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LOW ALLOY STEELS THAT MINIMIZE THE
HYDROGEN-CARBIDE REACTION

R.J. Kar, E.R. Parker, and V.F. Zackay

Final Technical Report - Part I
October 1, 1978 to September 30, 1979

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FOREWORD

This report covers work performed under Contract DE-AM03-76SF00034 PA DE AT03-76ER70296 for the period October 1, 1978 through September 30, 1979. Part II of this report, covering work for the period October 1, 1979 to the end of the contract, will be submitted later in the calendar year. This work was administered under the Department of Energy Technology, with Dr. Ron Kostoff as Project Manager. This report was prepared by Dr. R.J. Kar, formerly of the Department of Materials Science and Mineral Engineering, University of California, Berkeley. He was assisted by the following personnel: Graduate Student Research Assistants P. Klenn and J. Youngs; Undergraduate Research Aid K. Pool.

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ABSTRACT

This report presents results obtained during the first year of a research program to investigate important metallurgical parameters that control the reactions of hydrogen with carbides in steels. Preliminary work included a detailed literature review of the phenomenon of decarburization and methane bubble formation in steels and a suitable experimental technique for investigating hydrogen attack in laboratory conditions was established. Detailed microstructural-mechanical property evaluations were carried out on two series of alloys; the first was based on a plain carbon steel to which binary and ternary alloy additions were made to vary the carbide structure and morphology and assess these effects on the observed hydrogen attack resistance. The second group of steels consisted of commercial Mn-Mo-Ni (A 533 B) and Cr-Mo (A 542 type) steels and their alloy modifications, with a view towards developing steels with improved hydrogen attack resistance.

Part II of this report, covering work accomplished from October 1, 1979 to the end of the contract, will be submitted separately.

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1. OBJECTIVE AND SCOPE

The objectives of this research program are dual in nature:

1. To establish the metallurgical variables that control the phenomenon of hydrogen attack in simple binary and ternary steels.
2. To investigate the hydrogen attack resistance of commercial low alloy steels that will have future application in thick wall pressure vessels.

The objectives necessarily overlap with a view towards possible future design of low alloy steels that will exhibit improved hydrogen attack resistance.

The research program has been divided into the following tasks:

Task 1: Design Criteria for Hydrogen Attack Studies

Task 2: Equipment Design for Hydrogen Attack Tests

Task 3: Metallurgical Characterization of Simple Binary and Ternary Alloy Systems.

Task 4: Hydrogen Attack Evaluation of Binary and Ternary Alloy Systems

Task 5: Metallurgical Characterization of Candidate Commercial Low Alloy Steels and Their Modifications for Hydrogen Attack Studies

Task 6: Hydrogen Attack Evaluation of Candidate Commercial Low Alloy Steels and Their Modifications.

Each task will be discussed in detail in the following sections. Each task has a goal that helps outline the work for the succeeding task. The successful completion of Task 1 will lead to the choice of a suitable technique for evaluating hydrogen attack resistance in the systems studied in Tasks 3 - 6. Task 2 will establish the design and equipment details for the experimental procedures that are undertaken in this investigation.

Tasks 3 and 5 will outline microstructure-mechanical property relationships in simple steels and commercial alloy systems that will be used for evaluating hydrogen attack behavior as will be outlined in Tasks 4 and 6 respectively.

2. PROGRESS SUMMARY

The program is essentially on schedule. Tasks 1 and 2 have essentially been completed with considerable progress having been achieved in Tasks 3 - 6.

2.1 Task 1: Design Criteria For Hydrogen Attack Studies

During the past year, a detailed literature review was undertaken to collate experimental techniques used and alloy systems investigated in past hydrogen attack investigations. Particular attention was paid towards establishing important material parameters and the choice of a suitable method for detection of hydrogen attack in the alloys to be investigated.

2.2 Task 2: Equipment Design For Hydrogen Attack Tests

In this Task, high pressure, high temperature hydrogen attack equipment was designed and fabricated with a view towards exposing experimental samples to hydrogen at pressures and temperatures typical of coal gasifiers and/or hydrogenation plants. Considerable effort was expended towards establishing safety measures for trouble-free operation of the experimental set-up. The equipment is currently undergoing preliminary evaluation for future long-term exposures.

2.3 Task 3: Metallurgical Characterization of Simple Binary and Ternary Alloy Systems

In this task, suitable compositions of plain carbon and ternary alloy steels were established for further study. Ternary additions consisted of singular additions of Cr, Mo and W to the base plain carbon steel. The tempering response of these systems was evaluated with a view towards correlating microstructure-mechanical property relationships with observed hydrogen attack behavior. Microstructural evaluation of suitably heat-treated specimens for hydrogen attack studies is nearing the final stages

of completion and some preliminary results are presented.

