of the unexposed alloy, whereas the strength of the 0.5Mn + 0.5Ni modification has increased after exposure although the ductilities of both alloys have changed very little. Figure 1 shows the results of the impact energy test from three alloys with unexposed and hydrogen-exposed conditions. Steels with 0.5Mn + 0.5Ni modifications have not only experienced a considerable raise in the 50 ft-lb impact energy transition temperature (about 130°C) but also a 50% reduction in upper shelf energy. Alloys with 0.5Mn + 0.5Ni + 0.02V and 0.5Mn + 1Ni + 0.75Cr modifications have also shown an extensive increase in transition temperature (130°C and 170°C, respectively) but showed very little change in upper shelf energy. It seems clear that hydrogen pressure of 2000 psi has deteriorated the impact properties of 0.5Mn + 1Ni modified samples, when compared to the results of 1500 psi hydrogen exposure previously reported. It has done less damage to the impact properties of those alloys modified with 0.5Mn + 0.5Ni + 0.02V and 0.75Cr + 0.5Mn + 1Ni. The cross-sectional views of intergranular bubbles of simulated cooled and tempered 2.25Cr-1Mo steel and its modifications, after exposure to hydrogen at 550°C and 2000 psi for 1000 hours, are shown in Figure 2. Careful

examinations of the broad range of sample surfaces have revealed that only a few voids have formed, mainly at grain boundary carbide sites, in most of the samples. The appearances of bubble size and shape indicate that the densities of bubbles are similar among three steels, whereas the bubbles in 1%Mn and 0.5Mn + 0.5Ni modified steels are much larger than those of the base steel. The individual bubbles in a micrograph of 0.5Mn + 0.5Ni modified steel were seen growing to link up with each other and occasionally extending along grain boundaries. It is also noted that there is a low density of visible carbides in the ferrite matrix while there are extensively grown large carbides along the grain boundary. Conclusively, the steels modified with 0.5Mn + 0.5Ni + 0.02V and 0.75Cr + 0.5Mn + 1.0Ni appeared to have high resistance to hydrogen attack (reduced density and size of bubble formation) when compared to the base, 1%Mn, 0.5Mn + 0.5Ni and 0.5Mn + 1.0Ni modified steels. The detailed investigation of the bubble formation was conducted further on the Charpy impact specimens fractured at 0°C. Figure 3 shows the fracture surfaces of all three alloys which were composed mainly of intergranular fracture with considerable amounts of grain boundary facets. The bubbles in 0.5Mn + 0.5Ni + 0.02V modified steel appear to be much smaller and fewer in number than those observed on the fracture surfaces of the 0.5Mn + 1.0Ni or 0.5Mn + 1.0Ni + 0.75Cr modified steels. The fracture surfaces of 0.75Cr + 0.5Mn + 1.0Ni modified steel exhibits a mixture of small bubbles on the grain facets and a few large bubbles along the phase boundaries. The observation of the characteristics of bubble formation seems to be consistent with the result obtained during the impact energy test; large bubbles lowered the upper shelf energy while a high density of bubbles led to an increase in transition temperature. Further detailed microstructural examination on various compositional effects on hydrogen resistance, using transmission electron microscopy, will be needed and is currently in progress.

Fig. 1 Impact Properties of 2.25Cr-1Mo Steels Modified with 0.5Mn + 1.0Ni, 0.5Mn + 0.5Ni + 0.02V, and 0.5Mn + 1.0Ni + 0.75Cr, Simulated Cooled ($12'' - 1/4T$) and Tempered at 650°C for 4 Hours; Hydrogen Exposed under 2000 psi at 550°C for 1000 hours.

Fig. 2a SEM Photomicrograph of the base
2.25Cr-1Mo Steel

Fig. 2b SEM Photomicrograph of the 1%Mn
Modified Steel

Fig. 2c SEM Photomicrograph of the 0.5Mn + 0.5Ni + 0.002V Modified Steel

Fig. 2d SEM Photomicrograph of the 0.5Mn + 1.0Ni Modified Steel

Fig. 2e SEM Photomicrograph of the 0.75Cr + 0.5Mn + 1.0Ni Modified Steel; Simulated Cooled (12" - 1/4T) and Tempered at 650°C for 4 hours, then Hydrogen Exposed at 550°C, 2000 psi for 1000 hours

Fig. 3a SEM Fractographs of 0.5Mn + 0.5Ni + 0.02V Modified Steel after Hydrogen Exposure and Fracture at 0°C.

Fig. 3b SEM Fractographs of 0.5Mn + 1.0Ni Modified Steel after Hydrogen Exposure and Fracture at 0°C.

Fig. 3c SEM Fractographs of 0.75Cr + 0.5Mn + 1.0Ni Modified Steel after Hydrogen Exposure and Fracture at 0°C.

UTN-3.1 - INVESTIGATION OF THE TRANSFORMATIONAL CHARACTERISTICS
AND COLD CRACKING SENSITIVITY OF MODIFIED 9 Cr-1 Mo Steel

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INTRODUCTION

When compared to conventional austenitic stainless steels advanced modified 9 Cr-1 Mo Ferritic steels offer improved engineering properties. These improvements include: higher yield strength, higher thermal conductivity, lower thermal expansion and improved resistance to stress corrosion cracking.

The University of Tennessee (UT) is currently studying the weldability of this steel. This report describes the status and progress of the work at The University of Tennessee. The main objective of the University of Tennessee weldability study of modified 9 Cr-1 Mo is to document the transformation characteristics and cold cracking behavior of this advanced alloy. This study includes a comparison of the cracking behavior of four modified heats of 9 Cr-1 Mo with one heat each of standard 9 Cr-1 Mo and HT-9 (12 Cr-1 Mo-V-0.2C).

The on-heating and on-cooling transformation behavior of the modified 9 Cr-1 Mo are presently being determined using dilatometric and electric resistivity measurements. The Battelle test and UT Hydrogen Sensitivity Test are being used to evaluate the cold cracking sensitivity of the alloy.

RESULTS FROM PRIOR QUARTERS

Transformation Studies

The dilatometric technique employing the Gleeble apparatus was used to determine the on heating and on cooling transformation temperatures of both standard and modified 9 Cr-1 Mo. The heating rate and starting microstructure have thus far been shown to influence the Ac_1 and Ac_3 temperatures in both the standard and modified 9 Cr-1 Mo. The difference in chemistry between the standard and modified 9 Cr-1 Mo results in an apparent lower Ac_1 and Ac_3 temperature for the modified 9 Cr-1 Mo. The M_s for both standard and modified material is approximately the same. Initial isothermal transformation studies indicate a markedly different response in the modified 9 Cr-1 Mo materials wherein the austenite is stable for longer hold times, indicative of a shift in the ferrite nose of the TTT diagram.

Stress Relief Cracking Evaluation

The stress relief cracking potential of standard and modified 9 Cr-1 Mo was evaluated. The initial studies indicate that the modified 9 Cr-1 Mo alloy is not susceptible to stress relief cracking.

Weldability Testing

Battelle Underbead Crack Test

Although research at Battelle as well as research at The University of Tennessee has shown the Battelle underbead crack test is useful in rating the underbead cracking tendency of plain carbon and low alloy steels, it was found that this test could not effectively evaluate the weldabilities of 9 Cr-1 Mo and 12 Cr-1 Mo steels. Even matching electrode compositions of high moisture content failed to produce HAZ cracking in either the modified or standard 9 Cr-1 Mo samples. Autogenous welds with 10% H_2 in Argon produced no HAZ cracking. It is considered that either the inherent restraint produced in the Battelle test is

not adequate to reveal the crack sensitivities of 9 Cr and 12 Cr steels or that the Hydrogen diffusion solubility sensitivity is markedly different for the lower Cr materials.

University of Tennessee Hydrogen Sensitivity Test

The initial results of this investigation into the Hydrogen cracking susceptibilities of standard and modified 9 Cr-1 Mo have shown the materials are comparable under identical test conditions. The necessity for the presence of hydrogen to produce cracking in the test has also been demonstrated.

Initial results have shown the 12% Cr-1 Mo (HT-9) material is significantly more susceptible to Hydrogen cracking than either the standard or modified 9 Cr-1 Mo.

DISCUSSION OF CURRENT ACTIVITIES

Hydrogen Sensitivity Tests

The susceptibilities of standard 9 Cr-1 Mo, modified 9 Cr-1 Mo and 12 Cr-1 Mo (HT-9) are currently being evaluated using the UT Hydrogen Sensitivity Test which is described in the quarterly report on "Transformation Characteristics and Cold Cracking Sensitivity of Modified 9 Cr-1 Mo Steel" for the period July-September 1981. This test allows the evaluation of cracking as a function of preheat, post weld hold, strain level and straining temperature.

Test Results For 9 Cr-1 Mo

Tests have now been completed on standard and modified 9 Cr-1 Mo samples welded and bent at 30°C (85°F). After welding at room temperature these samples were allowed to cool in the fixture (Direct Cool to Room Temperature) for 2 minutes. The samples were then bent to 4% augmented strain at room temperature. As shown in Table 1, all modified samples cracked while the standard 9 Cr-1 Mo sample did not. Except for heat 148, a reduction in restraint to 2% and 1% did not eliminate

cracking in the modified 9 Cr-1 Mo materials. Heat 148 exhibited no cracking at 1% strain. Testing is now underway to verify the performance of heat 148 at the 1% strain level. An increase in preheat to 100°C (212°F) with a Direct Cool to Room Temperature (DCRT) of 15 minutes allowed all modified samples to undergo 4% restraint with no cracking.

Further tests were conducted on both standard and modified 9 Cr-1 Mo samples which were bent below the apparent DBTT [0°C(32°F)]. Samples welded at 30°C (85°F) cooled in the fixture and bent at 0°C with 4% strain have been reported previously. Both standard and modified 9 Cr-1 Mo heats cracked under these conditions. Results from this test period show that a reduction to 2% or 1% strain did not eliminate cracking in either material.

The preheat temperature was increased to 100°C (212°F) for the standard and modified 9 Cr-1 Mo steels and they were strained at 4% and 0°C temperature. The modified heats cracked while the standard composition did not. A reduction of restraint to 2% still produced cracking in all modified heats. A further reduction in strain to 1% produced no cracks in the modified alloys.

All modified heats which had previously cracked when strained to 4% at 0°C and 100°C preheat were welded at 200°C (392°F) preheat. These modified heats were again strained using 4% augmented strain at 0°C. With these conditions the modified heats 383 and 394 showed cracking while heats 148 and 176 did not. From the materials chemistry (Table 3), it can be seen that the separation in the performance of the modified heats is apparently due to a difference in Si content. The higher Si heats 383 and 394 exhibited cracking while the lower Si heats 148 and 176 did not. When welded at 300°C (572°F) and strained at 0°C, heats 383 and 394 showed no cracking.

Variations in welding parameters which will double energy input are currently under consideration. These tests will be conducted on both standard and modified 9 Cr-1 Mo for 30°C preheat, 0°C bend and 1% strain. These results will document the effect of energy input on cracking tendency.

Results of Test on 12% Cr-1 Mo (HT-9)

All UT Hydrogen Sensitivity Tests on HT-9 are summarized in Table 2. During the last quarter it was shown that preheats ranging from 30°C to 315°C (85°F-600°F) failed to prevent cracking in HT-9 samples strained at 30°C under all levels of restraint. With the preheat temperature raised to 375°C (707°F) it was found that 4% strain at 30°C produced cracking while the 2% and 1% strain levels did not. When the HT-9 samples were strained below the DBTT (0°C) it was found that cracking could be produced at 2% strain but not at 1%.

Since preheat above 375°C is considered excessive, a series of tests are being conducted to evaluate the effect of a post weld hold. HT-9 samples welded at 375°C and post weld held at 375°C for 2 hours did not exhibit cracking at 2% augmented strain.

Conclusion

The initial results of the hydrogen sensitivity test for standard and modified 9 Cr-1 Mo indicate that the susceptibilities of these two materials towards hydrogen induced cracking were similar. More extensive testing using higher preheats and varying strain levels now indicate the modified 9 Cr-1 Mo alloys are slightly less resistant than the standard 9 Cr-1 Mo material. Additional testing with strains employed below the apparent DBTT have shown that Si content may affect the hydrogen sensitivity of the modified alloys.

Extensive testing of HT-9 has confirmed that this alloy is more susceptible to hydrogen induced cracking than either standard or modified 9 Cr-1 Mo. It has been found that high temperature post weld heat treatments (750°C/1hr) are necessary to prevent cracking at high levels of strain (4%). Post weld holds at 375°C/2hr have been found sufficient to prevent cracking at 2% strain.

Duplicate samples have been performed on standard 9 Cr, modified 9 Cr and HT-9 under all test conditions and the UT Hydrogen Sensitivity Test has thus far proven reproducible for the test conditions and materials evaluated.

Transformation Diagrams Using Electrical Resistivity Measurements

The continuous cooling diagrams for standard 9 Cr-1 Mo and one modified heat (no. 176) have been determined using electrical resistivity measurements (ERM). Metallographic examination is now underway to confirm the transformation points observed.

Table 1. Summary of Hydrogen Sensitivity Test
for Standard 9 Cr-1 Mo and Modified
9 Cr-1 Mo.

Heat No.	Preheat Temp. (°C)	Post Weld Hold	Bend Temp. (°C)	Strain	Result
Std. 9 Cr	30	DCRT (2 Min.)	30	4%	No Cracking
Mod. 148,176,383,394	30	"	30	1%	Cracked
Mod. 148	30	"	30	1%	No Cracking
Mod. 148,176,383,394	100	DCRT (15 Min.)	30	4%	No Cracking
Std. 9 Cr	30	DCRT (2 Min.)	0	4,2,1%	Cracked
Mod. 148,176,383,394	30	"	0	4,2,1%	Cracked
Std. 9 Cr	100	DCRT (15 Min.)	0	4%	No Cracking
Mod. 148,176,383,394	100	"	0	4%	Cracked
Mod. 148,176,383,394	100	"	0	2%	Cracked
Mod. 148,176,383,394	100	"	0	1%	No Cracking
Mod. 148,176	200	DCRT (18 Min.)	0	4%	No Cracking
Mod. 383,394	200	"	0	4%	Cracked
Mod. 383,394	200	"	0	2%	No Cracking
Mod. 383,394	300	DCRT (20 Min.)	0	4%	No Cracking

Table 2. Summary of Hydrogen Sensitivity Test for HT-9

Heat No.	Preheat Temp. (°C)	Post Weld Hold	Bend Temp. (°C)	Strain	Result
HT-9	30-315	DCRT (2-20 Min.)	30	4,2,1%	Cracked
HT-9	375	DCRT (25 Min.)	30	4%	Cracked
HT-9	375	"	30	2,1%	No Cracking
HT-9	375	"	0	2%	Cracked
HT-9	375	"	0	1%	No Cracking
HT-9	375	DCRT, 375°C/2Hr	30	4%	Cracked
HT-9	375	"	30	2%	No Cracking
HT-9	375	DCRT, 750°C/2Hr	30	4%	No Cracking

Table 3. Plate Chemistry - 9Cr

Heat No.	30176-1	30383-1	30394	10148	K48603F	9-607
Type	Mod 9Cr	Mod 9Cr	Mod 9Cr	Mod 9Cr	STD - 9Cr	HT - 9
C	.081	.083	.084	0.089	0.065	0.20
Mn	.37	.46	.46	0.47	0.41	0.61
P	.010	.010	.010	0.021	0.025	0.016
S	.003	.004	.003	0.006	0.004	0.007
Si	.11	.41	.40	0.28	0.44	0.26
Ni	.09	.09	.09	0.16		0.54
Cr	8.61	8.46	8.57	9.24	9.12	11.65
Mo	.89	1.02	1.02	0.96	0.96	1.02
V	.209	.198	.198	0.21		0.29
Cb/Ta	.072	.072	.073	0.054		0.01
Ti	.004	.005	.005	0.002		<0.01
Co	0.10	.055	.055	0.019		0.09
Cu	.04	.03	.04	0.08		0.03
Al	.007	.002	.014	0.002		0.009
B	<.001	<.001	<.001	<0.001		0.001
W	<.01	.05	.05	0.01		0.61
As	.001	<.001	<.001	0.002		0.004
Sn	<.001	<.001	<.001	0.004		0.001
Zr	<.-01	<.001	<.001	0.001		0.002
Fe						
N	0.055	0.051	0.053	0.035		0.041
O				0.008		0.013

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CSM-3.2 - CHARACTERIZING AND IMPROVING THE TOUGHNESS OF THICK-SECTIONED
2½Cr-1Mo ELECTROSLAG WELDMENTS

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INTRODUCTION

The electroslag welding process produces large single pass welds by consuming a wire electrode in an ohmically heated flux pool. The process has been particularly appealing for thick-section welding because of its high deposition rate. Application of electroslag welding is currently hindered, however, by the lack of fundamental understanding of critical process variables, thermal history, and heat treatment of the heat affected zone, and the influence of flux and alloy chemistry on the structure and properties of the weld fusion zone. Careful control of process variables and process chemistry are critical to fabrication. The welding potential and electrode velocity control the deposition rate, heat input, and thermal history of the heat affected zone. The electrode polarity, current density, and flux and metal compositions control electrochemical reactions which have a dominant influence on the weld metal chemistry. The post-weld heat treatment strongly affects the final mechanical properties of the weldment, especially in 2½Cr-1Mo steel. The objective of this program is to characterize the effects of process variables, chemical variables, and post-weld heat treatment, and to apply straight-forward metallurgical knowledge in optimizing the properties of 4-inch thick 2½Cr-1Mo steel electroslag weldments.

RESULTS FROM PRIOR QUARTERS

Process Control

Prior research on process control has produced a mathematical model for heat transport in the parent metal plates, an energy balance which accounts for heat utilization in electroslag welding, and process control plots to predict correct settings for operating variables. The results

have shown that a low heat input to the parent metal plates is obtained by operating at high currents and electrode velocities, and that a low heat input substantially increases fusion zone toughness and response to post-weld heat treatment. The enhanced fusion zone toughness is the result of the finer bainitic structure caused by more rapid cooling.

Process Chemistry

Prior research on process chemistry has concentrated on the influence of electrochemical reactions and on the modification of commercial oxide based fluxes to prevent alloy element oxidation losses. Electrochemistry experiments demonstrated that alloy elements are oxidized at the anodic wire electrode and reduced at the cathodic weld pool, and that the current in the flux is carried by ionic conduction. Welding experiments with a commercial oxide-based flux showed that chromium oxide additions to the flux could counteract the effects of chromium oxide losses, and that the flux chemistry will change to balance chromium activity between the flux and metal phases. It was also demonstrated that continuous oxygen pickup will be observed with oxide based fluxes, particularly with fluxes which are high in transition oxides.

Post-Weld Heat Treatment

Post-weld heat treatment studies during prior quarters have shown that excellent fusion zone toughness can be obtained by a combination of low heat input during welding and post-weld heat treatment at a temperature below the A_1 temperature. The optimum post-weld heat treating temperature was found to be 730C. A temperature of 690C was too low, while 760C was above the A_1 temperature and resulted in partial re-austenitization and the formation of polygonal ferrite. The fact that 760C exceeded the A_1 temperature in weldments high in austenitizers such as nickel and manganese was quantified by direct dilatometric measurement of the transformation temperatures.

DISCUSSION OF CURRENT ACTIVITIES

Work on process control during the last quarter has concentrated on further characterizing the microstructural differences in 4-inch thick $2\frac{1}{4}\text{Cr-1Mo}$ steel electroslog weldments made at different heat inputs. As was shown in a previous report (see ORNL/FMP-81/3, pp. 86 and 87), varying the heat input from 0.35 kJ/mm^2 to 0.64 kJ/mm^2 raised the 54J (40 ft-lb) transition temperature of weld fusion zones post-weld heat treated at 732°C from approximately -50°C to 50°C , and lowered the upper shelf energy from approximately 190J to 80J. These data are again shown in Figures 1 and 2. Ferrite lath spacing and carbide lath spacing were shown to increase with increasing heat input; however, other microstructural features such as dendrite arm spacing, chromium grain size, and grain orientation are also known to vary with heat input, and these features are being characterized. Figures 3 and 4 are low magnification optical micrographs of the fusion zones from weldments B_3 (0.35 kJ/mm^2) and A_1 (0.64 kJ/mm^2), the same weldments for which CVN toughness data are plotted in Figures 1 and 2. Figure 5 is a similar micrograph of the fusion zone from a high heat input (0.70 kJ/mm^2) weldment for which CVN testing is not yet complete. Each micrograph was taken midway between the centerline and the fusion line (i.e., at quarter weld width), and on a plane perpendicular to the short transverse direction (i.e., on a plane parallel to the direction of welding, viewed in a direction parallel to the plate thickness). The vertical axis of the micrographs is, in each case, parallel to the direction of welding.

Both orientation and size of the columnar grains are strongly dependent on the heat input of welding. Welding at low heat input (Figure 3) creates a deep molten metal pool, with solidification isotherms nearly parallel to the direction of welding at the quarter weld width location. The major axes of the columnar grains at the quarter weld width location in the fusion zone of low heat input electroslog weldments are therefore nearly perpendicular to the direction of welding. In contrast, welding at high heat input (Figures 4 and 5) creates a shallow molten metal pool, with solidification isotherms nearly perpendicular to the direction of welding. In this case, columnar grains

grains at the quarter weld width location grow in a direction nearly parallel to the direction of welding.

Columnar grain sizes qualitatively are shown to increase with heat input in Figures 3 through 5. This fact has been quantified for a series of welds made at various heat inputs, then microscopically examined at both the fusion zone centerline and quarter weld width positions. Specimens were prepared with the plane of polish perpendicular to the major axes of the columnar grains. The results of this analysis are shown in Figure 6. Columnar grain size was found to be linearly dependent on heat input, to be significantly larger at the quarter weld width than at the centerline location in low heat input welds, and to be slightly more sensitive to heat input at the centerline than at the quarter weld width. As a result, grain size for the high heat input welds was virtually independent of position in the fusion zone. This fact may help explain why the CVN toughness of weld metal from high heat input welds is not sensitive to location within the fusion zone, while the CVN toughness of weld metal taken from the quarter weld width location of low heat input welds is significantly better than the toughness of weld metal taken from the centerline.

Process Chemistry

Current process chemistry research is concentrating on the influence of alloy oxide flux additions on the chemistry of the fusion zone. Welds were produced in a water cooled steel crucible using Cr_2O_3 and MnO_2 additions to a commercial oxide based flux:

1. Commercial Flux
2. Commercial Flux + 5% Cr_2O_3
3. Commercial Flux + 10% Cr_2O_3
4. Commercial Flux + 15% Cr_2O_3
5. Commercial Flux + 5% MnO_2
6. Commercial Flux + 5% MnO_2 + 5% Cr_2O_3
7. Commercial Flux + 5% MnO_2 + 10% Cr_2O_3
8. Commercial Flux + 5% MnO_2 + 15% Cr_2O_3

Chemical analyses were made of the welds at heights of 1,2,4,8, and 14 inches from the base of the weld. These analyses showed that the pickup or loss of a particular alloy element from the flux is strongly dependent on its position on the electrochemical series. Table I gives a tentative electrochemical series for oxidation reactions in molten fluxes. Elements at the top of the series are more easily oxidized than elements at the bottom, and elements at the bottom are more easily reduced. Previous electrochemical data indicates that oxidation reactions as far down the series as the oxidation of iron from the ferrous to the ferric state occur at the anode; however, reduction reactions at the cathode are more difficult, and the reduction of elements low on the series occurs in preference to those at the top. Figures 7, 8, and 9 show the changes of chromium, manganese, and silicon concentration for fluxes with Cr_2O_3 additions. All three elements are oxidized at the anode, but silicon and manganese are not reduced at the cathode when a large concentration of chromium cations is present in the flux. Data for welds with MnO_2 flux additions indicate that an increased manganese concentration in the flux suppresses the cathodic reduction of silicon which is higher on the electrochemical series, but not the reduction of chromium which is lower on the series.

Figures 10, 11, 12, and 13 present data on oxygen and nitrogen concentrations for the same series of welds. Figure 10 shows oxygen concentration as a function of distance from the starting tab for welds with Cr_2O_3 additions to the flux. The minimum oxygen pickup of around 100ppm was observed for the welds with 0% and 5% Cr_2O_3 additions. The welds with 10% and 15% Cr_2O_3 additions showed substantial oxygen pickup to values as high as 800ppm. This oxygen pickup is expected based on the increased oxygen content in the flux and on the general observation that multivalent transition elements are capable of transporting oxygen from the flux/air interface to the flux/metal interface. The oxygen concentrations in Figure 10 are observed to fall with increasing distance along the weld, as the Cr_2O_3 content in the flux is lowered by cathodic reduction.

Figure 11 shows the oxygen concentrations for welds produced using a 5% MnO_2 addition to the flux along with the Cr_2O_3 additions. The MnO_2 addition produces much lower oxygen concentrations, even when the flux contains 15% Cr_2O_3 . The oxygen concentrations range from 150 to 300ppm over the entire length of the weld. This behavior was unexpected, because manganese in the +4 oxidation state is a powerful oxidizing agent, and it is capable of oxidizing molybdenum, nickel, chromium, and iron to higher oxidation states. The MnO_2 addition was expected to increase rather than decrease the weld metal oxygen content. Normal flux deoxidation practice employs the addition of a strong reducing agent such as aluminum (see Table I). One possible explanation for the reduced oxygen caused by the MnO_2 addition is that the Mn^{+4} ion forms a strong octahedral coordination complex with oxygen anions in the flux. Thus, the oxygen anions are bound in complex anions, their activity in the melt is lowered, and the discharge of oxygen anions at the anode is hindered. A clear understanding of the influence of MnO_2 additions to the flux will require more experimental and theoretical work.

Figure 12 gives the nitrogen concentrations for welds produced with Cr_2O_3 additions to the flux, and Figure 13 gives the nitrogen values for welds produced with both MnO_2 and Cr_2O_3 additions. Some nitrogen refining is observed for the unaltered commercial flux; the Cr_2O_3 additions inhibit this refining to a small extent; and the 10% and 15% Cr_2O_3 additions cause a small nitrogen pickup in the initial portion of the weld. The MnO_2 additions cause a small nitrogen pickup along the whole length of the weld. This behavior is not well understood at the present time, but the nitrogen concentrations in the weld metal are small, and the influence on mechanical properties is expected to be negligible.

Three conclusions can be based on the oxygen concentration data presented in Figures 10 and 11. First, a minimum oxygen pickup of around 100ppm is observed for oxide based electroslog welding fluxes. Second, 10% and 15% Cr_2O_3 additions to the flux cause a dramatic increase in weld metal oxygen content. A 5% Cr_2O_3 addition, which is sufficient to maintain weld chromium content, causes no more oxygen pickup than

does the use of an oxide based flux. Third, MnO_2 additions eliminate the large oxygen pickup observed for fluxes with high Cr_2O_3 contents.

Table I - Tentative Electrochemical Series for Alloy Element
Reactions in Electroslog Welding

Figure 1 - The influence of welding heat input on fusion zone Charpy Impact transition temperature for 2 1/4Cr-1Mo steel electros lag weldments post-weld heat treated at 732C.

Figure 2 - The influence of welding heat input on the upper shelf Charpy Impact energies of 2 1/4Cr-1Mo steel electroslag weldments post-weld heat treated at 732C.

Figure 3 - The columnar grain structure in the fusion zone of a low heat input (0.35 kJ/mm^2), 4-inch thick $2\frac{1}{2}\text{Cr-1Mo}$ steel electroslag weldment. The view is parallel to the short transverse direction at the quarter weld width position with the vertical dimension of the photograph parallel to the direction of welding. Etched in 2% nital solution.

Figure 5 - The columnar grain structure in the fusion zone of a high heat input (0.70 kJ/mm^2), 4-inch thick $2\frac{1}{2}\text{Cr-1Mo}$ steel electroslag weldment. The location, orientation of specimen relative to the welding direction, and sample preparation were the same as for the specimens of Figures 3 and 4.

Figure 6 - The change in columnar grain size as a function of heat input during welding for weld metal from 4-inch thick 2 1/4Cr-1Mo steel electros slag weldments.

Figure 7 - The change in fusion zone chromium content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel electroslag welds produced using a commercial oxide-based flux with 0%, 5%, 10%, and 15% Cr_2O_3 additions. Positive ΔCr values indicate chromium pickup from the flux, and negative values indicate chromium oxidation losses.

Figure 8 - The change in fusion zone manganese content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel electroslag welds produced using a commercial oxide-based flux with 0%, 5%, 10%, and 15% Cr_2O_3 additions. Positive ΔMn values indicate manganese pickup from the flux, and negative values indicate manganese oxidation losses.

Figure 9 - The change in fusion zone silicon content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}$ -1Mo steel electroslag welds produced using a commercial oxide-based flux with 0%, 5%, 10%, and 15% Cr_2O_3 additions. Positive values of ΔSi indicate silicon pickup from the flux, and negative values indicate silicon oxidation losses.

Figure 10 - Fusion zone oxygen content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel welds produced using a commercial oxide-based flux with 0%, 5%, 10% and 15% Cr_2O_3 additions.

Figure 11 - Fusion zone oxygen content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel welds produced using a commercial oxide-based flux with a 5% MnO_2 addition, and 0%, 5%, 10%, and 15% Cr_2O_3 additions.

Figure 12 - Fusion zone nitrogen content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel welds produced using a commercial oxide-based flux with 0%, 5%, 10%, and 15% Cr_2O_3 additions.

Figure 13 - Fusion zone nitrogen content as a function of distance from the starting tab for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel welds produced using a commercial oxide-based flux with a 0%, 5%, 10%, and 15% Cr_2O_3 additions.

PNST-3.2 — AN X-RAY STUDY OF RESIDUAL STRESSES
IN NARROW-GROOVE TIG WELDMENTS

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INTRODUCTION

This study is to compare the residual stress field resulting from narrow gap hot wire gas tungsten arc (GTA) welding to conventional vee groove submerged arc welding for thick plates. It has been proposed that narrow gap (groove) welding could lead to the reduction of stress relief treatment in heavy 2.25 Cr - 1 Mo Steel sections. Furthermore, the low distortion resulting from the GTA process alone may be indicative of lower residual stress inducement. As an integral part of this project, procedures for measuring three-dimensional residual stress contours in thick, low alloy steel plate will be developed. Procedures will focus on the application of a new type of x-ray stress analyzer based upon a position sensitive scintillation x-ray detector developed by the principal investigator. Both x-ray and stress relief techniques will be applied to provide three-dimensional stress contours in the 2.25 Cr - 1 Mo Steel weldments.

RESULTS FROM PRIOR QUARTERS

In the first quarter ordering of components for the x-ray stress analyzer was initiated and the task I literature search begun and was completed in the second quarter.

The following predicted as-welded stress distributions were derived through the literature search by comparing similarities in the stress distributions reported by various investigators. The various methods used by these investigators are quite diverse, ranging from hole drilling to x-ray diffraction methods. The resulting data, however, seem to be fairly consistent regardless of the method used. Allowances have to be made for differences in measurement methods, e.g., strain gages average the stresses over a larger area and volume than x-ray methods, therefore there are limits to how steep a gradient a method such as hole drilling can resolve.

The residual stress data gleaned from the literature suggests three-dimensional stress patterns as illustrated in Figs. 1 and 2 for thick as-welded multi-pass low alloy steel plate weldments. Both figures show the stress on a scale from 0 to 100 pct of the yield strength of the parent metal.

Figure 1 shows the predicted planar stresses on the surface, at one-quarter thickness, and at the center of the weldment parallel to and perpendicular to the weld center line. The solid line designated A and E shows the behavior of the stress in the weldment top and bottom surface perpendicular to the weld (σ_x) on a traverse from the weld toe (weld fusion line) to a distance of about two plate thicknesses (2T). The dotted line designated A and E depicts the stresses in the direction parallel to the weld center line (σ_y) along the same traverse. The lines designated B and D show the predicted stress behavior in the plane parallel to the surface and at a distance of one-quarter plate thickness from the top or bottom surface; the solid line for stresses perpendicular and the dotted line for stresses parallel to the weld center line. The lines designated C show the stress in the plane parallel to the plate surfaces at the center of the weldment; the solid line for stresses perpendicular to the weld center line and the dotted line, for those parallel.

Figure 2 shows the predicted through thickness stresses in a direction perpendicular to plate surface at the weld fusion line as seen at the weld fusion line (A), at a distance of one half a plate

Fig. 1 Predicted as-welded stresses in the plane of the surface (A and E), at a plane parallel to the surface and one-quarter plate thickness below (B and D), and at the center plane (C). The solid lines show stresses perpendicular to the weld center line and the dotted lines parallel.

Fig. 2 Predicted as-welded stresses in the direction perpendicular to the surface plane and in a traverse through the thickness of the welded plates at the weld fusion line (WFL) seen on the surface (A), at a distance of one half a plate thickness from the WFL (B), and at a distance one plate thickness from the WFL (C).

thickness from the weld fusion line (B), and at a full plate thickness from the weld fusion line (C).

The conclusion to be drawn from Figs. 1 and 2 is that they show the predicted three-dimensional as-welded residual stress distribution of a thick plate weldment joined by a multi-pass procedure. The highest tensile stresses are in the plate surface near the weld fusion line (WFL) and are often near yield in the as-welded condition.

Also, in the second quarter, the design of the stress measurement carriage apparatus was completed and fabrication initiated and the major electronic equipment components procured. Assembly of the x-ray stress measurement instrument and computer controller was initiated in the third quarter as well as the search for an A387 plate source and weldment specimen fabricator.

In the fourth quarter initial software data refinement listings were written and x-ray stress data was synthesized to test the software. The search for suitable steel plate sources and weldment fabricators progressed as well as the survey of logistics problems in specimen machining, handling, and transportation.

In the fifth quarter calibration and test fixtures for x-ray residual stress measurement were designed and fabricated. Design and fabrication of the stress head X-Y carriage continued, and procurement, assembly, and testing of the computer controller for the stress instrument progressed. Simultaneously, writing of software for data refinement continued.

In the sixth quarter fabrication, assembly, and testing of the X-Y positioning stage and x-ray source was completed, and the frame for its mounting and positioning was designed. Incident x-ray beam collimators for the stress head were designed and fabricated as well as a special film holder for film camera work. Assembly of the x-ray stress analyzer computer controller was completed and found operational with the initial utility software. The software for K-alpha-two stripping and Lorentz-Polarization and Absorption correction was completed and tested on synthetic data. Figure 3 shows the raw data typical of that which is expected to be produced by the unique position

Fig. 3 X-ray diffraction raw data as collected by position sensitive scintillation detector and displayed on a CRT. Chromium K-alpha-one and two radiation as diffracted from the (311) planes of ferrite at a Bragg angle of 78 degrees; with the incident x-ray beam striking the specimen surface at 25 degrees to the surface normal.

sensitive scintillation x-ray detector to be applied to x-ray stress measurement in this program. The peaks represent the K-alpha-one and two doublet of chromium radiation diffracted by the (211) crystallographic planes of ferritic steel at a Bragg angle of approximately 78 degrees. The two different peaks are diffracted from groups of ferritic grains with different crystallographic orientations to the specimen surface. This data was synthesized from data produced by previous prototypes of the detector concept. Figure 4 shows the result of the data refinement programs including K-alpha-two stripping and Lorentz-Polarization and Absorption correction. Stress will be calculated through finding the apex of each of the peaks shown in Fig. 4, ascertaining the location of each apex with respect to the center of the figure; then substituting these values into a stress calculation algorithm based upon the single exposure x-ray stress equation.

In the seventh quarter, the x-ray stress instrument was completed and installed in the laboratory. Training in the operation and maintenance of the instrument was accomplished. Testing to characterize the operational parameters of the instrument as applied to x-ray stress measurement are in progress.

In the eighth quarter test methods to evaluate the accuracy and precision capabilities of the x-ray stress instrument were developed. The test revealed corrections necessary for obtaining accurate stress measurements and provided the constants to be used in stress calculations. Simultaneously, development of procedures for electropolishing low alloy steel specimens were initiated.

DISCUSSION OF CURRENT ACTIVITIES

Testing to characterize the stress measurement capabilities of the position sensitive scintillation x-ray detector based stress analyzer is continuing on low alloy steel specimens. Two new Reticon diode arrays have been procured to replace those originally installed

Fig. 4 Raw data from Fig. 3 refined by correcting for electronic dark current and gain and applying a K-alpha-two stripping routine and Lorentz-Polarization and Absorption corrections.

in the instrument. These specially selected components should reduce the scatter of the precision of measurement by at least one third. Testing of the software is continuing and should be aided by the reduced scatter of the new diode arrays.

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CU-3.3 - HYDROGEN ATTACK IN Cr-Mo STEELS
AT ELEVATED TEMPERATURES

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INTRODUCTION

When a carbon or low alloy steel is exposed to high pressure hydrogen at elevated temperatures, it is well established that in addition to surface decarburization, internal damage or hydrogen attack will occur as a result of the formation of methane bubbles at the grain boundaries (1-6). It is also known that in the presence of an applied stress, the stress-rupture strength of these steels will be reduced with a loss in ductility at much lower hydrogen pressures whereas in the unstressed condition hydrogen attack would not be detected (1,2).

Current interests in coal conversion and other energy technology for which structural components are exposed to high temperature and high pressure hydrogen, has increased the need for more extensive materials performance data under these conditions (7). This type of data is required to establish various mechanical design criteria to insure the integrity of structural components.

Cr-Mo steels have been identified as potential structural materials for coal conversion plants. This project is designed to obtain micro-structure and mechanical property data of these steels under the simultaneous influence of high temperature and high pressure hydrogen and an applied stress. In particular the work will include an experimental determination of the kinetics of nucleation and growth of gas bubbles or cavities in 2½ Cr-1Mo steels at elevated temperatures under the influence of high pressure hydrogen and applied stress, and the development of kinetic equations for estimating the number density and size distribution of grain boundary bubbles or cavities as a function of time under conditions of interest to coal conversion plant operations (7).

The nucleation of methane bubbles at the grain boundaries, when low alloy steel is exposed to high pressure and high temperature hydrogen, has been found to be heterogeneous in nature and dependent upon the stability of the carbides present (8-10). Second phase particles at the grain boundary and grain boundary steps are favored high energy sites for nucleation. According to the current microscopic concepts of nucleation, the size of the critical nucleus and the magnitude of the free energy barrier of nucleation are roughly determined by the ratio of a surface tension term and the internal methane pressure (3). The time required to build up the internal methane pressure in a bubble of critical size can be expected to be a significant portion of the incubation time observed during hydrogen attack. For steels of high chromium content the stability of the carbides could be such that the equilibrium methane pressure may not be sufficient to cause the nucleation of methane bubbles.

In the presence of an applied stress, depending on the magnitude of the applied stress, grain boundary sliding will occur and cause deformation incompatibility at grain boundary steps and second phase particles. This deformation incompatibility can produce large tensile stresses at these sites which will enhance the rate of bubble or cavity nucleation (4,11). Under these circumstances, the size of the critical nucleus will be determined roughly by the ratio of a surface tension term and the sum of the internal methane pressure and the hydrostatic component of the tensile stresses. One can see that an applied stress can reduce significantly the size of the critical nucleus through the tensile stresses produced by deformation incompatibility and thus increase the probability of bubble or cavity nucleation.

The enhanced bubble or cavity nucleation caused by an applied stress can be responsible in part for the observed accelerated hydrogen attack (1,2,9,10). Theoretically, the presently available capabilities are not able to quantitatively predict the magnitude of this effect. One of the objectives of this work is, therefore, to determine experimentally the effect of applied stress enhanced bubble or cavity nucleation and to develop analytic correlations for data extrapolation based on experimental data.

If the equilibrium methane pressure resulting from CH_4 reaction is sufficient to cause bubble nucleation (as long as the internal methane pressure is greater than $2\gamma/R$ where γ is the surface tension of the bubble and R is the radius), the bubble will grow as a function of time in the absence of an applied stress. There can be different rate limiting mechanisms. First, the bubble growth can be controlled by the rate of supply of vacancies with the grain boundary being the source of vacancies (4). For this type of growth the internal methane pressure will always be greater than $2\gamma/R$. The bubble can grow by creep with internal pressure also greater than $2\gamma/R$ (12). If one removes the specimen from the hydrogen environment, the bubble will continue to grow at elevated temperatures until the magnitude of the internal pressure approaches that of $2\gamma/R$.

The bubble growth can also be controlled by the rate of formation of methane. For this rate limiting mechanism, the magnitude of internal methane pressure will be larger than, but close to that of, $2\gamma/R$ because there is a sufficient supply of vacancies or creep deformation to maintain the internal methane pressure near $2\gamma/R$. If one removes from the hydrogen environment a specimen containing bubbles whose growth is limited by methane formation, the bubble will not continue to grow when exposed to elevated temperatures.

It should be noted that for practical interests, a coal conversion plant will be operated under conditions (temperature and hydrogen pressure) where the rate of bubble growth under the influence of internal methane pressure would ordinarily be extremely small. However, the hydrogen environment could be sufficient with the aid of an applied stress, to nucleate grain boundary bubbles or cavities which could grow under the influence of this stress resulting in accumulated damage. In this work the growth kinetics under an applied stress will also, therefore, be investigated in detail. An important product of this work is the capability to estimate based on cavity nucleation and growth data, the number density and size distribution of grain boundary bubbles or cavities as a function of time under conditions of interest to coal conversion plant operations (7).

For thin wall components the design criteria for service at elevated temperatures are usually based on deformation limits due to creep, stress to rupture life and creep-fatigue interactions. These properties will be influenced by cavity formation especially the long term performance. For example, stress-rupture tests under high pressure hydrogen at high temperature have shown reduced life as compared to that in air or high pressure helium (2,6,13).

For thick wall components, design criteria are usually based on crack growth rate and fracture toughness. The existence of grain boundary bubbles or cavities is expected also to influence these properties.

RESULTS FROM PRIOR QUARTERS

For coal conversion technology a part of the materials requirement should represent an optimum combination of strength and resistance to hydrogen attack (7,14). In general, for a given Cr-Mo steel, a heat treatment procedure involving quenching and tempering at low temperatures and short durations, will produce high strength and carbides of low stability and thus, low resistance to hydrogen attack (15). On the other hand, a heat treatment procedure involving normalizing and tempering at high temperatures and long durations, will produce low strength and carbides of high stability and thus, high resistance to hydrogen attack. At the present the required heat treatment procedure is to be determined. An objective of this program is to, therefore, produce a part of the required information for materials selection.

We are fortunate in having received, through the courtesy of Drs. R.A. Swift and J.A. Gulya of Lukens Steel, both a normalized and tempered and a quenched and tempered piece of A387 steel which represent the two limiting heat treatment conditions of interest. These two materials will be the main sources of specimens for the present program.

In addition, some work will be done on an A542 steel obtained from Professor R.P. Wei at Lehigh University (properties are given in Table 1.)

Specific conditions of heat treatment, properties and composition of the normalized and tempered A387 steel are given in Table 2. Similar data for the quenched and tempered material are also given in Table 2.