2.4 Task 4: Hydrogen Attack Evaluation of Binary and Ternary Alloy Systems

Progress in this task has been slow due to the delay of equipment design and construction outlined in Task 2. Currently, heat-treated specimens are being machined for long-term exposure in the hydrogen-filled autoclaves. It is planned to conduct interrupted tests of total duration between 1000 - 1200 hours. The degree of attack will be continuously monitored through the use of suitable experimental methods. The results will be presented when available.

2.5 Task 5: Metallurgical Characterization of Candidate Commercial Low Alloy Steels And Their Modifications

Considerable progress has been achieved in this task which is essentially complete. The commercial alloy systems chosen for investigation consist of the Mn-Mo-Ni (A 533 type) and Cr-Mo (A 542 type) steels and their modifications. Detailed microstructural characterization of thick-section simulated plates has been carried out and some of the highlights of these results are discussed in relation to their expected hydrogen attack behavior.

2.6 Task 6: Hydrogen Attack Evaluation of Candidate Commercial Low Alloy Steels and Their Modifications

In this task, heat treatments of thick section simulated plates have been performed for future hydrogen exposures. Specimens are currently awaiting completion of the safety measures outlined in Task 2 before high pressure and temperature hydrogen exposures can be undertaken. The results of this task will be presented when available.

3. TECHNICAL PROGRESS

3.1 Task 1: Design Criteria for Hydrogen Attack Studies

Hydrogen attack is a phenomenon that occurs in plain carbon and low alloy steels when exposed to high pressure hydrogen at elevated temperatures.⁽¹⁾ Hydrogen diffusing into the pre-existing microvoids combines with carbon in the steel to form methane. The non-diffusing methane expands the voids to fissures causing swelling of the material and eventual mechanical property degradation.^(1,2,3)

In the past, little was known about the effect of hydrogen in relation to microstructure as a variable. Selection of steels for petrochemical applications was governed by the well known⁽¹⁾ Nelson diagrams which outlined temperature and pressure conditions for carbon and low alloy steels containing Cr and Mo and defined regimes where these steels would be safe from attack. Early work by Naumann⁽²⁾ suggested that alloying elements could play an important role in governing the hydrogen attack susceptibility of a steel. However, little has been done to elucidate the effect of alloying elements such as chromium, molybdenum, tungsten, vanadium, nickel, manganese or silicon which normally occur in steels.

During the past decade considerable effort has been undertaken towards understanding the phenomenon of hydrogen attack in plain carbon steels. The work of Vitovec⁽³⁾, Westphal and Worzala⁽⁴⁾, Shewmon⁽⁵⁾, Sagues et al⁽⁶⁾ has helped gain an insight into the phenomena of bubble nucleation and growth in plain carbon steels.

It is generally accepted that in plain carbon steels, hydrogen attack manifests itself initially as a process of decarburization where carbon in interstitial solid solution combines with hydrogen to form methane.

The carbon loss from ferrite sets up a concentration gradient between the carbides and ferrite which leads to dissociation of the carbides.

In the past, hydrogen attack has been measured using a number of different techniques. Some of the more prominent techniques used include specific gravity or weight loss measurements, mechanical tests notably reduction of area measurements during tensile testing, detection of attack by mass spectrometric measurement of outgassed effluent, dilatometry, microstructural examination, etc.

After a detailed literature review and establishment of the merits and demerits of the various techniques that have been used in the past, it was decided to use the following techniques to study hydrogen attack:

1. Reduction of area measurements in tensile tests: The normalized difference in reduction of area between charged and uncharged heat treated specimens will serve as an index for assessing hydrogen attack susceptibility of a steel.

2. Microstructural examination of charged specimens for occurrence of bubbles at inclusions, carbide-ferrite interfaces, etc., as determined by optical techniques.

3. Scanning electron microscopic examination of fractured Charpy impact specimens for evidence of bubbles and/or voids.

3.1.1 Material Parameters for Attack Evaluation

Based on a detailed literature review, material parameters that are considered important to this investigation include the following:

- a) Chemical composition of the steel: Elements typically found in steel such as chromium, tungsten, molybdenum, nickel, manganese are important because these are important carbide formers and/or affect the type of carbide that forms in the steel.

b) Thermodynamic stability of alloy carbides: Past work⁽⁷⁾ presents evidence that the stability of a carbide renders a steel more resistant to hydrogen attack. Thus, an understanding of the relative stabilities of complex carbides in high pressure hydrogen is an important parameter that must be considered.

c) Morphology of Second Phase Precipitates: The phenomenon of hydrogen attack has been considered to be an "internal surface" problem. Hence, it is important to assess the morphological effect of second phase precipitates such as alloy carbides, inclusions, etc. and their relation to the hydrogen attack resistance of the steel.

d) Tempering response of the steel: The effect of prolonged tempering of a steel at pressures and temperatures typical of gasifiers will lead to changes in microstructure, more notably in the type of alloy carbide that will form on tempering. Thus, the tempering response of the steel must be characterized and correlated with the hydrogen attack response of the heat treated steel.

e) Effect of Impurities: Hydrogen attack occurs in temperature regimes where tramp elements such as P, As, Sb, Sn, etc. can have deleterious effects in that these segregate to grain boundaries and lead to poor impact properties. It is important to distinguish between these effects and those that occur due to hydrogen attack, particularly in assessing commercial steels, where complex interactions between tramp impurities and alloying elements such as chromium, molybdenum, nickel or manganese are known to occur.

3.2 Task 2: Equipment Design for Hydrogen Attack Tests

The design work for assessing hydrogen attack resistance of steels in this research program was primarily carried out by J. Youngs

and P. Klenn. An overall view of the equipment which has been installed is shown in Figure 1 and a schematic diagram of the system is outlined in Figure 2. The attack equipment consists of high temperature-pressure autoclaves (1 gallon capacity each) which have maximum allowable working conditions of 2450 psig hydrogen at 650°C. Each vessel is suitably equipped with ancillary equipment to allow maximum flexibility.

Heating of the high pressure autoclaves is accomplished by electrical heating. The hydrogen is supplied through a bottled cylinder by means of high pressure pipes, the pressure being continuously monitored through high pressure gauges. As outlined in the schematic diagram (Figure 2) the system also includes an inert gas supply, which is used to backfill the autoclaves at the start and end of each high temperature hydrogen experiment.

In order to prevent accidental overheating of the autoclaves, load limit control devices have also been incorporated into the system. These are connected in series with the main power supply so that in case of accidental equipment malfunction, the system is shut down. In addition an elapsed time clock records the time up to the overheat onto the shut off. Accidental overpressurization of the autoclaves is prevented by incorporation of gas relief valves and rupture discs in the system. The rupture discs are designed to perforate at an accidental pressure of 3000 psig hydrogen and the gas relief valve will vent the excess hydrogen away from the equipment cells to safety.

In order to facilitate loading and unloading of the high pressure autoclaves, such as before and after each experimental run, the equipment design incorporates lifting and moving of the autoclaves by means of specialized lifting devices.

The specialized lifting devices have been designed by Youngs and consist of lifting plates which are secured to each exposure chamber by bolts. Each plate has three "lug-locks" and is used to move the exposure chamber with the help of a 1 ton capacity hand winch.

Currently the high pressure hydrogen equipment is awaiting certification by the U.C. Berkeley Campus Safety Committee and the Lawrence Berkeley Laboratory Safety Department. It is proposed to have the system in operation early in 1980.

3.3 Task 3: Metallurgical Characterization of Simple Binary and Ternary Alloy Systems

As outlined in Task 1, it is known that alloying additions of stable carbide forming elements are considered important in governing the hydrogen attack resistance of a steel. However, studies to date⁽²⁾ have only been empirical, and little attempt has been made to characterize the type of carbide that presumably would impart hydrogen attack resistance. It is primarily to approach this gap in the understanding of the complex phenomenon of hydrogen attack, that is the basis of this task. Thus, the outline of this task, in brief, is to characterize and identify carbides of differing thermodynamic stabilities i.e., Fe_3C , M_7C_3 , M_2C , etc. that are known to form in simple alloy steels,⁽⁸⁾ and correlate the hydrogen attack resistance of these steels with the absence or presence of these carbides.

The basis for alloy systems investigated in this task center around a plain carbon steel (nominal composition 0.15%C - 0.5%Mn) to which singular additions of 2 atomic percent Cr, Mo or W have been made. The nominal composition of the steels investigated are outlined in Table 1. The purpose of these additions, as mentioned earlier, is to vary the chemical composition, structure and morphology of the carbides that form,

and correlate these with the observed hydrogen attack resistance of the steel.

3.3.1 Choice of Austenitization Temperature

The preliminary basis for subsequent evaluation of the different steels chosen for this task centered around eliminating microstructural variables such as prior austenite grain size, effect of primary undissolved carbides, varying initial as-quenched microstructures, etc. from the study. This was to ensure that these variables would in no way affect the observed hydrogen attack response of the steels and therefore any observed changes could then be directly correlated to the carbide structure, composition and morphology. For this purpose it was necessary to evaluate the as-quenched microstructures and subsequent tempering response of the alloy steels.

3.3.1.1 0.15C - 0.5Mn Base Alloy: The base alloy was austenitized at 900°C, 1000°C and 1100°C for 1 hour and the subsequent tempering response of the steel after austenitizing at these temperatures is shown in Figure 3. The initial as-quenched microstructures subsequent to austenitizing at the different temperatures are shown in Figure 4.