TABLE 1

PROPERTIES OF 2½ Cr-1 Mo (A542) STEEL PLATE

(Lukens Steel Heat C7158; A542, Class 2)

<u>Supplier's Analysis</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Al</u>
Ladle	0.11	0.43	0.007	0.016	0.24	ND*	2.33	0.93	ND
Check	0.10	0.45	0.012	0.018	0.23	ND	2.36	0.92	ND

*ND -- Not Determined

Heat Treatment

Austenitized 1650-1700°F, 1 hour per inch of thickness minimum,
water quench + tempered 1180°F, 90 minutes per inch of thickness
minimum, water quench.

Mechanical Properties

<u>Lehigh Data</u> ¹⁶	<u>Yield Strength ksi (MN/m²)</u>	<u>Tensile Strength ksi (MN/m²)</u>	<u>Reduction of Area Percent</u>	<u>Elongation in 2 in. (5.08cm) Percent</u>
Longitudinal	108.8 (750)	118.3 (815)	62	20
	108.3 (746)	119.3 (822)	63	21
	<u>108.8 (750)</u>	<u>118.8 (819)</u>	<u>63</u>	<u>20</u>
(Av.)	108.6 (748)	118.8 (819)	63	21
Transverse	110.8 (763)	119.8 (825)	50	17
	<u>109.3 (753)</u>	<u>119.8 (825)</u>	<u>51</u>	<u>18</u>
(Av.)	110.1 (759)	119.8 (825)	51	17

TABLE 2

PROPERTIES OF 2½ Cr-1 Mo (A387) STEEL PLATE - 12 in. THICK
(Lukens Steel Heat B3085; A387 - Grade 22)

<u>Lukens¹⁷ Analysis</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Al</u>
Ladle	0.13	0.52	0.01	0.01	0.23	0.18	2.23	0.95	0.21

Normalized and Tempered Heat Treatment

Austenitized 1675°F, 12 hours, air cool + tempered 1275°F, 12 hours, air cool

Mechanical Properties

<u>Lukens Data¹⁷</u>	<u>Yield Strength ksi</u>	<u>Tensile Strength ksi</u>	<u>Reduction of Area Percent</u>	<u>Elongation Percent</u>
Transverse	42.			
Transverse	42.4	77.4	64.3	24.3

Quenched and Tempered Heat Treatment

Austenitized 1675°F, 12 hours, Waterquenched + tempered 1275°F, 8 hours, waterquench

Mechanical Properties

<u>Lukens Data¹⁷</u>	<u>Yield Strength ksi</u>	<u>Tensile Strength ksi</u>	<u>Reduction of Area Percent</u>	<u>Elongation Percent</u>
Longitudinal	68.0	85.7	76.9	26.5

Both types of material are sections from the surface of a 12 inch (305mm) thick plate. The quenched and tempered steel shows a microstructure of tempered bainite with no proeutectoid ferrite, whereas the normalized material shows a microstructure of both bainite and proeutectoid ferrite (18).

During the first phase of this project (contract period September, 1978 - August, 1980) a major portion of the work concentrated on the investigation of the normalized and tempered A387 steel. Information obtained on this material includes:

1. The incubation time and rate of methane bubble nucleation as a function of temperature and hydrogen pressure.
2. The effect of applied stress on the incubation time and rate of methane bubble nucleation.
3. The rate of stress induced cavity growth at the grain boundary.
4. Analytical equations for methane bubble nucleation.

A detailed description of the above results is given in a final report for the contract period September, 1978 - August, 1980.

At the end of the previous contract period the work on the quenched and tempered A387 began. This switch of emphasis was made upon the advice of Dr. Joe Long of ORNL, even though the planned test matrix for the normalized and tempered material had not been completely carried out. The quenched and tempered A387 is currently a favored candidate structural material because of its high strength. Based on current results, it might also be a better choice compared to the normalized and tempered material from the viewpoint of hydrogen attack. This is because a saturation methane bubble nucleation behavior was observed in the quenched and tempered steel. The saturation number of methane bubbles may not be significantly different in the quenched and tempered and normalized and tempered A387 steels. On the other hand, the rate of stress induced cavity growth was found to be significantly slower in the former material.

In the previous quarterly report we have summarized all the available nucleation data on normalized and tempered as well as quenched and tempered materials. We have analyzed these data using a nucleation

model based on classical nucleation theories. This model together with fitted parameters can be used for data extrapolation to conditions which are not accessible experimentally at the present.

DISCUSSION OF CURRENT ACTIVITIES

During this quarter we continued the investigation of the nucleation of methane bubbles on a quenched and tempered 2½ Cr-1Mo steel. In this report the new data on nucleation as a function of hydrogen pressure, exposure time, temperature and applied stress will be presented. Such data are expected to establish a basis upon which a quantitative theory will be developed for extrapolation to a variety of hydrogen exposure conditions.

In the previous quarter (19) we devoted a considerable amount of effort to evaluating a model, based upon classical nucleation theory, in terms of the data then available. The model was shown to be consistent with the temperature, hydrogen pressure and stress dependence observed, which included the results from experiments on both the quenched and tempered and the normalized and tempered materials.

In the following, the model will again be examined by comparing its predictions with the latest data.

A. Nucleation Theory

The adaptation of the classical nucleation theory (20,21) for the present interest has been discussed in previous quarterly reports (8,9) and summarized in the last report (19). According to the nucleation model, the formation of the methane bubble results from the condensation of vacancies fed along the grain boundary. The methane pressure provides the driving force in the absence of an applied stress. The free energy, ΔG , associated with a vacancy cluster of a particular size is given as:

$$\Delta G = -\alpha n + \beta n^{2/3} \quad (1)$$

where n is the number of vacancies in the nucleus, αn represents the volume free energy term and $\beta n^{2/3}$ is the surface energy term. Assuming β and the number of available nucleation sites to be independent of temperature, it can be shown (19) that incubation times τ_1 and τ_2 and the rates of nucleation, $\dot{N}_1$ and $\dot{N}_2$, for two different hydrogen exposure conditions are related by the following equations:

$$\tau_1/\tau_2 = \frac{T_1}{T_2} \left(\frac{\alpha_2}{\alpha_1}\right)^3 e^{G_{gb}(1/RT_1 - 1/RT_2)} \quad (2)$$

and

$$\dot{N}_1/\dot{N}_2 = \left(\frac{T_2}{T_1}\right)^{1/2} \left(\frac{\alpha_1}{\alpha_2}\right) e^{-G_{gb}(1/RT_1 - 1/RT_2)} \quad (3)$$

where G_{gb} is the activation energy for grain boundary self-diffusion and RT retains its usual meaning. G_{gb} is taken to be 41500 cal/mole (22). It is important to note that, in arriving at Equation 3, the energy barrier to nucleation is assumed small. This assumption can be justified by the observed temperature dependence of $\dot{N}$ between 550°C and 600°C as discussed in the previous quarterly report (19).

In the same report, based on the observed dependencies of both $\dot{N}$ and τ on hydrogen pressure and temperature, and on the estimate of methane pressure as a function of hydrogen pressure and temperature in the chromium steels, we have taken α in Equation 1 to depend on the methane pressure as $\alpha \sim P_{CH_4}^{1/3}$. This dependence is non-physical compared to a linear dependence on P_{CH_4} , reflecting a more complicated physical situation, and yields the observed dependence of the τ and $\dot{N}$ on hydrogen pressure according to the available data.

The effects of stress on $\dot{N}$ and τ are introduced through a modification of the volume free energy term in Equation 1, such that α becomes:

$$\alpha = \alpha_{\sigma=0} + \sigma_{conc.} \Omega \quad (4)$$

where $\alpha_{\sigma=0}$ is the volume free energy term in the absence of a stress, $\sigma_{\text{conc.}}$ is a measure of the stress concentration at the nucleation site and Ω is the atomic volume.

According to the model, $\sigma_{\text{conc.}}$ is taken to be independent of hydrogen pressure and P_{CH_4} . It is expected that the same value of $\sigma_{\text{conc.}}$ can be used to estimate N and τ under different hydrogen pressures, for a given applied stress.

B. Nucleation Data in the Absence of Applied Stress

In the present quarter data were obtained for low hydrogen pressures and low temperatures which required long exposure times. One test was performed at 600°C under a hydrogen pressure of 1000 psi to explore the effects of hydrogen pressure on nucleation. Other tests were at 500°C and under a hydrogen pressure of 2000 psi.

In the experiment, tensile specimens were hydrogen exposed for specified lengths of time. After exposure, the specimens were given the creep growth treatment, designed to grow the nucleated cavities to sizes large enough for observation in a scanning electron microscope (23). From micrographs of the sectioned, etched and polished specimens estimates of the grain boundary cavity number densities were made.

Figure 1 shows the cavity number density versus exposure time for specimens of the quenched and tempered steel subjected to a hydrogen pressure of 2000 psi at the temperatures 600°C, 550°C and 500°C. The new data obtained this quarter were for 500°C and exposure times 50 and 180 days. Both of these data lie near the base line value, suggesting an incubation period of longer than 180 days. The base line represents the grain boundary cavity number density resulting from the creep growth treatment alone. Calculations based on the nucleation model described earlier and the parameters given in the previous quarterly predicted an incubation period of about 90 days at 500°C in the absence of an applied stress.

Figures 2a and 2b show the grain boundary cavity number densities as functions of exposure time for both normalized and tempered and quenched

Figure 1. Grain boundary cavity density vs. hydrogen exposure time for the A387 quenched and tempered steel. Data for hydrogen exposure at 600°C , 550°C and 500°C are presented. The symbols are experimental data points and the lines are calculated. The data obtained this quarter are for 50 and 180 days at 500°C .

Figure 2. Grain boundary cavity density vs. hydrogen exposure time for both the A387 quenched and tempered and normalized and tempered steels. Data for 2000 psi and 1000 psi hydrogen exposure at 600°C are presented. The data obtained this quarter are from the quenched and tempered material at $P_{\text{H}_2} = 2000$ psi. The symbols are experimental data points and the lines are calculated.

and tempered steels exposed to hydrogen pressures of 1000 psi and 2000 psi at 600°C respectively. The data for the normalized and tempered specimens were obtained in our earlier work. They suggest that lowering the hydrogen pressure by a factor of two affected the nucleation in a normalized and tempered material by roughly doubling the period of incubation and decreasing the rate of nucleation slightly, if any. Because of the similarity of the two materials, we expect the effect to be similar for the quenched and tempered material. The new data on the quenched and tempered material obtained in this quarter showed an incubation period near or longer than 20 days under $P_{H_2} = 1000$ psi. The calculation predicts an incubation period of 17 days for the same condition.

Table 3 summarizes the results of our nucleation measurements and calculations for the quenched and tempered material in the absence of an applied stress. The calculations were made by using Equations 2 and 3 and the data for $T = 600^\circ\text{C}$, $P_{H_2} = 2000$ psi data as the reference. The calculation of the methane pressure was given in the previous report.

C. Stress Enhanced Nucleation

New data were collected also on the quenched and tempered steel under a tensile stress. Tests were completed for $T = 550^\circ\text{C}$ and $P_{H_2} = 2000$ psi under an applied stress of 16 ksi. Figure 3 shows micrographs of specimens having undergone various lengths of exposure under those conditions. Figure 4 compares the observed grain boundary cavity number densities for the quenched and tempered steel, with and without the influence of applied stress, at 550°C. As was shown by the data of 600°C (19), the present data show also that the applied stress shortened the incubation period and increased the rate of nucleation. No saturation effect was observed in the data of the stressed specimens in Figure 4. This might simply be because longer exposure times are required. From the ratios of incubation times and rates of nucleation, we obtained for the stress concentration term a value of $\sigma_{\text{conc.}} = 400$ MPa under an applied stress of 16 ksi at 550°C. The estimated methane pressure is

TABLE 3

INCUBATION TIMES AND RATES OF NUCLEATION

Quenched and Tempered Materials

<u>Exposure Conditions</u>		<u>Experimental</u>		<u>Theoretical</u>	
Temp.	P _{H₂}	$\dot{N}$	τ	$\dot{N}$	τ
(°C)	(psi)	($\mu\text{m}^{-2}\text{day}^{-1}$)	(days)	($\mu\text{m}^{-2}\text{day}^{-1}$)	(days)
600	2000	2.0×10^{-1}	8.8	9.50×10^{-2}	8.8
550	2000	3.9×10^{-2}	15	2.58×10^{-2}	26
500	2000	-	>180 $\neq$	5.70×10^{-3}	92
600	1000	-	> 20 $\neq$	7.58×10^{-2}	17.2

$\neq$ Data obtained this quarter; the experimental values may be modified as more data becomes available

Figure 3. SEM photomicrographs of polished and etched specimens of A387 quenched and tempered $2\frac{1}{4}$ Cr-1Mo steels. The specimens were hydrogen exposed at conditions of 2000 psi and 550°C with a 16 ksi applied stress for a) 10, b) 23 and c) 32½ days. After hydrogen exposure the specimens underwent creep growth treatments for periods varying from 9 to 13 days at 600°C, under a 16 ksi stress in argon. The stress axis is indicated by the arrow.

Figure 4. Grain boundary cavity density vs. hydrogen exposure time for the A387 quenched and tempered steel. Data for hydrogen exposure (550°C, 2000 psi) with and without applied stress (16 ksi) are compared. The data obtained this quarter are for hydrogen exposure involving stress. The symbols are experimental data points and the lines are calculated.

510 MPa for the same conditions and $P_{H_2} = 2000$ psi. At 600°C and under the same stress and hydrogen pressure the estimated effective stress concentration and methane pressure are 770 MPa and 370 MPa, respectively. Table 4 summarizes the results of the nucleation measurements and calculations for the quenched and tempered material under stress at $P_{H_2} = 2000$ psi.

Tests were performed also during this quarter to investigate the effect of varying hydrogen pressure under an applied stress. Figure 5 shows the observed grain boundary cavity number densities from specimens of the quenched and tempered steel exposed at two different hydrogen pressures at 600°C while under a tensile stress of 16 ksi. Also included is a measurement for a specimen crept in air at the same temperature and stress level. The data for $P_{H_2} = 2000$ psi were obtained in our earlier work. The data, collected this quarter, were for a hydrogen pressure of 200 psi.

By using the value of $\sigma_{conc.}$ (770 MPa) estimated based on the data for $P_{H_2} = 2000$ psi and an applied stress of 16 ksi at 600°C, we can calculate from Equations 2 and 3 the value of τ and $\dot{N}$ for $P_{H_2} = 200$ psi and $P_{H_2} = 0$ under, otherwise, the same conditions. The results of the calculations are shown as the lines in Figure 5 and summarized in Table 5. The estimated methane pressures are 370 MPa for $P_{H_2} = 2000$ psi, 15 MPa for $P_{H_2} = 200$ psi. It is seen from Figure 5 that calculations yielded incubation periods much shorter than the ones observed experimentally.

D. Discussion

The new data obtained during this quarter allowed a further test of the nucleation model as described in sections B and C. We note, for example, that the data for $P_{H_2} = 2000$ psi at 500°C indicate an incubation stage longer than 180 days, compared to a 90 day incubation period predicted by extrapolation from data of higher temperatures. We expect

TABLE 4

THE EFFECT OF APPLIED STRESS

Quenched and Tempered

Temp. (°C)	P_{H_2} (psi)	Stress (MPa)	<u>Calculated</u>		<u>Experimental</u>		<u>Calculated</u>
			τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	$\sigma_{\text{conc.}}$ (MPa)
600	2000	110	.3	2.9×10^{-1}	.5	4.0×10^{-1}	770
550	2000	110	3.3	6.4×10^{-2}	4	$8.8 \times 10^{-2} \neq$	400

 $\neq$ Data obtained this quarter

TABLE 5

16 KSI STRESS, PLUS 200 PSI H_2 AT 600°C

Quenched and Tempered

<u>Calculated (using stress concentration from 600°C, 2000 psi data)</u>			<u>Experimental</u>	
τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	$\sigma_{\text{conc.}}$ (MPa)	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)
.6	2.3×10^{-1}	770	$6 < \tau < 14$	-

Figure 5. Grain boundary cavity density vs. exposure time for the A387 quenched and tempered material. Data is presented for exposure (600°C, 16 ksi applied stress) in hydrogen at 2000 psi and 200 psi and in air at 0 psi. The symbols are data points and the lines are calculated, using the stress concentration obtained from the data at 600°C, 2000 psi, 16 ksi to obtain predictions for the other two conditions.

that further modification of the model involving the adjustment of the values of various parameters, will be made when a larger increment of the new data becomes available. At this time, we suspect that, a most likely candidate for further attention would be the value of the carbon activity, a parameter which determines methane fugacity, and thus, the functional dependence of P_{CH_4} on P_{H_2} and T (19). The carbon activity has not been measured for the Cr-Mo steels and is almost certainly dependent on time at elevated temperatures.

The hydrogen pressure dependence of the nucleation data at 600°C under a stress of 16 ksi suggests that the present nucleation model grossly underestimates the incubation time for lower hydrogen pressures, or in air. This result could mean that the relative value of $\alpha_{\sigma=0}$ and $\sigma_{conc.}$ in Equation 4 requires further adjustment or that the nucleation model used is too simple for the simultaneous effect of hydrogen pressure and applied stress.

E. Future Work

During the next quarter we should begin to obtain data for the quenched and tempered specimens under stress at 500°C. We have already initiated the required experiments.

In the area of stress induced cavity growth, stress-to-rupture data are being obtained at 600°C in air for creep specimens with prior hydrogen exposure. These data are expected to yield cavity growth rate as a function of applied stress level.

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ORNL-3.3(B) -- EFFECTS OF HEAT TREATMENT ON MICROSTRUCTURE
AND MECHANICAL PROPERTIES OF Cr-Mo STEELS

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INTRODUCTION

This program is a new effort in FY 1982 and has the general concept of examining the effects of various heat treatment procedures on the microstructure and mechanical properties of modified chromium-molybdenum steels. It is related to a previous program, "Evaluation of Fracture Toughness of Pressure Vessel Steels," but is specifically directed at an understanding of microstructural changes that occur in the modified alloys and the effects of those changes on mechanical properties. The former program examined mechanical properties, particularly fracture toughness, of several steels considered to be candidates for the construction of large second-generation commercial pressure vessels, including SA-516, grade 70 (C-Mn-Si); SA-204, grade B (C-1/2 Mo); SA-533, grade B, class 1 (Mn-1/2 Mo-1/2 Ni); SA-387, grade 22, class 2 (2 1/4 Cr-1 Mo); and A-543, grade B, class 1 (Ni-Cr-Mo). Minimum specified tensile strengths range from 450 MPa for the SA-204, grade B, to 725 MPa for the A-543, grade B, class 1. The modified alloys referred to are all 2 1/4 Cr-1 Mo steels with either Ti-V-B or Ni-V additions to increase both the hardenability and the high-temperature strength over those of standard 2 1/4 Cr-1 Mo as specified by SA-387.

The scope of work of the new program on detailed examination of the modified chromium-molybdenum steels includes the identification of microstructures and microstructural constituents obtained from various heat treatment schedules and the verification of published continuous-cooling transformation diagrams. The effects of time and temperature on microstructure and mechanical properties from postweld heat treatments will be examined to characterize and compare tempering parameters for the various alloys. Characterization of each steel will be through the use of

metallurgical tools such as transmission electron microscopy, scanning electron fractography, microprobe analysis, energy dispersive x-ray analysis, and optical light microscopy. Mechanical properties of interest include tensile, Charpy impact, and fracture toughness.

Fracture toughness behavior will be examined with advanced elastic-plastic methodology such as the computer-controlled J -integral unloading compliance test to characterize not only initiation toughness but also resistance to ductile tearing (e.g., tearing modulus). Further, high-temperature aging under no stress, creep stress, and strain-cycling conditions will be introduced to simulate service-related softening and to verify metallurgical and mechanical stability of a damage accumulation model. Again, extensive microscopic analyses and mechanical property tests will be performed in these evaluations. An integral part of the program is a study of weldability for all the alloys mentioned. Initial studies will concentrate on the simulation of base materials heat-affected zones that would arise from different welding processes and conditions. Mechanical properties tests and metallurgical analyses will be performed as outlined previously.

RESULTS FROM PRIOR QUARTERS

Although the emphasis of the AR&TD Program on pressure vessel steels has shifted toward an exclusive investigation and comparison of modified and unmodified Cr-Mo steels, there exists some prior work germane to the subject.

Recent investigations have emphasized testing of modified 2 1/4 Cr-1 Mo steels. We have examined the tensile and Charpy impact toughness of Japan Steel Works (JSW) Ti-V-B modified alloy plate (29 mm thick) when subjected to various heat treatments, including the simulation of water quenching of 254- to 305-mm-thick plate. The tensile properties of the U.S. Steel Ni-V modified alloy fabricated with three different deoxidizing processes were also determined after various heat treatments that simulated water quenching for plate thickness as done for the JSW

steel. These results were reported in previous quarterly reports of this series. Charpy impact toughness specimens were machined from the U.S. Steel Ni-V modified alloy for testing this quarter.

DISCUSSION OF CURRENT ACTIVITIES

V-Ti-B Modified 2 1/4 Cr-1 Mo Steel

Work began this quarter on characterizing the steel sections received from the Japan Steel Works (JSW), which were taken from a 16t casting and forge-reduced to various thicknesses. The as-received material was produced by melting in a basic electric furnace, vacuum casting, and forging, followed by normalizing at 1020°C for 15 h, air cooling and tempering at 700°C for 10 h, and furnace cooling. A further heat treatment (called a "quality" heat treatment) was performed by holding the material at 950°C for 7 h, followed by a water quench, and at 650°C for 15 h, followed by an air cool. The so-called quality heat treatment improved significantly the Charpy V-notch (C_v) toughness. For instance, previous work¹ on an earlier JSW heat of modified 2 1/4 Cr-1 Mo steel showed that the quality heat treatment decreased the transition regime from 116 to -51°C at the 68-J energy level and increased the upper shelf from 136 to 272 J for one particular specimen orientation.

Four blocks of steel forged from the 16t casting have been supplied to ORNL. The average chemical compositions of these blocks — designated A through D — are listed in Table 1.

The four blocks of steel are currently being cut into manageable sizes for the examinations described earlier in this report.

High-Temperature Damage Accumulation in Ti-V-B Modified 2 1/4 Cr-1 Mo Steel

Twelve creep-rupture tests at 482, 510, and 538°C have been started on the Ti-V-B-modified 2 1/4 Cr-1 Mo steel provided to us by JSW. Typical plots for the log creep rate versus accumulated creep strain (Fig. 1)

Table 1. Results of the check analyses for the modified 2 1/4 Cr-1 Mo forged steel samples

Element	Composition (wt %)			
	Block A	Block B	Block C	Block D
C	0.14	0.14	0.11	0.11
Si	0.06	0.07	0.06	0.06
Mn	0.48	0.49	0.46	0.47
P	0.010	0.008	0.006	0.006
S	0.006	0.007	0.005	0.006
Ni	0.15	0.16	0.15	0.15
Cr	2.33	2.34	2.29	2.30
Mo	1.02	1.00	0.95	0.95
V	0.26	0.26	0.26	0.26
Ti	0.034	0.032	0.030	0.036
B	0.0018	0.0024	0.0022	0.0026
Al	0.007	0.015	0.019	0.024
Sn	0.007	0.008	0.007	0.007
As	0.008	0.009	0.009	0.008
Sb	0.0020	0.0017	0.0015	0.0014
Cu	0.09	0.08	0.08	0.08
N	0.0092	0.0085	0.0071	0.0076
O	0.0023			

Source of data: T. Ishiguro et al., "Mechanical and Metallurgical Properties of a 16-Ton Medium Size 2 1/4 Cr-1 Mo-1/4 V-Ti-B Pressure Vessel Steel Sample for Elevated Temperature Applications," Japan Steel Works Data Sheet Series No. CLR-B, MR81-2, Muroran, Hokkaido, Japan, March 1981.

for tests at 482°C reveal an initial decrease in creep rate followed by an increase after less than 1% strain. We consider this acceleration in creep rate to be a manifestation of internal damage in the material. For exploratory analysis, we have assumed that the following rate equation holds for time-dependent deformation under uniaxial stresses:

$$\dot{\epsilon} = A \sinh[\beta(\sigma - \alpha)/I] , \quad (1)$$

Fig. 1. Creep rate versus strain for Ti-V-B-modified 2 1/4 Cr-1 Mo steel at 482°C.

where $\dot{\epsilon}$ is the creep rate, A is a temperature-dependent constant related to the deformation process, β is a material constant, σ is applied stress, and α and I are state variables related to the metallurgical structure. We chose α to be a kinematic hardening state variable that reflects the movement of the point in stress space where the strain rate is zero. We chose I to be an isotropic hardening state variable that reflects changes in the global hardness as a function of deformation history. With reference to Fig. 1, we assume that the initial decrease in creep rate with increasing creep strain is a manifestation of a shift in α .

Initially, α is zero but increases toward the value of the applied stress as gliding dislocations are immobilized through interaction with other dislocations or precipitate particles. Eventually, α attains a stable value that depends on the applied stress. We assume that the value of I decreases gradually as a result of an increase in the total dislocation density or the Ostwald ripening of the vanadium and titanium carbides that are responsible for the initial high strength of the alloy. It is apparent from Eq. (1) that a decrease in I will produce an increase in $\dot{\epsilon}$ and an apparent increase in the damage rate. Thus, our studies of damage accumulation will focus on the behavior of the isotropic hardening state variable I . To determine I , one must devise special tests and analysis methods and relate changes in I to changes in microstructure.

At high stresses Eq. (1) becomes:

$$\dot{\epsilon} = A/2 \exp[\beta(\sigma - \alpha)/I] , \quad (2)$$

and at the start of the creep test α is near zero; hence,

$$\dot{\epsilon}_0 = A/2 \exp[\beta(\sigma/I_0)] , \quad (3)$$

or

$$\ln \dot{\epsilon}_0 = \ln A/2 + (\beta/I_0)\sigma , \quad (4)$$

where the subscript zero refers to the initial conditions. Equation (4) shows that a plot of $\ln \dot{\epsilon}$ versus σ should produce a strain line with the slope β/I_0 . Our data at 482 and 538°C more or less conform to Eq. (4) and indicate that β/I_0 is independent of temperature.

Further analysis of Eq. (2) results in the following relation at the condition of minimum creep rate:

$$\dot{\alpha}/\dot{I} = -(\sigma - \alpha)/I . \quad (5)$$

Experimentally, we should be able to evaluate α at this point by strain transient dip tests and to evaluate I from yield stress probes in tension and compression.

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UCSB-3.3 — ANALYSIS OF HYDROGEN ATTACK
ON PRESSURE VESSEL STEELS

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INTRODUCTION

Steels used for fabrication of coal conversion vessels are exposed to hydrogen at high temperatures and pressures ($T \sim 450^\circ\text{C}$ and $P_{\text{H}_2} \sim 15$ MPa). Under these conditions hydrogen readily diffuses into the metal matrix and may react with carbon at internal surfaces to form methane. This phenomenon, known as hydrogen attack (HA), can result in internal decarburization and the nucleation, growth and eventual coalescence of grain boundary cavities. These microstructural changes, in turn, result in severe degradation of mechanical properties. Hence, HA may be a serious failure mechanism for thick-walled pressure vessels.

Selection of "safe" hydrogen pressure and temperature limits have been based on the empirical Nelson Curves; these curves have been developed for various broad alloy classes and qualitative failure criteria. However, because of limited data and operating experience under the conditions pertinent to coal conversion technologies and probable requirements for fail-safe operation, Nelson curves may not be adequate for designing thick-walled pressure vessels.

The purpose of this research is to develop physical models of the HA process describing important mechanisms and containing pertinent environmental and metallurgical parameters. These models are then used to statistically correlate engineering and laboratory data and to extrapolate the data to predict HA behavior under actual vessel service conditions.

RESULTS FROM PRIOR QUARTERS

Hydrogen Attack in Carbon Steels

Hydrogen attack data of McKimpson¹ on carbon steel was analysed to identify mechanisms of nucleation and growth of cavities during incubation stage. The first step in this effort was to develop an accurate basis for calculating equilibrium methane pressures as controlled by carbon activity (hence, Fe_3C carbide) and hydrogen pressure. Further, it was shown that the rate of nucleation of HA cavities was not consistent with the classical nucleation mechanisms. Hence, a nucleation model was developed based on unstable growth of a fraction of a pre-existing distribution of microvoids and/or gas bubbles. The model predicts cavity spacings of $\sim 1\text{-}2\text{ }\mu\text{m}$ at high hydrogen pressures and higher spacings at low hydrogen pressures. These are qualitatively consistent with experimental observations of cavity spacings. A major advantage of the model is that it has few adjustable parameters which can be measured, in principle, by laboratory experiments.

It was also shown that the growth of HA cavities is consistent with a constrained diffusion growth model.² The analysis indicated growth by vacancy diffusion along the grain boundary provided the methane pressure in the cavity exceeds a threshold pressure. Further, threshold pressure, measured experimentally, decreases with increases in temperature. It is well established that two-phase interfaces are not good sources or sinks for vacancies. For diffusional growth of cavities to continue, the atoms removed from the cavity should be plated uniformly along the grain boundary, otherwise internal stresses will be generated at the precipitates in the grain boundary which oppose the growth of the cavity. A constrained cavity growth model was developed in which the internal stresses at the precipitates were relieved by local plastic deformation of matrix. The predictions of the model were in excellent agreement with McKimpson's¹ data.

The model was also used to calculate incubation times for hydrogen attack in carbon steels which were in good agreement with a number of

experimental observations. A Nelson-type curve constructed using the model was also found to be in good agreement with published versions.

HA in $2\frac{1}{4}$ Cr - 1 Mo Steels

The constrained diffusion growth model developed for carbon steel was extended to $2\frac{1}{4}$ Cr - 1 Mo steels by considering two carbide species, M_3C tempered carbide and Cr_7C_3 carbide with higher stability. Experimental data indicates that HA cavities are generally observed on only a fraction of grain boundaries. Often cavities are closely spaced on isolated grain boundaries surrounded by a cage of uncavitated grains^{1,3}. Under these conditions the cavity growth rate may be determined by the rate of deformation of cage and not by the diffusional kinetics. A cavity growth model based on geometric constraints was developed for HA conditions. The model was calibrated using the recent dilatometry data of Yu and Shemon⁴ on a quenched and tempered $2\frac{1}{4}$ Cr - 1 Mo steel. Further, the model predicts that $2\frac{1}{4}$ Cr - 1 Mo steels containing unstable carbide M_3C carbide are susceptible to HA where as steels containing higher stability carbides such as Cr_7C_3 and Mo_2C are unlikely to suffer HA. This is consistent with the experimental observation of Geiger and Angelis⁵. The Nelson curve predicted by the calibrated model lies above the standard API decarburization curve.

The effect of external stresses on HA cavity growth rates was also considered. The growth rates predicted by the model in the presence of an external stress were considerably higher than those in absence of the stress. The model predicts decrease in rupture time for creep tests under hydrogen exposure conditions which is consistent with the experimental observations^{6,7}. Further, the applied stress will shift the Nelson curve to lower temperatures and hydrogen pressures.

A creep fracture map $2\frac{1}{4}$ Cr - 1 Mo steel was constructed using simple models for high temperature fracture such as transgranular, triple point cracking and cavitation fracture. Both the rupture times and fracture modes predicted for the alloy were in good agreement with the data. The effects of HA on the creep fracture map was also

considered. The creep fracture map under hydrogen exposure conditions indicates the dominance of regime of intergranular fracture and the reduction in rupture times.

DISCUSSION OF CURRENT ACTIVITIES

HA in 2½ Cr - 1 Mo steels

In previous quarterly reports we have presented a grain boundary bubble growth model based on geometric constraints due to inhomogeneous distribution of cavities. The model has been developed further during this quarter. Particularly, effects of diffusion creep of matrix on the cavity growth are considered here.

Figure 1 shows schematically a cavitated boundary between grains A and B being surrounded by uncavitated grains. If the strain rate on the cavitated boundary due to atom plating is greater than that of the surrounding material, then cavity growth will be constrained. Assuming that the methane pressure within the cavities is constant and equal to equilibrium methane pressure, P_o , a force balance results in

$$f_b \frac{\pi}{4} x^2 P_o - \frac{\pi x}{2 l} \cdot \gamma = \sigma_1 \cdot f_b + \sigma_2 (1 - f_b) \quad (1)$$

where f_b is the fraction of grain boundaries cavitated, σ_1 is the stress over the cavitated region, σ_2 is the stress in the uncavitated region, γ is the surface energy and $x = r/l$, r is the radius of the cavity and l is the cavity half spacing.

Further the strain rate in cavitated and uncavitated regions should be the same. Strain rate in the cavitated region is given by

$$\dot{\epsilon}_c = \frac{dv/dt}{\pi l^2 d} \quad (2)$$

where dv/dt is the cavity growth rate and d is the grain size. The cavity growth rate is assumed to occur by vacancy diffusion along the grain boundary⁸ and is given by

Fig. 1. Schematic diagram showing geometric constraint for cavity growth.

$$\frac{dv}{dt} = \frac{2\pi\Omega\delta_b D_b}{kT} (\sigma_1 + P_o - \frac{2\gamma}{r}) f(x) \quad (3)$$

where δ_b is the width of grain boundary, D_b is boundary diffusivity, Ω is atomic volume, k is the Boltzmann's constant, T is temperature in degrees Kelvin and $f(x)$ is boundary ligament stress term.

$$f(x) = \frac{1 - x^2}{x^2 (1 - \frac{x^2}{4}) - \frac{3}{4} - \ln x} \quad (4)$$

The stress σ_2 in the uncavitated region or cage will be determined by the deformation mechanisms in that region. In the previous report we assumed that deformation in cage occurs by power-law creep as given by

$$\dot{\epsilon}_g = B \sigma_2^n \quad (5)$$

where $\dot{\epsilon}_g$ is the minimum or steady-state creep rate, and B and n are constants for materials.

It is fairly well established that the power-law creep parameters B and n are sensitive to applied stress and temperature. For example, Cane⁹ has reported for 2½ Cr - 1 Mo steel n decreasing from a value ~ 12 for stresses greater than 150 MPa to ~ 4 for $\sigma < 150$ MPa at 565°C. Further, the apparent activation energy for creep also varies with temperature. Hence, extrapolation of high temperature power-law creep data to lower temperatures and stresses may result in under estimation of creep rates. This factor together with use of minimum creep rate in equation (5) makes the analysis less conservative.

Diffusion creep is often found to be dominant in fine grained materials at low stresses. Unlike the uncertainties involved with power-law creep extrapolations to low stresses, the form of the rate equations for diffusion creep are well established. Further, the Nelson curves predicted by the model will be lower bound curves since

the diffusion creep predicts maximum creep rates at low stresses and temperatures. Hence, deformation of the cage by diffusion creep is considered in the present analysis.

COMPARISON OF EXPERIMENTAL DATA

We again will calibrate our model using the kinetic data of Yu and Shewmon⁴ for a quenched and tempered 2½ Cr - 1 Mo steel. The presence of M_3C carbide in the steel is assumed because the analysis, even with diffusion creep, showed that the equilibrium pressures of higher stability carbides Cr_7C_3 and Mo_2C appear to be too low (less than 50 MPa) to cause the observed expansion rates. The equilibrium constant, K_o , for methane reaction for M_3C carbide was taken from the work of Geiger and Angelis⁵ as

$$K_o = 1.95 \times 10^{-6} \exp \left(\frac{12121}{T} \right) \text{ MPa}^{-1} \quad (6)$$

The rate equation for diffusion creep is given by¹⁰⁻¹²

$$\dot{\epsilon} = \frac{14D_l \Omega \sigma}{kTd^2} + \frac{14\Omega \delta_b D_b \Omega \sigma}{kTd^3} \quad (7)$$

where D_l is the lattice diffusivity. The first term on the right hand side of equation (7) gives the strain rate for vacancy flow through the lattice (Nabarro-Herring creep^{10,11}) and the second term is for the vacancy flow along the grain boundary (Coble creep¹²). The former is dominant at high temperatures and the latter at low temperatures.

Figure 2 shows the comparison between the model predictions and the temperature cycling data for Yu and Shewmon⁴ for hydrogen pressure of 20.3 MPa. The parameters used in the correlation are given in Table 1. The cavity growth rate, dv/dt , predicted by the model (equation (3)) was converted to specimen expansion rate, DLDT, using the relationship

$$DLDT = \frac{1}{3} \rho_c \frac{dv}{dt} \quad (8)$$

Fig. 2. Comparison between model predictions and experimental data of Yu and Shewmon⁴.

TABLE I

Parameters used for 2½ Cr - 1 Mo Steel in Comparison Between
the Model Predictions and Experimental Data

Parameter	Value	Reference
R	$8.314 \text{ J K}^{-1} \text{ mole}^{-1}$	
Ω	$1.18 \times 10^{-29} \text{ m}^3$	
k	$1.38 \times 10^{-23} \text{ J K}^{-1}$	
d	$5 \times 10^{-5} \text{ m}$	4
K_o	$1.95 \times 10^{-6} \exp \left(\frac{12121}{T} \right) \text{ MPa}^{-1}$	5
N_c	$2.5 \times 10^{11} \text{ m}^{-2}$	6,7
$\delta_b D_b$	$1.1 \times 10^{-12} \exp \left(- \frac{173700}{RT} \right) \text{ m}^3 \text{ s}^{-1}$	16
D_l	$2.0 \times 10^{-4} \exp \left(- \frac{251000}{RT} \right) \text{ m}^2 \text{ s}^{-1}$	17
G	$6.4 \times 10^4 (1 - (T - 300) 4.7 \times 10^{-4}) \text{ MPa}$	18
γ	1.95 J m^{-2}	19

where ρ_c is the volume cavity density given by $\rho_c = 3f_b N_c / d$ and N_c is the local cavity density on the cavitated grain facet.

As discussed in detail in the previous report the important parameter in the model is f_b . It is evident from Figure 2 that agreement between the Yu and Shewmon⁴ data and the model is achieved for $f_b \sim 0.1$. Even though apparent activation energy, ~ 135 kJ mole, predicted by the model is considerably less than the experimental value of $\sim 206 \pm 38$ kJ mole⁻¹, the absolute magnitudes of expansion rates are in good agreement. Taking values for $f_b = 0.1$ and $x = 0.1$, the model predictions are compared with the hydrogen pressure cycling data as shown in Figure 3. Again the expansion rates predicted by the model are in reasonable agreement with the data. However, the hydrogen pressure exponent ~ 1 predicted by the model is also significantly less than the experimental values of 1.7 ± 0.7 and 2.8 ± 1.2 at 570 and 580°C respectively.

In the previous report we had shown that the data given in Figures 2 and 3 can be modeled using $f_b \sim 0.15$ when deformation in the cage occurs by power-law creep as

$$\dot{\epsilon} = 7.8 \times 10^7 \sigma^4 \exp \left(- \frac{400000}{RT} \right) \text{ s}^{-1}, \text{ for } \sigma < 150 \text{ MPa} \quad (9)$$

$$\dot{\epsilon} = 5.1 \times 10^{-10} \sigma^{12} \exp \left(- \frac{400000}{RT} \right) \text{ s}^{-1}, \text{ for } \sigma > 150 \text{ MPa} \quad (10)$$

The temperature and hydrogen pressure dependence predicted by this model were in somewhat better agreement with the experimental data; however, it must be emphasized that the data is taken over a very limited range of temperatures and pressures, and is subject to considerable uncertainty. Hence, it is useful to seek other indications of the rate controlling mechanism.

Figure 4 shows a high temperature deformation mechanism map for 2½ Cr - 1 Mo steels. The map is constructed assuming that diffusion creep rate in the material is given by equation (7) and using equations (9) and (10) for power-law creep. A thick line separates the regions of power-law creep and diffusion creep. Also shown in the

Fig. 3. Comparison between model predictions and experimental data of Yu and Shewmon⁴.

Fig. 4. High temperature deformation mechanism map for 2½ Cr - 1 Mo steel with grain size 50 μm. The stresses, σ_2 , in the cage predicted by the model for power-law and diffusion creep accommodation are shown.

Figure 4 are the stresses, σ_2 , in the cage estimated for two deformation mechanisms considered in the correlation. Clearly, the stresses predicted for the diffusion creep accommodation are lower than those for the power-law creep, and in fact, the stresses predicted for the latter also lie in the diffusion creep region of the map. This would suggest that matrix deformation by diffusion creep will be dominant. Since application of the model involves extrapolation to even lower temperatures and stresses, it would seem imprudent (nonconservative) to simply base the calculations on power-law creep models. Stated differently, use of the diffusion creep model might be expected to result in a lower bound prediction (within the basic assumptions of the model). Therefore, such a calculation was carried out.

Figure 5 shows the Nelson-type curve predicted by the calibrated model based on a failure criteria of 0.1% swelling at 100,000 hours for $2\frac{1}{2}$ Cr - 1 Mo steel. Also shown in Figure 5 are the standard API decarburization curve(1) and the model prediction based on power-law creep accommodation(2). The Nelson curve predicted by diffusion creep accommodation model(3) lies below that predicted by the power-law creep accommodation. Hence, the Nelson curve obtained in the the present analysis might serve as an estimated lower bound curve. The lowering of the Nelson curve to $\sim 450^\circ\text{C}$ would indicate that hydrogen attack may be a problem in the pressure vessels used for coal conversion technologies.

The Nelson curve predicted by the diffusion creep accommodation model also suggests that HA may occur in $2\frac{1}{2}$ Cr - 1 Mo steels even at low hydrogen pressures. This arises because equation (7) which was used to model diffusion creep in the material, implies that grain boundaries are perfect sources and sinks for vacancies. However, grain boundaries in $2\frac{1}{2}$ Cr - 1 Mo steels in tempered condition contain high density of carbides. It is well established that the presence of hard particles in the grain boundaries will result in inhibition of diffusion creep¹³⁻¹⁴. The particle/matrix boundary can not readily emit or absorb vacancies and hence, an internal stress will develop at the particles which will oppose diffusion creep. A threshold stress,

Fig. 5. Comparison between Nelson type curves predicted by the model and the API decarburization curve for 2 1/4 Cr - 1 Mo steel.

1. Standard API surface decarburization curve.
2. Power-law creep accommodation.
3. Diffusion creep accommodation.
4. Diffusion creep accommodation with threshold stress of 10 MPa.

σ_o , will result below which deformation will cease and the diffusion creep rate will be given by

$$\dot{\epsilon} = \frac{14 D_o \Omega (\sigma - \sigma_o)}{kT d^2} + \frac{14 \pi \delta_b D_b \Omega (\sigma - \sigma_o)}{kT d^3} \quad (11)$$

Harris¹⁵ has developed a crude energy balance model for threshold stress in which vacancies will be generated and absorbed by punching out interstitial and vacancy loops respectively, in matrix regions adjacent to the particles. The magnitude of threshold stress is given by

$$\sigma_o = N_p \cdot \frac{Gbr}{2} \ln \left(\frac{r_p}{b} \right) \quad (12)$$

where N_p is the particle density, b is the Burgers vector, r_p is the particle radius and G is the shear modulus of the matrix. Taking $N_p \sim 10^{12} \text{ m}^{-2}$, $r_p \sim 2.5 \times 10^{-7} \text{ m}$, $b \sim 2.5 \times 10^{-10} \text{ m}$ and $G \sim 4.8 \times 10^4 \text{ MPa}$, the threshold stress estimated is $\sim 10 \text{ MPa}$. This appears to be a reasonable magnitude for threshold stress. However, comparison with experimental data could not be made because of lack of diffusion creep data.

The threshold stress can be included in the cavity growth model by modifying equation (1) as

$$f_b \cdot \frac{\pi}{4} x^2 \cdot P_o - \frac{\pi}{2} \frac{x}{l} \cdot \gamma - \sigma_o = \sigma_1 \cdot f_b + \sigma_2 \cdot (1 - f_b) \quad (13)$$

Physically, the threshold stress has the same effect as an external hydrostatic pressure. The rest of the analysis remains the same. The effect of a threshold stress of 10 MPa on the Nelson curve(4) is also shown in Figure 5. As expected, the effect is large at low hydrogen pressures and has negligible effect at large hydrogen pressures. The threshold hydrogen pressure for hydrogen attack is increased to $\sim 6.5 \text{ MPa}$.

The analysis presented in this section is based on the assumption that diffusion creep occurs in 2½ Cr - 1 Mo steel. However, it should

be emphasized that we have not found direct experimental evidence for diffusion creep in the material. The creep rates are probably too low to be measured in most laboratory tests. However, diffusion creep may be important for the long-time, low-temperature and low-stress conditions typical of coal conversion pressure vessels. Further, the analysis yields lower bound Nelson curves for design purposes.

HA Exposure Facility

For the purpose of investigation of HA in $2\frac{1}{2}$ Cr - 1 Mo steel a hydrogen exposure facility is being set up. The equipment is schematically shown in Figure 6. The autoclave is made of a seamless tube (2" I.D. x 3.5" O.D. x 26" length) of 316 stainless steel. The autoclave is rated for 3000 psi at 600°C. Both the autoclave and the high pressure fittings were supplied by High Pressure Equipment Co., Erie, PA. The autoclave is heated externally by a three zone electric resistance furnace. The power for the three zones can be adjusted through separate variacs. Furnace is controlled by a Leeds and Northrop proportional plus automatic reset controller. Placement of the control thermocouple can be varied. A thermocouple well is provided in the autoclave which will be used to measure temperature along the length of the tube.

Currently tests are being done to measure the extent of uniform temperature zone by changing the power inputs to the furnace zones. Because of large heat loss through the stainless steel tube wall we have been able to obtain only ~ 6" of uniform zone ($\pm 2^\circ\text{C}$) in the center. Attempts will be made to increase the uniform zone by using separate controllers for the outer zones and the central zone of the furnace. The goal is to develop a ~ 10" uniform zone. In addition, experiments are being conducted to determine if it is possible to produce several smaller uniform zones (2-3") at different temperatures (2 to 3 values). This would facilitate conducting kinetic studies by allowing prolonged exposures at different temperatures.

Because of the limited exposure volume we are currently attempting to optimize the experimental matrix. A section of the Lukins 12" plate

Fig. 6. Schematic diagram of experimental set up for HA study.

has been requested from Oak Ridge National Laboratory for our initial studies. Plans call for reheat treating this alloy to produce a range of carbide species with 3 to 4 metallurgical conditions (including the as-received); further, we will subject some of this material to $\sim 1\text{-}2\%$ prior creep strain.

These alloys will be exposed to hydrogen at approximately 3000 psi at temperature of 525 to 550°C. The accumulation of HA damage will be monitored using nonconservative dimensional changes induced by the growth of HA cavities. This will be accomplished by periodically measuring length change using a precision profilometer and a paired, unexposed reference bar (as well as a thermal control); strain rates of $< 10^{-11} \text{ s}^{-1}$ should be resolvable using this procedure.

Upon the accumulation of significant damage (e.g. strains $> 10^{-5}$ to 10^{-4}) the alloys will be subject to mechanical testing (initially, tensile and instrumented Charpy V-notch tests) and microstructural examination (using transmission and scanning electron microscopy and energy-dispersive x-ray analysis). These initial studies are expected to involve hydrogen exposure periods of 1500-2000 hours.

SUMMARY AND CONCLUSIONS

The effect of diffusion creep accommodation of matrix in an HA cavity growth model based on geometric constraints is considered. The cavity growth rates predicted by the model are consistent with the recent dilatometry data on $2\frac{1}{2}\text{ Cr} - 1\text{ Mo}$ steel. It has been shown that the Nelson curve predicted by the calibrated model lies well below the curve obtained in the previous report based on power-law creep accommodation of matrix. Hence, it might be used as a lower bound Nelson curve. The effect of threshold stress ($\sim 10\text{ MPa}$) for diffusion creep is to increase the threshold hydrogen pressure to $\sim 6.5\text{ MPa}$. The present analysis supports the conclusion arrived earlier that $2\frac{1}{2}\text{ Cr} - 1\text{ Mo}$ steels containing unstable carbide M_3C are susceptible for HA where a steels containing higher stability carbides such as Cr_7C_3 and Mo_2C are less likely to suffer HA. Finally, a description of our new HA experimental facility is given along with a tentative research plan.

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WEC-3.3 — STUDY TO OPTIMIZE Cr-Mo STEELS to RESIST
HYDROGEN AND TEMPER EMBRITTLEMENT

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INTRODUCTION

The primary objective of this program is to evaluate a range of Cr-Mo steels in order to assess the role of compositional variables on the susceptibility to hydrogen and temper embrittlement. The program is divided into two phases. Phase I is designed to establish the hydrogen embrittlement susceptibility of commercial 2-1/4Cr-1Mo steels provided by the American Petroleum Industry. This phase consists of two parts. The first part is to assess the hydrogen embrittlement characteristics of the steels at conventional strength levels (Ultimate Tensile Strength, UTS, in the range 60-80 ksi or 400-550 MPa). The second part is to measure the hydrogen embrittlement susceptibility of the peak hardness zone (PHZ) in the heat affected zone (HAZ) adjacent to the weld. Since few large weld samples were available, tests were also to be conducted on plate material heat treated to a higher strength level corresponding to that of the PHZ. This corresponds to an UTS of the order 100-110 ksi or 690-760 MPa.

Phase II consists of an evaluation of 32 laboratory heats with compositions arranged according to a statistical design and tempered in a bainitic condition to two strength levels, corresponding to the ranges used in Phase I. The primary evaluations are for temper embrittlement and hydrogen embrittlement. Comparison of the data generated from the laboratory heats can be made with commercial samples from Phase I of the program for hydrogen embrittlement and with an independent API program for temper embrittlement. Based upon the data to be generated in Phase

II, it is anticipated that compositional areas with high or low susceptibility to either form of embrittlement may be identified.

The original intention was to use a simple rising load test on fatigue precracked Charpy specimens for the hydrogen embrittlement study. However, because the yield strength of this class of steel is so low, a study of the effect of specimen size on the validity of the data was included in Phase I. Consequently, tests were carried out on 1T, 2T and 3T Compact Tension (CT) specimens for comparison.

As a result of this study, it became clear that the inexpensive Charpy test would not yield reliable data. Moreover, the rising load test on a standard CT specimen would not necessarily give the value of the threshold stress intensity in the H_2S environment (K_{Isc}). Two factors of considerable importance, i.e. the incubation time and plane-stress pinning of the crack, had to be considered in some detail. A review of the effects is given in Quarterly Report #4.

Since the revision of the test technique necessitated the use of larger specimens and a more complex test procedure, the scope of the program (but not the primary objectives) had to be revised. To date, it appears that the method for evaluating the hydrogen embrittlement susceptibility of the higher strength steels (690-760 MPa) is resolved.

The same technique that would satisfactorily produce cracking in the steels tempered to a higher strength level was totally unsuccessful for steels of a lower strength level. In order to obtain a screening test for the low strength steels, it was decided to introduce a more potent environment. The results of tests on both high and low strength steels subjected to the same (mechanical) test procedure using hydrogen sulfide gas saturated with water vapor for the environment appeared to be quite satisfactory in that steels over the entire strength level range were embrittled.

This report gives an example of the quality of a model derived from the regression analyses in predicting the temper embrittlement of commercial steels.

RESULTS FROM PRIOR QUARTERS

Temper embrittlement data for 32 heats of Cr-Mo steel, with Cr, Mo, Mn, Si, C and P as primary compositional variables, was generated for the steels tempered to two strength levels. The regression analyses of the data included eight independent variables, viz Cr, Mo, Mn, Si, C, P strength level (SL) and percentage of ferrite in the steel (PF). The dependent variables were the 40 ft-lb transition temperature (40ft-lbTT), the fracture appearance transition temperature (FATT) and the shift in the transition temperatures due to temper embrittlement termed $\Delta T(40)$ and $\Delta FATT$ respectively. The analyses were made very complex by the inclusion of the additional two independent variables SL and PF. Predictive models representing the embrittlement data derived from the study showed a significant improvement over currently available expressions.

DISCUSSION OF CURRENT ACTIVITIES

The second phase of the program has two components: i) the investigation of the effect of compositional variables (Mo, Cr, Mn, Si, C and P) on the susceptibility of the steels to temper embrittlement, and ii) the effect of the same variables on hydrogen embrittlement. The statistically designed set of 32 heats have been tempered to two strength levels. The temper embrittlement tests and the regression analyses of data have been completed. The models are currently being assessed by comparing predictions from the models with data obtained from independent tests. The independent test data was obtained from an American Petroleum Institute (API) program on temper embrittlement of Cr-Mo steels.⁽¹⁾ Hydrogen embrittlement tests on steels tempered to a higher strength level have been completed and the tests on the lower strength level steels are continuing. Tensile test data from all the samples, at both strength levels, has been obtained. These results will be used in the analysis of the hydrogen embrittlement data.

Temper Embrittlement Study

In the previous quarterly report the complexity of the regression analysis was discussed. The primary problem was associated with the inclusion of three extra independent variables in the analysis, viz strength level (SL), percentage ferrite (PF) and grain size (GS), in addition to the compositional variables Mo, Cr, Mn, Si, C and P. It was found that grain size was not an important variable within the range found in the laboratory samples. Analyses were attempted for samples with no ferrite and samples which had some percentage of ferrite in the otherwise bainitic structure. The results of these analyses were then inspected to assess the role of ferrite in temper embrittlement. This investigation showed that PF can influence temper embrittlement but the issue was clouded to some extent because PF is a function of the composition which is also included in the analysis.

It was found that the most important terms for the high strength set of samples were also present in the expressions for the low strength set. The analysis was therefore extended to produce a model for $\Delta T(40)$ for both high and low strength sets. This proved to be reasonably successful in that models with only eight terms had correlation coefficients of $>.8$. One of these models included the terms (in descending order of importance) MnP, CrC, P, MoP, SiP, CrP, Cr and SL. The terms MnP and SiP are commonly used in expressions relating temper embrittlement to composition^{(2),(3)}. However the term CrC, which always appears as an important term in these analyses does not appear to have been recognized before.

The plot of the observations (experimental data) compared with the model predictions is shown in Fig. 1. The scatter in this data is about $\pm 25^{\circ}\text{F}$ to 30°F .

The acid test of any model based upon the statistical design employed in this study lies in the quality of prediction of independent data. Fortunately in an earlier study for the API,⁽¹⁾ commercial steel samples were identically embrittled. (875°F for 1000 hrs). The comparison of this data with the predictions from the model described above are shown

in Fig. 2. It can be seen that the fit is reasonably good. Of particular interest is the prediction of the observed de-embrittlement of some samples.

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Fig. 1. Comparison of the predicted and observed 40 ft-lb transition temperatures for the laboratory heats using a model with eight terms

Fig. 2. Comparison of the predicted and observed 40 ft-lb transition temperatures for laboratory heats (open circles) and commercial steels (full circles) using a model with eight terms.

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MPC-3.4 - CORROSION IN
COAL LIQUEFACTION PROCESSES

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INTRODUCTION

A research program to study the corrosiveness of various coal liquefaction process fluids is being conducted at Southwest Research Institute (SwRI) under the technical direction of The Metal Properties Council, Inc. (MPC). The program includes two major tasks: (1) corrosion tests utilizing representative coal liquids obtained from liquefaction pilot plants; and (2) quantitative chemical analysis of the coal liquids used in the corrosion tests.

The objectives of this program are to:

- Determine the general susceptibility of carbon steels, stainless steels, and nickel-base alloys to corrosion in coal liquids.
- Identify and measure concentrations of suspected corrosive species in coal liquids before and after corrosion tests.
- Determine effects of temperature on the corrosion of metals and on the stability of corrosive species in coal liquids.
- Relate extent, type of corrosion, and corrosion mechanism(s) to corrosive species present in coal liquids.
- Provide background data for the interpretation of results of in-situ corrosion tests and failures in liquefaction plants.

As these objectives indicate, the major thrust of the program is directed toward determining the chemical species present in coal liquids which are responsible for corrosion, rather than toward the generation of corrosion-rate data suitable for use in plant design.

A detailed description of the program test matrix and test procedures may be found in the quarterly report for the period ending December 31, 1980. The current report summarizes data reported in previous quarters and presents new data developed during the period from October 1, 1981, through December 31, 1981. Latest liquids supplied to SwRI through December 31, 1981, are shown in Table 1. Thirty-seven liquids from three liquefaction processes--Solvent Refined Coal (SRC), H-Coal, and Exxon Donor Solvent (EDS)-- are received. The samples are from six pilot plants. Nine coals or coal mixtures were used in the production of the 37 samples. A four-position code number identifies each sample according to: plant, process, and mode; sample point or other description provided by pilot plant personnel; sequence number, for two or more samples obtained at the same location; and coal in use at the time the sample was taken. In cases where a plant has been operated in more than one process mode, different first-position identifiers are used for each of the modes.

RESULTS FROM PRIOR QUARTERS

The two major program task areas are: (1) the performance of corrosion coupon exposure tests utilizing coal liquids obtained from liquefaction pilot plants; and (2) quantitative chemical analyses of the coal liquids used in the corrosion tests. Results of 135 corrosion test exposures using 25 coal liquids were reported in the quarterly progress report for the period ending September 30, 1981.^(*) The duration of these tests was 100 hours. Results of 119 chemical analyses were reported in the same report; these analyses included 25 as-received liquids, 81 liquids removed from autoclaves after corrosion test exposures, and 13 liquids removed from autoclaves after "blank" exposures (tests in which no metallic coupons were exposed). Procedures used for corrosion test exposures and analytical test methods employed were reported in the quarterly progress report for the period ending December 31, 1980.

(*) In this report Coal Liquid G117 (from EDS ECLP Plant operating in the Bottoms Recycle Mode) was incorrectly identified as E817.

TABLE 1
LATEST COAL LIQUIDS SUPPLIED TO SwRI

<u>Plant Location/Process</u>	<u>Code</u>	<u>Description</u>	<u>Coal Liquid Sample</u>		<u>Boiling Range</u>	<u>Coal Used</u>
			<u>Date</u>	<u>Collected</u>		
Baytown, TX/EDS(ECLP)	E716	Light Atmospheric Gas Oil (Tray 23)	5-27-81		Medium	Illinois #6
Baytown, TX/EDS(CLPP)	G117 ⁽⁹⁾	Solvent Hydro- genation Feed	8/81		High	Big Brown
Baytown, TX/EDS(ECLP-- Bottoms Recycle Mode)	H429	Light Vacuum Gas Oil	Note (8)		Medium	Wyoming Sub- bituminous
Catlettsberg, KY/H-Coal	F116	Startup Oil	Note (8)		High	Illinois #6
Catlettsberg, KY/H-Coal	F216	Fractionation Column Bottoms	Note (8)		Medium	Illinois #6
Catlettsberg, KY/H-Coal	F316	Light Oil Point 210	Note (8)		Medium	Illinois #6
Catlettsberg, KY/H-Coal	F416	Fractionation Column Side Draw	Note (8)		Low	Illinois #6
Catlettsberg, KY/H-Coal	F516	Q207 Bottoms	Note (8)		Low	Illinois #6

(8) Collection date not reported.

(9) Sample G117 was incorrectly identified as Sample E817 in earlier reports.

With a few exceptions for carbon steel, corrosion rates of the six alloys tested have been low, and no significant corrosion has occurred in any of the austenitic alloys (Type 316 stainless steel, Hastelloy C-276, and Incoloy 825). Comparison of the chemical compositions of as-received fluids with corrosion rates for carbon steel and Type 410 stainless steel in tests at 500°F suggests that the corrosion susceptibility of these alloys depends upon the concentrations of three species--phenols, chlorides, and nitrogen compounds.

A specialized test procedure, developed to determine the quantities of weak and strong amines present in coal liquids, was described in the quarterly report for the period ending September 30, 1981. In addition, two series of special corrosion test exposures have been conducted. The first was performed to determine the effects of the ratio of solution volume to coupon surface area in 100-hour tests. These tests were described in the quarterly report for the period ending June 30, 1981; results indicate no significant differences in corrosion rates for ratios of $1 \text{ cm}^3/\text{cm}^2$, $20 \text{ cm}^3/\text{cm}^2$, and $80 \text{ cm}^3/\text{cm}^2$.

The second series of special tests was performed to evaluate the effects of exposure time and possible depletion of corrosive species on corrosion rate. Tests conducted are detailed in the quarterly reports for the periods ending June 30, 1981, and September 30, 1981. Results of tests in two coal liquids showed no change in rates of carbon steel with exposure time; additional coupons added to the solutions as some of the original coupons were removed corroded at essentially the same rate in 10- to 30-hour tests as did coupons exposed for 100 hours. In a third coal liquid, corrosion rates decreased with exposure time and replacement coupons exposed for 10-hour periods also displayed lower rates than did coupons removed after the first 10 hours of exposure; further, the 10-hour rate of the second set of replacement coupons was lower than that of the first set of replacements. Examination of the coupons indicated the decrease of the rate with exposure time was due in part to the formation of a protective film of corrosion product on coupons, but the behavior of the replacement coupons suggests the decrease also was due in part to a decreased concentration of corrosive species.

DISCUSSION OF CURRENT ACTIVITIES

Corrosion Tests

Corrosion coupon exposures of six alloys are being performed in coal liquid samples selected from those listed in Table 1. The test alloys used in the coupon exposures are separated into two groups. Group I consists of carbon steel (A515, Gr. 70), 5Cr-1/2Mo steel (A387, Gr.5), and Type 410 stainless steel. (Duplicate coupons of each alloy are exposed in each test.) Group II consists of Type 316 stainless steel, Hastelloy C-276, and Incoloy 825. Duplicate coupons of Type 316 stainless steel and single specimens of Hastelloy C-276 and Incoloy 825 are exposed in each test. (Prior to the July-September 1981 quarter, duplicate samples of Type 316 stainless steel and Hastelloy C-276 were exposed in autoclaves designed to test four coupons. When Incoloy 825 was added to the test program during the July-September 1981 quarter, it was decided to replace one of the Hastelloy C-276 coupons with an Incoloy 825 coupon.)

Results from 16 exposures of Group I alloys completed in the current quarter are given in Table 2. Results of 5 earlier exposures, for which rate calculations were incomplete at the end of the previous quarter, also are included in Table 2. Results from 15 new exposures of Group II alloys and completed results of 9 earlier tests are given in Table 3.

Chemical Analyses of Coal Liquids

Quantitative chemical analyses are performed on the as-received coal liquids and the post-test liquids from autoclave tests. Analyses are being made to determine concentrations of the following suspected corrosive species:

- Total Nitrogen
- Chlorine Compounds
 - Total Chlorine
 - Water Soluble Chlorides

TABLE 2
CORROSION RATE DATA FROM GROUP I ALLOYS

Coal Liquid(a)	Test Temp. (°F)	Corrosion Rate (mils/year)		
		A515(b)	A387(c)	Type 410 SS(d)
A311	350	Nil	2.1	1.0
A311	350	4.5	2.5	1.6
A311(e)	425	4.5	8.1	5.4
A311(e)	425	5.1	8.2	6.3
A411	350	4.3	0.3	0.3
A411	350	4.1	0.3	0.5
C218	500	4.1	9.2	0.5
C218	500	4.7	10.4	0.4
C318	500	0.5	0.5	0.6
C318	500	0.5	0.4	0.2
C318	650	4.7	0.7	0.7
C318	650	5.0	1.3	0.8
D125(e)	500	3.4	3.4	0.8
D125(e)	500	3.5	4.4	1.1
E316(e)	500	2.5	1.9	1.5
E316(e)	500	2.4	1.6	1.2
E416(e)	500	9.9	8.1	3.4
E416(e)	500	9.4	7.7	3.8
F116	500	0.3	0.3	0.3
F116	500	0.3	0.4	0.3
F116	650	10.0	8.6	0.9
F116	650	11.8	8.1	1.5
F216	425	0.5	0.1	0.2
F216	425	0.6	0.2	0.2
F216	500	1.0	1.2	0.5
F216	500	1.0	1.5	0.7
F216	575	2.5	1.8	0.7
F216	575	(g)	(g)	(g)

(a) See Table 1.

(b) ASTM A515, Grade 70.

(c) ASTM A387, Grade 5.

(d) Type 410 Stainless Steel.

(e) Test conducted in earlier quarter; rate calculation completed in current quarter.

(f) Sample G117 was incorrectly identified as Sample E817 in earlier reports.

(g) Not completed.

TABLE 2 (Continued)
CORROSION RATE DATA FROM GROUP I ALLOYS

Coal Liquid (a)	Test Temp. (°F)	Corrosion Rate (mils/year)		
		A515 (b)	A387 (c)	Type 410 SS (d)
F316	425	13.6	10.8	8.2
F316	425	12.7	13.0	8.4
F316	500	10.7	9.2	3.7
F316	500	12.0	8.8	4.5
F316	575	8.3	6.2	4.1
F316	575	(g)	(g)	(g)
G117(e,f)	500	4.7	2.4	0.8
G117(e,f)	500	4.5	3.7	1.0
H429	425	3.5	0.4	0.3
H429	425	4.6	0.4	0.3
H429	500	4.0	3.4	0.3
H429	500	3.9	3.7	0.3
H429	575	5.4	2.3	0.5
H429	575	5.2	2.1	0.4

(a) See Table 1.

(b) ASTM A515, Grade 70.

(c) ASTM A387, Grade 5.

(d) Type 410 Stainless Steel.

(e) Test conducted in earlier quarter; rate calculation completed in current quarter.

(f) Sample G117 was incorrectly identified as Sample E817 in earlier reports.

(g) Not completed.

TABLE 3
CORROSION RATE DATA FROM GROUP II ALLOYS

Coal Liquid (a)	Test Temp. (°F)	Corrosion Rate (mils/year)		
		Type 316 SS (b)	C-276 (c)	IN 825 (d)
C218	350	Nil	<0.1	<0.1
C218	350	<0.1	(e)	(e)
C218	500	Nil	<0.1	<0.1
C218	500	<0.4	(e)	(e)
C318	500	<0.1	0.1	<0.1
C318	500	0.1	(e)	(e)
C318	650	0.7	<0.1	Nil
C318	650	0.8	(e)	(e)
D114 (f)	500	0.2	<0.1	0.2
D114 (f)	500	Nil	(e)	(e)
D114 (f)	650	0.5	0.4	0.7
D114 (f)	650	0.2	(e)	(e)
D125 (f)	500	0.5	0.3	0.4
D125 (f)	500	<0.1	(e)	(e)
D125 (f)	650	0.3	<0.1	<0.1
D125 (f)	650	0.3	(e)	(e)
D314 (f)	350	Nil	Nil	Nil
D314 (f)	350	0.2	(e)	(e)
D425 (f)	650	0.1	Nil	Nil
D425 (f)	650	<0.1	(e)	(e)
E316 (f)	500	1.1	0.1	0.1
E316 (f)	500	0.2	(e)	(e)
E416 (f)	500	0.2	0.1	<0.1
E416 (f)	500	0.1	(e)	(e)
F116	500	Nil	<0.1	Nil
F116	500	<0.1	(e)	(e)
F116	650	0.2	Nil	Nil
F116	650	<0.1	(e)	(e)

(a) See Table 1.

(b) Type 316 Stainless Steel.

(c) Hastelloy C-276.

(d) Incoloy 825.

(e) Only one coupon exposed in test.

(f) Test conducted in earlier quarter; rate calculation completed in current quarter.

TABLE 3 (Continued)
CORROSION RATE DATA FROM GROUP II ALLOYS

Coal Liquid (a)	Test Temp. (°F)	Corrosion Rate (mils/year)		
		Type 316 SS (b)	C-276 (c)	IN 825 (d)
F216	425	Nil	Nil	Nil
F216	425	Nil	(e)	(e)
F216	500	<0.1	<0.1	<0.1
F216	500	<0.1	(e)	(e)
F216	575	0.3	<0.1	<0.1
F216	575	(g)	(e)	(e)
F316	425	<0.1	<0.1	Nil
F316	425	0.1	(e)	(e)
F316	500	0.1	<0.1	<0.1
F316	500	0.1	(e)	(e)
F316	575	0.5	0.2	<0.1
F316	575	(g)	(e)	(e)
G117 (f,h)	500	1.0	0.5	0.5
G117 (f,h)	500	Nil	(e)	(e)
H429	425	<0.1	Nil	Nil
H429	425	<0.1	(e)	(e)
H429	500	<0.1	Nil	<0.1
H429	500	<0.1	(e)	(e)
H429	575	<0.1	<0.1	<0.1
H429	575	<0.1	(e)	(e)

(a) See Table 1.

(b) Type 316 Stainless Steel

(c) Hastelloy C-276.

(d) Incoloy 825.

(e) Only one coupon exposed in test.

(f) Test conducted in earlier quarter; rate calculation completed in current quarter.

(g) Not completed.

(h) Sample G117 was incorrectly identified as Sample E817 in earlier reports.

- Oxygen Compounds
 - Organic Acids
 - Phenols
 - Water
- Sulfur Compounds
 - Total Sulfur
 - Hydrogen Sulfide
 - Elemental Sulfur, including reactive polysulfidic sulfur
 - Mercaptans
 - Disulfides, including nonreactive polysulfidic sulfur and disulfides formed by removal of sulfur from reactive polysulfides

In addition to analyses of liquids, analyses for hydrogen sulfide and mercaptans are also being performed on gases present in autoclaves at the completion of autoclave tests. Results of chemical analyses performed in the current quarter on 6 additional liquids are given in Tables 4 through 9. Chemical analyses were curtailed during this quarter, pending extension of the program, and none of these analyses are complete.

In addition to the chemical analyses originally incorporated in the test matrix, a method has been developed for determining the relative quantities of "weak base" amines and "strong base" amines. Results of such analyses on four coal liquid samples were reported in the quarterly report for the period ending September 30, 1981. During the current quarter the extracted "weak base" and "strong base" amines from two of the four samples were analyzed in a mass spectrometer to determine the compounds present in the extracts. Results of these analyses are as follows:

- Sample B312 (Ft. Lewis, WA/SRC-I, Wash Solvent Column Bottoms, Point 411)

Strong Base Extract, 0.11 weight percent.

Major constituents: tetrahydroquinoline;
tetrahydromethylquinoline; dihydrodimethyl,
1 H-indole; tetrahydrodimethylisoquinoline;

TABLE 4
RESULTS OF CHEMICAL ANALYSES OF SAMPLE C218
(Ft. Lewis, WA/SRC-II, Middle Distillate)

<u>Species</u>	<u>AS Received</u>	<u>Group II 350°F</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>
Total Sulfur wt.%	0.29		0.28	0.30
Elemental & Reactive Polysulfide Sulfur wt.%				
Disulfide Sulfur wt.%				
Hydrogen Sulfide Sulfur wt.%	0			0
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	N/A	0.0023	0.0096	0.0228
Mercaptan Sulfur wt.%	0.0209		0.0719	0.048
Mercaptan Sulfur In Autoclave Gas Phase g/l	N/A	0	0	0
Phenol % OH ⁻	2.71		2.46	2.35
Phenol % as p-Cresol	17.21		15.64	14.92
Acid Number mg KOH/g	0.001		0	0.031
Base Number mg KOH/g	0		0.50	0.004
Water ppm	393		696	890
Total Chlorides ppm				
Water Soluble Chlorides ppm				
Total Nitrogen wt.%	0.98		1.02	0.97
Ash mg/l	0.6		3.6	3.1

TABLE 5
RESULTS OF CHEMICAL ANALYSES OF SAMPLE C318
(Ft. Lewis, WA/SRC-II, Heavy Distillate)

<u>Species</u>	<u>As Received</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>	<u>Group I 650°F</u>	<u>Group II 650°F</u>
Total Sulfur wt.%	0.50	0.52		0.52	0.51
Elemental & Reactive Polysulfide Sulfur wt.%					
Disulfide Sulfur wt.%					
Hydrogen Sulfide Sulfur wt.%	0			0	0
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	N/A	0.0871	0.0179	0.0321	0.0787
Mercaptan Sulfur wt.%	0.0042	0.0036		0.0043	0.0093
Mercaptan Sulfur In Autoclave Gas Phase g/l	N/A	0	0	0	0
Phenol % OH ⁻	0.55	0.50		0.46	0.47
Phenol % as p-Cresol	3.50	3.18		2.95	2.98
Acid Number mg KOH/g	0.014	0		0	0.005
Base Number mg KOH/g	0	0		0	0
Water ppm	526	787		433	805
Total Chlorides ppm					
Water Soluble Chlorides ppm					
Total Nitrogen wt.%	1.23	1.25		1.23	1.20
Ash mg/l	23.7	3.1		7.1	6.3

TABLE 6
RESULTS OF CHEMICAL ANALYSES OF SAMPLE D114
(Trenton, NJ/H-Coal, Vacuum Still Overhead)

<u>Species</u>	<u>As Received</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>	<u>Group I 650°F</u>	<u>Group II 650°F</u>
Total Sulfur wt.%	0.02			0.01	0.01
Elemental & Reactive Polysulfide Sulfur wt.%	0.0034			0.0020	0.0007
Disulfide Sulfur wt.%					
Hydrogen Sulfide Sulfur wt.%	0			0	0
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	N/A	0.0046	0.0030	0.0322	0.0092
Mercaptan Sulfur wt.%	0.0059			0.0050	0.0044
Mercaptan Sulfur In Autoclave Gas Phase g/l	N/A	0.0022	0.0017	0.0021	Nil
Phenol % OH ⁻	0.41			0.43	0.46
Phenol % as p-Cresol	2.62			2.72	2.89
Acid Number mg KOH/g	0.02			0.005	0.015
Base Number mg KOH/g	0			0	0
Water ppm	138			260	230
Total Chlorides ppm					
Water Soluble Chlorides ppm					
Total Nitrogen wt.%	0.35			0.45	0.46
Ash mg/l	0.4			5.3	6.3

TABLE 7
RESULTS OF CHEMICAL ANALYSES OF SAMPLE D125
(Trenton, NJ/H-Coal, Vacuum Still Overhead)

<u>Species</u>	<u>As Received</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>	<u>Group I 650°F</u>	<u>Group II 650°F</u>
Total Sulfur wt.%	0.11			0.08	0.09
Elemental & Reactive Polysulfide Sulfur wt.%	0.0944			0.0046	0.0045
Disulfide Sulfur wt.%					
Hydrogen Sulfide Sulfur wt.%	0			0	0
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	N/A	0.0037	0.0107	0.0131	0.0579
Mercaptan Sulfur wt.%	0.0087			0.0075	0.0101
Mercaptan Sulfur In Autoclave Gas Phase g/l	N/A	0.0004	0.0013	0.0013	Nil
Phenol % OH ⁻	0.31			0.31	0.28
Phenol % as p-Cresol	1.96			1.95	1.79
Acid Number mg KOH/g	0.084			0.02	0
Base Number mg KOH/g	0			0	0
Water ppm	371			576	894
Total Chlorides ppm					
Water Soluble Chlorides ppm					
Total Nitrogen wt.%	0.76			0.82	0.83
Ash mg/l	2.5			9.8	2.0

TABLE 8
RESULTS OF CHEMICAL ANALYSES OF SAMPLE G117(*)
(Baytown, TX/EDS(CLPP), Solvent Hydrogenation Feed)

<u>Species</u>	<u>As Received</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>	<u>Group I 650°F</u>	<u>Group II 650°F</u>
Total Sulfur wt.%	0.05			0.04	0.05
Elemental & Reactive Polysulfide Sulfur wt.%	0.0021			0.0036	0.0030
Disulfide Sulfur wt.%					
Hydrogen Sulfide Sulfur wt.%	0			0	0
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	N/A	0.0621	0.0403	0.0382	0.1069
Mercaptan Sulfur wt.%	0.0034			0.0027	0.0037
Mercaptan Sulfur In Autoclave Gas Phase g/l	N/A	0.0076	0.0013	0.0022	0.0072
Phenol % OH ⁻	0.80			0.80	0.78
Phenol % as p-Cresol	5.06			5.07	4.95
Acid Number mg KOH/g	0.084			0	0.015
Base Number mg KOH/g	0			0	0
Water ppm	689			560	705
Total Chlorides ppm					
Water Soluble Chlorides ppm					
Total Nitrogen wt.%	0.39			0.43	0.41
Ash mg/l				2.5	10.7

(*)Sample G117 was incorrectly identified as Sample E817 in earlier reports.

TABLE 9
RESULTS OF CHEMICAL ANALYSES OF SAMPLE F116
(Catlettsberg, KY/H-Coal, Startup Oil)

<u>Species</u>	<u>As Received</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>	<u>Group I 650°F</u>	<u>Group II 650°F</u>
Total Sulfur wt.%	0.09		0.09	0.08	0.08
Elemental & Reactive Polysulfide Sulfur wt.%					
Disulfide Sulfur wt.%					
Hydrogen Sulfide Sulfur wt.%					
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	N/A	0.0002	0.0597	0.1353	0.2794
Mercaptan Sulfur wt.%	0.0048	0.0059	0.0068	0.0002	0.0033
Mercaptan Sulfur In Autoclave Gas Phase g/l	N/A	0.0002	Nil	Nil	Nil
Phenol % OH ⁻	0.10		0.10	0.13	0.16
Phenol % as p-Cresol	0.66		0.64	0.81	1.02
Acid Number mg KOH/g	0		0	0	0
Base Number mg KOH/g	0		0	0	0
Water ppm	95		142	121	117
Total Chlorides ppm					
Water Soluble Chlorides ppm					
Total Nitrogen wt.%	0.21		0.22	0.21	0.19
Ash mg/l	3.0	3.0	3.0		2.3

tetramethylpyridine; 2,5-dimethyl, 1 H-benzimidazole;
trimethyl pyridine; tetramethyl pyridine; ethyl-
dimethyl pyridine.

Weak Base Extract, 5.63 weight percent.

Major constituents: methylquinoline; methyliso-
quinoline; dimethylquinoline; benzoquinoline.

• Sample E416 (Baytown, TX/EDS(ECLP), Light Vacuum Gas Oil)

Strong Base Extract, 0.05 weight percent.

Major constituents: 1,2,3,4-tetrahydro-6-
methylquinoline; 1,2,3,4-tetrahydro dimethyl-
quinoline.

Weak Base Extract, 2.40 weight percent.

Major constituents: methyl acridine; dimethyl
acridine; ethyl acridine.

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ORNL-3.4 — CORROSION IN COAL-DERIVED LIQUIDS

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A. STRESS CORROSION CRACKING

V. B. Baylor, J. R. Keiser, J. F. Newsome, and M. Howell

INTRODUCTION

This work is being performed to assess the resistance of various materials to stress corrosion cracking in coal liquefaction plants.

RESULTS FROM PRIOR QUARTERS

During prior quarters, racks of U-bend specimens were exposed in the Wilsonville, Alabama, and Fort Lewis, Washington solvent refined coal (SRC) pilot plants; the Catlettsburg, Kentucky, H-Coal pilot plant; and the Baytown, Texas, Exxon Coal Liquefaction pilot plant. From weight change measurements, corrosion rates were calculated for all specimens. Selected specimens were examined by standard metallographic procedures. The results of all pilot plant stress corrosion tests through September 1981 are reported in detail elsewhere.^{1,2}

DISCUSSION OF CURRENT ACTIVITIES

During this quarter, a second set of specimens exposed at ECLP was examined. The exposure locations and conditions and the calculated corrosion rates are given in Table 1. In the liquefaction overhead the exposure time was 2660 h; in the other locations it was 2465 h. Visual examination showed no evidence of cracking on any of the specimens. Some pitting was found on the carbon steel samples and on several of the type

Table 1. Corrosion rates of U-bend specimens exposed at the Exxon Coal Liquefaction Pilot Plant from February to September 1981

Exposure site	Environment	Corrosion rate [mm/year (mils/year)]			
		Carbon steel	Type 304 stainless steel, sensitized and unsensitized	Ferralium ^a	Incoloy ^b 825
Liquefaction overhead piping from D-105 separator	Sour water, 65°C, 13.3 MPa (2000 psi)		<0.01 (0.19) <<0.01 (0.06)	c	<0.01 (0.14)
Liquefaction overhead piping into E-108 condenser	Hydrocarbon, 290°C, 13.8 MPa (2000 psi)		0.08 (3.23)	c	0.01 (0.42)
Hydrogenation overhead piping from E-302 condenser	Hydrocarbon-sour water, temperature and pressure proprietary	0.07 (2.71)	0.01 (0.24) 0.01 (0.34)	c	<0.01 (0.15)
Hydrogenation overhead piping from T-301 scrubber	Sour water, temperature and pressure proprietary	0.03 (0.99)	c 0.01 (0.15)		0.01 (0.28)
Solvent fractionator overhead piping into D-304 reflux drum	Sour water-hydrocarbon, 120°C, 0.34 MPa (50 psi)	0.01 (0.59)	<0.01 (0.14) <0.01 (0.11)		
Solvent fractionator overhead piping from E-304B condenser	Sour water-hydrocarbon, 120°C, 0.34 MPa (50 psi)	0.02 (0.98)	<0.01 (0.16) <0.01 (0.14)		

^aTrademark of Langley Alloys Limited.

^bTrade name of Huntington Alloys.

^cSpecimen gained weight.

304 stainless steel specimens. The Ferralium* and Incoloy† 825 showed no signs of attack. These results are consistent with specimens from the first set, which also had very low corrosion rates with minimal attack. During this quarter, replacement racks were prepared and shipped to both ECLP and the H-Coal Pilot Plant.

Laboratory tests to study stress cracking in sulfur acids with and without chloride additions as a function of aging conditions were also initiated. We are first using ASTM E262 Practice B to determine the relative degree of sensitization by measuring the susceptibility to intergranular attack. A range of materials has been aged at 400, 500, and 600°C for 10 to 10,000 h. The samples aged for 10 h have been exposed to the boiling 50% sulfuric acid-ferric sulfate solution for 120 h.

Calculated penetration rates averaged from three samples are given in Table 2. The results for the austenitic stainless steels and Incoloy 800 show that the corrosion rate is almost the same after aging for 10 h at 400 and 500°C but increases dramatically for specimens aged for 10 h at 600°C (except for type 347, which is stabilized to resist sensitization). These data indicate that the austenitic stainless steels (except as noted) have been sensitized for 10 h at 600°C, as indicated by the increased susceptibility to intergranular attack. This behavior is consistent with that usually observed for these steels (except for type 321, which should be sensitization resistant).

We will be testing U-bend specimens aged under identical conditions in polythionic acid with and without chloride additions. Our in situ specimens and failure analysis have confirmed these species as the primary corrosive agents in stress-corrosion cracking in coal liquefaction systems. We hope to determine the susceptibility to cracking as a function of the chloride content of the process stream and exposure time.

*Trademark of Langley Alloys Limited.

†Trade name of Huntington Alloys.

Table 2. Penetration rates after exposure to boiling 50% sulfuric acid-ferric sulfate solution for 120 h

Material	Penetration rate [mm/year (mils/year)] ^a					
	400°C ^b /752°F		500°C ^b /932°F		600°C ^b /1112°F	
Type 304 SS	0.887	(34.94)	1.594	(62.73)	11.789	(464.12)
Type 304L SS	0.627	(24.66)	0.483	(19.00)	2.187	(86.10)
Type 316 SS	0.552	(21.72)	0.509	(20.03)	3.146	(123.85)
Type 316L SS	0.601	(23.68)	0.458	(18.02)	1.115	(43.89)
Type 317 SS	0.272	(10.72)	0.386	(15.21)	1.716	(67.57)
Type 317LM SS	0.334	(13.16)	0.341	(13.42)	1.282	(50.33)
Type 321 SS	0.828	(32.59)	0.870	(34.26)	12.468	(490.88)
Type 347 SS	0.579	(22.78)	0.504	(19.84)	0.562	(22.13)
Type 310 SS	0.123	(4.85)	0.142	(5.58)	2.839	(111.77)
E-Brite 26-1 ^c	2.781	(109.50)	0.422	(16.60)	0.350	(13.78)
Carpenter 20 Cb-3 ^d	0.136	(5.35)	0.141	(5.55)	0.290	(11.42)
Incoloy 800	0.217	(8.55)	0.440	(17.30)	1.313	(51.69)
Incoloy 825	1.623	(63.89)	0.225	(8.86)	0.321	(12.66)
Hastelloy G-3 ^e	0.236	(9.29)	0.221	(8.71)	0.628	(24.71)
Hastelloy C-276	5.077	(199.86)	6.621	(260.66)	8.303	(326.91)

^aAverage of three specimens.

^bAging temperature, specimens aged for 10 h.

^cTrade name of Allegheny Ludlum.

^dTrade name of Carpenter Technology.

^eTrade name of Cabot Corporation.

B. GENERAL CORROSION

J. R. Keiser, M. Howell, and J. F. Newsome

INTRODUCTION

The purpose of this work is to determine the potential for general corrosion in coal liquefaction plants. The corrosivity of the fluids is measured by exposing corrosion coupons in a number of vessels in the Fort Lewis and Wilsonville SRC pilot plants and the Catlettsburg H-Coal pilot plant.

RESULTS FROM PRIOR QUARTERS

Corrosion coupons have been exposed in a number of vessels in the Fort Lewis and Wilsonville SRC pilot plants, and results from examination of these samples have been reported in prior quarters. These studies have shown that sulfidation can be a serious problem in the reaction and separation areas, and a chloride-related mechanism causes serious corrosion problems in the fractionation area.

DISCUSSION OF CURRENT ACTIVITIES

During September, a rack of coupons for the Wilsonville hydrotreater was rebuilt and shipped. Two racks of coupons that had been exposed 3526 h in the Wilsonville vacuum column were examined at ORNL. Results (Table 3) indicate that, except for carbon steel exposed below tray 8, all

Table 3. Calculated corrosion rates for coupons
exposed 3526 h in the Wilsonville T-102
vacuum column

Alloy ^a	Corrosion Rate [mm/year (mils/year)]	
	Rack location	
	Top of column	Bottom of column
Type 347 SS	<0.0001 (<0.05)	<0.0001 (<0.05)
Type 304L SS	<0.0001 (<0.05)	<0.0001 (<0.05)
18 Cr-2 Mo	<0.0001 (<0.05)	<0.0001 (<0.05)
Type 321 SS	<0.0001 (<0.05)	<0.0001 (<0.05)
26 Cr-1 Mo stabilized		<0.0001 (<0.05)
Type 409 SS		0.0001 (0.05)
Type 410 SS	<0.0001 (<0.05)	0.0003 (0.14)
20 Cr-4 Mo	<0.0001 (<0.05)	
9 Cr-1 Mo		0.0021 (0.8)
7 Cr-1 Mo (0.14 Nb)		0.0023 (0.9)
7 Cr-1 Mo (0.37 Nb)		0.0032 (1.2)
5 Cr-1 Mo (0.13 Nb)		0.0032 (1.3)
9 Cr-1 Mo modified		0.0034 (1.3)
5 Cr-1 Mo (0.38 Nb)		0.0043 (1.7)
Carbon steel	0.0013 (0.5)	0.0041 (16.0)

^aAlso exposed in top rack were 316 SS, 317 SS, Inconel 600, Incolloys 800 and 825, Hastelloys G and C-276, and titanium, all of which have corrosion rates less than 0.0001 mm/year (<0.05 mils/year).

tested alloys had corrosion rates of less than 0.05 mm/year (2 mils/year). Racks of new coupons were installed in the tower.

Coupon racks supplied by ORNL were removed from the Fort Lewis wash solvent and light ends columns after plant operations were stopped in July 1981. These racks were reportedly prepared for shipment to ORNL, but records do not indicate they were shipped. Unfortunately, the personnel remaining at Fort Lewis are unable to locate the racks; we are therefore assuming that they were inadvertently discarded.

Chemical analyses are being performed on three samples (one process water and two oil) collected at the Baytown pilot plant during operation with Wyodak subbituminous coal. These results will be compared with those for samples to be collected during operation with Illinois No. 6 coal in early 1982.

Five racks of coupons to be exposed in the T-201 atmospheric fractionator at the ECLP were shipped to Baytown as replacements for five racks that were removed from the column. The latter five racks were returned to ORNL, where they were cleaned and weighed, and corrosion rates were calculated. Results of these calculations are given in Table 4. It should be noted that the pilot plant operated for about one week on Illinois No. 6 (bituminous) coal and for about ten weeks on (subbituminous) coal from the Wyodak mine. On the basis of corrosion probe measurements and knowledge of the chlorine content of the coals, we expected that corrosion would be more severe during operations on Illinois coal than on Wyodak coal. Significant corrosion was noted on the carbon steel and 410 stainless steel coupons exposed on trays 21 and 23. We speculate that much of this corrosion occurred during the initial operation on Illinois coal.

We have reported that type 321 stainless steel showed the lowest corrosion rate of all austenitic stainless steels exposed in the 204 to 260°C (400–500°F) range of the fractionation columns at the SRC pilot plants.³ The 321 sample exposed on tray 23 of the ECLP fractionator had an unexpectedly high corrosion rate. It may be that conditions in the ECLP fractionator are sufficiently different from those in the SRC towers that type 321 stainless steel behaves much differently in the two locations. However, it may also be that the sample exposed on tray 23 was

Table 4. Calculated corrosion rates for first set of coupons exposed 1896 h in the Exxon Coal Liquefaction Pilot Plant T-201 atmospheric fractionator

Alloy	Corrosion rate [mm/year (mils/year)]				
	Tray 26	Tray 25	Tray 23	Tray 21	Tray 20
Carbon steel	0.58 (23)	1.47 (58)	4.86 (191)	4.54 (179)	2.69 (108)
Type 410 SS	0.010 (0.4)	0.045 (1.8)	2.10 (83)	2.62 (103)	0.46 (18)
Type 321 SS	<0.003 (<0.1)	<0.003 (<0.1)	0.166 (6.5)	0.009 (0.4)	<0.003 (<0.1)
Aluminized 304 SS	0.016 (0.6)	0.017 (0.7)	0.011 (0.4)	0.008 (0.3)	0.010 (0.4)
Incoloy 600	<i>a</i>	<i>a</i>	<0.003 (<0.1)	0.003 (0.1)	<i>a</i>
Incoloy 601	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Type 304 SS	0	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Type 316 SS	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Incoloy 825	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Type 316 SS	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Type 316L SS	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Ferrallium	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Haynes 20 modified	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Zirconium	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Type 347 SS	<i>a</i>	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Titanium	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)	<0.003 (<0.1)
Incoloy 625	<i>a</i>	<0.003 (<0.1)	<i>a</i>	<0.003 (<0.1)	<0.003 (<0.1)
Hastelloy C-276	<0.003 (<0.1)	<0.003 (<0.1)	0	<0.003 (<0.1)	<0.003 (<0.1)

^aWeight gain indicates presence of a tightly adherent scale not removed by ultrasonic cleaning.

not properly handled. Whichever the case, additional coupon exposures should provide enlightening data.

A paper on "Corrosion in Coal Liquefaction Systems" was presented at the Sixth Annual Conference on Materials for Coal Conversion and Utilization, Gaithersburg, Maryland, October 13-15, 1981.

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BCL-3.5 - EVALUATION OF ADVANCED MATERIALS
FOR SLURRY EROSION SERVICE

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INTRODUCTION

This program is intended to address the needs of coal liquefaction pilot plants for erosion-resistant materials for trim, wear inserts or liners for letdown valves or pumps, through screening of candidate materials, characterization of the erosion behavior of generic materials, and investigation of routes to improving these materials.

RESULTS FROM PRIOR QUARTERS

Materials screening activities confirmed earlier trends of the increased erosion resistance of WC-cermets with decreasing binder level for a series of WC-Co materials. In addition, diamond/Si-SiC compacts which contained a high volume fraction of fine diamond particles exhibited promising resistance to slurry erosion. In attempts to modify the surface microstructure and hardness in a direction likely to improve erosion resistance, two Haynes Stellite hardfacing alloys were subjected to laser surface melting, and the resulting surfaces were characterized by metallography.

DISCUSSION OF CURRENT ACTIVITIES

The activities in each of the three main tasks of this program are discussed below.

Task I. Materials Screening Activities

A substantial amount of the experimental effort during this quarter was expended on screening studies. The results for a number of standard, new, or modified cermet materials exposed to the standardized slurry erosion test conditions (1 hr in 8% by weight solids/anthracene oil slurry, at 343 C (650 F), 100 m/s, 20°), are listed in Table 1.

The standard of comparison is a specimen of K-701 cemented tungsten carbide, which is run periodically throughout the test cycle. Note that the values for the standard in this series of tests are lower than in those reported in the previous quarter, 1.9 to 3.5 μm (average 2.8 μm) versus 3.4 to 5.6 μm (average 4.3 μm); this is a result of a slow degradation in the erosive quality of the test slurry, which is minimized by a regular rejuvenation procedure described earlier. If a comparison between the behavior of materials tested at different times is desired, a value of erosion depth of the material of interest divided by that for K-701 in the same test series might be considered. The measured crater length is not currently used in any quantitative way, but only serves as a qualitative aid to visualizing the extent of erosion damage.

The extensive series of cobalt-bound WC material again exhibited a trend to increased erosion resistance (under the given test conditions) with decreasing binder content, with a "low" cobalt content, micrograin WC material, Kennametal SPZ 313, exhibiting the lowest erosion of the series, in duplicate tests. Surprisingly, however, a binderless WC grade, Kennametal SP-278, eroded at a faster rate than the WC-Co grades; the modes of erosion have not yet been examined, and a further binderless grade has yet to be tested.

TABLE 1. NEW AND MODIFIED CERMETS

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
K-701	Reference	Kennametal	WC-10% Co-4% Cr	1.9-3.5 (Av = 2.8)	1.07-3.43 x 10 ³
WC (binderless)	WCX	Kennametal	tungsten monocarbide	--	--
WC (binderless)	SP-278	"	--	8.5	3.00 x 10 ³
WC-TaC-Co	K-602	"	<1.5% Co	3.3	3.34 x 10 ³
WC-Co	K-6T	"	low Co	--	--
WC-Co	SPZ313	"	low Co, micrograin WC	1.5/None	0.70 x 10 ³
WC-Co	K-11	"	2.8% Co	2.5	2.51 x 10 ³
WC-Co	K-68	"	5.8% Co	2.0	3.23 x 10 ³
WC-Co	K-3406	"	7.8% Co	3.3	0.84 x 10 ³
WC-Co	K-3560	"	9.5% Co	--	--
WC-Co	K-3109	"	12.2% Co	4.3	1.84 x 10 ³
WC-Co-multicarbides	CRZ 316-25	"	--	--	--
WC-Ni-multicarbides	SP269	"	--	--	--
WC-Ni	K-801	"	6% Ni	11.4	2.59 x 10 ³
WC-Ni	K-803	"	--	7.1	3.35 x 10 ³
WC-Ni-Mo	K-165	"	--	53.3	2.44 x 10 ³
WC-Ni-Cu-Fe	W-2	"	94% W, 2.6% (Ni, Cu, Fe)	too deep	to measure
WC-Ni-Cu-Fe	W-11	"	--	too deep	to measure
WC-Co-Cr	K-701	"	8.5% Co, 4.5% Cr	1.8	3.56 x 10 ³
WC-Co-Cr	K-703	"	6.0% Co, 1.0% Cr	1.2	2.08 x 10 ³
WC-Co-Cr	K-714	"	14% Co+Cr	2.0	2.84 x 10 ³
WC-TiCN	SP293A	"	high Ti, fine grained	--	--
WC-TiCN	SP293B	"	HIP-version of SP293A	--	--
WC-proprietary binder	SP317	"	--	--	--

TABLE 1. (Continued)

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
Coated WC-Co-Cr	K701/TMT 745A	Turbine Metal Technology	--	--	--
Coated WC-Co-Cr	K703/TMT 745A	Turbine Metal Technology	--	--	--
Coated WC-Co-Cr	K703/Si ₃ N ₄	Kennametal	4.5-5.0 μm thick coating	--	--
B ₄ C-Ni	256	ORNL	98% B ₄ C, 2% Ni	Specimen broken during test assembly	
B ₄ C-Ni	260	"	94% B ₄ C, 6% Ni	7.1	1.15×10^3
B ₄ C-Co	257	"	98% B ₄ C, 2% Co	6.6	0.90×10^3
B ₄ C-Co	259	"	96% B ₄ C, 4% Co	6.0	1.32×10^3
B ₄ C-Co	263	"	92% B ₄ C, 8% Co	1.9	0.76×10^3
B ₄ C-SiB ₄	320	"	0.9/0.1 molar B ₄ C/SiB ₄	too deep to measure	
B ₄ C-SiB ₄ -Co	342	"	4% Co+B ₄ C/SiB ₄ , 0.9/0.1	111.7	1.19×10^3
B ₄ C-SiB ₄ -Ni	343	"	6% Ni+B ₄ C/SiB ₄ , 0.9/0.1	68.6	1.34×10^3
B ₄ C-SiB ₄ -Ni	347	"	10% Ni+B ₄ C/SiB ₄ , 0.9/0.1	25.0	0.98×10^3

The Co-Cr-bound WC cermets exhibited the same trend, with K-703 (7% binder) giving a slightly better result than K-701 (13% binder), and a similar result to the SPZ 313 Co-bound grade.

The Ni-bound WC grades, K-801 and -803, were less resistant to slurry erosion in this test than the Co-bound materials of similar binder content, a result consistent with earlier testing.

Other binder materials, such as Ni-Mo, and Ni-Cu-Fe at a 2.6% level (suggesting substoichiometric WC), did not lead to promising erosion behavior.

A series of Co-bound B_4C -base cermets exhibited erosion values of a low order, with one composition performing almost as well as the best of the WC-cermets. The trend with these materials was to increased erosion resistance with increased binder content over the range 2 to 8% Co. The erosion observed on a single Ni-bound composition of this series was of a similar but slightly greater degree than that of the equivalent Co-bound specimen. A similar trend with binder content was found with B_4C - SiB_4 (0.9 to 0.1 molar ratio) material. With no binder, the erosion crater was too deep to traverse with the Talysurf profilometer, while additions to 10% Ni (or Co) reduced the depth of erosion substantially, though not to the low levels of the B_4C -Co cermets. Currently this trend to improved erosion behavior with increasing binder content is not understood; single phase B_4C in the same test exhibits good erosion resistance with a value of 11 μm ($B_4C/K701 = 1.6$) but, of course, has the mechanical properties of a ceramic.

Three ceramics were tested, and duplicate tests of each were run because of concern over the possible effect of surface finish. As can be seen from Table 2, the differences between as received and ground finishes were small. Hot-pressed alumina materials have not performed well in this test in the past; the erosion behavior of K-060 and K-090 rank amongst the best observed for this class of ceramics. The performance of the SiAlON material, however, was excellent and similar to that of the best WC- and B_4C -cermets.

TABLE 2. EROSION TESTING OF CERAMICS

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
Al_2O_3	K-060	Kennametal	Hot Pressed-SNG452T	17.8/22.3	$1.44/3.87 \times 10^3$
$\text{Al}_2\text{O}_3\text{-TiC}$	K-090	Kennametal	Hot Pressed	21.3/19.1	$1.22/3.66 \times 10^3$
SiAlON	Kyon 2000	Kennametal	--	1.4/2.3	$1.02/2.35 \times 10^3$

Four pieces of trim taken from service in the Wilsonville SRC-1 pilot plant were erosion tested in an attempt to investigate the causes of inconsistent trim performance experienced at that plant in recent operation. Sections of the trim stems were surface finished so that both transverse faces were flat and parallel, and then they were exposed in the screening test. The sections were positioned in the erosion rig so that the test crater was situated close to the service-worn surface. The results in Table 3 indicate that two samples, E-1200 and E-2000, performed in a manner typical of K-703 and GEM 505-type materials, whereas one material (E-288) eroded in a way which suggests that it was a defective sample of K-703, or an inferior grade. The result for sample E-4000 was inconclusive, because of an apparently rough surface finish, and will be repeated. Metallographic comparisons of these specimens with on-grade materials is in progress.

TABLE 3. TRIM FROM PILOT PLANTS

Material	Specimen Designation	Source	Erosion Crater	
			Depth (μm)	Length (μm)
K703	E-288	Wilsonville (McCartney)	too deep to measure	
K703	E-1200	Wilsonville (McCartney)	2.8	1.27×10^3
GEM 550	E-2000	Wilsonville (GEMOCO)	3.8	1.28×10^3
GEM 550	E-4000	Wilsonville (GEMOCO)	~5, to be repeated	
TMT-5	--	H-Coal (Catlettsburg)	--	--
TMT-Gracoat	--	Anonymous (valve)	--	--

A TMT-5-coated WC-cermet trim piece from a Willis choke valve used in the Catlettsburg H-coal demonstration plant was examined by scanning microscopy and metallography. The surface features both in the worn areas near the flow holes and in regions apparently remote from wear, were essentially identical with no physical evidence of a coating. The surface morphologies were in fact similar to those of WC-Co cermets after moderate erosion, having WC grains exposed and standing slightly above the general surface. EDAX surface analysis showed no essential difference in composition (elements > Na) between worn and remote surfaces; however, metallography revealed a modified surface layer some 10 to 15 μm deep, apparently resulting from a diffusion treatment. The physical characteristics of this coating will be compared with those of other, as-received, coatings from the same manufacturer, before the specimen is committed to erosion testing.

Task II. Characterization of the Erosion Behavior of New Materials

The objective of this task is to investigate the mechanisms by which specific classes of advanced ceramics are degraded by erosive coal-derived slurries. In order to provide as consistent an erosion condition as possible for use in short term erosion runs designed to investigate the time dependence of erosion damage, modifications have been made to the erosion test rig to permit once-through passage of the test slurry. The initial use of this system will be to study the degradation of one batch of coal-derived (Wilsonville solids/anthracene oil) slurry by measuring the wear on a standard specimen as the slurry is passed through the test rig a known number of times.

Following this, a well characterized, artificial slurry consisting of a Harbison-Walker fused silica suspended in anthracene oil will be used in studies of cumulative damage on selected targets. The slurry will be passed through the test rig once, and discarded. Anthracene oil was retained as the carrier fluid because of its particular viscosity characteristics, and because it is a cost effective choice. Both sets of once-through experiments await the release of the

erosion rig from screening studies.

Examination of the eroded surface of a reaction-bonded SiC ceramic, Norton Noralide NC-430, has shown a "mechanically-etched" structure, which is the result of preferential removal of free silicon at the grain boundaries, leaving behind more wear resistant, protruding SiC grains. After the initial removal of the free silicon, the wear rate of the material must be increasingly determined by the wear rate of the SiC grains due to the shadowing effect, particularly at low impingement angles. The large SiC grains revealed several interesting and some unexpected features of material removal: the eroded grain surfaces were extremely smooth with a polished appearance, and some macroscopic ripples were noted in some eroded grains in the direction of the slurry flow. No evidence of elastic-plastic indentation cracking was noted in any of the eroded grains. These observations suggest that the mechanism of material removal must be ductile in nature with the particle interaction with the surface confined to extremely fine scale not resolved by scanning electron microscopy. Secondly, all the grain surfaces of SiC do not erode at the same rate. This is suggested by two observations. Some SiC grains appeared to have been eroded significantly more than neighboring grains, which still showed the grinding marks from the original surface finish (target surfaces were finish ground with a 600-grit diamond wheel). The uneven wear of the grain faces is also suggested by development of facets in some eroded grains, as shown in Figure 1, where the original ground surface has undergone only moderate erosion (A), while the facet at B shows pronounced erosion

The smooth surfaces of the eroded SiC grains and the lack of any evidence of chipping by lateral cracking imply that the particle impact conditions in the erosion test are below a threshold to initiate indentation fracture ⁽¹⁾. Material removal below the threshold is expected to be by a plastic cutting mechanism, in the general manner discussed, for example, by Finney, et al ⁽²⁾. The relevant material parameter controlling the erosion rate in this regime is the hardness of the target. Erosion rate in the sub-threshold regime is typically one order of magnitude smaller than the wear rate associated with the lateral

FIGURE 1. FEATURES OF A LARGE SiC GRAIN IN THE ERODED SURFACE OF RS-SiC SHOWING ORIGINAL, GROUND SURFACE (A) AND AN ERODED FACET (B)

fracture mechanism⁽³⁾. This coupled with the high hardness of SiC might explain the low wear rates observed for generic SiC targets in the slurry wear evaluation program and in plant trials with SiC valve trims⁽⁴⁾. Erosion faceting observed on the SiC grains is also consistent with a hardness-controlled, subthreshold wear mechanism. It is known that SiC crystals exhibit significant anisotropy in microhardness depending on crystal orientation and direction⁽⁵⁾. Microhardness measurements with a Knoop indenter at 200 gm load on a polished surface of reaction-bonded SiC indicated that microhardness ranged from 2400 to 3000 kg/mm² among the individual SiC grains. The uneven wear rates on the grain surfaces may well be a consequence of the anisotropy of the hardness of the SiC grains in different planes.

Task III. Approaches to the Development of New Materials

The results of erosion testing of the laser surface melted

Stellite materials, although the data are currently only qualitative, were disappointing since little superiority was observed for the modified materials compared to the starting alloys. The test condition was less severe than that used for screening cermets and ceramics (56 m/s vs 100 m/s), but may still have been too severe for metallic materials. Further developments of the laser surface melting technique have been to incorporate titanium carbide into the alloy surface by melting in place a mixed carbide/alloy powder. The resulting surface layer consisted of the typical alloy dendritic structure with incorporated and reprecipitated TiC particles up to 100 - 150 μm in size. Qualitatively, this material performed better than unmodified Stellite 6B in the erosion test. Refinements of this technique are planned to increase the volume fraction of TiC in the surface layer. However, this type of coating structure already suggests promise for use in sliding wear applications, and attempts will be made to obtain some simple comparative abrasive wear test results.

Analysis of the erosion behavior of B_4C suggested that while promising, the resistance to erosion was impaired by the presence of fine porosity, or a finely dispersed impurity content which was easily removed by erosion. Consideration was given to densification of this material by HIP-processing. However, discussion with the Norton Company on causes of the observed porosity/impurity have raised the possibility that the phenomenon may be an artifact of surface preparation techniques; experiments are in progress at Norton and BCL to establish the existence and/or identity of this feature.

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LBL-3.5 — COAL LIQUEFACTION ALLOY TEST PROGRAM

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INTRODUCTION

The objective of this program is to carry out a generic research program to determine and understand the mechanisms of erosion and corrosion and combined erosion-corrosion of metals, coatings and scales on metals. The service environments simulated are solid particle-gas and solid particle-liquid flows and static elevated temperature corrosion atmospheres that are representative of those in fossil energy conversion and utilization processes. Bare materials and materials coated with metal and ceramic protective layers are exposed to test conditions at both low and high temperatures that represent the conditions in piping systems, fuel passages, cyclones,

combustion chambers, pumps, valves and heat exchanger of coal conversion, oil shale retorting and synthetic fuels utilization systems.

The program is divided into 5 tasks as follows:

1. Erosion behavior of materials
2. Erosion-Corrosion behavior of metals and coatings
3. Effect of flow passage geometry on erosion behavior
4. Behavior of materials in liquid slurry flows
5. Corrosion of materials in oil shale retort environments

DISCUSSION OF CURRENT ACTIVITIES

TASK 1. EROSION BEHAVIOR OF MATERIALS

A. ELEVATED TEMPERATURE EROSION

Elevated temperature testing of an aluminum alloy, 1100-0, and a stainless steel, 310SS, was conducted in the new tester. The test device used is similar in construction to the room temperature tester that has been used for several years in this program except that all of the flow passages of the gas and particles and the specimen location area under the nozzle have been encapsulated in a single, resistance heating type furnace. Figure 1 is a sketch of the tester. The tester can be operated up to 900°C with inert or oxidizing gases and the specimens cooled after testing in an inert atmosphere.

Erosion behavior is determined by weight loss measurements and observation of the eroded specimens in the scanning electron microscope (SEM). Specimens were exposed to 240 μ m diam. SiC particles at a velocity of 30mps at temperatures up to 800°C.

The erosion weight loss of both the 1100-0 aluminum and 310SS at an impingement angle of 30° followed the same pattern as a function of the test temperature (See table 1). These two alloys are both single phase FCC metals but have great differences in strength, modulus of elasticity and other properties. As the temperature was increased up to a homologous temperature range of 0.3 - 0.4, the erosion rate decreased. At a homologous temperature of 0.5 - 0.6 for both metals, the highest erosion rate was measured, considerably greater than the room temperature rate. The initial decrease in erosion rate and subsequent increase relative to the room temperature rate is the result of changes in the plastic deformation characteristics of the alloys and the surface deformation temperature. At a still higher homologous temperature range of 0.6 - 0.8, the erosion rates for both alloys had decreased to the lowest levels in the test series. At the highest test temperature, considerable amounts of SiC were detected in the surface of the specimens and could account for the low weight loss measured particularly for the negative weight loss (actual gain in weight) of the aluminum alloy. It is interesting to note how close the erosion rates of the two alloys are at the various homologous temperatures with the exception of the highest test temperature where the aluminum

added weight because of embedded SiC particles. The strength differences between the two materials are great at the test temperatures. The difference in the tensile strength at the homologous test temperatures are shown in Table 1; the 310SS is, by far, the stronger of the two alloys at all temperatures.

TABLE 1

EROSION RATE $\text{g/g} \times 10^5$

ALLOY	HOMOLOGOUS TEMPERATURE ($T_{\text{test}}/T_{\text{melt}}$ in $^{\circ}\text{K}$)			
	$\frac{0.2 - 0.3}{2.2}$	$\frac{0.3 - 0.4}{1.1}$	$\frac{0.5 - 0.6}{2.8}$	$\frac{0.6 - 0.8}{-3.0}$ (wt. gain)
1100-0 Al				
310SS	1.9	1.2	2.7	1.2
Δ TENSILE STRENGTH IN KSI (310SS-1100) Al	77	73	70	40

B. EFFECT OF PARTICLE VARIATIONS

Cold rolled 1020 plain carbon steel was erosion tested to determine what effect a variation in the strength/hardness and shape of the impinging particles had on the resulting erosion rate. Particles of minerals listed in Table 2 were used as well as spherical and

angular steel shot. The average particle size for the minerals was 250 μ m. The average size of the steel shot was 200 μ m.

TABLE 2

ABRASIVE PARTICLES HARDNESS

ABRASIVE PARTICLE		MOHS HARDNESS	VICKERS HARDNESS (kg/mm ²)
Calcite	CaCO ₂	3	115
Apatite	Ca ₅ (PO ₄) ₃		
	(OH, F, Cl)	5	300
Sand	SiO ₂	7	700
Alumina	Al ₂ O ₃	9	1900
Silicon Carbide	SiC	>9	3000

The steel specimens were eroded at a particle velocity of 60mps and impingement angles of 30° and 90° in an erosion tester that used air as the carrier gas. The nozzle diameter was 0.8cm and the distance from the nozzle to the specimen was 1.3 cm.

Figure 2 is a curve of the resulting erosion rate when the 1020 steel was eroded by the different minerals. It can be seen that the soft particles, calcite and apatite, cause a smaller amount of erosion

to occur than do the 3 harder erodent materials. The harder materials, above a Vickers hardness of 700, caused essentially the same erosion rate in the carbon steel. This indicates that for ductile metal target materials, the hardness of the eroding particles is not a factor once a minimum hardness has been reached. SiO_2 , Al_2O_3 and SiC all erode a steel the same.

An analysis of the specimen surfaces after the erosion had occurred and microscopic observation of the particles after impact indicated that it was not the hardness but the structural integrity of the particles that determined the erosion rate. The soft materials, calcite and apatite, broke up upon impact, markedly reducing the force that they could impart to the target metal to cause erosion. The sand, alumina and silicon carbide did not change size upon impact, thereby striking the target material with approximately the same force and causing the same amount of erosion to occur. The softer materials also deposited upon the target surface as they disintegrated in a smearing type of mechanism that helped to protect the eroding surface from erosion by subsequent particles.

The angular shape steel shot caused four times as much erosion to occur on the 1020 steel as the spherical steel shot did, indicating that there is a significant effect of particle shape on erosion if the shapes are sufficiently different. There are visual differences in the angularity of the SiO_2 , Al_2O_3 and SiC particles, but they all are sufficiently angular in shape to cause the same amount of

erosion to occur. Figure 3 shows the surface of the 1020 steel after steady state erosion has been reached with angular and spherical steel shot. The nature of the surface deformation is markedly different, indicative of the efficiency with which each shape of particle can produce platelets and erosion.

TASK 3. EFFECT OF FLOW PASSAGE GEOMETRY

The slurry loop used to determine the effect of piping geometry variations on the resultant erosion behavior of the steel alloys of its construction was refurbished to bring it up to required safety standards and to provide a means of ready slurry waste disposal. A larger pump was also provided for and the basic piping diameter reduced from 5 cm to 3.8cm so that higher velocities could be achieved, resulting in more measureable erosion in reasonable test duration.

Waste Disposal and Safety Considerations

In order to provide a means for disposing of the used slurry that was safe and effective, a surplus 1000 - gallon steel tank was acquired. After leak detection and corrosion inspection per LBL's Environmental Health and Safety (EHS) guidelines, the tank was fitted with a manway, coated with asphalt and sunk into the ground just downhill of the loop site. The concrete retaining wall that rings the site was completed, replacing a temporary sand bag section. This

wall, coupled with the asphalt paving of the loop area, provides total protection of the surrounding area from system leaks and spills. The slope of the asphalt drains away liquids towards the waste tank where the drain manifold can direct spilled slurry into the waste tank and rainwater down the side of the adjacent hill.

In keeping with spirit of efficient energy use, when the waste tank becomes full it is pumped out by a local waste disposal firm. The kerosene is recycled and the coal particles are pressed into bricks for burning in a fireplace.

Other safety precautions involved the installation of an on-site phone and emergency number listing, installation of an electrical 'crash-off' switch just 'uphill' from the test site (this switch cuts all electrical power to the site in case of an emergency), and the location of a 300 pound chemical fire extinguisher within easy reach of any operational personnel. All pipe supports were designed to conform to seismic safety standards.

Pump Selection

Both pumps previously employed in the slurry loop had proven to be somewhat inadequate in one way or another. The initial pump, a 6" Moyno positive displacement type, did not have the pumping capacity necessary to conduct tests at desired flow velocities in the 5 cm dia pipe used for the loop. Being run almost at its full capacity, the

abrasicve slurry took its toll on the wetted areas of the pump and its consequent performance suffered.

The next pump, a sliding vane type, was acquired on loan from the Blackmer Pump Division of the Dover Corporation. Only minor problems were encountered with this pump; its major drawbacks were its small capacity and its internal pressure protection system which plugged up with coal. The low flow capacities required that small diameter (3/4" - 1") pipe loops be used in order to get any meaningful test results. The basic design and performance of the pump was promising.

The Blackmer Pump Division was most cooperative in supplying a modified, larger size pump. In February 1982 a 6" Blackmer HXLS6 pump will be delivered to the site on a shared cost basis at an extremely low cost to the program. It was necessary to make some minor modifications at the factory in order to incorporate improvements that had grown out of the experience gained in the previous experimentation with a sliding-vane type pump. The modifications included a housing cast from an experimental material, the application of external rather than internal pressure protection, and an extra-long shaft to accomodate the large belt-drive equipment that will be employed in driving it.

Loop Configuration.

The loop design now utilizes mostly flanged and welded connections but its modular design will permit easy modification of loop geometry and components. A systematic examination of the performance of various materials (carbon-steel, stainless steel and cast iron, primarily) in various flow geometries (regular and long-radius elbows, large radius bends, line-flow and branch-flow in 'tees', etc.) will be conducted. Other aspects of testing will include an analysis of the effect of construction techniques, namely, mis-alignment of flanges and sections of straight pipe as well as poor welds (over-penetration). Areas of extreme turbulence near pump suction and discharge sections and around valves will also be investigated.

Two 'test spools' (short easily removable sections of straight pipe) are provided to make the installation of valves and smaller sub-loops quick and easy. It is conceivable that in the near future valve and pump manufacturers will cooperate to use this and similar test equipment to determine which materials and equipment design will be most suitable for use in coal-conversion systems. Table 3 is a listing of the functional characteristics of the Slurry-loop compared to those of the SRC-II pilot plant in Washington State

TABLE 3

Slurry Loop Characteristics

	LBL Slurry Loop	SRC -II Pilot Plant
NOM Pipe DIAMETER	1 1/2"	3"
Flow Rate	to 1300 t/day	125 t/day
Flow Velocity	to 10mps (30 fps)	3 mps (10 fps)
Ave. Slurry Composition	30 - 50 wt% coal and kerosene	40 wt% coal and process solvent
Temperature	25°C	to 200°C

TASK 4. BEHAVIOR OF MATERIALS IN LIQUID SLURRY FLOWS

Additional testing was carried out in the slurry pot tester and jet impingement tester to determine the behavior of materials in coal-kerosene slurries. Figure 4 plots the cumulative erosion of 304SS and A53 mild steel in a -30 mesh coal-kerosene slurry at 94°C (200°F). The larger particle size coal reversed the order of erosion between the 304SS and the A53 mild steel from that experienced using -200 mesh coal at 94°C. The rates of erosion at the 5 hour exposure time were 8.75 times higher for the 304SS using the larger - 30 mesh coal and 6.25 times higher for the A53 mild steel than was measured for each alloy when the - 200 mesh coal was used.

In a 50 wt coal-kerosene slurry using -200 mesh size coal, shown in figure 5, the greater weight of coal in the slurry resulted

in 1.7 times as much erosion for 304SS but only 1.1 times as much erosion for the A53 steel compared to a 30 weight coal-kerosene slurry exposure at the same 94°C test temperature. The order of erosion rate was also reversed. Thus, the effect of larger coal particles and more coal in the slurry increasing the erosion rate determined initially at 25°C was also seen at 94°C.

The jet impingement tester was used to determine the effect of impingement angle on spheroidized 1020 steel. Figure 6 shows the resulting curve. Unlike the 2 1/2 Cr 1Mo and 5Cr 1/2Mo steels tested earlier, the initial peak erosion did not occur at the same angle for both velocities tested. The peak was shifted 10° to 50° from 40° for the higher velocity flow. All other aspects of the curve shapes and positions were similar to those determined for other steel alloys. The absolute rates of erosion for the spheroidized 1020 steel were also higher only at the higher velocity compared to the other steels tested and reported in the last quarterly report. The reason for the differences observed are being investigated.

TASK 5. CORROSION OF MATERIALS IN OIL SHALE RETORT ENVIRONMENT

HIGH TEMPERATURE CORROSION IN IN-SITU RETORTS.

A small crucible holding 15 gm of shale into which individual small specimens of alloys can be immersed wholly or partially was constructed for use in a furnace where higher and more controlled temperatures could be achieved. The higher temperatures were required

as they normally occur in actual below ground retorts where the shale surrounding the retort insulates it to a greater degree than occurs in the above ground retorts where all of the corrosion tests to date have been performed. The more controlled temperatures were required to be able to establish the basis for the occurrence of observed corrosion products on the specimens.

A series of tests were performed on 304 stainless steel at 1000°C to determine whether periodic replenishment of the crucible with 15 grams of fresh shale during 48 hour exposures would better maintain the corrosivity of the small amount of shale in the crucible. Runs were completed replacing the shale twice (after each 16 hrs.) once (after 24 hrs) and leaving the initial shale for 48 total hours. Results showed that maximum attack occurred when the initial shale was left in the crucible for 48 hours because this time period allowed more extensive interaction between the samples and the reactive gases from the shale to occur. The 16 and 24 hour replacement periods allowed the reactive gases to clear the crucible when the shale was replaced.

Figure 7 shows 304SS after a 48 hour non-replenished shale run. There is an outer scale of primarily chromium sulfide with a thin chromium oxide layer between the outer scale and the substrate metal. There are also areas of internal sulfidation primarily along grain boundaries resulting from the inability of the chromium oxide layer to act as a diffusion barrier to sulfur. This breakdown of the

Cr_2O_3 protective scale duplicates the behavior of austenitic stainless steels in in-situ retort exposures at LETC. The ability of the laboratory crucible to simulate the corrosion conditions that occur in large scale retorts was demonstrated.

The effect of chromium content in steel alloys exposed to oil shale retorting conditions were determined using the small laboratory crucible at a test temperature of 1000°C for 48 hours exposure. 15gm of fresh, finely ground Anvil points, Green River Shale with a 1.7 % sulfur content was used in each test of a 1.3cm x 1cm x 0.3cm size specimen. The steels that were tested were 1018 mild steel, 2 1/4Cr 1Mo steel 5Cr 1/2Mo steel, and 9Cr 1Mo steel. 410 ferritic and 304 and 310 austenitic stainless steels will also be tested.

Figure 8 shows a cross section of the mild steel with x-rays for iron and sulfur. The structure above the solid region of iron is iron oxide scale. The sulfur present is in small MnS inclusions that are normally present in the as-rolled steel. No sulfide formation was observed either externally or internally in this steel which contains no chromium. Of the four steels tested in this series, the 1018 underwent the greatest amount of corrosion.

Figure 9 shows the corrosion product that formed on the 2 1/4Cr 1Mo steel. An entirely different corrosion process took place on this steel. The heavy, outer scale was primarily iron sulfide with a small amount of chromium in it. Internal sulfidation also occurred, forming

primarily iron sulfide with some possible chromium sulfide. Some MnS inclusions in the as-rolled steel can also be seen. There is possibly some chromium oxide at the scale-metal interface, but it could also be chromium sulfide. The presence of the small amount of chromium, not enough to form a protective oxide layer, appeared to catalyze the formation of sulfides, primarily iron sulfide. The amount of corrodant, however, was less than that which formed on the 1018 steel.

Figure 10 is a cross-section of the 5Cr 1/2Mo steel exposed in the same oil shale environment as the previous two specimens. Yet another pattern of corrosion products occurred at this level of chromium. A thin, external, interrupted layer of iron oxide formed with no sulfur in it. Along the scale metal interface line a partial layer of chromium oxide appears as darker gray in the secondary electron image, upper left photo in figure 10. Some chromium oxide extends upward into the thin iron oxide layer. Starting beneath the chromium oxide layer are regions of internal sulfidation. No sulfide formation occurred from the bottom of the interrupted chromium oxide band upward to the external surface. It can be seen by comparing figures 9 and 10 that much less corrosion occurred on the 5 Cr containing steel compared to the steel containing 2 1/4 Cr.

The last steel in the test series so far is the 9Cr 1Mo steel; it is shown in Figure 11. In this steel, essentially no free scale formed during the 48 hour exposure. Even at only 9 Cr a continuous appearing Cr_2O_3 scale formed on the surface with no evidence of

any iron corrosion products above it. A rather extensive network of internal Cr_2O_3 formed, which is known to occur at intermediate chromium contents in austenitic stainless steels with 18 or more percent chromium. The Cr_2O_3 forms in a semi-chromium depleted zone beneath a surface Cr_2O_3 barrier scale. In the case of the 9 Cr content steel, the zone of ideal Cr content to form internal Cr_2O_3 was quite large. There was essentially no sulfide formation in the specimen, either externally or internally.

Thus, in the four alloys tested under the same oil shale exposure conditions, a different corrosion behavior occurred for each alloy, see figure 12. The occurrence of the various oxides and sulfides that formed on each alloy can be explained reasonably well using the equilibrium stability diagrams for Po_2 and Ps_2 . The occurrence of corrosion product in one form or another is primarily due to shifts in the compound formation lines on the stability diagram because of partial depletion of the reacting elements as they form corrosion products. The formation of iron sulfide scale on the 2 1/4Cr 1Mo steel rather than the iron oxide that formed on the Cr 1018 steel may be due to some subtle effect of the relatively small amount of either Cr or Mo present to promote sulfide formation by some catalytic type mechanism.

Thermowell Performance Analysis

Analysis of a plain carbon steel pipe used as a thermowell

protector in an actual underground in-situ retort in Utah shows a high level of corrosion with the formation of a porous, layered scale on the base metal shown on the right side of figure 13. The x-ray map shows that there are three layers: a layer next to the base metal of iron oxide with a small amount of sulfur in it, a middle layer of iron sulfide and an outer layer of iron oxide. At other locations along the 0.25" thick pipe, the metal was completely consumed, leaving layers of the iron oxide and iron sulfide. The severe attack observed is typical of that experienced by non-chromium containing alloys in in-situ oil shale retorts.

LOW TEMPERATURE CORROSION IN ABOVE - GROUND RETORTS. Test were performed to determine the nature of the corrosion problem in above - ground retorts where the operating temperatures are below 750°C, mostly around 500° - 550°C. As in the high temperature exposures, the tests consisted of both field and laboratory exposed samples. 7.5cm x 2.5cm x 6mm samples were exposed in a large scale, above ground retort in Colorado at temperatures to 500°C. Other exposures were made in LBL's 7.5cm diam. retort at a test temperature of 550°C. Studies of the effect of partial and total immersion in shale oil on the corrosion of steel were also conducted at temperatures to 300°C.

Tests samples of plain carbon and several 300 series stainless steels in the large scale above-ground retort showed mild corrosion (<20 mils/yr) only on the 1018 carbon steel after 400 hours of exposure. Very little corrosion was observed on the stainless

steels. Tests of several low alloy and stainless steels in the LBL 7.5cm diam. Retort at 550° for 48 hours again showed mild attack only on the plain carbon 1018 steel. Exposure of steels partially immersed in shale oil at 300°C for 100 hours showed essentially no corrosion on stainless steels and only mild corrosion on 1018 steel.

ELEVATED TEMPERATURE EROSION-CORROSION TESTER

XBL 821-7741

Figure 1
Elevated temperature erosion tester

Figure 2
Effect of particle hardness on erosivity of impacting particles

XBL 8110-7180

10 μm

1020 STEEL ERODED BY STEEL GRIT

$$V = 80 \text{ m/sec}$$

$$\alpha = 30^\circ$$

$$E_R = 5.3 \times 10^{-4} \frac{\text{g}}{\text{g}}$$

10 μm

1020 STEEL ERODED BY STEEL SHOT

$$V = 80 \text{ m/sec}$$

$$\alpha = 30^\circ$$

$$E_R = 1.4 \times 10^{-4} \frac{\text{g}}{\text{g}}$$

Figure 3
Appearance of 1020 steel surface eroded by angular
and spherical steel shot.

XBL 8110-7149

Figure 4
Erosion of 304SS and A53 mild steel in 30 wt % ,
30 mesh coal-kerosene slurry at 94°

XBL 8110-7190

Figure 5
Erosion of 304SS and A53 mild steel in 50 wt %,
-200 mesh coal-kerosene slurry at 94°C

Figure 6
Effect of impingement angle on spheroidized 1020 steel

XBL 8110-7144

10 μ m

Fe Map

Cr Map

S Map

304SS, 48hrs., 1000°C

Figure 7

Corrosion scale formed on 304SS in laboratory crucible test

35 μ m

Fe Map

1018 Steel

S Map

Figure 8 - Cross section of corroded 1018 steel from crucible tests

25 μm

Fe Map

Cr Map

S Map

2 1/4Cr-1Mo Steel

Figure 9 - Cross section of corroded 2 1/4Cr-1Mo steel from crucible tests

20 μm

Fe Map

Cr Map

S Map

5Cr- $\frac{1}{2}$ Mo Steel

Figure 10 - Cross section of corroded 5Cr $\frac{1}{2}$ Mo steel from crucible tests

25 μ m

Fe Map

Cr Map

S Map

9Cr-1Mo Steel

Figure 11 - Cross section of corroded 9Cr1Mo steel from crucible tests

FIGURE 12
MORPHOLOGY OF SURFACE AREA OF
4 STEELS OF VARYING Cr CONTENT

	1018 (0% Cr)	2 $\frac{1}{4}$ Cr1Mo	5Cr $\frac{1}{2}$ Mo	9Cr1Mo
SCALE-METAL INTERFACE		FeS ₂	Fe ₂ O ₃	
	Fe ₂ O ₃	Cr ₂ O ₃	Cr ₂ O ₃	Cr ₂ O ₃
		MoS ₂	MoS ₂	Cr ₂ O ₃
		INTERNAL SULFIDE	INTERNAL SULFIDE	INTERNAL OXIDE
	BASE METAL	BASE METAL	BASE METAL	BASE METAL

100 μ m

Plain Carbon Steel Pipe from
in-situ retort

Fe Map

S Map

Figure 13 - Corrosion scale on a plain carbon steel pipe from an in-situ retort

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PART III — MATERIALS FOR COAL GASIFICATION

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ANL-4.1, -4.3, -4.4 - CORROSION OF ALLOYS
FOR COAL GASIFICATION ENVIRONMENTS

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SUMMARY OF CURRENT ACTIVITIES

The purposes of this program are to (1) experimentally evaluate the high-temperature corrosion behavior of iron- and nickel-base alloys in gas environments with a wide range of oxygen, sulfur, and carbon potentials, (2) develop mechanical-property data on several Fe-Cr-Ni alloys exposed to complex gas mixtures typical of coal-conversion process environments, (3) develop corrosion information in the temperature range 400 to 750°C in simulated low- and intermediate-Btu gasification atmospheres using internally cooled specimens of selected commercial materials, (4) develop an approach that is based upon available thermodynamic and kinetic information for evaluating possible corrosion problems in coal-conversion systems, and (5) monitor technical aspects of gasification-materials programs funded by DOE/FE.

The effects of mixed-gas environments on mechanical properties must be known to establish the design and performance requirements of various components in a coal-gasification system. Metallic materials for internal members and external heat exchangers in a gasification system must operate under environmental conditions that strongly influence their mechanical properties. The stress-rupture strength of the best of these materials is quite low in the temperature range (800-1000°C) that typifies most second-generation gasification processes. The gasification environment may result in even lower levels of stress-rupture strength and low ductility owing to intergranular penetration of sulfur into the base metal.

During this reporting period, two constant-load creep-test machines were equipped with high-temperature environmental chambers capable of operation in mixed-gas atmospheres. Two additional machines are presently

being modified to handle the complex gases. In addition, two machines are being used to develop baseline data in an air environment. The present tests are being conducted on Incoloy 800 H cylindrical specimens designed as per ASTM specifications. The control tests are conducted in air and the mixed-gas tests are conducted in a medium-Btu gas environment that simulates the U-Gas process. Table I lists the U-Gas process chemistry and the calculated and experimentally used values for oxygen and sulfur partial pressures.

Figures 1 and 2 show the creep strain-time plots for specimens tested at 843°C, 55.2 MPa and 927°C, 41.4 MPa, respectively. Table II lists the pertinent creep data obtained from these preliminary creep tests. The results show that even though minimum creep rates are the same or lower in the U-Gas environment compared to those in air, the rupture ductility and rupture times are significantly lower in the mixed-gas environment. Additional tests are being conducted at lower stress levels and other temperatures to establish the role of mixed-gas atmospheres on the creep properties of Incoloy 800 H.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

¹Materials Technology for Coal-conversion Processes: Progress Report for October-December 1981, Argonne National Laboratory Report ANL/FE-82-9 (in preparation).

Table I. U-Gas Process Chemistry and Calculated and Experimentally Used Values for Oxygen and Sulfur Partial Pressures in the Test Program

<u>U-Gas Chemistry (Mole Percent)</u>				
	CO	21.50		
	CO ₂	14.23		
	H ₂	26.17		
	H ₂ O	33.16		
	CH ₄	3.53		
	H ₂ S	0.79		
	COS	0.03		
	N ₂	0.57		
	NH ₃	0.02		
T (°C)	<u>Calculated</u>		<u>Experimental</u>	
	843	927	843	927
p _{O₂} (atm)	2 x 10 ⁻¹⁸	1.0 x 10 ⁻¹⁶	1.3 x 10 ⁻¹⁸	7.8 x 10 ⁻¹⁷
p _{S₂} (atm)	2 x 10 ⁻⁷	8.5 x 10 ⁻⁷	2 x 10 ⁻⁷	8.9 x 10 ⁻⁷

Table II. Creep Data for Incoloy 800 H

<u>T (°C)</u>	<u>σ (ksi)</u>	<u>t_r (h)</u>	<u>ε_r (%)</u>	<u>$\dot{\epsilon}_{III}$ (s⁻¹)</u>	<u>Environment</u>
843	8	79.6	38.3	9.3 x 10 ⁻⁷	air
	8	27.3	8.6	3.4 x 10 ⁻⁷	U-Gas
927	6	16.9	38.5	3.8 x 10 ⁻⁶	air
	6	6.3	16.8	3.3 x 10 ⁻⁶	U-Gas

Fig. 1. Creep Strain-Time Curves for Incoloy 800 H Specimens Tested in Air and Mixed-gas Environments at 843°C.

Fig. 2. Creep Strain-Time Curves for Incoloy 800 H Specimens Tested in Air and Mixed-gas Environments at 927°C.

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INEL-4.3 — THE EFFECT OF COAL GASIFICATION ATMOSPHERES
ON BIAXIAL CREEP OF ALLOYS

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INTRODUCTION

Several processes have been proposed for production of high-Btu coal gas, but none has been developed commercially. Concern exists regarding the integrity of construction materials under the relatively severe process conditions anticipated. No other industrial process is sufficiently similar to alleviate these concerns. A test program was, therefore, begun under the sponsorship of the American Gas Association to evaluate the behavior of various proposed construction materials in the coal gasification environments of greatest concern. This work has continued under the sponsorship of ERDA, DOE, and the Gas Research Institute. The Metal Properties Council (MPC) has been the prime contractor and has provided technical guidance.

Exposure of candidate materials, in both laboratory-simulated environments and pilot plants, has been used to evaluate such effects as corrosion, erosion-corrosion, and the possible effects of coal gasification atmospheres (CGAs) upon selected mechanical properties. Most of the corrosion and erosion-corrosion work has been done by the Illinois Institute of Technology Research Institute (IITRI). The mechanical properties work has been conducted primarily at the Southwest Research Institute (SwRI) on nine candidate alloys for gasifier internals. Impact, uniaxial stress rupture, tensile, and some fatigue properties have been measured there.

Many potential applications of these candidate alloys involve biaxial loading. A DOE-sponsored test program was, therefore, initiated by EG&G Idaho, Inc., at the Idaho National Engineering Laboratory (INEL) to measure the biaxial stress rupture strength, life, and ductility of four candidate alloys for gasifier internals under simulated CGA conditions. The data from the tests would be used to confirm any trends observed in the uniaxial stress rupture tests, demonstrate the differences caused by biaxial loading, and produce an empirical correlation between uniaxial and biaxial rupture strengths. Cyclic creep testing of these four alloys in CGA is planned for the future.

RESULTS FROM PRIOR QUARTERS

Two systems were designed and built to perform the described testing: one to test tubular specimens in air at atmospheric pressure, the other to test tubular specimens in various high-pressure simulated CGAs. The input compositions of these atmospheres are shown in Table 1.

TABLE 1. SIMULATED CGA COMPOSITIONS

	<u>MPC^a</u>	<u>Bigas</u>	<u>Synthane</u>	<u>Battelle</u>
H ₂	24	15	18	48
CO	18	12	10	26
CO ₂	12	13	18	5
CH ₄	5	7	16	6
H ₂ O vapor	40	52	37	14
NH ₃	1.0	1.06	0.6	0.6
H ₂ S	0.5	0.53	0.3	0.3

a. Composition used at IITRI, SwRI, and INEL (Reference).

Target 100-h biaxial stress rupture tests were completed on the four selected alloys (Type 310 stainless steel, Incoloy 800H, Haynes 188, and IN-657). These alloys were shown by gaseous corrosion tests at IITRI to have comparatively good corrosion resistance to a simulated CGA. The rupture behavior was first determined in air at atmospheric pressure and then comparative tests were run at 1000 psi in air, an MPC reference CGA, and three widely differing simulated gasification pilot plant atmospheres. The temperature range used was 1200-1800°F. The results of these tests are presented in Figures 1-4. Note that two different heats of Type 310 stainless steel were tested.

These experiments have shown that, except at temperatures of 1800°F, the biaxial stress rupture behavior of these alloys is affected very little, if at all, by a nominal 100-h exposure to a simulated CGA. The disagreement in values observed at 1800°F was postulated to be due to cyclic creep loading arising from the gas pressure control system (discussed in current activities). At lower temperatures, the biaxial stress rupture life/strength was usually close to the mean of the values of uniaxial stress rupture life/strength from several alloy heats reported in the literature. The biaxial ductility of a few percent at tube rupture was generally unchanged by exposure to CGA.

More recently, target 500-h tests were run at 1500°F in the MPC composition atmosphere, using the high-pressure system, to determine whether longer exposure to CGA will affect stress rupture behavior. No change in stress rupture behavior was detected in these longer-term tests.

The atmospheric pressure test system (APTS) was remodeled to permit the simultaneous testing of four specimens at atmospheric pressure in a simulated CGA. The partial pressures of oxygen and sulfur are controlled to achieve this simulation. Continuous gas flow is used to prevent depletion of the various chemical species. Automatic flow control also gives better control of gas composition than manual control.

Figure 1. Rupture parameter of biaxially loaded Type 310 SS in various atmospheres.

Figure 2. Rupture parameter of biaxially loaded Incoloy 800H in various atmospheres.

Figure 3. Rupture parameter of biaxially loaded Haynes 188 in various atmospheres.

Figure 4. Rupture parameter of biaxially loaded IN-657 in various atmospheres.

Duplicate specimens of all four alloys were exposed in the remodeled APTS to a simulated medium-Btu CGA (simulating MPC composition) at 1650°F with a target life of 500 h. The calculated partial pressures of oxygen and sulfur at 1650°F were 6.4×10^{-17} atm and 3.2×10^{-7} atm, respectively. The results of these tests are also shown in Figures 1-4. The trend of these data is consistent with previous results at and below 1650°F. This is also true for the values of strain at rupture. This consistency indicates that tests performed in the remodeled APTS are valid and also that a nominal 500-h exposure at and below 1650°F to a simulated medium-Btu gas has no adverse effect on the stress-rupture behavior.

Tests in a simulated medium-Btu CGA at 1800°F with goal lifetimes of 500 h were not made, for two reasons: first, extrapolation of the corrosion observed in tests at lower temperatures or for shorter times at 1800°F suggested that corrosion might cause premature rupture in these tests; and second, interest in, and anticipated use of, these alloys at 1800°F has decreased greatly.

An extra test of IN-657 was conducted in the high pressure system in an attempt to assess whether cyclic creep was the correct explanation for the reduced life of all four alloys when tested in this system at 1800°F. A throttling valve added to the system reduced the fluctuation in the 1000 psi pressure from a nominal value of 40 psi to 28 psi. This change increased the rupture life to approximately that observed when the environmental pressure was constant. The higher value is represented by the data point labeled "reduced ΔP " in Figure 4. The increase in life supports the cyclic creep postulate but more work is needed to verify cyclic loading as the cause of reduced life.

DISCUSSION OF CURRENT ACTIVITIES

Exposure of the four alloys to a simulated low-Btu gas in the remodeled APTS was begun late last quarter and has continued during

this quarter. Biaxial stress rupture tests of duplicate specimens at 1500 and 1650°F with a target life of 500 h are planned. The oxygen and sulfur partial pressures to be used in the gas are given in Table 2. The results of the first 1650°F test are shown in Figures 1-4. No adverse effect on stress rupture life was noted. Little specimen corrosion was observed in this test. The rupture life recorded in the second test at 1650°F was much shorter. Moreover, the specimens in this test showed enough corrosion that rupture was probably accelerated by corrosion. The most obvious difference between these two runs was the use of a new reactor in the second run. It is believed that the Alonized coating on this new reactor acted as an oxygen getter and resulted in a more sulfidizing atmosphere. The cause of this variation in corrosion is being investigated. Reproducibility will be obtained before the low-Btu tests are continued.

TABLE 2. OXYGEN AND SULFUR PARTIAL PRESSURES IN SIMULATED LOW-BTU GAS

Temperature (°F)	P_{O_2} (atm)	P_{S_2} (atm)
1650	3×10^{-18}	3.7×10^{-7}
1500	1×10^{-19}	1.3×10^{-7}

Additional modifications are being made to the the high pressure CGA system in the attempt to verify that the cyclic creep load was the cause of the reduced stress rupture life observed at 1800°F. Efforts are under way to reduce the cyclic stress, inherent in the system operation, from the approximately 40 psi present in the original system design to 10 psi. An accompanying increase in stress rupture life would verify the one data point obtained for IN-657 (discussed in the prior section) and substantiate cyclic creep as the cause of the reduced rupture life. Efforts to analytically evaluate the probability of cyclic creep damage in this circumstance were hampered by the lack

of adequate high-temperature mechanical properties data. If the cyclic creep effect is verified, a test apparatus to examine this effect systematically will be designed and built.

MPC-4.4(A) - CORROSION OF METALS AND REFRACTORIES
IN COAL GASIFICATION PILOT PLANTS

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INTRODUCTION

The MPC coal gasification pilot plant corrosion evaluation program (Phases IIa and b) is directed to a critical assessment of potential corrosion problems in various coal gasification environments. Fabricated assemblies of metal and refractory coupons were exposed to the diverse environments at preselected locations having significant corrosion potential. The corrosion data, together with those from the Phases I and III laboratory tests, permit increased confidence in materials selection and corrosion rate prediction for coal gasification plants. The program includes metals and refractories: metals have been exposed in both high-temperature gasifier locations and in lower temperature quench system locations; refractories have been exposed only in gasifier environments.

RESULTS FROM PRIOR QUARTERS

Since the initiation of the Phase II corrosion monitoring program in 1974, active testing has been conducted in eight coal gasification pilot plants (see Table 2-1). Gasifier units, except in the BI-GAS process (entrained flow gasifier), have been of the fluid bed type. Test racks, positioned in these units, have been exposed to low-velocity gas/particulate impingement (fluid bed freeboard section; entrained flow off-gas). Quench system test sites have also experienced only low-velocity solid/liquid or vapor impingement in product gas quench towers, solid/liquid separators, and slurry mix tanks.

TABLE 2-1. STATUS OF PHASE II PILOT PLANT
CORROSION MONITORING, DECEMBER 1981

Pilot Plant	Number of Test Locations		Exposure in Progress	Number of Exposures Completed	Completion of Test Program
	Metals	Refractories			
HYGAS	11	1	-	4	Yes
CONOCO COAL	4	2	-	3	Yes
Synthane	7	1	-	2	Yes
Battelle	5	2	-	1	Yes
BI-GAS	7 + 2 ^a	1	3rd ^b	2	No
U-Gas	3 + 2 ^c	1	3rd ^c	2	No
Westinghouse	7	1	1st	0	No
PEATGAS	7	0	1st	0	No
GEGAS ^d	Test locations finalized. ^e				
Mountain Fuel ^f	Preliminary assessment of potential test locations.				

^aTwo new test racks were added (loc. 5 and loc. 6) inlines 401 and 601 in the BI-GAS process.

^bTest racks installed in October 1981.

^cTwo new test locations (loc. 5 and 6) in newly installed venturi scrubber systems were added.

^dGeneral Electric's Advanced Fixed Bed gasifier (Lurgi type) at Research Center near Schenectady, New York.

^eDesign of test racks to begin on receipt of drawings.

^fMountain Fuel Resources' proposed 3000 lb/hr downflow entrained flow gasifier to be built near Salt Lake City, Utah.

Metals

Phase I laboratory testing and Phase II pilot plant gasification corrosion monitoring have shown a number of high-temperature alloys to be suitable for gasifier applications if operating temperatures are below 1600°F. In contrast, a number of alloys, including Monel 400 and IN-600, were consistently found to have unacceptable corrosion rates (>20 mpy) and are regarded as unsuitable for gasifier internals.

Of the alloys tested, those appropriate for use in the temperature range 1600°-1800°F appear to be limited to Fe-Cr-Ni types with greater than about 25% Cr, and the higher Cr cobalt-base alloys. The diffusion zone formed by pack aluminizing of alloys IN-800 and Type 310 has shown some promise for corrosion protection, but the coating itself incurs many cracks due to thermal cycling. The cracks form short circuit corrosion paths up to the diffusion zone, thereby undermining the corrosion protection of the Al_2O_3 coating. In the CONOCO COAL regenerator (non-gasifier environment), pack-aluminized alloys outperformed their uncoated counterparts.

Accumulated Phase II data for coal pretreatment and gasifier quench systems show that uncoated carbon steel and other iron-base alloys (2½Cr-1Mo, silicon iron, cast iron, Ni-Resist, Ni-Cu Resist) corroded at unacceptable rates (>10 mpy) in almost all low-temperature pilot plant locations. To date, stainless steel Types 329, 316, 304, and 18-18-2 and EBRITE 26-1 appear more acceptable than Types 430 and 410, the latter two being susceptible to deep localized corrosion in many test locations.

Refractories

Current data (up to 1981) have shown very limited degradation of dense refractories exposed in six pilot plants under non-slagging conditions. In general, it appears that refractories with compositions of greater than 60% alumina and less than 30% porosity have experienced little degradation during exposure. Phosphate-bonded materials, originally thought to be unlikely to withstand the gasifier environments, have shown no significant attack.

There are exceptions to the generalized rule: Alfrax bubble alumina, with greater than 30% porosity, has shown no significant deterioration, whereas silicon nitride bonded silicon carbide with less than 30% porosity has deteriorated in atmospheres of high steam content.

DISCUSSION OF CURRENT ACTIVITIES

A summary of quarterly work activities for 1981 is given in Table 2-2. Corrosion monitoring in the HYGAS process has been completed; a topical report on materials testing in this pilot plant has been issued for MPC committee review. Topical reports have also been issued for testing completed in the Synthane and CONOCO COAL (CO₂-Acceptor) processes. Similar reports will be available for the U-Gas and BI-GAS processes where materials testing is continuing.

Discussions were held with General Electric (GEGAS process) and Mountain Fuel Resources (proposed pilot plant) personnel to identify potential material test locations. Preliminary discussion documents outlining potential material test sites and hypothetical rack designs were then forwarded to each firm for approval. Details of rack design and materials selection will be finalized during early 1982.

Corrosion Data--Metals

Materials and Method of Analysis

The nominal compositions of Phase II test alloys are given in Table 2-3. Pack-aluminized alloys Type 310, IN-800, and carbon steel A515 are also included. During welding of the bead-on-plate U-bends, the backside of the specimen is shielded by argon gas. Only alloy 18SR received post-weld heat treatment.

Corrosion after exposure was determined by both gravimetric and metallographic analysis of exposed specimens. However, different techniques were applied to specimens exposed in the quench system and gasifier. Wherever possible, the results of both gravimetric and metallographic measurements were incorporated in generation of corrosion data, along with supplementary SEM analysis, as required.

TABLE 2-2. PHASE II ACTIVITIES DURING 1981

Quarter	Progress
I	<ol style="list-style-type: none"> 1. Completion of the Phase II contribution to the 1980 Annual Report. 2. Fabrication of first-exposure racks for PEATGAS pilot plant. 3. Initiation of corrosion analysis of specimens from the fourth exposure in HYGAS. 4. Initiation of first exposure in Westinghouse PDU.
II	<ol style="list-style-type: none"> 1. Completion of HYGAS fourth exposure corrosion analysis. 2. Discussion with GEGAS and Mountain Fuel Resources personnel to identify potential materials test locations. 3. Compilation of materials selection list for inclusion in exposures during 1981 program for ORNL. 4. Phase II contributions to the MPC Semiannual Meeting. 5. Initiation of first exposure in PEATGAS.
III	<ol style="list-style-type: none"> 1. Completion of corrosion analysis of U-Gas gasifier second-exposure coupons. 2. Completed physical property measurement of reference refractory specimens for BI-GAS (3rd exposure), U-Gas (2nd exposure), and Westinghouse (2nd exposure). 3. Corrosion monitoring discussion documents were forwarded to General Electric and Mountain Fuel Resources for review. 4. Completion of CONOCO COAL "topical report." 5. Completion of rack fabrication for BI-GAS (3rd exposure), U-Gas (3rd exposure), and Westinghouse (2nd exposure) pilot plants. 6. Completion of corrosion analysis of second-exposure U-Gas quench system coupons.
IV	<ol style="list-style-type: none"> 1. Compilation of up-dated materials selection list for inclusion in exposures during 1981/1982 for ORNL. 2. Issued HYGAS and Synthane topical reports for MPC Phase II Committee review. 3. Initiated third exposure in U-Gas pilot plant. 4. Completed corrosion analysis in second exposure coupons from the BI-GAS pilot plant. 5. Completed detailed analysis of selected coupons from the U-Gas and Synthane pilot plants. 6. Continued effort on U-Gas and BI-GAS topical reports.

TABLE 2-3. NOMINAL CHEMICAL COMPOSITIONS OF PHASE II TEST ALLOYS

Alloy	C	Mn	Si	Fe	Ni	Cr	Co	Al	Mo	Others
Carbon steel A515	0.22	0.62	0.2	Bal						
A515 (Al) ^a										
Carbon- $\frac{1}{2}$ Mo	0.15	0.45	<0.03	Bal					0.5	
1 $\frac{1}{2}$ Cr- $\frac{1}{2}$ Mo	0.15	0.40	0.5	Bal		1.25			0.5	
2 $\frac{1}{2}$ Cr-1Mo	0.15	0.45	<0.3	Bal		2.25			1.0	
5Cr- $\frac{1}{2}$ Mo	0.15	0.45	0.23	Bal		5.6			0.5	
Cast iron (A-278)	3.02	0.67	1.93	Bal	1.6				0.4	
Si-iron (A-518)	1.1	1.5	14.5	Bal		0.5			0.5	0.5Cu
Ni-Resist (A-439 D2B)	2.8	0.91	2.81	Bal	19.8	3.1				
Ni-Resist (Cu) (A-436 1B)	3.0	1.5	2.80	Bal	17.5	3.5				6.5Cu
405	0.08	1.0	1.0	Bal		13.0				0.2Al
410	0.13	0.35	0.54	Bal	0.5	12.0			0.1	
430	0.06	0.36	0.62	Bal		0.4				
446	0.10	0.45	0.38	74.6	0.4	24.0				
26-1	0.02	0.27	0.43	Bal	0.3	25.6			1.0	0.42Ti
329	0.05	0.5	0.4	Bal	4.3	27.1			1.4	
HC-250	3.03	0.5	0.7	68.1	0.1	27.5			0.01	
HK-40	0.4	2.0	2.0	Bal	20.0	28.0			0.5	
HL-40	0.47	0.6	1.4	47.1	19.4	30.9			0.01	
HL40-3Si	0.42	0.7	2.4	45.8	19.3	31.4			0.01	
304	0.05	1.45	0.54	70.0	9.1	18.8			0.34	
309	0.11	0.54	0.74	60.5	14.7	23.0				
310	0.06	1.71	0.68	52.2	20.2	25.0				
310(Al) ^a										
314	0.06	1.90	2.21	51.6	20.0	24.0				
316	0.05	1.65	0.43	65.3	13.9	17.1			2.5	
321	0.04	1.60	0.40	Bal	10.0	17.7			0.4	0.35Cu, 0.2Ti
347	0.08	2.0	1.0	Bal	9-13	17-19				Cb+Ta, 10 X C min
Crutemp 25	0.07	1.5	0.6	47.2	24.8	25.4			0.4	
18-18-2	0.05	1.35	2.0	Bal	18.2	18.1				0.08Cu
20Cb3	0.03	0.56	0.50	Bal	33.0	19.4			2.1	3.1Cu, 0.91Cb+Ta
21-6-9	0.04	8.2	0.7	62.9	6.8	20.7			0.22	
22-13-5	0.05	5.3	0.5	Bal	13.5	21.1			2.25	0.14Cb, 0.2V, 0.3N
IN-800	0.03	0.80	0.33	47.1	30.8	20.6	0.10	0.32		0.42Ti
IN-800(Al) ^a										
IN-793	0.03	0.72	0.40	43.2	32.2	21.4	0.02	1.76		
IN-825	0.04	0.56	0.30	28.3	42.0	21.9		0.06	3.2	2.1Cu, 0.7Ti
RA-330	0.05	1.5	1.3	Bal	36.0	19.1				0.19Cu
RA-333	0.05	1.5	1.4	15.5	45.0	26.3	2.5		3.8	2.7W
30/50W	0.51	0.87	1.0	Bal	48.7	27.9				3.6W
IN-600	0.05	0.15	0.20	7.0	76.5	15.8	0.08			
IN-625	0.05	0.2	0.2	2.5	61.0	21.5	1.0 max	0.2	9.0	0.2Ti, Cb+Ta 3.6
IN-601	0.04	0.24	0.19	15.9	59.5	22.5	0.03	1.19		
Alloy X	0.09	0.69	0.44	19.5	44.6	21.9	2.5	0.21	9.1	0.5W
IN-671	0.06	0.06	0.39	1.1	47.8	50.2				0.24Ti
556	0.1	1.5	0.4	Bal	20.0	22.0	20.0	0.3	3.0	2.5W, 0.02La, 1.0Cb+Ta
IN-617	0.07				54.0	22.0	12.5	1.0	9.0	
N155	0.10	1.3	0.6	29.0	19.8	20.9	19.5		3.0	1.1Cb+Ta, 2.8W
T63WC	0.52	0.10	1.4	Bal	36.0	28.2	15.0			5W
188	0.09	0.6	0.4	1.2	22.9	22.0	Bal	0.22	0.6	0.07La, 14.5W
150	0.08	0.5	0.5	18.0	1.4	27.9	Bal		0.1	
6B	1.0	1.4	0.5	1.9	2.8	28.1	57.1		1.2	4.8W
CN7M	0.07	1.5	1.5	42.3	29.0	20.5				3.0Cu min
Titanium 50A	0.02			0.14						0.14N, Bal Ti
Monel 400	0.14	1.06	0.14	1.9	63.6					33.2Cu
Al-Bronze (CDA 954)				3.3	2.0			10.36		Bal Cu

^aPack aluminized

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Gravimetric analysis of specimens exposed in quench systems was conducted after chemical removal of surface scales. Surface scales were removed according to NACE Standard TM01-69. Any specimen exposed in the quench system equipment with gravimetrically calculated corrosion of greater than 1 mil was subsequently sectioned for metallographic measurements of metal loss. Pit depth measurements were made by optical microscopy using depth-of-focus technique.

U-bend specimens from pilot plant exposures were cleaned and examined at 30X under a binocular microscope for stress-corrosion cracks. Visual observations of stressed U-bend specimens are also included in the data tables.

Metallography in conjunction with weight loss measurements was employed for all specimens exposed to gasifier type environments. The metallographic techniques have been described in detail in earlier annual reports on this program. Briefly, loss of metal through both scaling and internal corrosion was determined using the original specimen dimensions. Scaling and internal corrosion were then summed up to obtain a total corrosion parameter. Only the scaling metal loss determined metallographically can be compared with the calculated metal loss obtained from weight change. Significant internal corrosion can occur with little weight change.

The time dependence of corrosion rates for test alloys exposed in various pilot plants is not known. Thus, corrosion data obtained in this report assume linear corrosion behavior. This assumption assists comparison of corrosion losses from specimens exposed for different durations under highly transient conditions. Quoted linear corrosion rates are in terms of mils per year (mpy).

In pilot plant corrosion data, both operational and total exposure times were used in the corrosion rate calculations for quench system environments. This was necessary since the relative contribution of operation and standby conditions to metal loss could not be assessed.

For high-temperature gas phase exposures in the gasifiers, linear corrosion rates were based only on the operational exposure times. In gasifier exposures it was not considered likely that standby or shutdown conditions would have made any significant contribution to the corrosion of the high-temperature alloys.

HYGAS Pilot Plant

Post-exposure metallographic and gravimetric analyses of corrosion coupons were completed during the reporting period. This section is a discussion of corrosion data for the following locations in HYGAS for the fourth exposure:

<u>Location No.</u>	<u>Process Unit</u>	<u>Rack Position</u>
1	Fluidized bed pretreater	Freeboard section
3	Pretreater quench tower	Off-gas
4	Feed slurry mix tank	Slurry phase
6	Steam-oxygen gasifier	Freeboard section
7	Second-stage hydrogasifier	Freeboard section
9	First-stage hydrogasifier	Freeboard section
10	Slurry dryer	Freeboard section
11	Prequench tower	Aqueous phase
12	Quench separator	Oil/water phase
13	Product gas quench tower	Off-gas
14	Char slurry mix tank	Slurry phase

The fourth exposure period encompassed HYGAS runs 83 to 87. During these test runs, washed Western Kentucky coals No. 9 and No. 11 were processed under demonstration plant operating conditions.

Location 1 - Fluidized Bed Pretreater. In the fluidized bed pretreater, the caking tendency of coals with high swelling indices is destroyed by mild oxidation at 750° to 800°F with air and steam. The specimen rack was exposed to the gases at 3 to 5 ft above bed level.

The corrosion performance of most stainless steels for the fourth exposure parallels that of the second and third exposures. Austenitics (Types 304 and 316) incurred the least corrosion attack with linear corrosion rates of <2.5 mpy after 1803 hr. Martensitic Type 410 experienced mild localized attack to a maximum of 2.4 mils in scattered areas. Previous results from this location have shown that Type 410 incurs corrosion attack resulting in rates as high as 22 mpy (2nd exposure, 1790 hr) and as low as 0.7 mpy (1st exposure, 1719 hr); corrosion by internal penetration has always been the major mode of attack. In all four exposures, the austenitics have consistently performed well compared to martensitic Type 410, which contains only 12% Cr.

Carbon steel and aluminized carbon steel incurred corrosion rates of 18 and 51.6 mpy, respectively, during the fourth exposure. The uncoated carbon steel suffered localized corrosion attack with minimal scaling loss, as in the second exposure period. The aluminized coupons, however, incurred corrosion attack at cracks in the coating, the penetration extending to the diffusion layer. Considerable loss of the coating (3.5 mils) also occurred.

No evidence of stress-corrosion cracking was found in Type 304 or Type 316 welded U-bends.

Location 3 - Pretreater Quench Tower. This test site was near the top tray in the upper portion of the tower. Gases produced from pretreatment of caking coals are cooled from 750°F to approximately 180°F at 1.1 psig by contacting with process water.

The corrosion data shows all average corrosion loss values to be <0.1 mil except for carbon steel (max. 39.4 mils). Carbon steel experienced uniform overall corrosion at the rate of 192 mpy. Pits were measured on Type 410, to a maximum of 3.0 mils. Austenitic steels Type 316 and Type 304 suffered no observable pitting and incurred corrosion rates of <0.5 mpy.

Stress-corrosion cracks were not found in welded U-bend specimens of carbon steel, Type 316, or Type 304.

Location 4 - Feed Slurry Mix Tank. In this process vessel, pre-treated coal and toluene are slurried for introduction into the HYGAS multistage reactor. The coupon rack is immersed in the slurry phase at a temperature of 85°F and pressure of 5 psig.

Due to the short duration of the operational exposure (1004 hr), the corrosion rates for carbon steel and Type 410 are higher when compared to the three previous exposures. After the 1004 hr exposure, carbon steel experienced maximum uniform corrosion (13.1 mils) at a rate of 114 mpy as determined from metallographic data. Martensitic Type 410 experienced mild pitting attack (7.8 mils max) and corrosion to the extent of 2.3 mils in 1004 hr. Type 304 stainless experienced only minor overall corrosion loss of <1 mpy; pitting attack was not observed.

No welded U-bends were exposed during the fourth exposure.

Location 6 - Steam-Oxygen Gasifier. In the fluid bed steam-oxygen gasifier, char produced in the upper gasifier stages is reacted with steam and O₂ at 1500-1750°F. The test rack was positioned on a dipleg in the freeboard section of the reactor.

Due to the short time of the exposure (671 hr), the linear corrosion rates for most alloys were higher than those in the three previous exposures. Alloys IN-800, Type 309, Type 310, Type 446, and IN-671 incurred the least amount of degradation of the alloys tested, with corrosion rates of <20 mpy. IN-671 and Type 446 suffered considerable scaling loss but minimum attack due to internal penetration. Type 310 experienced the least corrosive attack (5.2 mpy). Alloy RA-333 suffered localized corrosion at the sample edge to the extent of 6.3 mils (82.2 mpy).

The aluminized alloys, Type 310 and IN-800, experienced the same mode of attack in other pilot plant exposures. An isolated area of attack on the 310(Al) specimen penetrated well into the diffusion layer. This resulted in a measured corrosion rate of 99.2 mpy, which is approximately twice that for IN-800(Al) (54.8 mpy).

Location 7 - Second-Stage Hydrogasifier. In this reactor, the gases produced by the steam-oxygen gasifier are reacted with partially devolatilized char. As in location 6, the corrosion rack test site is in the freeboard section above the fluidized bed.

In general, the corrosion rates obtained were lower than those in the steam-oxygen gasifier. The average operating temperature in the second-stage hydrogasifier was 1525°F, compared to an average of 1675°F in the steam-oxygen gasifier. The better performing materials (IN-671, Type 310, Type 309, Type 446, RA-333) suffered minimal scaling loss and internal penetration with rates of <4 mpy. This is in general agreement with earlier exposures for uncoated samples. Aluminized IN-800 and Type 310 experienced corrosion rates of 56 and 106 mpy, respectively.

Location 9 - First-Stage Hydrogasifier. This spouting bed fluidized reactor functions to separate partially reacted char from the gas phase; at the operating temperature (900°-1100°F) some hydrogenation reactions do occur. The corrosion test site was situated near the reactor side wall in the freeboard section (gas phase).

It was observed that the stainless steels, especially the austenitic steels, suffered minor attack (linear rates of <20 mpy); previous longer term exposures gave similar results. However, in this fourth exposure period, 21-6-9 incurred corrosion attack via internal penetration (7.3 mils) to the extent of 71 mpy (linear rate); earlier longer exposures--second (1355 hr) and third (2292 hr)--resulted in corrosion rates of 13 mpy and 3.1 mpy, respectively. Ferritic Type 430 experienced only minor attack (<20 mpy).

Location 10 - Slurry Dryer. Toluene, used as a coal particle transport medium, is flashed off in the slurry dryer at 500° to 600°F. The remaining coal particles are partially devolatilized in the fluidized process gas stream. The coupon racks were located in the gas phase (freeboard) near the reactor side wall.

The operating temperatures in this vessel were the lowest in the HYGAS gasifier, and a broader range of materials was selected for testing. The short operational exposure time (924 hr) resulted in high corrosion

rates for Type 430 (26.5 mpy) and the low alloy steels ($\frac{1}{2}$ Mo and 5Cr- $\frac{1}{2}$ Mo--about 50 mpy); their corrosion rates in the third exposure were less than 20 mpy. The $\frac{1}{2}$ Mo and 5Cr- $\frac{1}{2}$ Mo low alloy steels in the 3rd exposure period (2292 hr) suffered losses equivalent to linear corrosion rates of 10.3 and 16.4 mpy, respectively.

The austenitic steels and titanium 50A incurred overall corrosion attack of approximately 0.2 mil (2 mpy). Type 410 suffered only minor attack, via internal penetration, not exceeding 1.4 mils in 924 hr of exposure. These alloys, including titanium 50A, have shown low corrosion rates in all four exposure periods.

Location 11 - Product Gas Prequench Tower. The prequench tower functions to reduce product gas temperature from 500° to 135°F by contacting with cool process water. The quenching operation causes toluene and water to condense from the gas and collect in the bottom section of the tower. The corrosion test rack is located in the bottom collection section where the temperature approaches 250°F at pressures of 600 to 900 psig. The exposure period was 823 hr.

The austenitic steels (Type 304, 18-18-2), ferritic alloy 26-1, and titanium 50A sustained the least corrosion at rates of <1.1 mpy. Alloy Type 304 experienced pitting toward the sample edge (9.0 mils max). Martensitic Type 410 suffered semi-localized corrosion as well as pitting (10.6 mils max). Localized corrosion resulted in a metallographically determined rate of 64.9 mpy under operating conditions. Aluminum bronze showed relatively better corrosion resistance than Type 410. This was also the case during the second exposure period.

Corrosion loss measurements on cast iron, Ni-Cu Resist, and Ni-Resist by metallographic methods resulted in corrosion rates between 103 and 158 mpy. Carbon steel, with a maximum corrosion loss of 17.8 mils, had the highest corrosion rate (78.2 mpy) in this location.

Stress-corrosion cracks were not detected in welded U-bends of Type 304, 18-18-2, or 26-1.

Location 12 - Quench Separator. This process unit separates water and toluene by decantation. Temperatures vary in the range of 95° to 120°F at pressures of 600 to 900 psig. The corrosion rack was positioned where contact was made with the water/toluene liquid phase.

The corrosion data were based on 924 hr of exposure to the operating conditions. As in previous exposure, carbon steel suffered uniform corrosion loss at 291 mpy. Type 410 and Type 430 incurred extensive semi-localized corrosion losses and pitting with rates of 88.2 mpy and 66.4 mpy, respectively. Mild pitting was detected on Type 304 with a corrosion rate of <1.0 mpy.

Stress-corrosion cracks were not detected in welded U-bends of carbon steel on Type 304.

Location 13 - Product Gas Quench Tower. This unit reduces the product gas temperature from 130° to 95°F by contacting with cool process water. The coupon rack was located in the top of the tower where cooled product gas contacts the samples.

This location proved to be the most aggressive for carbon steel (555 mpy) and Type 410 (75.8 mpy) compared to other locations. Heavy pitting and deep localized areas of corrosion were observed on Type 410 (17.4 mils max). The austenitic steel Type 304 sustained deep pitting attack to a maximum of 14.2 mils; overall corrosion was minimal.

No stress-corrosion cracks were detected in the Type 304 welded U-bend specimens.

Location 14 - Char Slurry Mix Tank. Gasifier char is slurried with water at 600 to 900 psig in the slurry mix tank. Corrosion coupons are positioned in the char/water slurry at a constant temperature of 100°F.

The trend of increasing corrosion loss parallels that in other locations: Type 304 < Type 410 < carbon steel. Type 304 stainless incurred milder pitting compared to Type 410.

No stress-corrosion cracks were observed in U-bend specimens of Type 304 or carbon steel.

U-Gas Pilot Plant

During the reporting period, post-exposure metallographic analysis was completed for second-exposure corrosion coupons from the U-Gas gasifier, product gas scrubber, and scrubber sludge tank.

The second-exposure period encompassed U-Gas runs 201 to VEGG-3. During the exposure the following coals were gasified:

<u>U-Gas Run No.</u>	<u>Coal Gasified</u>
157-160	Pittsburgh No. 8 Bituminous
201-206	Western Kentucky No. 6 Bituminous
VEGG-1	Australian Bituminous
VEGG-2	Wyoming Subbituminous
VEGG-3	Polish Bituminous

Location 1 - Gasifier. The corrosion racks were situated in the gasifier freeboard section just below the internal cyclone. Temperatures at this test location are approximately 150°F less than the bed temperature (1835°-1953°F). In general, the cobalt-base and nickel-base alloys showed better corrosion performance than iron-base alloys.

Alloys 188, 6B, and X incurred the least corrosion losses which resulted in equivalent linear corrosion rates of <15 mpy during the 1581 hr exposure period. Marginal performance was obtained with N155, IN-671, RA-333, IN-800(A1), and T63WC with linear rates of <31 mpy but >20 mpy. Higher corrosion losses (>5.5 mils) resulted for HL-40, HK-40, Type 310(A1, and Type 310; equivalent linear corrosion rates were >31 mpy.

From a qualitative compositional standpoint, higher chromium content in the alloy was not a sufficient criterion for better corrosion resistance under the test conditions. This can be seen by comparing corrosion losses for T63WC, HK-40, and HL-40 to 188, Alloy X, and N155. The first three alloys contain 28.0 to 30.9% Cr, while the latter three have 20.9 to 22.0 wt% Cr. Cobalt and nickel content compositions were also important. For alloys containing Ni, Cr, and Co (188, 6B, Alloy X, N155, RA-333, T63WC) as major constituents, the higher the weight percent ratio of (Co + Ni)/Cr, the better performing the alloy.

For coated alloys, IN-800(Al) corroded at half the corrosion rate of Type 310(Al). The corrosion attack was predominantly along cracks in the bulk coating for both alloys.

In addition to standard corrosion analyses, exposed specimens (Type 310, Type 310(Al), HK-40, IN-671, 188) from the second exposure were examined by SEM EDX spot analysis method. A limited number of X-ray maps of elements were also taken. The outer surface of the oxide scales was analyzed in the as-received condition. Following surface analyses, each specimen was carefully cross sectioned and mounted. Spot analyses were conducted on the sectioned metal surface starting from the scale/metal interface and proceeding into the interior region of each specimen.

It was found that chromium and iron were depleted at the scale/metal interface while nickel enrichment was observed. The buildup of nickel at the interface has resulted in nickel sulfide formation, as shown by X-ray maps in Fig. 2-1. Analysis of the scale in cross-section was not possible since the oxide scale separated from the metal during polishing. The scales were probably mixed oxides with variable amounts of Cr, Fe, Ni, and S.

For pack-aluminized Type 310, chromium concentration dropped sharply in the diffusion zone, but a considerable amount of aluminum was present. The concentration of other elements did not show any appreciable changes. The internal particles present in the cross-section of 310(Al) were mainly aluminum-rich oxide as one would expect from thermodynamic considerations. The normalized concentration (of internal oxides) was 95.8% Al, 1.3% Fe, 2.9% Ni.

Chromium and nickel concentration decreased appreciably at the scale/metal interface of alloy HK-40, and a corresponding increase in Fe and Si was observed. The drop in chromium at the metal/scale interface was more than for Type 310. The increase of silicon at the interface in HK-40 would be useful for corrosion protection.

Chromium concentration dropped appreciably with a corresponding increase in nickel in IN-671. Chromium was lower by 27% in the examined area, but the microstructure did not show signs of excessive internal sulfidation-oxidation. There are, however, other areas on the samples

Figure 2-1. Analysis of surface scale formed on Type 310 specimen exposed for 1581 hr in the U-Gas gasifier (temperature 1850°F, pressure 10.1-42 psig). (a) Electron micrograph, and X-ray maps of (b) Ni, (c) S, (d) Fe, and (e) Cr. (2500X)

which exhibited this type of attack. Minor elements were not depleted and hence are not shown. The scales formed on IN-671 were complex, and the following normalized compositions were recorded:

Scale (near the metal:	3.9% S, 94.4% Cr, 1.7% Fe
Internal gray sulfide:	46% S, 49% Fe, 2% Ti, 1% Al
Isolated place in the middle of the oxide:	42% Ti, 52% Cr, 4% Ni, 1% S (Ti is expected to come from process debris.)

In cobalt-base alloy 188, chromium and nickel concentrations decreased by approximately 15% at the metal/scale interface. The alloying elements tungsten and cobalt showed enrichment at the interface. Analysis of the scale indicated the following normalized composition: 95.3% Cr, 1.9% Si, 2.8% Co, with no nickel.

Location 2 - Product Gas Scrubber. This test site was below the tower internal demister plate. Temperatures ranged from 170° to 185°F, and pressures ranged from 10.1 to 42 psig. Untreated city water is utilized in the scrubbing operation.

The test materials can be ranked according to their average corrosion losses as follows: titanium 50A < CN7M < Type 329 < IN-800 < (Types 304, 316) < IN-600 < carbon steel < Type 410 < 430 < HC-250. The corrosion losses incurred by Types 329, 316, 304, IN-800, and IN-600 are excessively high, considering their excellent performance in all other quench systems in the Phase II program to date.

The highly localized attack of Type 329 and CN7M was confined to isolated areas; edge effects were also present. Irregular corrosion was observed on IN-800 and Types 304 and 316. The corroded surface on nickel-base alloy IN-600 appeared smoother in texture. Of the metals experiencing severe corrosion attack, carbon steel was not as adversely affected as were Types 410, 430, and HC-250, on the basis of gravimetric analysis. Chromium, nickel, and molybdenum were important as alloying elements for better corrosion performance in this environment. Titanium 50A proved to be the best performing material. It was observed that the welds and heat-affected zones on welded U-bend specimens were noticeably attacked.

Location 3 - Scrubber Sludge Tank. This test location is in the aqueous phase inside the scrubber sludge tank (open to atmosphere). Foul process water from the product gas scrubber is piped into the sludge tank; temperature is between 70° and 85°F.

Materials tested were similar to those for test location 2. Alloys HC-250 and Types 410 and 430 were similar in their corrosion performance. Corrosion losses did not exceed 1.5 mils (1581 hr), and maximum pit depths were in the range 5.0-7.3 mils. The remaining alloys including titanium 50A were the better performing materials, and carbon steel A515 the poorest performing metal.

Stress-corrosion cracks were not observed on any exposed U-bend specimens.

BI-GAS Pilot Plant

During the reporting period post-exposure metallographic and gravimetric analyses of corrosion coupons were performed. This section is a discussion of corrosion data for the following locations in the BI-GAS second exposure:

<u>Location No.</u>	<u>Process Unit</u>	<u>Rack Position</u>
1	Entrained flow gasifier	Off-gas
3	Gasifier slag quench	Vapor phase
4	Gasifier slag quench	Aqueous phase
7	Gas washer	Vapor phase
10	Vent gas washer	Aqueous phase
13	Recycle gas washer	Aqueous phase

The second exposure period encompassed BI-GAS tests G-5 to G-17F. During these test runs, washed Montana Rosebud subbituminous coal was processed.

Neg. No. 53979

200X

(a)

Neg. No. 53983

200X

(b)

Figure 2-2. Microstructure of (a) Type 310(Al) and (b) IN-800(Al) after second exposure (1784 hr) in the BI-GAS gasifier.

Location 1 - Gasifier. Two reaction zones (coal/steam and char/oxygen/steam) in the entrained flow gasifier produce the desired product gas. The specimen rack was exposed to the product gas/char at 25 to 30 ft above the steam/coal reactor. During the exposure period (1784 hr), temperature at the test site ranged from 1525°-1750°F at constant pressure (750 psig).

Acceptable corrosion behavior was exhibited by all uncoated alloys; equivalent linear rates were <15 mpy. Alloy N155 (19.8 wt% Ni, 20.9 wt% Cr, 19.5 wt% Co) was the best performing material.

The uncoated alloys included iron, nickel, and cobalt-base alloys with chromium content in the range 20.6 to 28.1 wt%. Arranging these alloys, except IN-671, in two groups:

Group 1: Alloys with chromium concentration in the range 20.6 to 22.0 wt%.

Group 2: Alloys with chromium concentration in the range 25.0 to 28.1 wt%.

shows a qualitative trend in corrosion performance by considering the weight percent ratio Cr/Ni. Increasing the nickel content detracts from corrosion performance in each group of alloys. This trend is suggested in the chromium range 20-28 wt%. However, differences in performance between groups 1 and 2 were not obvious from alloy composition. Similar trends were apparent in first-exposure alloy performance. It was also noted that alloys with 19.1 to 21.4 wt% Cr ranked higher in corrosion performance than alloys containing 25 to 26.2 wt% Cr.

The pack-aluminized alloys IN-800 and Type 310 showed similar corrosion behavior as in the first exposure period. Figure 2-2 shows the corrosion attack incurred by these coated alloys. The bulk coating (Al_2O_3) on Type 310 has been particularly affected after 1784 hr of exposure.

Locations 3, 4 - Gasifier Slag Quench. This lower section of the gasifier vessel is situated directly below the char/oxygen reaction zone slag nozzle. Molten slag drips directly into the slag quench water bath. Specimen racks were situated in the aqueous phase (location 3) and in the vapor phase (location 4) above the bath. The materials selection list for both test locations is the same except for Type 329 in location 4.

Carbon steel A515 and low-alloy steel 2½Cr-1Mo experienced somewhat higher corrosion attack in the aqueous phase (60°-75°F) compared to the vapor phase (400°-600°F). In both cases, corrosion losses progressed at unacceptable rates. These results agree with corrosion data from the first-exposure period of 1043 hr under similar conditions. High alloy steels exposed in the slag quench vessel showed increased corrosion in the vapor phase compared to the aqueous environment. Pitting attack was observed on all alloys exposed in the vapor phase. Ferritic alloy 26-1 exhibited better corrosion performance than Types 304, 316, and 405. First-exposure results did not show this difference in corrosion behavior.

Welded U-bend specimens did not incur stress-corrosion cracking in either test location. However, slag droplets melted through specimens of Types 329 and 304 in the U-bend region.

Location 7 - Gas Washer. Product gas from the feed char vessel (V-402) receives a water scrubbing in gas washer V-501 to remove fine particulates and undergoes a drop in temperature from 800° to 450°F. The corrosion monitoring rack was positioned on baffle No. 1 just opposite the manway. Temperature at the rack site is approximately 500°F.

Alloys 20Cb-3, Types 304 and 316 exhibited minimal corrosion losses (<0.1 mil) during the exposure period. Type 405 incurred somewhat greater corrosion loss (0.4 mil) and mild pitting after 1784 hr of exposure under operating conditions. Monel 400 and carbon steel A515 underwent extensive corrosion to give linear corrosion rates of >20 mpy.

Stress-corrosion cracks were not observed in any exposed U-bend samples.

Location 10 - Vent Gas Washer. Absorbed gases in process water from gas washer V-501 and lock-hopper V-303 are released in vent gas washer V-502 by pressure reduction and a water wash to reduce the temperature. Baffle No. 1 in the bottom of the tower was the attachment site for this corrosion rack. Temperatures at the test site ranged from 230° to 260°F.

Carbon steel A515 and Types 405 and 304 were evaluated in the vent gas washer aqueous environment. After 1784 hr of exposure, Types 405 and 304 exhibited corrosion performance much superior to carbon steel A515.

Welded U-bends exposed in the aqueous environment did not incur stress-corrosion cracking.

Location 13 - Recycle Gas Washer. The recycle gas washer (V-202) is part of the coal preparation system for the gasifier. Vent gases from the coal cyclone vessel (V-306) undergo water scrubbing to remove coal fines and moisture. The test rack was positioned on baffle No. 6 in the gas washer aqueous phase. Nominal temperature at the site is 300°F.

The materials selection list for the recycle gas washer V-202 parallels that for vent gas washer V-501. The austenitic stainless steels showed minimal overall corrosion losses (~0.1 mil) compared to nickel-base alloy Monel 400 (5.3 mils). Results for carbon steel A515 and low-alloy steel 2½Cr-1Mo showed high corrosion rates.

Corrosion Data--Refractories

Specimen Fabrication

The current list of candidate refractories from which materials have been selected for exposure in various coal gasification pilot plants is shown in Table 2-4. Priorities for testing established by the Phase IIb Refractories Subcommittee are shown in this table. The list of materials has been revised several times during the program based on the results of pilot plant exposures. Most lightweight insulating refractories, which were significantly attacked in CONOCO COAL plant exposures, have been deleted since these materials would not normally be exposed to the gasification atmospheres. Additional phosphate-bonded refractories were added because of their promising performance.

The standard specimen size for exposure is a 3/4 in. slice cut from a 9 in. straight brick. The specimen measures 2½ x 4½ x 3/4 in. This specimen was used in the U-Gas pilot plants and other pilot plants. However, the BI-GAS and Westinghouse pilot plant specimens were smaller due to the restricted space for exposure. These specimens are described in the sections covering these pilot plants.

Bricks were supplied by the manufacturer. If possible, monolithic refractories were also obtained as bricks from the manufacturer. However, some of the monolithics were prepared at IITRI following the manufacturer's instructions. The mix was formed into 9 in. straights in wooden molds and cured for 48 hr at room temperature and 100% relative humidity.

Specimens were prepared from the 9 in. straight samples as follows:

1. Specimens were rough cut from bricks with a diamond saw.
2. The surface of the specimens was ground with a 165 micron diamond disk until smooth.
3. Holes in the BI-GAS and Westinghouse specimens were diamond core drilled.
4. Code cuts to identify the refractory were made with a diamond saw, if possible.

TABLE 2-4. SUMMARY OF CANDIDATE PILOT-PLANT REFRACTORY TEST MATERIALS

No.	Trade Name	Priority Rating	Manufacturer	Form	Bond	Alumina Content, wt%
1	Castolast G	-	Harbison-Walker	Dense Castable	Calcium Aluminate	90+
2	Mizzou	1	A. P. Green	Dense Castable	Calcium Aluminate	60
3	Purolite 30	-	Kaiser	Light Castable	Calcium Aluminate	90+
4	Greencast-97L	-	A. P. Green	Light Castable	Calcium Aluminate	90+
5	Super Brikcast A	2	Grefco	Dense Castable	Calcium Aluminate	54
6	Litecast 75-28	9	Grefco	Light Castable	Calcium Aluminate	54
7	MUL-8	-	A. P. Green	Fired Brick (dense)	Vitreous (Mullite)	70
8	Chemal 85B	3	C-E Refractories	Fired Brick (dense)	Phosphate	85
9	Kricor	-	Kaiser	Fired Brick (dense)	Self-bonded	90+
10	H-W Corundum	-	Harbison-Walker	Fired Brick (dense)	Self-bonded	99+
11	Insulcor	-	Babcock & Wilcox	Fired Brick (light)	Vitreous	77
12	Alfrax B101	-	Carborundum Co.	Fired Brick (light)	Self-bonded	98+
13	Monofrax A	-	Carborundum Co.	Fused Cast Brick (dense)	Self-bonded	99+
14	Refrax 20	7	Carborundum Co.	Fired Brick (dense)	Nitride	(SiC)
15	Alumex 70HD	-	Kaiser	Fired Brick (dense)	Vitreous (Mullite)	70
16	Boron Carbide	-	Norton Co.	Hot-pressed coupon	Self-bonded	Very Low
17	Zircon	-	C-E Refractories	Coupon	Vitreous	Low
18	AZS	-	Carborundum Co.	Fused Cast Brick (dense)	Vitreous	Unknown
19	Harbide	-	Harbison-Walker	Fired Brick	Clay	(SiC)
20	Ufala TI	6	Harbison-Walker	Fired Brick (Tar Impreg)	Vitreous	60
21	KX99	12	A. P. Green	Fired Brick (dense)	Vitreous	45-50

TABLE 2-4 (cont.)

No.	Trade Name	Priority Rating	Manufacturer	Form	Bond	Alumina Content, wt%
22	Chemal 111	10	C-E Refractories	Dense Mortar	Phosphate	88
23	Super Harbond	-	Harbison-Walker	Mortar	Vitreous (Clay)	Unknown
24	Wasp 60	11	C-E Refractories	Ramming Mix	Phosphate	60
25	Brikram 90	4	General Refractories	Ramming Mix	Phosphate	90
26	Litecast 80	-	General Refractories	Light Castable	Calcium Aluminate	52
27	Greencast 97	-	A. P. Green	Dense Castable	Calcium Aluminate	90+
28	Hi-Lumnite	-	C-E Refractories	Fired Brick (dense)	Vitreous (Mullite)	70+
29	Altex 85B	8	General Refractories	Fired Brick (dense)	Phosphate	85
30	Alumex P8	-	Kaiser	Fired Brick (dense)	Phosphate	80+
31	CS 612	-	Kaiser	Fired Brick (dense)	Cr ₂ O ₃ /Al ₂ O ₃ solid-solution	90
32	Resco Cast AA-22	5	Resco Chemical	Dense Castable	Phosphate	90+
33	Corpatch 95	-	Kaiser	Dense Mortar/Patching Mix	Phosphate	90+
34	Crystolon 63	-	Norton Co.	Coupons/Bricks	Oxynitride	(SiC)
35	Alfrax 57	-	Carborundum Co.	Light Castable	Calcium Aluminate	90+
36	TR 90	=	C-E Refractories	Dense Patching Mix/Mortar	Phosphate	90
37	Blu-Ram	-	C-E Refractories	Dense Ramming Mix	Phosphate	70
38	Blu-Ram HS	-	C-E Refractories	Dense Ramming Mix	Phosphate	70
39	H-W Ruby	-	Harbison-Walker	Dense Brick	Cr ₂ O ₃ /Al ₂ O ₃ solid-solution	90
40	Serv	-	Didier Taylor	Dense Brick	Cr ₂ O ₃ /Al ₂ O ₃ solid-solution	84

5. The specimens were brushed in running water and rinsed in distilled water to remove machining debris.
6. After drying overnight at 250°F (120°C) the specimens were fired for four hours at 1500°F (815°C).
7. The specimens were removed hot from the kiln and cooled in a desiccator to prevent hydration.

Specimen No. 20, a tar-impregnated dense 60% alumina brick, was gently dried for 24 hr under an infrared lamp instead of in a dryer and was not fired to avoid removing the tar impregnation by oxidation.

Specimen Analyses

Three criteria are used to evaluate specimens after exposure:

1. Visual appearance
2. Physical properties
3. Abrasion resistance.

Visual appearance provides evidence of apparent changes in the form of "skin" development, pitting, and crumbling. For the most part, such changes were observed on only a limited number of samples exposed in the pilot plants.

After initial visual inspection and photography, one half of each of the exposed specimens was sent to the manufacturer for analysis. This procedure was initiated in 1978 in order to obtain additional information on the effect of exposure. It has proved very helpful even though not all of manufacturers have participated. If the specimens are broken, fragments equivalent to approximately one half of the specimen are sent to the manufacturer. If the specimens are intact, they are halved by controlled fracture. This technique, developed during 1979, insures that the sample sent to the manufacturer for analysis is uncontaminated and truly in the "as-received" condition. Previously, specimens were halved by diamond sawing using either water or, later, kerosine. For the new technique, the specimen was grooved transversely to a depth of 1/8 in. with a dry silicon carbide wheel and then fractured in three-point bending. In addition to

avoiding contamination, the technique provided a fresh fracture surface for examination. This was often more revealing than examining a cut surface.

The specimen half retained at IITRI was calcined at 1500°F for 4 hr in air to oxidize the char and other material that had formed a coating on the specimen which would interfere with determination of density, porosity, and abrasion resistance. A second visual examination of the specimens was then made for any new features which may have been revealed by calcination.

Color photography was used to document the appearance of the specimens in the "as-received" condition and after calcination. Both of the exposed surfaces, as well as the fracture surfaces, were photographed.

The liquid immersion method, based on ASTM Method C20-46, was used to measure the physical properties: the apparent porosity, apparent specific gravity, and bulk density. Kerosine was used as the displacing medium, instead of water, because some of the exposed specimens are readily hydrated. To insure complete penetration, the specimens were evacuated for 2 hr, then the kerosene was introduced and evacuation continued for 3 to 4 hr, well after gas bubbles were no longer escaping from pores in the specimens.

Porosity is the percentage of air spaces or voids between solid particles of material composing the refractory. The total porosity consists of closed pores, which do not communicate with the surface, and open pores, which do communicate and can be infiltrated by liquid. The percentage of open pores constitutes the apparent porosity, P_a , which is calculated by:

$$P_a = 100 \frac{W_s - W_d}{W_s - W_u} \%$$

where W_s is the saturated weight with the open pores filled with liquid

W_d is the dry weight

W_u is the weight of the saturated specimens submerged in the liquid.

A decrease in the apparent porosity may indicate that pores have been filled with a deposit, while an increase may indicate either an increase in size and/or number of pores and/or the formation of cracks.

The apparent specific gravity, SG_a , is the specific gravity of the specimen including the closed pores. It is calculated by:

$$SG_a = \frac{W_d \times d_L}{W_d - W_u}$$

where d_L is the density of the liquid.

A decrease in apparent specific gravity indicates an expansion of the closed pores and/or a decrease in density of the solid material due to phase change, oxidation, or other reaction. An increase in apparent specific gravity indicates a decrease in closed porosity because of sintering, cracking, opening of closed porosity, and/or an increase in the density of the solid material due to phase change or reaction.

The bulk density, d_b , is the dry weight of the specimen divided by the total volume of the specimen, including both open and closed pore volume. It is calculated by:

$$d_b = \frac{W_d \times d_L}{W_s - W_u}$$

This is the usual density reported for ceramic materials. An increase in bulk density may be due to weight increase, filling of pores, and/or sintering. A decrease in bulk density may be due to weight loss and/or bloating or swelling of the specimen.

Comparison of changes in apparent porosity, apparent specific gravity, and bulk density, together with the results of visual examination and manufacturer's analyses, can usually give a clear picture of the effects of exposure on refractories.

Abrasion resistance was evaluated using the Rotating Rod Abrasion Test discussed in detail in the 1975 and 1976 Annual Reports. The laboratory abrasion test is not intended to simulate abrasion or erosion conditions experienced in the coal gasification environment but, rather, to show changes due to environmental exposure.

Results and Discussion

Specimens were prepared for the following coal gasification pilot plants: BI-GAS, 3rd exposure, location 1; U-Gas, 2nd exposure; and Westinghouse, 2nd exposure, off-gas location 1. Two specimens were prepared, one for test and one for reference. If possible, the reference specimen was cut from the same brick immediately adjacent to the test specimen. Physical property measurements were made on test and reference specimens.

The U-Gas specimens are solid rectangular shapes, 4 x 2 x 3/4 in. The BI-GAS and Westinghouse specimens are smaller due to limited access. The reference specimens for these are solid rectangular shapes of the same external dimensions.

The property values of test and reference specimens are quite close, within 10%, for most refractories.

BI-GAS Pilot Plant Second-Exposure Results

Specimens were returned from the second exposure in the BI-GAS coal gasification pilot plant. The specimens were supported on a tripod rack in location No. 1, gasifier off-gas. One of the specimens was not returned to IITRI, and several were fractured due to cracking in the support notches (see Fig. 2-3) even though the specimen design had been changed to increase its strength following similar specimen breakage during the first exposure. The missing specimen was No. 18, a dense fused cast brick.

Physical property measurements were made on the returned specimens but except for specimen No. 6 there was very little change in the apparent specific gravity of the specimens. This suggests that there was no change in mineralogy due to exposure. Specimens No. 2 and 21 showed an increase in apparent porosity and little change in bulk density, which suggests there was some opening of closed porosity due to exposure. Specimens No. 6 and 32 showed an increase in apparent porosity and a concomitant decrease in bulk density which suggests an increase in total porosity due to exposure. Specimen No. 25 showed a decrease in apparent porosity and little change in bulk density, which is probably due to pore filling during exposure. Specimen No. 29, an 85% alumina, phosphate-bonded, dense brick, was unchanged by exposure.

A more detailed analysis will be made upon completion of the rotating rod abrasion tests and receipt of the results of the analyses.

Neg. No. 54109

Figure 2-3. Refractory specimens recovered from second exposure in the BI-GAS coal gasification pilot plant.

PROJECTED WORK FOR THE NEXT YEAR

The work plan for 1982 includes the following:

1. Continued corrosion monitoring of metals and refractories in the following pilot plants:
 - BI-GAS (3rd exposure)
 - U-Gas (3rd exposure)
 - Westinghouse PDU (2nd exposure)
 - PEATGAS (complete 1st exposure and begin 2nd exposure)
2. Initiate corrosion monitoring of metals in GEGAS:
 - Materials selection and rack fabrication
 - Begin 1st exposure
3. Initiate corrosion monitoring of metals and refractories at Mountain Fuel Resources:
 - Materials selection, rack fabrication
 - Begin 1st exposure in early 1982
4. Post-corrosion analysis of metals and refractories from Westinghouse PDU, 1st exposure.
5. Amend HYGAS, U-Gas, and BI-GAS topical reports after receipt of reviewers' comments.
6. Carry out detailed metallographic and SEM examination of selected coupons from the Phase IIa program.

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MPC 4.4(B) - EROSION-CORROSION OF MATERIALS
IN COAL GASIFICATION PILOT PLANTS

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INTRODUCTION

The MPC program on materials for coal gasification is subdivided into several phases. The objective of the Phase IV testing program is to provide baseline data on the erosion-corrosion resistance of materials potentially useful for the construction of gasifier internals. The results provide information additional to that from the Phase I high-temperature gas corrosion program as a basis for materials selection decisions.

Two high-temperature test reactors have been constructed for the Phase IV erosion-corrosion testing program, one operating at atmospheric pressure and the other at pressures of up to 1000 psi.* Both reactors utilize as a test environment the simulated coal gasification atmosphere approved by MPC.

In the 1981 program, alloys were evaluated under several combinations of test conditions encompassing temperatures of 1650° and 1800°F, erodent velocities of 25 to 150 fps, operating pressures of atmospheric to 1000 psi, erodents of low, medium, and high sulfur chars and inert Al_2O_3 , and times of 50 to 250 hr. A primary objective of the 1981 program is to provide information on the interrelation of metal loss, exposure time, and erodent velocity.

* All pressures are gauge values, i.e., psig.

RESULTS FROM PRIOR QUARTERS

The Phase IV erosion-corrosion testing program has been in progress at IITRI since 1976. Atmospheric and high pressure test facilities were designed and constructed for the program, and testing in these facilities commenced in 1976 and late 1978, respectively.

By the end of 1980 a total of 3327 hr of atmospheric pressure testing and 1710 hr of high-pressure testing had been completed. Test schedules were designed to generate useful engineering data at an early stage. This remains largely the objective of the present work, though the need for a more systematic and detailed investigation of erosion-corrosion mechanisms to improve confidence in extrapolations is being increasingly recognized.

Prior to commencement of the 1981 program, the erosion-corrosion behavior of 22 alloys and 10 refractories in a range of simulated gasifier environments had been investigated. Testing had entailed temperatures of 1500°-1800°F, alumina and high- and low-sulfur erodents at velocities of 10-200 fps, H₂S levels of 0.1-1.0 v/o, and pressures of atmospheric up to 1000 psig. Test durations were limited to 250 hr in the atmospheric and 100 hr in the high-pressure unit. From the results, several general trends in the erosion-corrosion behavior of the alloys tested could be tentatively identified:

1. Good corrosion resistance was a necessary but not a sufficient requirement for good erosion-corrosion resistance.
2. Erosion-corrosion losses increased as pressure increased, but might peak at 500 psig.
3. Erosion-corrosion losses increased with increasing temperature and H₂S level.
4. Erosion-corrosion losses appeared independent of char particle size, in the range 106 to 600 μ m.
5. Some of the chars were considerably more aggressive than others.

These conclusions were regarded as highly tentative because, first, test times were short--maximums of 250 hr in the atmospheric and 100 hr

in the high-pressure reactors--and, secondly, only a few data points were available from the broad matrix generated by the large number of variables acting in the system. The 1981 program, described below, was designed to provide data from longer tests and to fill in additional points in the data matrix.

A summary of quarterly work activities for 1981 is given in Table 4-1.

DISCUSSION OF CURRENT ACTIVITIES

Test Program and Equipment Status

In 1981 tests as well as in the previous two years, the following variables were kept constant:

a) Erodent feed rate	0.3 lb/100 acfm
b) Index rate	1 specimen position/30 min
c) Impingement angle	Fixed at 45° at start of test

Atmospheric Reactor

During 1981, 1150 hr of atmospheric pressure tests were completed and the test program is shown in Table 4-2. The status of the program is also given in Table 4-2 as of 11 December 1981, which was the cutoff date for this report.

High Pressure Reactor

The testing for 1981 in the high-pressure reactor completed 750 hr of testing by 11 December 1981 as shown in Table 4-2.

Test Materials

Table 4-3 defines the materials test groups approved by MPC for erosion-corrosion testing. Groups A, B, and C consisted primarily of alloys selected because of their high corrosion resistance, established by Phase I testing. Test group R consisted of ten refractories selected by the Phase IIb Subcommittee and two reference alloys, 800 and 671, which were used as reference alloys in all test groups.

TABLE 4-1. PHASE IV ACTIVITIES DURING 1981

Quarter	Atmospheric Reactor	High Pressure Reactor
I	Specific repairs to the high temperature support bearing and internal seals. Completed test 45 and began test 44.	General equipment rebuilding and overhaul of the internal reactor and the diaphragm compressor.
II	Completed: Test 44 100 hr 47 250 hr 49 100 hr and began: 46 250 hr	Completed repairs and completed Test HP31 50 hr HP32 50 hr began interrupted test: HP34 200 hr
III	Completed: Test 46 250 hr began interrupted tests: 50 200 hr 51 200 hr	Began and continued interrupted tests: HP33 200 hr HP34 200 hr HP35 200 hr
IV	Completed: Test 50 200 hr began or continued interrupted tests: 51 200 hr 52 200 hr	Completed tests: HP33 200 hr HP34 200 hr HP35 200 hr HP30 50 hr

Erodents

Four erodents were used in the test program. These were coarse FMC char, coarse spent char, coarse Al_2O_3 , and coarse coke char. The first three erodents were used in testing during 1980, and the fourth erodent, coarse coke char, was approved as the new standard erodent and was used in many of the 1981 tests. The ultimate and ash analyses for all main erodents used to date are given in Table 4-4.

Post-Exposure Analysis

The post-exposure analysis of erosion-corrosion specimens has been described in detail in past reports, but will be summarized here. The $1 \times 1 \times \frac{1}{4}$ in. samples are weighed before exposure (W_1), then after exposure before cleaning. The cleaning is done in two stages. First, the

TABLE 4-2. SUMMARY OF APPROVED 1981 EROSION-CORROSION TESTS

Test No.	Completed	Erodent ^a	Press., psig	Temp., °F	H ₂ S, v/o	Vel., fps	Time, hr	Alloy Series
<u>ATMOSPHERIC</u>								
44	X	Spent	0.3	1800	0.1	100	100	A
45	X	Spent	0.3	1800	0.5	100	100	A
46	X	FMC	0.3	1800	1.0	50	250	C
47	X	FMC	0.3	1650	1.0	50	250	A
49	X	Coke	0.3	1800	1.0	100	100	A
50	X	Coke	0.3	1800	1.0	25	200 ^b	A
51	c	Coke	0.3	1800	1.0	50	200 ^b	A
52	d	Coke	0.3	1800	1.0	100	200 ^b	A
53		Coke	0.3	1800	1.0	150	100 ^e	A
Total							1500	
<u>HIGH PRESSURE</u>								
HP29		FMC	1000	1650	1.0	50	250	A
HP30	X	Al ₂ O ₃	600	1800	1.0	100	50	A
HP31	X	Spent	1000	1650	1.0	100	50	A
HP32	X	Coke	1000	1800	1.0	100	100	A
HP33	X	Coke	500	1800	1.0	25	200 ^b	A
HP34	X	Coke	500	1800	1.0	50	200 ^b	A
HP35	X	Coke	500	1800	1.0	100	200 ^b	A
Total							1000	

^aErodent size: 300 to 600 μm (-30 +50 mesh).

^bSpecimens to be inspected at 50, 100, and 200 hours.

^c100 hours of testing completed.

^d50 hours of testing completed.

^eSpecimens to be inspected at 50 and 100 hours.

TABLE 4-3. MATERIAL SELECTION FOR EROSION-CORROSION TEST GROUPS

Series A	Series B ^a	Series C	Series D	Series R
800 ^b	800 ^b	800 ^b	800 ^b	800 ^b
671 ^b	671 ^b	671 ^b	671 ^b	671 ^b
446	446	32X	The 10 best alloys from groups A & C	<u>Brick</u>
188	188	N155		90% alumina, self-bond (Kricor)
601	601	T63WC		85% alumina, phosphate bond (Chemal 85B)
310	310	150		70% alumina, mullite (Alumex)
310(A1)		6B		60% alumina, pitch impregnated (Ufala TI)
800(A1)		Alloy X		45% alumina, fire brick (KX-99)
Crutemp 25		HK-40		90% alumina-10% chromia (HW Ruby)
RA-333		30/50W		<u>Castable</u>
LM-1866		HL-40		90% alumina, calcium aluminate bond (Castolast G)
Co-Cr-W No. 1		<u>Alternates</u>		60% alumina, calcium aluminate bond (Superbrikcast A)
		Fe-36Cr-36Ni		<u>Insulating Refractory</u>
		Fe-31Cr-36Ni		54% alumina castable, calcium aluminate bond (Litecast 75-28)
		Fe-31Cr-28Ni		77% alumina brick, vitreous bond (Insulcor)
		Fe-31Cr-44Ni		
		329		

^aDuplicate samples.^bReference materials.

TABLE 4-4. ULTIMATE AND ASH ANALYSES OF ERODENTS

Component	Analysis of Erodents, wt%				
	FMC ^a	Husky ^b	Coke ^c	Spent ^d	Al ₂ O ₃ ^e
<u>Ultimate</u>					
C	75.92	74.30	87.18	83.26	-
H	2.21	2.04	0.34	1.05	-
N	0.77	0.64	0.90	0.48	-
Cl	0.03	0.02	0.07	0.03	-
S	2.69	1.89	0.81	0.14	-
Ash	14.73	17.56	10.08	13.04	100
<u>Ash</u>					
SiO ₂	44.00	19.97	49.42	40.31	0.06
Al ₂ O ₃	24.31	10.94	24.72	24.38	+99.5
TiO ₂	1.03	0.48	1.20	1.14	-
Fe ₂ O ₃	22.36	7.66	14.24	1.85	-
CaO	2.11	22.17	3.57	22.30	-
MgO	0.94	8.65	1.61	6.90	-
K ₂ O	2.53	0.60	1.89	0.50	-
Na ₂ O	0.27	2.41	1.24	0.57	0.21
SO ₃	1.65	25.71	1.00	0.27	-
P ₂ O ₅	0.27	0.15	0.33	0.08	-
SrO	-	0.50	0.01	-	-
BaO	0.01	0.10	0.08	-	-
Mn ₃ O ₄	-	0.11	0.23	-	-
Unknown	0.54	0.55	0.46	1.70	-

^aWestern Kentucky coal prepared by COED process.

^bWestern coal processed by the Husky Oil Company.

^cMetallurgical coke.

^dMontana rosebud coal which has been through the BI-GAS gasifier.

^eAlcoa Chemical tubular alumina, grade T61.

erosion surface (6.45 cm^2) is cleaned by glass beading, and the sample is weighed (W_2). This is followed by cleaning the other five sides (12.9 cm^2) of the sample by glass beading, and a final weight (W_3) taken. The weight loss data are then calculated based on the following equations:

$$\begin{aligned} W_{EC} &= (W_1 - W_2)1000/6.45 \\ &= \text{erosion-corrosion weight loss in mg per cm}^2. \\ W_C &= (W_2 - W_3)1000/12.9 \\ &= \text{corrosion weight loss in mg per cm}^2. \end{aligned}$$

The initial sample thickness (t_1) is measured by micrometer before exposure; then, after exposure and after final cleaning, the specimen is measured at two points. The first point is an average sample thickness (t_2) away from any erosion-corrosion pit. The second measurement (t_3) is at the deepest point in the erosion-corrosion pit. These three measurements are illustrated in Fig. 4-1 and used in the following equations:

$$\begin{aligned} t_C &= \frac{t_1 - t_2}{2} \times 1000 \\ &= \text{average corrosion loss in mils.} \\ t_{EC} &= \left[t_1 - \left(t_3 + \frac{t_1 - t_2}{2} \right) \right] \times 1000 \\ &= \text{maximum erosion-corrosion loss in mils.} \end{aligned}$$

The gravimetric measurements provide only a rough estimate of material properties since, in most cases, the erosion-corrosion damage is localized in small areas. For this reason the erosion-corrosion thickness loss is the term used in all analyses presented in this and past reports. The cleaning of the specimens after the test presented no problems until the interrupted tests began in 1981. At that time the specimen examination technique was reviewed, and an interruption was considered the same as a completed test so the specimens were cleaned at each interruption. To determine if this method would change the alloy response, a check was made in high-pressure test HP35. This was done by inserting 310 samples when

Figure 4-1. Schematic diagram of erosion-corrosion specimen and micrometer measurements taken and calculated.

the alloys 800, 601, and Crutemp 25 had to be removed from the test. By the end of test HP35, the 12 data points shown in Table 4-5 were generated, and a comparison of the data shows two factors. The first point is it seems to make no difference in the results if the specimens are cleaned between tests or not. The second point, a new development, is that material loss seems to increase in steps. These sudden variations are still not well understood and need much more investigation to permit any conclusions, but indicate that if a stepwise increase is stopped or has stopped, it might not recommence when the test restarts.

TABLE 4-5. SUMMARY OF 310 SAMPLES IN TEST HP35

Sample No.	Erosion-Corrosion Loss, ^a mils			
	50 hr	100 hr	150 hr	200 hr
<u>Cleaned at Interruptions</u>				
D497	28.3	102.9	105.9	133.7
D497B	20.1	51.3	91.1	
<u>Not Cleaned at Interruptions</u>				
D497A	107.0	104.9	106.8	
D497C	1.7	57.1		

^aCumulative loss for the indicated periods.

Atmospheric Pressure Test Results

Test 44

Test 44 was operated with Series A alloys at 1800°F-100 fps-100 hr-1.0 v/o H₂S with coarse spent char. This test shows very minor attack on all the alloys, with Co-Cr-W No. 1 losing the least, 0.6 mils, and 800(Al) the most, 2.6 mils. All of the alloys fall between these two values of maximum erosion-corrosion metal loss.

Test 45

Test 45 was operated with Series A alloys at 1800°F-100 fps-100 hr-0.5 v/o H₂S with coarse spent char. The micrometric erosion-corrosion data show the alloys falling into four groups. The most severely attacked was Alloy 800, which lost 10.4 mils in the 100-hr test. The second group was made up of alloys 800(Al), 310(Al), and LM-1866. These lost from 2.4 to 3.7 mils. Alloys 446, 601, RA-333, Crutemp 25, 310, and 671 make up the third group, with losses of 1.3 to 1.7 mils. Co-Cr-W No. 1 and 188 showed the least attack, losing only 0.3 and 0.7 mil, respectively.

Test 46

Test 46 was completed and operated with Series C alloys at 1800°F-50 fps-250 hr-1.0 v/o H₂S with coarse FMC erodent. The test could not be run for the full 250 hr but had to be stopped at 192 hr because of a breakdown of the FMC erodent. This erodent has been used several times and now seems to be breaking up. The data for maximum erosion-corrosion metal loss fall into two groups. The least attacked group lost from 0.7 to 4.8 mils and consists of the alloys 671, HL-40, N155, 329, 150, Alloy X, 6B, 30/50W, and 32X. The most attacked alloys were 31Cr-36Ni, 800, and HK-40 which lost 9.0, 9.4, and 14.5 mils, respectively.

Test 47

Test 47 was completed and operated with Series A alloys at 1650°F-50 fps-250 hr-1.0 v/o H₂S with coarse FMC char as the erodent. The

micrometric data for maximum erosion-corrosion metal loss shows that the alloys can be divided into two groups. The first group of alloys--310, 671, 188, and Co-Cr-W No. 1--lost from 0.6 to 1.0 mil in the 250 hr of testing, while the rest of the alloys lost from 3.0 to 7.8 mils in the test.

Test 49

Test 49 was also completed and was run under the conditions of 1800°F-100 fps-1.0 v/o H₂S with coarse coke char on Series A alloys. The data for maximum erosion-corrosion metal loss fall into three different groups; the most attacked group includes alloys LM-1866, 446, and Crutemp 25, and lost from 7.8 to 8.7 mils. The mid-range group contains alloys 800, 601, 310, and RA-333; these lost 2.8 to 5.6 mils, while the rest of the alloys only lost 0.9 to 1.8 mils in the 100-hr test.

Test 50

50 Hours. This was the first interruption of test 50 after 50 hr of testing. This test was operated with Series A alloys under the conditions of 1800°F-25 fps-1.0 v/o H₂S and coarse coke erodent with a total time of 200 hr. The data from this first interruption give very low maximum erosion-corrosion losses between 0.4 and 1.0 mil for 800 and aluminized 310, respectively.

100 Hours.* After an additional 50 hr of exposure very little material loss had occurred, ranging from 0.5 mil for Co-Cr-W No. 1 to 2.8 mils for 188.

200 Hours. After 200 hr of exposure there was little material loss, ranging from 0.7 mil for Co-Cr-W No. 1 to 3.3 mils for LM-1866.

* All time periods for test interruptions are cumulative hours; hence, the data presented are cumulative.

Test 51

50 Hours. Test 51 completed the first 50 hr of exposure, operating at 1800°F-25 fps-1.0 v/o H₂S-coarse coke erodent on Series A samples. The alloys can be grouped in the following way: Good alloys Co-Cr-W No. 1, 671, LM-1866, 310(Al), and 800(Al) lost little metal--only 0.7 to 2.4 mils; whereas alloys 188, 310, Crutemp 25, 446, and 601 lost from 4.9 to 8.7 mils; and the poorest alloys, 800 and RA-333, lost 14.1 and 18.6 mils, respectively.

100 Hours. This exposure was run, but analysis has not been completed and therefore will be presented in the next quarterly report.

Test 52

Only 50 hr of testing was completed. The operating conditions of this test were 1800°F-100 fps-1.0 v/o H₂S with coke erodent on Series A alloys. The alloy response from this test seems to classify the alloys into two groups, the better alloys including alloys 800(Al), 310(Al), Co-Cr-W No. 1, RA-333, and 671 after losing 0.9 to 3.7 mils. The rest of the alloys lost 5.1 to 8.9 mils.

High Pressure Test Results

Test HP30 - 600 psig

Test HP30 used Series A alloys under the conditions of 1800°F-100 fps-50 hr-1.0 v/o H₂S with coarse Al₂O₃ erodent at 600 psig. This test was completed, but the analysis is still under way and will be presented in the next quarterly report.

Test HP31 - 1000 psig

Test HP31 was completed and operated on Series A alloys at 1650°F-1000 psig-100 fps-50 hr-1.0 v/o H₂S and coarse spent char. The data seem to fall into two groups: alloys 800(Al), 310, 310(Al), LM-1866, 446, Crutemp 25, and Co-Cr-W No. 1 were the least damaged alloys losing only 0.8 to 3.8 mils as measured by maximum erosion-corrosion metal loss. The rest of the alloys lost 12.5 to 48.2 mils in the 50-hr test.

Test HP32 - 1000 psig

Test HP32 was completed and operated at 1800°F-1000 psig-100 fps-50 hr-1.0 v/o H₂S and coarse coke erodent. The data of this test, with respect to maximum erosion-corrosion metal loss, can be put into four groups. The first group consists of alloys with the most resistance to metal loss, losing only 0.9 to 3.1 mils, and includes alloys 310(A1), LM-1866, 671, and Co-Cr-W No. 1. The next group contains alloys 800(A1) and 446 which lost 5.2 and 10.8 mils, respectively. The third group comprises alloys 188, 310, Crutemp 25, 800, and RA-333, which lost 23.7 to 98.5 mils. Alloy 601 exhibited the most damage and was completely penetrated during the 50-hr test.

Test HP33 - 500 psig

50 Hours. Test HP33 completed 50 hr of testing under the conditions of 1800°F-25 fps-1.0 v/o H₂S-Series A alloys and coarse coke erodent. This summary shows maximum erosion-corrosion metal loss falling between 0.5 and 3.6 mils for alloys Co-Cr-W No. 1 and 310(A1), respectively.

100 Hours. The data from this test after the second 50 hr showed that little material loss occurred. Corrosion losses ranging from 0.7 mils for Co-Cr-W No. 1 to 4.3 mils for 446 were observed.

200 Hours. The final 100 hr of testing resulted in large material losses. Some alloys--Co-Cr-W No. 1, 310(A1), 800(A1), 188, 671, and LM-1866--show little material loss, from 0.9 to 3.5 mils, while the rest of the alloys lost 8.0 to 18.0 mils during the total 200 hr of testing.

Test HP34 - 500 psig

50 Hours. The first 50 hr of testing on HP34 has been completed under the conditions of 1800°F-50 fps-1.0 v/o H₂S-coarse coke erodent on Series A alloys. Alloy 188 exhibits the most resistance to erosion-corrosion attack and RA-333 the poorest.

100 Hours. The second 50 hr of this test has the alloys falling into 3 groups. The best alloys are Co-Cr-W No. 1, 188, 800(A1), 310(A1), and 671 which lost from 1.6 to 3.9 mils; alloys LM-1866 and 446 lost

7.6 and 8.3 mils, respectively, thereby falling into the second group. The rest of the alloys lost from 10.4 to 21.0 mils in the total 100 hr exposure.

200 Hours. The data for the final 100 hr of exposure shows Co-Cr-W No. 1 as the best alloy, having lost 1.6 mils, and 800 the worst, losing 43.5 mils.

Test HP35 - 500 psig

50 Hours. Test HP35 was run under the conditions of 1800°F-100 fps-1.0 v/o H₂S-coarse coke erodent and Series A alloys. Alloys 800 and 601 were removed from the test after 50 hr because of damage, and were replaced with 310 samples. The analysis of this test shows alloys 310(A1) and Co-Cr-W No. 1 losing the least metal of all alloys--1.0 and 0.4 mils in 50 hr, respectively. The least resistant alloys, which are still in the test, are 310 and 446. These lost 28.3 and 4.0 mils, respectively, after 50 hr.

100 Hours. Results were about the same as the 50-hr test in that 310(A1) and Co-Cr-W No. 1 were the best alloys, and 310, 446, and Crutemp 25 the worst alloys remaining in the test. Crutemp 25 lost 95.0 mils and was removed from the test and replaced by a 310 sample.

150 Hours. The alloys exhibit the same response as in the two earlier tests.

200 Hours. The data for the end of the 200-hr test show a major change from the earlier tests. The difference lies with 800(A1), which lost 91.1 mils; this was a very local attack area and seemed to be a "holing" of the aluminized coating. The data for the additional 310 samples were given in an earlier section (see Table 4-5).

Evaluation of Erosion-Corrosion Results

The erosion-corrosion results for the 1981 tests are summarized in Tables 4-6 and 4-7 for the atmospheric and high pressure units, respectively. The following sections examine the effect of some variables and

TABLE 4-6. SUMMARY OF MICROMETRIC MEASUREMENTS OF EROSION-CORROSION METAL LOSS FOR ALLOYS TESTED IN THE ATMOSPHERIC UNIT - 1981

Test No.:	44	45	46	47	49	50			51	52
Test Parameters										
Temp., °F	1800	1800	1800	1650	1800	1800			1800	1800
Velocity, fps	100	100	50	50	100	25			50	100
Time, hr	100	100	250	100	100	50	100	200	50	50
H ₂ S, v/o	0.1	0.5	1.0	1.0	1.0	1.0			1.0	1.0
Erodent	Spent	Spent	FMC	FMC	Coke	Coke			Coke	Coke
Pressure, psig	0.3	0.3	0.3	0.3	0.3	0.3			0.3	0.3
Alloy Series	A	A	C	A	A	A			A	A
Maximum Erosion-Corrosion Loss, mils										
800	0.7	10.4	9.4	6.0	3.6	0.4	1.7	1.3	14.1	5.1
800(A1)	2.7	3.7	-	4.1	1.4	0.8	1.3	1.7	2.4	0.9
601	1.7	1.4	-	4.9	4.2	0.4	1.2	2.0	8.7	5.7
310	1.0	1.3	-	0.8	5.6	0.5	2.0	2.0	7.7	5.6
310(A1)	2.0	3.5	-	7.8	1.7	1.0	1.5	1.5	1.7	1.2
RA 333	0.7	1.4	-	3.0	2.8	0.5	2.1	2.1	18.6	1.9
LM 1866	1.4	2.4	-	4.6	8.1	0.5	1.0	3.3	1.7	5.7
446	1.9	1.7	-	4.3	8.7	0.5	1.6	2.2	8.4	5.5
671	1.6	1.3	1.5	1.0	1.1	0.8	1.5	1.5	1.6	3.7
Crutemp 25	1.4	1.4	-	4.3	7.8	0.4	1.8	1.6	7.8	8.9
188	1.0	0.7	-	0.6	0.9	0.4	2.8	2.9	4.9	5.8
Co-Cr-W No. 1	0.6	0.3	-	0.6	1.8	0.5	0.5	0.7	0.7	1.3
150	-	-	4.8	-	-	-	-	-	-	-
N155	-	-	1.1	-	-	-	-	-	-	-
32X	-	-	1.2	-	-	-	-	-	-	-
Alloy X	-	-	0.7	-	-	-	-	-	-	-
HK-40	-	-	14.5	-	-	-	-	-	-	-
30/50W	-	-	1.9	-	-	-	-	-	-	-
6B	-	-	1.0	-	-	-	-	-	-	-
HL-40	-	-	1.8	-	-	-	-	-	-	-
329	-	-	2.6	-	-	-	-	-	-	-
31Cr-36Ni	-	-	9.0	-	-	-	-	-	-	-

TABLE 4-7. SUMMARY OF MICROMETRIC MEASUREMENTS OF EROSION-CORROSION METAL LOSS
FOR ALLOYS TESTED IN THE HIGH PRESSURE UNIT - 1981

Test No.:	HP31	HP32	HP33			HP34			HP35			
Test Parameters												
Temp., °F	1650	1800	1800			1800			1800			
Velocity, fps	100	100	25			50			100			
Time, hr	50	50	50	100	200	50	100	200	50	100	150	200
H ₂ S, v/o	1.0	1.0	1.0			1.0			1.0			
Erodent	Spent	Coke	Coke			Coke			Coke			
Pressure, psig	1000	1000	500			500			500			
Alloy Series	A	A	A			A			A			
Maximum Erosion-Corrosion Loss, mils												
800	26.8	98.5	1.4	1.8	11.8	10.0	17.4	43.5	74.2	-	-	-
800(Al)	1.0	5.2	2.4	4.1	3.6	1.0	2.6	2.8	2.5	9.6	11.1	91.1
601	38.8	212.3	1.2	1.1	10.7	6.7	10.4	12.0	80.2	-	-	-
310	3.8	72.8	1.9	1.1	8.0	4.1	20.6	28.0	28.3	102.9	105.9	133.7
310(Al)	0.8	3.1	3.6	2.5	3.4	3.8	3.9	4.4	1.0	6.9	8.5	4.6
RA-333	48.2	86.4	1.2	2.0	18.0	18.1	21.0	22.7	8.7	15.6	15.3	96.9
LM 1866	1.7	0.9	1.1	2.4	3.5	1.5	7.6	7.2	1.4	78.0	79.9	124.6
446	2.2	10.8	0.7	4.3	11.2	1.1	8.3	8.9	4.0	88.4	88.2	97.1
671	12.5	1.2	1.3	1.4	1.9	1.8	3.5	2.7	2.2	11.0	13.3	16.5
Crutemp 25	2.9	64.0	1.8	2.5	10.0	10.6	12.5	25.1	30.8	95.0	-	-
188	44.7	23.7	1.2	1.4	2.0	1.0	1.6	2.5	15.3	27.6	26.7	30.6
Co-Cr-W No. 1	1.0	1.1	0.5	0.7	0.9	1.7	1.9	1.6	0.4	9.8	10.3	13.7

mainly concern tests conducted this year; other variables have been analyzed in previous reports.

Effect of Erodent Type

Atmospheric-1800°F-100 fps-100 hr-1.0 v/o H₂S. Figure 4-2, in bar graph form, summarizes the three types of maximum erosion-corrosion loss encountered during 1978-81. Alloy 601 exhibits a declining metal loss as the sulfur content of the erodent decreases; this trend is also exhibited by alloy RA-333. Alloy 188 shows no major difference in metal loss for the different erodents, and this response also occurred with alloys 671, 800(A1), and 310(A1). The last alloy shown is 800. This material incurred a very high material loss with the FMC erodent, the rest of the erodents giving lower losses. Such response is also true for alloys 310, LM-1866, 446, and Crutemp 25.

High Pressure (1000 psig)-1800°F-100 fps-50 hr-1.0 v/o H₂S. Figure 4-3 is a bar graph representation of the data from several tests (1978-81) under these conditions, including the 1981 test HP32, the first high

Figure 4-2. Effect of erodent type: 1800°F-100 fps-100 hr-1.0 v/o H₂S-0.3 psig. Test numbers are given in parentheses.

Figure 4-3. Effect of erodent type: 1800°F-100 fps-50 hr-1.0 v/o H_2S -1000 psig. Test numbers are given in parentheses.

pressure test done with coke as an erodent. Five different types of responses are illustrated with five alloys, each one representing a group of alloys. Alloy 800 illustrates the type of response where FMC, Husky, and spent chars as well as no erodent all give about the same total metal loss. Coke and Al_2O_3 tests gave much higher losses. Type 310 also exhibited a pattern similar to 800. Type 310(Al) is shown next, and it presents the case where all carbon-bearing erodents result in about the same loss but the inert Al_2O_3 causes major damage; 800(Al) also shows this result. Alloy LM-1866 exhibits the same erodent relationships as 671--namely, low losses with coke and spent char but higher losses with FMC, Husky, and no-erodent tests, the highest loss occurring with Al_2O_3 erodent. The most common type of response is typified by Alloy 446, wherein the medium-sulfur erodents cause higher material loss, with highest losses still occurring with Al_2O_3 . This pattern is also present in alloys 601, Crutemp 25, and RA-333. The final type of response is illustrated by 188, where FMC caused the severest attack and the rest of the erodents gave lower losses.

Effect of Temperature

High-Pressure (1000 psig)-100 fps-50 hr-1.0 v/o H_2S -Spent Char. The BI-GAS spent char that was first used in 1980 was tested this year at a lower temperature, and a summary plot of the data is presented in Fig. 4-4. The alloy response in the two tests falls into three types: the first one shown is for RA-333 and shows a declining loss with increasing temperature. This type of behavior also appeared with Alloys 671 and 188. Alloy 601 shows the opposite type of behavior, increasing loss with increasing temperature, and this second behavior also appears with 800. The third type of behavior is shown for 800(Al), but also holds for 310, 310(Al), LM-1866, 446, Crutemp 25, and Co-Cr-W No. 1: there is negligible change in loss with the temperature increase.

Effect of H_2S

Atmospheric-1800°F-100 fps-100 hr-Spent Char. Figure 4-5 shows a summary plot of the data from three tests done under these conditions with varying H_2S contents. The results show that, with the exception of Alloy

Figure 4-4. Effect of temperature: 100 fps-50 hr-1.0 v/o H₂S-1000 psig-spent erodent. Test numbers are given in parentheses.

Figure 4-5. Effect of H₂S: 1800°F-100 fps-100 hr-0.3 psig-spent erodent. Test numbers are given in parentheses.

800, there is no major difference in metal loss as the H_2S content increases from 0.1 to 1.0 v/o. Alloy 800 shows a maximum at 0.5 v/o H_2S .

Effect of Time

High Pressure (500 psig)-1800°F-100 fps-1.0 v/o H_2S -Coke Erodent.

Figure 4-6 shows a summary plot of the data from test HP35 that was interrupted every 50 hr. The results show that only Type 310(A1) was unaffected by the longer term tests. The next group of alloys, 800(A1) and RA-333, show little material loss up to 150 hr but a large increase in material loss between 150 and 200 hr. The third type of behavior, shown for 671 but also true for Co-Cr-W No. 1, is that of steadily increasing small material loss with increasing time with a larger initial increase between 50 and 100 hr. The last type of alloy response shown is for Type 310, but also holds for 446, LM-1866, and 188; the sequence is small losses after 50 hr, but a very large increase in losses by 100 hr, followed by a loss stabilization at longer times.

Effect of Pressure

1800°F-50 hr-100 fps-1.0 v/o H_2S -Coke Erodent. Figure 4-7 is a summary graph of the data from three tests done under these conditions; the pressures were 0.3, 500, and 1000 psig. The atmospheric test was 100 hr long, while the high pressure tests were only 50 hr in length. Therefore, for this plot the atmospheric losses were extrapolated based on linear rates to 50 hr. The plot shows four types of alloy behavior: the first type shown is for Alloy 800, but it also occurred with 188, which exhibits a large increase in material loss from atmospheric to 500 psig and then a slight increase to 1000 psig. The second behavior is that of Type 310, which shows an increase in material loss with an increase in pressure. Alloys Crutemp 25 and 601 behave in a like manner. The next type of alloy response shows no effect of pressure, over the range tested, and is represented by Type 310(A1), but also occurred with LM-1866, 671, and Co-Cr-W No. 1. The last alloy shown is 446, and shows no major difference between tests at atmospheric and 500 psig but a large increase when the pressure goes to 1000 psig. This response is also true for Alloys RA-333 and 800(A1).

Figure 4-6. Effect of time: 1800°F-100 fps-1.0 v/o H₂S-500 psig-coke erodent, test HP35.

Figure 4-7. Effect of pressure: 1800°F-100 fps-50 hr-1.0 v/o H₂S-coke erodent. Test numbers are given in parentheses.

Effect of Particle Velocity

High Pressure (500 psig)-1800°F-1.0 v/o H₂S-Coke Erodent. The effect of time on particle velocity was first examined this year, and a few interesting observations can be made. The data for 50 hr are given in Fig. 4-8 and for 200 hr in Fig. 4-9. The first alloy shown is 310(A1), and it exhibits no threshold velocity up to 100 fps and 200 hr. The next alloy shown is 310, and this alloy exhibits a threshold velocity between 50 and 100 fps after 50 hr, but this threshold seems to shift to between 25 and 50 fps after 200 hr; this also occurred to alloys 800 and Crutemp 25. The third behavior found is shown for alloy LM-1866. This alloy does not show a threshold velocity below 100 fps at 50 hr but does below 100 fps at 200 hr. Many of the alloys seem to follow this type of behavior--such as 446, Co-Cr-W No. 1, 800(A1), RA-333, and 671. Alloy 188 shown last on both plots seems to exhibit no change in velocity threshold between 50 and 200 hr; the results at both times give a threshold velocity between 50 and 100 fps.

PROJECTED WORK FOR THE NEXT YEAR

The program of erosion-corrosion testing for 1982 originally entailed 2000 hr atmospheric testing, 1300 hr high pressure testing, and final construction and shakedown of the second high-pressure vessel. This program has been scaled down, at the time of writing, to the following levels: 1400 hr of atmospheric testing and 1000 hr of high pressure tests. These projected test hours will be done in addition to the 1981 tests that remain to be completed. The specific tests for 1982 have not been finalized at this time, but will probably encompass three specific areas:

1. Effect of time, at 1650°F, on threshold velocity for long-term tests.
2. Effect of impingement angle at atmospheric and high pressure.
3. Effect of pressure on coke erodent with multiple samples.

Figure 4-8. Effect of velocity at 50 hr: 1800°F-1.0 v/o H₂S-500 psig-coke erodent. Tests at 25 fps (HP33), 50 fps (HP34), and 100 fps (HP35).

Figure 4-9. Effect of velocity at 200 hr: 1800°F-1.0 v/o H₂S-500 psig-coke erodent. Tests at 25 fps (HP33), 50 fps (HP34), and 100 fps (HP35).

ANL-4.5 -- NONDESTRUCTIVE TESTING: EROSION WEAR DETECTION

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SUMMARY OF CURRENT ACTIVITIES

The experimental EMAT and preamplifier were modified to resonate at 1.5 MHz. The modified system actually resonated at 1.3 MHz, owing to tolerances of discrete components. Initial tests showed generation and reception of horizontally polarized shear waves in aluminum, ferritic steel and stainless steel. The modification of the preamplifier caused an increase in the overload recovery time from 2 to 15 μ sec. The first reflected echo from the backwall of the material samples occurs within that time and cannot be discriminated from background noise. Experiments to lower the overload recovery time by a minimum of 50% were initiated.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

¹Materials Technology for Coal-conversion Processes: Progress Report for October-December 1981, Argonne National Laboratory Report ANL/FE-82-9 (in preparation).

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ANL-4.8 -- DEVELOPMENT OF THERMAL-SHOCK-RESISTANT REFRACTORIES

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SUMMARY OF CURRENT ACTIVITIES

The purpose of this new program is to develop a technology for improving the thermal-shock resistance of selected refractories that appear to have the necessary corrosion resistance for operation in slagging gasifiers.

MgCr_2O_4 has been synthesized by two different methods: (1) solution precipitation and polymerization with a subsequent firing to 900°C , and (2) calcining MgCO_3 and Cr_2O_3 at 1200°C for 48 h. Both methods produced phase-pure MgCr_2O_4 as determined by x-ray analysis. Cold-pressed MgCr_2O_4 pellets containing 5 and 10 wt % ZrO_2 have been sintered at 1650°C for 2 h in a $\text{CO}/\text{CO}_2 = 100:1$ atmosphere. The sintered pellets were ~74 to 86% dense. Characterization of the microstructures is in progress.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

¹Materials Technology for Coal-conversion Processes: Progress Report for October-December 1981, Argonne National Laboratory Report ANL/FE-82-9 (in preparation).

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ISU-4.8 — CREEP BEHAVIOR OF REFRACTORY CONCRETES

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INTRODUCTION

The three main objectives of this work have been:

1. Evaluate the long term creep strain of high-alumina refractory concretes as functions of composition and microstructure.
2. Determine the creep mechanisms of these materials as functions of the composition, stress, strain and temperature.
3. Obtain creep strain data useful for mathematical modeling.

This research (subcontract 7940) is a continuation of Contract DE-AS05-78OR13402 of the DOE Fossil Fuel Program.

RESULTS FROM PRIOR QUARTERS

Research on refractory concretes made from pure alumina aggregate or calcined kaolin aggregates and bonded with Ca-25 high purity calcium aluminate cement revealed that in the range from 1000 to 2200°F and from 500 to 3000 PSI the creep strain depended on temperature in an Arrhenius manner, and on stress in an exponential manner. The activation energy varied from about 33 kcal/mole to about 170 kcal/mole depending upon composition and previous thermal history.

High Purity Alumina Aggregate with High Purity Cement

When the concretes were initially heated breakdown of the hydraulic bond produced extremely fine grained calcium aluminate compounds. These sintered under stress as the temperature was increased and the load was applied. The activation energy of 33 kcal per mole was found for the neat cement on initial heating. That is close to the activation energy for calcium ion diffusion in calcium dialuminate and probably represents the rate controlling mechanism for the sintering process. After heating to high stresses and temperatures the temperature dependence was again Arrhenius when heated at lower temperatures. However, it increased to a maximum value of about 170 kcal/mole. This is similar to that of pure alpha alumina. At intermediate temperatures or stress the activation energy was intermediate. It appears that the creep is controlled initially by the stress aided sintering of the bond phase. After the particles have grown in size, compacted and been converted to higher aluminates, accompanied by changes in structure so that the coarse aggregate grains are in contact, the creep is dominated by the entire structure and the activation energy corresponds to that of the alumina grain to alumina grain bonding. Thus the creep of these concretes is very complex. Variations in coarse aggregate grain size and constitution should affect the creep process.

The stress exponent for these concretes was remarkably constant when determined by plotting log creep rate versus log stress at constant temperatures. The exponent also depended on previous thermal history. The creep of concretes on the first heating, constant temperature with increasing stress, gave stress exponents of about 0.5, less than that for viscous flow and plastic deformation. Because this stress exponent is too low to represent any known constant strain rate model it is apparent that the structure of the concrete is changing during the creep process. After initial compacting at the maximum stress the stress exponent increased to about 3.5. This could be associated with dislocation processes, which have stress exponents of 4 to 5, but probably is not. The fact that the exponent changes after initial creep, when recycled over the same stress range also indicates that the structure is changing.

The creep, especially on initial heating, depends upon the cement phase. The cement is less refractory than alumina so reducing the amount of cement might make it possible to use the concrete to higher temperatures. One of the recent improvements in commercial refractory concretes has been in reducing the amount of cement present - making it more refractory. Therefore, the creep of refractory concretes using tabular alumina aggregate was determined over a range of cement contents. The creep rate on initial heating was the same from about 7-1/2% to about 30%, the usual range of concentrations found in commercial concretes. However, the total strain to failure and the maximum stress and temperature at which failure occurred was reduced as the cement content was reduced. This could be important to gasifier linings because the low cement concretes will be more susceptible to damage whenever thermal expansion effects produce high stress.

Concrete specimens were subjected to the DOE gasifier atmosphere at the Illinois Institute of Technology at 1000°F for times up to 1000 hours. The creep resistance of these specimens was much better than specimens not heated in the gasifier atmosphere. This is in agreement with other results which indicate greater strength occurs when high pressure water vapor is present.

DISCUSSION OF CURRENT ACTIVITIES

Several changes in personnel were made during the quarter. Dr. J. R. Smyth left the University to work in industry. Mr. D. J. Bray graduated and went to work in industry also. Mr. Goo Dae Kim replaced Mr. Bray. The first part of the quarter was devoted in part to training new technicians and in renovating the creep furnace to which need periodic maintenance. One of the furnaces now has a differential LVDT installed to improve measurements of transient creep.

During this quarter major effort was expended on preparing the previous results for publication. The paper "Thermal/Strain History Effects on the Creep of Refractory Concrete" by D. J. Bray, J. R. Smyth and T. D. McGee received the first review by the American Ceramic Society. Only minor changes were needed and this paper should be

published in the near future. Two additional manuscripts are almost complete. One is on the effect of cement content on the creep behavior. The other is on the creep of specimens made with calcined kaolin aggregate and high purity Ca-25 calcium aluminate cement.

Experimental work during the quarter included X-ray diffraction analysis of the bond phases in specimens subjected to the DOE gasifier atmosphere, and to CO and steam atmospheres at atmospheric pressure.

Materials were ordered to begin the study of the effect of various cements on creep. These have been received, neat cement specimens have been cast and some of the core drilling has begun. During the next quarter the creep of these specimens will be studied. The differential LVDT is expected to provide better data for mathematical modeling purposes.

MIT-4.8 - THERMOMECHANICAL MODEL FOR REFRACTORY
CONCRETE LINER-ANCHOR INTERACTION

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INTRODUCTION

The objective of this study are: (a) to develop a numerical capability model to predict the stress and strain distribution during the heat-up and cool-down cycles of refractory concrete lined coal gasification vessels, (b) to provide a behavioral understanding of the degradation process in concrete such as cracking and creep, and (c) through parameter studies to arrive at specific guidelines for an optimal design. The model includes nonlinear stress-strain relations under multiaxial cyclic stress states and temperature-dependent creep laws. The objective is also to recommend design criteria which include optimum heating schedule, material property combinations, anchor configurations.

The approach taken to achieve these objectives includes both experimental and analytical studies. The experimental part of this work contains biaxial monotonic and cyclic compression tests on flat square refractory concrete specimens under different temperature environments. By using the test data, practical useful relationships between stress and strain and the failure criteria will be developed. The developed material model will then be utilized to perform simulation and parametric studies for a thorough understanding of the thermomechanical behavior of coal gasification vessels.

The technical work consists of the following tasks.

1. Organization of the Test Program: The test program is planned to achieve an efficient arrangement of testing equipment and selection of appropriate parameters so as to obtain most information out of a limited number of tests.

2. Biaxial Compression Tests: This task includes

- (a) Design, construction, and installation of a biaxial loading frame for applying compressive stresses to flat square specimens in two perpendicular principal directions.
- (b) Careful preparation, casting, placing, curing, and prefiring of refractory concrete specimens such that a close simulation of real situations will be obtained.
- (c) Uniaxial monotonic compression tests under different temperatures to obtain stress-strain curve in full range of loading in both orthogonal directions.
- (d) Uniaxial cyclic compression tests by monitoring strain increments under different temperatures to obtain full range of cyclic stress-strain curves.
- (e) Biaxial monotonic compression tests under different temperatures to obtain biaxial stress-strain curves for the full range of loading from zero to failure.
- (f) Special considerations to obtain the strain-softening characteristics.

3. Mathematical Modeling of Refractory Concrete:

Currently available material model for refractory concrete is based on the uniaxial compression tests with the assumption that its behavior is similar to that of ordinary concrete.¹ A more refined material model is needed to be used in predictive analysis to fully understand the behavior of coal gasification vessel linings.

4. Development of Creep Model: Creep plays an important role in the long-term behavior of coal gasification vessels under high temperature environment. Development of an improved creep model which takes into account the effect of temperature is warranted.

5. Development of Heat Transfer Model: Predictions obtained from previous analyses^{1,2} are not accurate since the response of the refractory materials to high temperature effects is highly dependent upon past temperature loading histories. Also, the critical condition of the vessel does not necessarily occur in the steady state. Development of a transient heat transfer model to predict

transient temperature distributions for subsequent stress analysis is required.

6. Numerical Simulation of Coal Gasification Vessel Tests: Due to the complex behavior of concrete and the liner anchor interaction, an accurate thermomechanical analysis is necessary to understand the behavior. Three-dimensional nonlinear finite element method together with the heat transfer model is utilized for the idealization of the structure and the response prediction.
7. Parameter Studies: The relative importance of each controlling parameter, such as the constitutive models, the material properties, anchor geometries, and heating rate, is assessed for economical and efficient design of the vessel structure.
8. Design Recommendations: Interpretation of the above parameter studies is made to provide specific guidelines for optimum design.

RESULTS FROM PRIOR QUARTERS

Experimental and analytical accomplishments from prior quarters are summarized below.

Experimental Work

During the past reporting periods details of the testing equipment, testing procedures, and the test results are presented. Results include mainly the stress-strain curves up to failure for 90% Al_2O_3 dense refractory concrete at room temperature, 1000°F, 1500°F, 2000°F and Litecast insulating refractory concrete at room temperature, 500°F, 1000°F, and 1500°F. At each temperature, proportional plane loading at four stress ratios (0.1, 0.153, 0.484, 1.0) are tested. Failure envelope plotted on biaxial plane shows significant biaxiality effect.

Analytical Work

A creep model for the 90% Al_2O_3 dense refractory concrete based on thermorheologically simple material behavior was developed using the test results from Iowa State University. Refinement of the model and extension to the insulating material are necessary.

An effective conductivity model for refractory concrete lining has been developed. Numerical solution of the transient heat transfer problem based on the Crank-Nicholson method has been implemented into a computer program. Verification of the program was made by comparing with analytical solution in a special case where material properties are constant.

DISCUSSION OF CURRENT ACTIVITIES

Constitutive Model for Refractory Concrete

The developed temperature dependent constitutive model for refractory concrete is reported in the following. The parameters are identified for a 90% Al_2O_3 dense refractory concrete and an insulating lightweight refractory concrete. The model is based on the nonlinear elastic orthotropic model which is widely used for ordinary concrete^{3,4}.

Failure Surface in the Principal Stress Space

The failure surface in the principal stress space is fitted from previously reported biaxial compression test data. To separate the effect of temperature from the multiaxial behavior, the function form of the failure surface is assumed to be separable.

$$F(\sigma_{ij}, T) = f(\sigma_{ij}) g(T) \quad (1)$$

where $F(\cdot)$ is the failure surface, σ_{ij} is the stress tensor and T the temperature. To estimate $g(T)$, the strength at different stress ratios are averaged at different temperatures. The average strength for both

materials are shown in Figure 1. $g(T)$ was then fitted by a cubic polynomial. With $g(T)$ obtained, one can then isolate the temperature effect. The normalized (with respect to temperature) strength data are plotted in Figure 2 and 3.

Two function forms as proposed by Hsieh, Ting, and Chen⁵ and Willam and Warnke⁶ were chosen and modified to fit $f(\sigma_{ij})$ through a least square nonlinear optimization program. The resulting failure surface on the biaxial plane as predicted by the two models are also shown in Figure 2 and 3. The modified model of Willam and Warnke gives much better fitting and has been adopted in the model.

Failure Surface in the Principal Strain Space

The failure strain of each biaxial compression test is shown in Figure 4. The failure strain does not show a definite trend with respect to different stress ratios. It is assumed in the model that the failure strain at each temperature is a constant. The average failure strain at different temperatures are shown in Figure 5 for both materials. Both curves are fitted by cubic polynomials.

Temperature Dependent Initial Modulus

The temperature dependent initial moduli for each material and each temperature were determined from experimental data. The moduli were then fitted by an exponentially decaying functions as shown in Figure 6 and 7.

Heat Transfer Analysis

The developed transient heat transfer analysis program is further verified by comparing with another heat transfer program⁷ and experimental results from B&W⁸. Comparison is made with Example 1 in Ref. 7. The result is shown in Figure 8. Agreement is generally good and both analysis predicted exactly the same shell temperature (so will be the heat loss). Note that the effect of anchors has been neglected in the developed program. The path 2 temperature profile

is the temperature distribution through anchor in the lining.

The transient heat transfer program is also used to simulate B&W Lining #1 and #2 first heat-up tests. Both linings were heated up to 1200°F at hot face. Parameters including high-conductivity process gas, amount of cracking in different portions of the lining, crack width, gap width and radiation distance were studied. Figure 9 and 10 shows the improvement of temperature profile predictions by incorporating adequate amount of cracking into the lining.

NEXT QUARTER ACTIVITY

During next quarter, the developed constitutive model and creep model will be incorporated into the stress analysis program to perform transient simulation analysis of the B&W linings and parameter studies especially the problem of optimum heating schedule. Final report will be issued after the next quarterly report.

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Figure 1 Average Strength of the Two Materials at Different Temperatures.

Figure 2 Failure Surface in Compression on the Biaxial Plane as fitted by Two Models on the Normalized Experimental Data. (f'_c is the Averaged Strength in Uniaxial Compression).

Figure 3 Failure Surface in Compression on the Biaxial Plane as fitted by Two Models on the Normalized Experimental Data. (f'_c is the Average Strength in Uniaxial Compression).

Figure 4 Failure Strain of the Two Materials Plotted on the Biaxial Principal Strain Plane.

Figure 5 Average Failure Strain for the Two Materials at Different Temperatures.

Figure 6 Experimental and Fitted Equation for the Initial Elastic Modulus of 90% Al_2O_3 Dense Refractory Concrete.

Figure 7 Experimental and Fitted Equation for the Initial Elastic Modulus of the Insulating Refractory Concrete.

Figure 8 Steady-State Temperature Profile as Predicted by the Transient Heat Transfer Program and CONBEC.

Figure 9 Predicted Temperature Profile for B&W Lining #1 1200°F Heat-Up Compared with Measurement.

Figure 10 Predicted Temperature Profile for B&W Lining #2 1200°F Heat-Up Compared with Measurements.

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VPI-4.8 — INVESTIGATION OF CARBON MONOXIDE DISINTEGRATION
OF REFRACTORIES IN COAL GASIFIERS

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INTRODUCTION

Refractories used in coal gasification vessels and piping are exposed to mixtures of hydrogen, steam, hydrogen sulfide, methane, carbon monoxide, and other gases over a wide range of temperatures and pressures. Many refractories are known to deteriorate when exposed for long periods of time to CO-containing atmospheres; especially if the temperature is below about 1300°F and if the refractory contains any iron containing compounds. It is, therefore, important to develop experience and engineering data on these refractories under simulated coal gasifying conditions and to attempt to determine the effect of each identifiable variable on the CO resistance of the refractories used in coal gasifiers.

The objectives of this investigation are to determine 1) whether or not CO disintegration is likely to occur in the refractories used in coal gasifiers, and 2) to identify the conditions under which CO disintegration of the refractories can be expected to be a serious problem. It is also a goal to this investigation to develop information that will assist in the identification of refractory deterioration or failure that is caused by CO disintegration.

The objectives of this study include:

- 1) A systematic study of the effects of pressure, temperature, gaseous mixtures, and iron impurities in coal gasifier refractories.
- 2) Conduct an intensive study of the CO disintegration at high pressures (500-1000 psi) of fiber reinforced refractories in order to
 - a) evaluate the deterioration that can be expected from the various iron based fibers, and
 - b) attempt to develop a fiber system that effectively resists disintegration.
- 3) Conduct a series of tests on insulating castables at high pressures to evaluate the extent of CO damage that can be expected in these back-up lining components.
- 4) Investigate the effect of alkali as an accelerator of CO disintegration.
- 5) Investigate the effect of early stages of CO disintegration of refractories on the abrasion (and possibly creep) resistance of the refractories.
- 6) Conduct a series of field examinations of gasifier linings to look for CO disintegration or related effects.
- 7) Prepare a comprehensive final report at the conclusion of this study that summarizes in reasonable detail the present knowledge of CO disintegration of gasifier refractories.

RESULTS FROM PRIOR QUARTERS

Based on the test data collected to date, the following observations have been made:

- 1) CO disintegration of high alumina castables is not likely to be a problem in coal gasifiers at atmospheric pressure. All gases added to CO tended to retard refractory disintegration compared with samples exposed to pure CO. A 1000 hr exposure to a simulated coal gasifier atmosphere did not produce any visible damage or strength loss in either castable examined.
- 2) CO disintegration of high alumina castables is a potential cause of refractory failure at high pressures. The time required for refrac-

tory deterioration rapidly decreases as pressure increases. The effect of even small amounts of iron impurities greatly accelerates the rate of disintegration.

- 3) In coal gasifiers, CO disintegration is likely to affect the abrasion resistance of the refractories long before any of the typical signs of CO disintegration are noted. The 50% Al_2O_3 castable is more susceptible to abrasion than the 90% Al_2O_3 castable.
- 4) The temperature range over which CO disintegration is active appears to be shifted to higher temperatures at high pressures.
- 5) Preliminary results suggest that alkali compounds, particularly K_2CO_3 , accelerate CO disintegration of high alumina castables.
- 6) The 50% Al_2O_3 castable disintegrates faster than the 90% Al_2O_3 castable, possibly a result of the higher iron content of the calcined kaolin used in the 50% Al_2O_3 refractory.
- 7) Stainless steel (AISI 316 and 446) reinforced castables possess very poor resistance to CO disintegration both at atmospheric and 1000 psi.

DISCUSSION OF CURRENT ACTIVITIES

Investigation of CO disintegration of 310 stainless steel fiber reinforced 90% Al_2O_3 and 50% Al_2O_3 castables began this period. In order to eliminate any variations due to casting conditions all samples of each composition were cast in a single batch. Both compositions were exposed to carbon monoxide and carbon monoxide/steam mixtures at 1000 psi/500°C for 50 hours. No 1100°C prefiring treatment was performed on the samples, but all test specimens were held at 500°C in the test vessel for 12 hours before introduction of the test gas mixture.

Visual examination of all exposed samples indicated that their interior had turned a uniform gray. No carbon deposition was found on any fiber surfaces and no samples displayed any apparent signs of degradation following exposure to the CO-containing atmospheres. This behavior contrasts previous observations made on non-fiber reinforced 90% Al_2O_3 castables doped with metallic iron particles where extensive carbon growth took place on the iron particles following CO exposure. These latter samples had completely disintegrated following an 1100°C

prefire and CO-exposure at 1000 psi/500°C for 50 hours. These differences between castables made with and without stainless steel fiber addition may be real, but they may also rise from the prefiring treatment given the non-fiber reinforced samples. The prefiring may well cause oxidation of the metallic iron additions, which in turn could catalyze the CO-disintegration reactions. Additional work is needed to evaluate the effect of the prefiring operation on CO-disintegration.

Following the visual inspection, strength and abrasion tests were performed on all the samples. These results are summarized in Table 1.

In pure CO, a substantial decrease in strength was observed in only 50 hours in both 50% and 90% Al_2O_3 samples. The 50% Al_2O_3 sustained more damage, probably because of the higher iron impurity levels contained in the calcined kaolin aggregate. The abrasion resistance, however, was not significantly affected in either castable.

Addition of 20% steam to CO caused a slight decrease in strength and a substantial decrease in abrasion resistance of the 90% Al_2O_3 samples. Following previous results, the 50% Al_2O_3 samples exhibited a strength increase, and an increase in abrasion resistance. The abrasion resistance was affected much more than the strength in this case.

Since carbon monoxide levels in coal gasifiers are typically under 80%, samples were tested in a mixture of 40% CO/40% N_2 /20% H_2O . Results of this test were similar to results of the 80% CO mixture with strength increasing in 50% alumina samples and decreasing in 90% alumina samples.

In general, a rapid loss of strength of 90% Al_2O_3 samples was observed in all atmospheres tested, with steam-containing atmospheres being more aggressive than pure CO. The strengthening effect observed in 50% alumina samples exposed to CO/steam mixtures follows observations made by other investigators. This strengthening has been attributed to the formation of mullite crystals. Further testing with longer exposure times is necessary to study the presumed strengthening effect. Longer exposure times would tend to accentuate any carbon monoxide degradation, since the 50 hour exposure time used may be insufficient to

TABLE 1. RESULTS OF EXPOSING 310 SS REINFORCED CASTABLES TO CO-CONTAINING
ATMOSPHERES AT 1000 PSI/500°C/50 HOURS

Sample Composition	Gas Composition (Vol.%)	Strength (Psi $\pm$ Std. Deviation)	Abrasion Resistance (Vol. Removed, cm ³)
50% Alumina	N ₂	3530 $\pm$ 340	2.53
90% Alumina	N ₂	3740 $\pm$ 400	1.86
50% Alumina	CO	2000 $\pm$ 370	2.26
90% Alumina	CO	2650 $\pm$ 430	2.29
50% Alumina	80% CO/20% H ₂ O	3800 $\pm$ 550	.82
90% Alumina	80% CO/20% H ₂ O	2250 $\pm$ 210	5.78
50% Alumina	40% CO/40% N ₂ /20% H ₂ O	3460 $\pm$ 400	1.04
90% Alumina	40% CO/40% N ₂ /20% H ₂ O	2180 $\pm$ 210	3.26

produce noticeable signs of reaction. Other fiber compositions will also be investigated.

ANL-4.9 -- CORROSION OF REFRACTORIES IN SLAGGING GASIFIERS

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SUMMARY OF CURRENT ACTIVITIES

Reflecting the recent change in philosophy of the AR&TD program, the purpose of this program has been modified to investigate the parameters that affect the corrosion of refractories in slagging gasifiers so that lining lifetimes can be optimized through the proper choice of refractory materials, coal selection or modification, and/or changes in process variables. The work described in previous quarterly reports, i.e., the evaluation of the corrosion resistance of commercial refractories via a gas-fired rotating-drum dynamic-slag corrosion test, will be reported under contract FTP 49570 with the Project Office of Fossil Energy.

With the aid of funding from the Solvent Refined Coal Project Office of Oak Ridge Operations, a controlled atmosphere rotating-spindle refractory-slag corrosion furnace has been designed and assembled.

Checkout of this furnace, the first of a projected three, was completed. Three tests of a 90% Al_2O_3 -10% Cr_2O_3 refractory at 1480°C and 100 rpm were completed. One test was completely successful and some data are available from the other two. The data are being analyzed. Several operational problems, normal to new equipment, have been solved. It is expected that a remaining relatively minor problem will be solved and two additional furnaces will be placed in operation during the next reporting period. Design of the viscosimeter, a modification of the corrosion test facility, is proceeding.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

¹Materials Technology for Coal-conversion Processes: Progress Report for October-December 1981, Argonne National Laboratory Report ANL/FE-82-9 (in preparation).

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IITRI-4.9 — DESIGN, ENGINEERING, AND EVALUATION
OF REFRACTORY LINERS FOR SLAGGING GASIFIERS

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INTRODUCTION

The objectives of this program under Department of Energy Contract No. DE-AC05-78ET13410, "Design, Engineering, and Evaluation of Refractory Liners for Slagging Gasifiers," are to design, construct, and operate a Refractory Test Facility for the evaluation of refractory liners under slagging gasifier conditions.

The program is composed of six tasks which can be grouped into three parts. The first part includes only Task A, Conceptual Liner Designs, which summarizes the state-of-the-art of the design of refractory liners for slagging coal gasifiers. The second part includes Task B, Design and Construction of Test System; Task C, Refractory Liner Tests; and Task D, Liner Design Evaluation. The test system constructed in Task B is used to test refractories under simulated slagging gasifier operating conditions. In the third part, the results of Tasks B, C, and D are to be used to prepare refractory liner design models and develop recommended design practices, which can then be incorporated into a handbook for gasifier designers and refractory suppliers.

RESULTS FROM PRIOR QUARTERS

The contract for this program was awarded at the end of September 1978. Work was started on 1 October 1978, on Tasks A, B, and E. Task A, Conceptual Liner Design, has been completed; Task B, Test System Design and Construction, is in progress. Task C, Liner Tests, and Task D, Liner Design Evaluation, will begin upon completion of Task B. Task E, Liner Model Development, is now inactive after an initial data compilation and theoretical model development effort. It will be activated as soon as

data are available from Task D. Task F, Liner Design Handbook, was active along with Task A since the report of both tasks will use the same format. It is now inactive until the completion of Tasks D and E. The principal efforts on this program during all prior quarters have been to design and construct the test facility, Task B.

Construction of the test unit was completed by 31 July 1981. A two-phase plan for integrated check-out and shakedown of the completed system was established and agreed to by DOE, Oak Ridge National Laboratory, and IITRI personnel. Phase I consists of the following tasks:

- a) rework control circuits
- b) put in a remote start/stop switch for slag tap torch
- c) install piping and valves for gas analyzer
- d) install gas detector
- e) wire optical pyrometer
- f) wire generator gas detector
- g) extend thermocouple wiring to data logger
- h) install data logger operating cable.

Phase II consists of the following tasks:

- Task 1) Run cold at atmospheric conditions (compressors, pumps, generator, and slag injection and removal system all run at same time to check entire system and familiarize ourselves with operation).
- Task 2) Run cold, but at a pressure of 100 psi.
- Task 3) Assemble auxiliary nozzle and equipment for low temperature heat-up of unit and dry-out of refractories.
- Task 4) Run through entire system with all burner systems to be fired at atmospheric conditions.
- Task 5) Go through complete start-up procedure with Davy McKee and burner people present.

This is considered to be a minimum shakedown schedule.

The work was to be completed by 30 October 1981. However, because of the need to conserve (requested by the ORO) funds, the work crew was cut in half, and because of the usual unanticipated equipment malfunction which always occurs when new equipment of this size (pilot plant scale) is first operated, only parts of Phase I and II were completed during the time period 1 July to 30 September 1981. The problems and work completed were discussed in the quarterly report ending 30 September 1981.

PROJECT STATUS

During this report period, 1 October to 31 December 1981, the Phase I tasks were completed, all systems were checked out and found to be operational. Task 1, cold running at atmospheric pressure and Task 2, cold running at 100 psi pressure, of Phase II shakedown of the test unit were completed during the previous quarter. The remaining tasks of Phase II-- Task 3) assemble auxiliary nozzle, Task 4) fire all burner systems at atmospheric temperature and heat up unit to 1500°F to dry out refractories and fire in castable refractories, and Task 5) fire up all burner systems at pressure (90 psi) and heat up the unit to 2700°-3000°F and run slag through system--were attempted during this quarter.

The report from Hercules on the Hazard Analysis of the test equipment and its operation was received during the first week in December. A preliminary analysis of the report was given on 15 October 1981 by C. A. Angoli of Hercules Incorporated Allegany Ballistics Laboratory, Cumberland, Maryland. In their opinion, the test vessel construction and operation procedure were satisfactory. However, there were a few items in the analysis that they thought should be done which would be of benefit to the project. These are listed below:

- 1) Install audible and visual alarms from gas detector outside of compressor enclosure and on the control panel - done.
- 2) Move gas compressor switch to outside of gas compressor enclosure - done.

- 3) Control room and gas compressor room exhaust fans should have flow switches - not to be done.
- 4) Both fans to start automatically - not to be done.
- 5) Overhead roof fan to start automatically - not to be done.
- 6) Additional gas alarms to be put on burner pipe rack - in process of being installed.
- 7) Platform on top vessel - will be done at a later date.
- 8) Face shields and breathing apparatus - purchased.
- 9) Flow switch for N₂ purge - not to be done.
- 10) Insulation around scrubber - done.
- 11) Level controls for slag tap vessel - designed and purchased.
- 12) Clock for control room - done.
- 13) Install limit switch on main burner gas and oxygen for gas lance purge valves and light on panel to indicate they are closed - not to be done.
- 14) Install controls on panel for slag tap vessel drain - done.

Phase II - Task 3, Heat-up burner installation

The main burner supplies too much heat even at low firing to safely heat up the test unit at approximately 100°-150°F per hour. In order to bring the unit up to a safe temperature (1500°F) to light the main burner, a North American "Aardvark 4492A" burner (Figure 1), a compact, high-velocity air heater was purchased and installed in the test unit. With suitably sized gas accessories, the Aardvark can deliver air at any temperature from 300° to 1600°F. Even higher temperatures are possible with suitably constructed hot air delivery piping and heating enclosures. Air temperature of the discharge of the Aardvark must be high enough to

overcome radiation losses in the distribution piping, and piping must be compatible with these temperatures. Insulation can be applied to the distribution piping as long as this does not cause excessive temperature buildup in the piping. A stainless steel smoke pipe (Figure 2) was used as the distribution pipe to bring the hot air through the slag tap vessel to the main test vessel. The original design consisted of a standard stainless smoke pipe without water cooling fitted through the flange cover of the lower manhole of the slag tap vessel (Figure 3).

A test run on 6 November 1981 heated up the flange cover rapidly to above 300°F. The system was rechecked, and an asbestos insulation was put in the smoke pipe to insulate it from the Aardvark mounting flange. On 10 November 1981, the unit was tested again. The flange cover did not heat excessively, but the pipe was hot. The slag tap vessel began to heat up, and the stove pipe was at red heat. Water was introduced into the bottom of the slag tap vessel, and the slag tap vessel water sprays were turned on. The water in the vessel was allowed to drain, and cold make-up water was continually introduced. This system appeared to keep the stove pipe from overheating. During the next two weeks all systems (control wiring, gas analyzer, thermocouples, igniters, flame sensors, pumps, and compressors) were rechecked, and the unit was made ready to attempt Task 4 of Phase II (heat up unit and fire all burner systems at atmospheric conditions).

Phase II - Task 4, Heat up test vessel and start main burner
and auxiliary torches at atmospheric conditions

Test was started on 2 December 1981. After six hours running time, the flange to which the Aardvark heater was fastened began to overheat. The heater was turned off, and the unit was shut down. It was discovered that the stove pipe had burned through just past the asbestos-lined section. The rest of the stove pipe had collapsed, and hot air was heating up the slag tap vessel. A decision was made to make a double pipe, of 7-in. OD section and 5-in. ID section with space between filled with Harbison-Walker castable 26. The new insulated smoke pipe was installed in the slag tap vessel. The castable in the notch was repaired before installation of the pipe. Damage was due to the water spray on the uncured castable.

A second test attempt was started on 8 December 1981. Again heat-up was done slowly, approximately 100°F per hour. After 5 hours of running time, the smoke pipe again heated up and the sprays were again turned on. After 9 hours running time, the temperature in test vessel approached 1000°F, but it was impossible to keep the smoke pipe cool and slag tap flange cover was beginning to heat up excessively. The heatup was kept on low heat until 8:45 a.m. on 10 December 1981 when the decision was made to shut down the run. The smoke pipe failed at the joint in the manway cover plate. The inner pipe had collapsed, the castable refractory eroded away, and the outer sheel burned through.

After this run, a new concept was devised for transmitting the hot gas from the Aardvark burner to the test vessel. A ceramic inner liner (zirconia) (5-in. ID with a 1/8-in. wall) was used, and a 7-in OD with a 1/8-in. thick 310 stainless pipe was used for the outer support. The space between the ceramic and the stainless was packed with Fiberfrax insulation. In order to avoid heating up the manway flange, a hanger was installed inside the slag tap vessel to hold the smoke pipe in place. The Aardvark burner was fitted to the end of the smoke pipe, Figure 4. To further insure cold running, the smoke pipe was water-cooled (Figure 5), and the ends of the distribution pipe were sealed with plastic refractory to hold the insulation in place, as shown in the figure.

Another test run was attempted on 29 December 1981 with the new distribution pipe (smoke pipe). No problems were encountered during heat up. The test-section refractories were heated to 1200°F, and the decision was made to turn on the main burner. The Aardvark unit was turned off, and an attempt to light the main burner was made at 10:00 on 29 December 1981. The burner started with a pop on the first try and ran for about 10 seconds. The flame scanner was very unstable, and the gas compressor shut off. There was difficulty in getting the gas compressor started, and the refractories were cooling rapidly. It was decided to start the Aardvark burner again. It would not start, and it appeared that the hot gas distribution pipe was plugged with debris from the explosive start of the main burner. After the run was terminated, it was determined that the debris was from the slag placed in the bottom of hearth section and old

bits of refractory left from previous runs. The pieces of refractory that blocked the flame scanner view of the Aardvark were cleaned out and at the next try, the unit start up explosively which cleaned out the distribution pipe. After this occurred, the distribution pipe was heating excessively (1200°F), and it was decided to abort the run without trying to light the main burner again. After cool-down and removal of the distribution pipe, the ceramic tube was found to be cracked and broken in several places. The ceramic tube was replaced with a spare tube, and a decision was made to change the operation of the Aardvark so that it could be operated with the main burner. The hot air distribution pipe was modified with the necessary change in piping and additional cooling coils before the end of the report period. The new design for the distribution pipe appears to work well, and the pipe can be heated to 1150°F without damage to the system. Another test run was scheduled for 4 January 1982.

Figure 6 is a view of the control room and data being taken from the data logger. Figure 7 is a view taken from IITRI's Tower Building during the 22 December 1981 run showing the water cooling tower in operation, and Figure 8 is a close-up of the tower during the same run. All systems tested appear to work satisfactory.

During the report period, the operating crew has worked well together, and learned a great deal about the operation of the test unit and how to handle emergency situations.

Figure 1. 4492A Aardvark burner used to heat up and dry out the test unit.

Figure 2. Stainless steel smoke pipe to bring hot air through the slag tap vessel to the test vessel.

Figure 4. Aardvark burner fitted to smoke pipe in manway of slag tap vessel.

Figure 5. Water cooling jackets on smoke pipe.

Figure 6. Control room.

Figure 7. View of water cooling tower in operation.

Figure 8. Close-up view of water cooling tower in operation.

PNST-4.9 — REFRACTORIES IN SLAGGING GASIFIERS*

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INTRODUCTION

This research is concerned with the high-temperature chemistry of oxide phases of importance as refractory materials in slagging coal gasifiers. Special attention is directed toward chromium oxide-containing phases (mainly Al_2O_3 - Cr_2O_3 solid solutions and various spinel phases involving Cr_2O_3 as a component). In order to provide the data-base needed for an understanding of such reactions, equilibrium relations are being determined for a number of oxide combinations of simplified coal-ash slags, mainly in the system CaO - FeO - Al_2O_3 - SiO_2 , with refractory oxide components (MgO , Al_2O_3 , Cr_2O_3). Because iron and chromium occur in several valence states in oxide phases, the equilibrium relations in systems involving these elements are dependent on the oxygen potential under which the reactions take place. The present studies, therefore, are carried out under carefully controlled atmospheric conditions. Most of the runs are made under the relatively reducing conditions of a CO_2 - H_2 atmosphere of ratio $\text{CO}_2/\text{H}_2 = 10/1$, while additional runs are being made in CO_2 or air.

RESULTS FROM PRIOR QUARTERS

Research done in previous quarters has established three important characteristics governing the behavior of chromium oxide in silicate systems of importance in slagging coal gasifiers, viz.: 1) The low solubility of Cr^{3+} in silicate melts, 2) The dissimilarity in crystal-chemical behavior of Cr^{3+} and Al^{3+} in solid phases of complex structures,

*Work performed under DOE/ORNL Subcontract Number 9006

and 3) The drastic increase in solubility of chromium in silicate melts and attendant drastic lowering of liquidus and solidus temperatures in such systems at very low oxygen potentials. Phase relations in a number of systems formed by various combinations of the most abundant oxide components in typical coal ash and of the most promising refractory components have been studied and summarized in previous reports. Particular emphasis during recent quarters has been placed on additions of various amounts of iron oxide to selected parts of the system $\text{CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$, and on the effects of oxygen potentials on such equilibria. Specifically, phase relations in the systems $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-FeAl}_2\text{O}_4$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-FeCr}_2\text{O}_4$ have been determined in $\text{CO}_2\text{-H}_2$ atmospheres of ratios $\text{CO}_2/\text{H}_2 = 10/1$, and the effects of increasing the oxygen potentials to those of CO_2 and air atmospheres have been studied in the systems $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeAl}_2\text{O}_4$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeAl}_2\text{O}_4$. The present activities, as summarized in the subsequent section, represents a continuation and extension of these previous studies.

DISCUSSION OF CURRENT ACTIVITIES

One major effort during the past quarter was the delineation of phase relations in FeO-containing silicate systems of particular importance in slagging coal gasifiers, and comparisons of the role of this component with that of MgO in analogous MgO-containing systems. Examples of results obtained are shown in Fig. 1, illustrating phase relations in the joins $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeAl}_2\text{O}_4$ and $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeCr}_2\text{O}_4$ of the systems $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Al}_2\text{O}_3$ and $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Cr}_2\text{O}_3$, respectively. The oxygen potential for which these diagrams apply are those generated by mixing CO_2 and H_2 in ratio 10:1. The crystalline phases occurring in stable equilibrium with liquid in the systems shown in Fig. 1 are spinel ($\text{FeAl}_2\text{O}_4\text{-FeCr}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solutions), sesquioxide ($\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The systems are not binary, as demonstrated by the presence of two crystalline phases and liquid (+ gas phase) over a temperature range.

An approximate phase diagram for the system $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-MgO-Cr}_2\text{O}_3$ is illustrated in Fig. 2, showing the existence of periclase, spinel

and sesquioxide, in addition to gehlenite, on the liquidus surface. The diagram is similar to that observed previously for the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-MgO-Cr}_2\text{O}_3$ except for the presence of gehlenite instead of anorthite as the primary silicate phase. In all cases, however, the most significant feature of the phase relations is the relatively low Cr_2O_3 content of the liquid phase in the silicate liquids at moderate temperatures ($\leq 1500^\circ\text{C}$), and the extreme degree of partitioning of chromium into the sesquioxide and spinel phases.

LEGENDS FOR DIAGRAMS

Fig. 1 Approximate liquid-solid phase relations along the join $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeAl}_2\text{O}_4$ (diagram on left) and the join $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeCr}_2\text{O}_4$ (diagram on right) of the systems $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Al}_2\text{O}_3$ and $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeCr}_2\text{O}_4$, respectively. Abbreviations used have the following meanings: W = wüstite; SP = spinel; SES = sesquioxide; AN = anorthite.

Fig. 2 Approximate phase relations in the system $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-MgO-Cr}_2\text{O}_3$ in a $\text{CO}_2\text{-H}_2$ atmosphere of CO_2/H_2 ratio = 10:1. Abbreviations used have the following meanings: PER = periclase; SP = spinel; SES = sesquioxide; GEH = gehlenite.

Fig. 1 Approximate liquid-solid phase relations along the join $\text{CaAl}_2\text{Si}_2\text{O}_8$ - FeAl_2O_4 (diagram on left) and the join $\text{CaAl}_2\text{Si}_2\text{O}_8$ - FeCr_2O_4 (diagram on right) of the systems $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{FeO-Al}_2\text{O}_3$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ - FeCr_2O_4 , respectively. Abbreviations used have the following meaning: W = wüstite; SP = spinel; SES = sesquioxide; AN = anorthite.

Fig. 2 Approximate phase relations in the system $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-MgO-Cr}_2\text{O}_3$ in a $\text{CO}_2\text{-H}_2$ atmosphere of CO_2/H_2 ratio = 10:1. Abbreviations used have the following meanings: PER = periclase; SP = spinel; SES = sesquioxide; GEH = gehlenite.

PART IV — MATERIALS FOR HEAT ENGINES AND HEAT RECOVERY

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ORNL-5.10, -5.11, -5.12 -- CERAMICS FOR HEAT ENGINES AND HEAT RECOVERY

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The organization of this section follows the task organization of the Structural Ceramics for Heat Engines and Heat Recovery section of the draft AR&TD Fossil Energy Materials Program Plan for FY 1982-86. The subtasks identified in the program plan are: (1) Powder Synthesis, (2) Fabrication and Microstructural Control, (3) Testing and Characterization, (4) Ceramic Joining and Joint Development, and (5) Structural Design Methodology and Data Analysis. Our in-house work currently supports only the first three subtasks.

A. SILICON CARBIDE SYNTHESIS AND PROCESSING

G. C. Wei and C. S. Morgan

INTRODUCTION

This task includes experimental investigations on synthesis and evaluation of SiC powders and processing of SiC ceramics for applications in heat engines and heat recovery systems.

DISCUSSION OF CURRENT ACTIVITIES

Hot pressing of silicon carbide powder (A-10 from Hermann C. Starck, Berlin) with additives such as BN (XK grade from Electroschmelzwerk Kempen GmbH), TiC (grade F from PPG Industries, Barberton, Ohio), Cr (lot 36094 from Union Carbide Corporation, Electro Metallurgical, Niagara Falls, New York), and Y₂C (lot 1592 from Cerac, Inc., Milwaukee, Wisconsin) was investigated. A silicon carbide powder* prepared by

*Lots 499-S-8 and 499-S-9 prepared by C. R. Kennedy, Oak Ridge National Laboratory.

reactions of Cab-O-Sil (grade M5 from Cabot Corporation, Boston, Massachusetts) with A-240 pitch (from Ashland Oil, Inc., Ashland, Kentucky) was also used in the hot pressing study.

The chemical analysis of the A-10 α -SiC powder (batch S2503) was reported by the vendor as follows: C, 30.03%; O, 0.49%; Fe, 0.01%; Al, 0.01%; and Ca, 0.006%. The average particle size is 0.65 μm , and the BET surface area is 17.12 m^2/g . Thermogravimetric analysis (TGA) results on this powder heated from room temperature to 1200°C at 0.67°C/s under flowing argon ($3.6 \times 10^{-6} \text{ m}^3/\text{s}$) showed no change in weight.

Powders were mixed by blending overnight and ball milling in a Spex mill for 10 min. The mixed powders were hot pressed for 2.7 ks (45 min) at 2000°C and 62 MPa (9000 psi); density results are shown in Table 1. Small additions of BN had a dramatic effect on the density of the SiC. The addition of 0.615 wt % BN increased the fractional density from 71 to nearly theoretical. The fractional density decreased steadily with increasing concentration of BN above 1.2%.

Small amounts of titanium carbide powder were mixed with the SiC-BN powders to obtain a tougher SiC. Hot pressed results, also shown in Table 4.6, indicate that high densities, 97.3% for specimen SC-18, were attained. The SiC-BN powders with added chromium were also hot pressed to high densities, for example, 93.9% for specimen SC-20. However, dopant Y_2C did not appear to enhance densification significantly during hot pressing.

Measurements of microtoughness of specimens SC-12 and SC-16 were performed with the indentation technique. Preliminary results indicate that the room-temperature toughness of SC-12 ($3.3 \text{ MPa}\cdot\text{m}^{1/2}$) or SC-18 ($4.7 \text{ MPa}\cdot\text{m}^{1/2}$) is higher than that of the sintered- β SiC ($3 \text{ MPa}\cdot\text{m}^{1/2}$). The BN and TiC dopants appear to improve the toughness of SiC ceramics.

A preliminary evaluation of the thermal shock resistance and toughness of SiC samples was made by quenching 10-mm-diam samples from 520°C in air to 70°C in water. Structural damage caused by the quenching was determined by clamping the sample in a rubber tube and observing helium leaks. Helium at 0.17 MPa was on the back side of the SiC, and bubbles were observed in alcohol. Specimen SC-12 (SiC — 0.615 wt % BN), which was 99.14% of theoretical, did not show helium leaks after ten successive quenches. After 15 quenches there were three small streams of bubbles.

Table 1. Results of hot pressing of silicon carbide powder with additives

Specimen	SiC	Additives (wt %)			Theoretical density (%)
		BN	TiC	Other	
SC-2	A-10 ^a	0			70.7
SC-12	A-10	0.615			99.4
SC-11	A-10	1.23			99.0
SC-13	A-10	0.326			98.9
SC-10	A-10	2.44			98.8
SC-8	A-10	4.76			97.7
SC-3	A-10	9.1			94.6
SC-6	A-10	16.1			92.5
SC-7	A-10	23.1			90.5
SC-14	A-10	0	9.1		72.2
SC-16	A-10	4.6	4.6		89.0
SC-18	A-10	4.7	2.3		97.3
SC-19	A-10	8.7	4.4		94.0
SC-24	A-10	40.0	35.0		90.5
SC-21	A-10	20.0	15.0		91.2
SC-23	A-10	30.0	25.0		90.9
SC-25	A-10			1 YC ₂	81.5
SC-26	499-S-8 ^b	1.23			98.9
SC-28	499-S-9 ^b	1.23			97.2
SC-29	499-S-9	2.44			94.7
SC-15	A-10	1.23		5 Cr metal	75.7
SC-20	A-10	7.0		5 Cr metal	93.9
SC-17	A-10	4.76		5 Cr metal	92.8
SC-27	A-10	1.23		1 vol % Cr metal	77.8

^aA-10 SiC from Hermann C. Starck, Berlin.

^b499-S-8 and 499-S-9 SiC prepared by C. R. Kennedy from Cab-O-Sil reacted at 1700°C with pitch (A-240).

Specimen SC-15, which contained 5 wt % Cr metal and was only 76% dense, had a fine porosity indicated by helium bubbles before quenching. During quenching the helium penetration decreased, presumably because water reacted with surfaces in tiny pores and blocked the helium flow, but concurrently the quenching did not cause cracks to develop. After 20 quenches there were no helium leaks. The sample was quenched 50 times without new leaks appearing.

Efforts to achieve SiC densification without hot pressing have been initiated. Samples cold pressed at 138 MPa were sintered under argon at 2000°C for 1 h. Results of sintering tests are given in Table 2. The highest densities achieved were above 87% of theoretical and were in material containing 4.76 wt % BN plus 2.5 or 5 wt % TiC.

A second hot press has been constructed from existing parts in order to increase the rate at which we can fabricate samples. The unit is induction heated. The induction hot press for heating up to 1850°C is completed and operational with manual control. However, an optimum coil design for heating up to 2000°C has not yet been found.

B. PROPERTY STUDIES

P. F. Becher

INTRODUCTION

The use of structural ceramics in heat exchanger (HX) applications must consider not only the long-term stability of these materials in the severe environments of coal-fired systems but also the microstructural-compositional factors that influence their chemical and mechanical response under such conditions. To this end, mechanical properties of several commercial silicon nitride and carbide ceramics are being examined before and after exposure to the hot combustion product environment of various coal-oil mixtures (COM) having different coal ash compositions.

In Combustion Exposure Test 2 (EC 2), flexural specimens are being studied for microstructural-compositional and mechanical changes brought about by long-term exposure at about 1220°C to the slag from the combustion of a basic COM.

RESULTS FROM PRIOR QUARTERS

In previous quarters, the fracture strengths before and after exposure to a viscous slag from the combustion of an acidic COM in CE-1 of several SiC and Si₃N₄ ceramics were characterized. At the same time, the microstructure of and the nature of second phases present in the

Table 2. SiC sintering results

Specimen	SiC	Additives (wt %)		Sintering conditions				Theoretical density (%)
		BN	Other	Cold pressing pressure (MPa)	Temperature (°C)	Time (h)	Atmosphere	
S-1	A-10	0.62		138	2000	1	Vac (6.7 mPa)	80.3
S-2	A-10	0.62		138	2000	1	Vac (6.7 mPa)	78.6
S-3	A-10	0.62		207	2000	1	Ar (101 kPa)	80.2
S-4	A-10	2.44		138	2000	1	Ar (101 kPa)	77.0
S-5	A-10	2.44		138	2000	1	Ar (101 kPa)	63.5
S-6	A-10	0.62	5 Cr	138	2000	1	Ar (101 kPa)	67.7
S-6(b)	A-10	0.62		138	2000	1	Ar (101 kPa)	71.2
S-14	A-10		9.0 TiC	138	2000	1	Ar (101 kPa)	72.2
S-15	A-10	1.23	5 Cr	138	2000	1	Ar (101 kPa)	75.7
S-16	A-10	4.76	5 TiC	138	2000	1	Ar (101 kPa)	87.8
S-7	A-10	4.76	5 TiC	138	2000	1	Ar (101 kPa)	87.2
S-7(b)	A-10	4.76	2.5 TiC	138	2000	1	Ar (101 kPa)	87.0
S-8	499-S-8	1.23		138	2000	1	Ar (101 kPa)	73.5
S-9	499-S-9	1.23		138	2000	1	Ar (101 kPa)	33.8
S-9(b)	499-S-9	1.23	1.23 Cr	138	2000	1	Ar (101 kPa)	33.0
S-12	499-S-9	9.1		138	2000	2	Ar (101 kPa)	70.4
S-12(b)	499-S-9	13.0		138	2000	2	Ar (101 kPa)	72.8

as-received materials were analyzed, and mechanisms responsible for the strength degradation as a result of the CE-1 exposure have been characterized by examining the changes in the second phases present in the surface region of the as-exposed ceramics. In addition, the effects of impurities on enhancing the surface oxidation of SiC and Si₃N₄ ceramics were presented. In the last quarter, the initial results of exposure of SiC and Si₃N₄ to a very fluid, basic slag produced during the combustion of a 20% coal-oil-mixture at 1230°C for about 240 h (CE-3) were discussed. Observations during CE-3 reveal a very much more rapid rate of corrosive attack and thinning of the SiC and Si₃N₄ ceramics by the fluid slag in CE-3 as compared to the behavior in CE-2.

DISCUSSION OF CURRENT ACTIVITIES

Samples of siliconized silicon carbide (KT-SiC*) have now been exposed for 2000 h at 1200°C in air to evaluate the long-term effects of high-temperature oxidation on fracture strength and surface and internal composition stability. Additional samples are being exposed for 5000 h under these same conditions. As previously reported,^{8,9} this material forms a very stable oxide layer and is not subject to degradation of strength by exposure to acidic coal slags at 1220°C, as were the other SiC and Si₃N₄ ceramics exposed in CE-1. As a result, we felt that this material should be quite stable under long-term oxidizing conditions. In fact, the measured four-point flexure strength σ_f after the exposure for 2000 h at 1200°C in air ($\sigma_f = 252$ MPa) shows a 20% increase in strength as compared with the as-received material ($\sigma_f = 209$ MPa). In addition, the oxide layer that formed on the KT-SiC was quite thin, as indicated by the grinding striations on the as-received surfaces that are still visible after the 2000-h oxidation exposure. The surface oxidation products in this material are primarily α -cristobalite. The internal oxidation of these samples, as well as the samples of the same material (which are now undergoing the 5000-h oxidation exposure), is being characterized by

*Product of Carborundum Corporation, Niagara Falls, N.Y.

transmission electron microscopy. Similar 2000- and 5000-h oxidation exposures are currently in progress for the NC-203* SiC and sintered α -SiC[†] ceramics in order to examine the effects of impurities on the long-term oxidation behavior of SiC.

In addition, Si₃N₄ and SiC ceramic flexure bars are currently being exposed in a laboratory furnace to the basic slag produced in the CE-2 test at 1200°C for 200 h in an oxidizing environment to examine the strength changes and the associated surface corrosion. As reported earlier,¹⁰ the results of the exposure to the basic slags formed in the CE-2 combustion exposure were incomplete because of the excessive thinning of the flexure test bars, and the current laboratory test will be used to complete the analysis of the effects of this basic slag.

*Product of Norton Company, Worcester, Mass.

†Product of Carborundum Corporation, Niagara Falls, N.Y.

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NBS-5.12 -- HIGH-TEMPERATURE APPLICATIONS
OF STRUCTURAL CERAMICS

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A. Dragoo and S. J. Schneider

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INTRODUCTION

The achievement of higher efficiency thermochemical engines and heat recovery systems requires the availability of high temperature, high performance structural materials. Structural ceramics such as SiC, Si₃N₄ and certain Al₂O₃-Si₃N₄ combinations have received particular attention for these applications due to their basic characteristics of good strengths coupled with good corrosion and thermal shock resistances. Even with these positive attributes, improved reliabilities and extended lifetimes under service conditions are necessary for structural ceramics to gain industrial acceptance and use. The problems are mechanical and/or chemical in nature and are enhanced by the fact that these materials are subjected to high temperatures, reactive environments and extreme thermal gradients.

With an objective of improved performance for heat engine/heat recovery applications the NBS program on structural ceramics addresses these problems through the determination of the critical factors which influence mechanical and microstructural behavior. The activities of the program are grouped under four major subtasks with each designed to develop key data, associated test methods and companion predictive models. The status of the subtasks are detailed in the following sections.

NBS-5.12(A) - HIGH-TEMPERATURE FRACTURE OF STRUCTURAL CERAMICS

RESULTS FROM PRIOR QUARTERS

Four-point flexural tests on notched bars of Si_5AlON_7 were completed and the results compared with previous work on an yttria-doped SiC (NCX-34) and with literature values for Si_3N_4 . Reduced scale testing rigs using SiC were manufactured to test small billets of experimental materials. Using these rigs, fifteen different compositions of Si_3N_4 + Y.A.G. materials, obtained from Professor Tien of the University of Michigan, were tested at 1300 °C in order to avoid oxidation. Further studies of Tien's Si_3N_4 were conducted to ascertain critical stress intensity factors and to clarify some inconsistencies in earlier results.

A literature survey of available data on fracture toughness, crack growth behavior and creep properties of SiC, Si_3N_4 and Sialon was completed.

Four-point bending tests under constant displacement rate were performed on several SiC and Sialon specimens. For α -SiC tested in air, the results showed little oxidation and high resistance to slow crack growth up to 1300 °C. For Sialon specimens ($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$), it was found that as z increases, the susceptibility to crack growth and oxidation decreases.

The asymptotic behavior of the stress intensity factors as a function of crack length for 4-point bending at small and large crack lengths was investigated in more detail. This work is useful for future numerical solution schemes. Also, an analysis of load-deflection curves which permit computation of crack growth behavior (v-K) without requiring a knowledge of Young's modulus or machine compliance was completed. High temperature four-point bending tests under constant displacement rates were performed on notched reaction sintered SiC specimens. Several ways of initiating cracks were tried before a chevron notch was used. This produced a stable crack growth period and a sharp crack.

A paper entitled "Slow Crack Growth in Sialon" was presented at the International Symposium on Fracture Mechanics of Ceramics, University Park, Pennsylvania on July 17, 1981. Another paper entitled "Effects of Deformation on the Fracture Behavior of Si_3N_4 and Sialons" was presented at the Second NATO Advanced Study Institute held at Falmer, England on August 7, 1981.

Further analyses of the four-point bend test were completed. One analysis allows the determination of the tensile creep behavior from the bending test of trapezoidal cross-sections. A further analysis deducing tensile behavior from bending and compression tests has been undertaken.

DISCUSSION OF CURRENT ACTIVITIES

A sensitivity study of the effects of the crack growth parameters on the load vs. displacement curves under bending was performed. The analytical results obtained from a time-dependent solution of nonlinear ordinary differential equations are capable of assessing the accuracy of the predicted stable crack growth behavior. Four-point bend data on SiC and Sialon obtained from previous experiments will be used to compare these analytical results in order to determine the confidence margins. A paper describing this work entitled "Effects of Crack Growth on the Load-Displacement Characteristics of Precracked Specimens Under Bending" is to be presented at the 84th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio in May, 1982.

Crack growth measurements are being conducted on Carborundum's HEXALLOY SA (a sintered α -SiC). Billets of this material with nominal dimensions of 50 X 50 X 12 mm have been machined both into double torsion specimens (25 X 50 X 1 mm) for the crack growth measurements and into single edged notched beam specimens (50 X 10 X 5 mm) for an independent determination of K_{IC} . Current experiments are being conducted at 1500 °C, whereas future tests will be done at 1200 °C and 1350 °C, respectively.

Long-term creep testing instrumentation is being assembled in order to test the specimens under the dead weight conditions and at elevated temperatures.

NBS-5.12(B) - CRACK GROWTH MECHANISM MAPS

RESULTS FROM PRIOR QUARTERS

Preliminary maps for Si_3N_4 have been drawn. A computer program for automatically drawing maps from v - K data has been written. Data for SiC has been collected with the aim of constructing a crack growth mechanism map. An evaluation of K_{IC} of SiC was made because its definition by ASTM E-399 conflicts with common usage in the ceramic community. A preliminary crack growth mechanism map for a commercial hot-pressed SiC was constructed from published information. The literature survey of fracture and crack growth mechanisms was completed for SiC, Si_3N_4 and Sialon.

A crack growth model based on diffusion mechanisms was developed. The model entails a grain-boundary crack growing in steady state due to applied stress by stress-assisted surface and grain-boundary self-diffusion. By further assuming the grains on either side of the crack behave elastically, the model predicts a unique v - K_I curve and a threshold K_I below which no crack growth will take place. A comparison of this model prediction with a set of creep crack growth data on Sialon at 1400 °C showed good agreement. The energy release rate associated with this crack growth model was also investigated. The results showed that J is the total amount of energy dissipation which consists of a portion consumed in the creation of new crack surfaces and the remaining portion lost in the mass transport processes. A paper describing this work will be published in the February, 1982 issue of the Journal of the American Ceramic Society.

The theoretical prediction of v - K_I functional relationship based on this diffusion-controlled crack growth mechanism was mapped into K_I - T space in order for the future data to fit in the diffusive crack growth area of the mechanism maps.

Data obtained for NCX34 from subtask (A) was analyzed in order to construct a crack growth mechanism map. A paper entitled "Crack Growth Mechanism Maps" was published in Advances in Fracture Research, ed. by

D. Francois, et al., Vol. 3, pp. 1313-1322 (Pergamon Press, 1981). This paper describes the concept of crack growth mechanism maps and details their construction.

DISCUSSION OF CURRENT ACTIVITIES

Specimens of SiC used in subtask (A) are being polished in order to determine the crack growth mechanism for the construction of the mechanism maps. These are interrupted tests and have been held under load at 1500 °C for several days. We are looking for evidence of creep cavities at or near the root of the notch. The results emanating from this investigation will be presented in an invited talk for the Gordon Research Conference of Solid State Studies in Ceramics at Plymouth State College, Plymouth, New Hampshire on August 10, 1982.

NBS-5.12(C) — MICROSTRUCTURE AND PHASE ALTERATION

RESULTS FROM PRIOR QUARTERS

X-ray analyses were performed on various Sialon and as-received silicon carbide samples. These analyses were based on standard x-ray diffraction data. In view of the wide variety of SiC polytypes, structure analysis of SiC may proceed best by determining the relative amounts of cubic and hexagonal packing in the c-axis direction.

Preliminary x-ray data obtained on alpha silicon carbide fracture specimens, oxidized before fracture, indicated tridymite and glass as the principal reaction products.

A literature survey was completed and a bibliography was compiled on oxidation of silicon carbide and on its high-temperature thermal and mechanical properties.

A high-temperature x-ray furnace was designed in which the SiC specimen serves as its own heating element.

DISCUSSION OF CURRENT ACTIVITIES

X-ray diffraction patterns were obtained for several different silicon carbide samples to verify d-spacings and intensities. These samples included:

- o NC203--a hot-pressed, very fine-grained silicon carbide;
- o NC430--a reaction-sintered silicon carbide with free silicon and large grains;
- o two Carborundum alpha silicon carbides, fine-grained, but of unknown specification; and
- o recently received Carborundum alpha silicon carbide: one sample cut parallel to the pressing direction, and one sample cut transverse to the pressing direction.

A small amount of silicon powder was sprinkled on the samples as a reference, and Cu K α -radiation was used. The 2 θ -values obtained are being converted to d-spacings. In general, most samples appear to contain several polytypes plus impurity phases.

Since the differences between silicon carbide polytypes arise from the relative amounts and arrangement of cubic and hexagonal stacking of planes of atoms in the [001] direction, development of a structural analysis is in progress which will determine the relative amounts of the two types of stacking in bulk samples. In this analysis all reflections are indexed on a hexagonal lattice. A computer program is being written to analyze observed (2 θ)-values and intensities on the basis of this model.

Oxidation Studies

A high-temperature laboratory furnace was returned to operation, and an oxidation study was begun using samples of NC203 and NC430. Two oxidation runs have been conducted at 1400 °C in air.

The high-temperature behavior of these two materials is markedly different. The NC203 sample shows very little apparent change for times up to three hours. Its x-ray diffraction pattern shows some diminishment of the silicon carbide peaks, the disappearance of some weak reflections

associated with impurities, and no evidence of a crystalline silica phase. On the other hand, during the first hour of the oxidation anneal, the NC430 sample became decorated with hard nubs of exuded silicon which were oxidized. The x-ray diffraction pattern of the oxidized sample showed a composite peak near $(2\theta) = 21^\circ$, which yielded d-values of 4.095 Å and 4.055 Å and were assigned, tentatively, to tridymite and cristobalite, respectively.

High-Temperature X-Ray Diffraction

A furnace housing (cover and endplate) for a high-temperature x-ray furnace was fabricated by the NBS instrument shop. An order was placed for the bonded ceramic fiber components which are required for the interior of the furnace. Electrodes were fabricated from silicon carbide heating elements.

The resistance heating concept was tested by mounting the electrodes in a test rig with a NC203 silicon carbide sample bridging the electrodes. Due to the high resistance of the NC203 sample, it was necessary to coat the underside of the sample with colloidal carbon. Sufficient sample conductivity then was obtained to heat the sample using a simple power supply (a 2.1 kVA variable transformer plus ammeter). A bright-red glow was obtained over the sample before the carbon burned off, as expected; and the resistance became too high for further heating to take place.

An improved high-temperature conductive coating which is stable in air is being sought. Two approaches are under investigation. The first approach consists of plasma-spraying one side of a specimen with molybdenum and converting the molybdenum to the disilicide by reaction with silicon nitride. The second approach consists of firing on a mixture of silicon carbide, a dopant, and a glass former.

The high-temperature x-ray diffraction furnace will be used for oxidation studies under this subtask and for studies of silicon carbide in reaction environments under subtask (D).

Model for Induced Microstresses and Microstrains

The strength and durability of ceramic materials is dependent in part on the occurrence of cracks in the bulk sample. The growth of cracks is influenced by the strain fields generated by impurity inclu-

sions, and the inclusions are often large on an atomic scale but small on a macroscopic scale. Therefore, we have initiated a study of the relationship between crack growth and extended inclusions in the context of continuum limit mechanics. We have identified several factors that need to be given consideration; including, (1) the stress-strain fields and stress intensity factors about an isolated crack in an isotropic medium, (2) the strain field and strain energy about an extended inclusion, (3) the effective interactions of inclusions (which may be generalized here to include the void of a crack) near a material interface, such as a grain boundary, and finally (4) the interaction of a crack with the stress field induced by an extended inclusion.

NBS-5.12(D) - MICROSTRUCTURE AND FRACTURE IN REACTIVE ENVIRONMENTS

RESULTS FROM PRIOR QUARTERS

The design of the environmental-mechanical testing apparatus and the order of the necessary components for its construction have been completed. An existing, displacement rate controlled, loading machine will be used to load a specimen (either notched-beam or double-torsion) in a gas tight laboratory box furnace. A gas blending system will control the flow and composition of a mixture of 5 gases (SO_2 , H_2O , CO_2 , O_2 , and N_2) through the furnace cavity at nominally atmospheric pressure.

That part of the gas blending system which will handle all the gases except H_2O has been delivered from a commercial supplier. The flow and composition of the gas mixture will be obtained through the mass flow control of the separate gases in devices which sense their thermal conductivities. The partial pressure of water vapor will be controlled by flow of the gas mixture through saturated water at a given temperature.

DISCUSSION OF CURRENT ACTIVITIES

The furnace system is still under construction by its manufacturer. Although delivery of the furnace system was to be the end of September

1981, the manufacturer's current estimate of delivery time is mid-January 1982. Besides the fabrication of the furnace system proper, it is being modified so that the load bearing rods may be introduced through sealed top and bottom ports.

Fabrication of the load bearing rod assembly has been completed. Silicon carbide rods are attached to fixtures of the loading machine through upper and lower bellows which will be sealed to the corresponding furnace ports. Special holders for the notched-beam and double-torsion specimens, respectively, have been obtained for insertion between the bearing rods.

Both notched-beam and double-torsion specimens of silicon carbide have been fabricated. Glass specimens of like geometry have been ordered so that the geometrical coefficients involved in the tests may be calibrated and compared with analysis for these test configurations.

Alteration of the laboratory room to provide water, drain, and gas exhaust has been completed. These services were needed to accomodate operation of the furnace and gas flow.

Presently we expect to complete assembly of the test apparatus by the end of January 1982. Verification of its operation will follow soon thereafter.

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PART V — MATERIALS FOR COMBUSTION SYSTEMS

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ANL-6.4 -- CORROSION OF ALLOYS IN FBC SYSTEMS

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SUMMARY OF CURRENT ACTIVITIES

The purposes of this program are to (1) experimentally evaluate the high-temperature corrosion behavior of iron- and nickel-base alloys in simulated combustion gas environments with a wide range of oxygen and sulfur potentials, and (2) evaluate deposit-induced hot-corrosion behavior of heat-exchanger and gas-turbine materials with and without coatings after exposure to multicomponent gas environments.

Deposit-induced hot-corrosion behavior of heat-exchanger and gas-turbine materials exposed to multicomponent gas environments is of considerable interest in advanced energy systems that utilize fossil fuels. For this purpose, characterization of environments in direct-combustion processes and evaluation of materials exposed to complex gas mixtures that simulate normal operating conditions and off-normal excursion situations are needed. In fluidized-bed combustion (FBC) systems, the presence of sulfated limestone and the low oxygen partial pressure lead to deposition of CaSO_4 . The presence of locally reducing oxygen partial pressures in the vicinity of the deposit can lead to sulfidation/hot corrosion of the heat-exchanger tube surface.

During the present quarter, a technical paper has been prepared on the corrosion behavior of materials for application in fluidized-bed coal-combustion systems.¹ In this paper, major concerns regarding the corrosion behavior of materials for use in FBC systems are discussed. The multicomponent gas environments in FBC systems are characterized using a thermodynamic approach. The results show that the oxygen partial pressures can reach very low values ($\leq 10^{-10}$ atm) and the sulfur partial pressures can attain values as high as 10^{-8} at a temperature of 850°C (1123 K), typical of FBC systems. Available information on direct

measurements of oxygen partial pressure in FBC systems shows p_{O_2} values in the range 10^{-2} to 10^{-14} atm at different locations within the same bed in both atmospheric and pressurized FBC systems. In addition, the measured p_{O_2} values fluctuate between the two values with time intervals of the order of less than a second. Corrosion experiments conducted in FBC-type gas environments (low p_{O_2} and moderate to high p_{S_2}) show that the candidate heat-exchanger materials develop unprotective oxide scales or thick sulfide scales. Furthermore, the presence of deposits such as $CaSO_4$ in the FBC atmosphere can lead to increases in scale thickness and alloy penetration. Similarly, the presence of alkali sulfates (which will be in excess of those prevalent in conventional petroleum fuels) can lead to accelerated degradation of blades and vanes in gas turbines of combined-cycle plants. The results presented show that significant additional work is needed to characterize the in-bed environment in FBC systems and to evaluate limits on alkali content of FBC effluent gas in order to establish material-design-performance envelopes for components in FBC systems.

A more detailed description of the work performed during the current quarter will be published elsewhere.²

¹K. Natesan, "Corrosion Behavior of Materials in Fluidized-Bed Coal-Combustion Systems," presented at the Symposium on High-Temperature Chemistry, Electrochemical Society Meeting, Denver, CO, October 11-16, 1981. To be published in the Symposium Proceedings.

²Materials Technology for Coal-conversion Processes: Progress Report for October-December 1981, Argonne National Laboratory Report ANL/FE-82-9 (in preparation).

ORNL-6.4 - HEAT EXCHANGER AND INTERNAL
STRUCTURAL MATERIALS FOR AFBC

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INTRODUCTION

The purpose of this task is to perform tests to evaluate the oxidation-sulfidation response of candidate heat exchanger alloys as a function of oxygen and sulfur partial pressures at 850°C and to determine the role of CaSO_4 in the corrosion process.

RESULTS FROM PRIOR QUARTERS

Attempts to simulate the growth of CaSO_4 scales by transport of gaseous $\text{CaOH}\cdot\text{nH}_2\text{O}$ were not successful. However, it was possible to form the CaSO_4 scale by direct contact of heated wires and CaSO_4 powder in a glass fluidized bed. A system was designed and constructed to measure the rate of gas-metal reactions when the respective pressures of sulfur and oxygen are rapidly cycled. Initial tests confirmed that pressure fluctuations of the desired magnitudes could be provided by the equipment, but gas inlet pressures were too high to accommodate the mass spectrometer. The pressures will be reduced by cryogenic cooling of the inlet gases.

DISCUSSION OF CURRENT ACTIVITIES

The differential thermal analysis (DTA) study of the chemical reactions between CaSO_4 and alloys or alloy constituents has shown that chromium is the only alloy constituent that does not form a sulfide. In this case CaO , Cr_2O_3 , and CaCr_2O_4 are the reaction products. This result may well have practical application in the corrosion prevention of fluidized-bed components. The accumulation of sulfides below a protective oxide scale disrupts the continuous development of the oxide. Hence, breakaway

corrosion may occur in an AFBC as a result of an oxidation-sulfidation reaction with either the gaseous environment or a CaSO_4 deposit. A CaCr_2O_4 coating may well prevent the initial formation of sulfides and, hence, stop breakaway corrosion.

Before we speculate further, we must first show that CaCr_2O_4 does not react further with excess CaSO_4 under AFBC conditions. To do this, the mixed oxide was formed by calcining a stoichiometric mixture of CaO and Cr_2O_3 in air at 1050°C for 72 h. An x-ray diffraction pattern of the product showed that CaCr_2O_4 had formed, but lines due to Cr_2O_3 were barely detectable. Because an optical examination showed that a liquid had not formed, the composition of the final oxide product must lie on the Cr_2O_3 side of the CaCr_2O_4 composition. A 1:1 mixture (by mass) of the above oxide product and CaSO_4 was held for 72 h at 850°C in oxygen and sulfur gas pressures of 10^2 and 10^{-24} Pa (10^{-3} and 10^{-29} atm), respectively. These values were chosen because they represent equilibrium stoichiometric combustion conditions of a high-sulfur coal² in an AFBC. In addition, CaSO_4 should not decompose; that is, the gas pressures exceed the decomposition pressures over CaSO_4 (ref. 3). We found that, after reaction, the above mixture showed a mass loss corresponding to about 5% of the starting mass. An x-ray diffraction pattern showed the presence of CaCr_2O_4 and CaSO_4 ; the lines due to Cr_2O_3 were absent. Apparently, the residual Cr_2O_3 reacted with CaSO_4 . On the basis of this experiment, we conclude that the mixed oxide would coexist with CaSO_4 under AFBC conditions.

Although a CaCr_2O_4 coating should provide a barrier to the gaseous environment in a fluidized combustor, the coating will act as a barrier between the base metal and the sulfate deposit. Considering that bed components are rapidly coated with sulfate during combustion, we conclude that the latter may be more important. The coating may be applied directly (e.g., by plasma spraying), but a self-forming coating may be a better alternative. If a chromium coating were applied, the mixed oxide would form in service by reaction with calcium sulfate. This alternative appears to be more attractive because the coating would be self-healing as long as chromium is not completely depleted.

Recently Hollingshead⁴ supported the above speculation by observing that several marine gas turbine engines were free of sulfidation after as many as 11,200 h of operation. The blade surfaces were partially covered by a zinc sulfate deposit. Under the sulfate deposit, a scale consisting mainly of chromic and zinc oxides was found. The source of the zinc was identified as the zinc-pigmented protective coating in the fuel tanks; the chromium, from the alloy itself. Laboratory crucible tests in which 2.5 or 5% zinc sulfate was added to a 90/10 Na₂SO₄/NaCl salt mixture reproduced the above observation.

The DTA study of the reactions between alloy 800 and CaSO₄ have been completed. The alloy specimens were in the form of fine lathe turnings or -50 mesh particles in order to determine the effect of particle size on the reaction. In both cases the reaction began at $T < 850^{\circ}\text{C}$, the turnings at about 600°C , and the -50 mesh particles at approximately 360°C . In addition to the difference in the onset of reaction we found a difference in the extent of reaction. An optical examination of the reaction products showed that the core of the lathe turnings contained unreacted metal but that the smaller particles were completely reacted. Further, in the lathe turnings, 67% of the possible SO₂ (from the decomposition of CaSO₄) was lost, but only 29% was lost in the smaller particles. These observations are indicative of a solid-state reaction. The observed enthalpic changes are shown below.

On heating:

1. broad exotherm beginning at 360 or 600°C ;
2. sharp endotherm at 990°C , which corresponds to $\text{Fe} + \text{FeS} = \text{Fe} + \text{liq}$;
and
3. changes corresponding to the following processes were barely detectable above the background:

FeO-FeS eutectic .

On cooling:

1. an exotherm at approximately 800°C , which possibly corresponds to the crossing of a liquidus boundary; and

2. a sharp exotherm at 530°C, which corresponds to an Ni_3S_2 crystal transition.

An optical examination showed that a liquid had been produced, and an x-ray diffraction pattern showed that $(\text{FeCr})_3\text{O}_4$, Ni_3S_2 , FeS , and CaO were present.

The experiments on corrosion under cyclic oxidation-sulfidation conditions are continuing. The entire system has now been assembled and tested. A nickel foil has been mounted as a test specimen to calibrate the response time of the measuring systems. In the process of performing this calibration, some difficulty with the valve drive circuits has been encountered. Work is in progress to remove this difficulty.

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