As seen in Figure 3, austenitization of the base alloy at 900°C resulted in a much lower hardness over the entire tempering range. Subsequent microstructural examination revealed that this was because the choice of 900°C resulted in incomplete austenitization, and free ferrite could be observed in the microstructure (Figure 4). This was eliminated by austenitizing at 1000°C. Moreover, as seen in Figures 3 and 4, there was no appreciable hardness increase or change in prior austenite grain size (ASTM 3-4) on increasing the austenitizing temperature to 1100°C. Therefore, the 1000°C austenitization temperature was chosen as the base for

the plain carbon steel.

3.3.1.2 0.5C - 0.5Mn - 2Cr Alloy: Preliminary heat treatments carried out on the 2Cr modified alloy (hereafter referred to as the chromium steel) revealed that austenitization at 900°C or 1000°C resulted in the presence of undissolved primary alloy carbides and it was necessary to austenitize the steel at 1050°C to eliminate undissolved carbides. The tempering response of the chromium steel is shown in Figure 5 and the as-quenched microstructures observed are shown in Figure 6.

Examination of the tempering response of the chromium steel (Fig 5) reveals that the chromium steel did not show a secondary hardening peak. This was because in the secondary hardening temperature range, the chromium carbides that precipitate coarsen extremely rapidly,⁽⁸⁾ so that there is no significant contribution towards the secondary hardening peak. However, comparison of Figures 3 and 5 reveals that over the entire tempering range, the chromium steel had a higher hardness than the base alloy.

3.3.1.3 0.15C - 0.5Mn - 3.5Mo Alloy: The molybdenum modified alloy (2 at % Mo) was austenitized at 1000°C, 1050°C and 1150°C. It was found that in order to completely eliminate undissolved alloy carbides, a minimum austenitization temperature of 1150°C was necessary. This resulted in a prior austenite grain size of ASTM 4, which was very similar to the base alloy. The as-quenched microstructures of the Mo alloy as a function of austenitization temperature are shown in Figures 7 a, b and c, and the tempering response is plotted in Figure 8. Examination of Figure 8 reveals that the Mo alloy exhibited a pronounced secondary hardening peak at 600°C at all three austenitization temperatures. Peak hardness is generally associated with the incipient precipitation of coherent or

semi-coherent precipitates⁽⁸⁾ (in this case alloy carbides), which primarily contribute to the hardness through substructural strengthening. Since the 1050°C austenitization resulted in a grain size similar to the base alloy, and with no primary carbides to be visually observed, this treatment was chosen for the Mo alloy.

3.3.1.4 0.15C-0.5C-0.5Mn-6.3W Alloy: The fourth steel chosen for study in this task consisted of the base alloy which was modified with 2 atomic pct W. This was because the structure and morphology of the carbide that form in this system at peak hardness i.e., W_2C , have a structure and morphology that is similar to the Mo_2C that forms in the Mo steel. Thus a direct comparison of the hydrogen attack susceptibility on the W steel can be made with that of the Mo steel and a correlation can be established relating the chemical composition of the alloy carbide with the observed hydrogen attack resistance, when the carbides have identical structures and morphologies.

In the preliminary heat treatments carried out on the W alloy, it was found that again a minimum austenitization temperature of 1150°C was necessary to dissolve primary alloy carbides. The as-quenched microstructure subsequent to austenitizing at different temperatures is shown in Figure 9 and the tempering response of the alloy is shown in Figure 10.

Examination of Figure 9 reveals that with the incipient dissolution of alloy carbides during austenitization, there was some tendency towards grain growth; however, the prior austenite grain size on austenitizing at 1150°C (ASTM 3-4) was extremely similar to the base alloy. For this purpose, it was decided to use this temperature for austenitizing for subsequent heat treatments for this alloy.

3.3.2 Microstructural Evaluation of Tempered Structure

Having established the austenitization temperatures and alloy systems chosen for this study, it was necessary to evaluate the carbide morphologies and structures, which could then be used as guidelines towards assessing the hydrogen attack response in the various steels.

3.3.2.1 0.15C - 0.5Mn Alloy: Microstructural assessment of the base alloy was carried out in the tempered condition using transmission electron microscopy. The tempered structures chosen for evaluation consisted of the steel being tempered at 600°C for 1 hour and tempered at 650°C for 1 hour.

As is fairly evident, the only carbide that exists in the plain carbon steel is of the type M_3C , primarily being Fe_3C , with some isomorphous Mn_3C . The choice of these two temperatures in this system was to vary the size of the M_3C carbides that formed, with little or no variation in chemical composition, and examine if the size of the carbide would have any effect on the subsequent hydrogen attack resistance of the steel.

Microstructural examination of the tempered structures was carried out using thin foils and carbon extraction replicas. These are shown in Figures 11 and 12. The microstructure on tempering at 600°C essentially consists of ferritic laths with carbide precipitation at lath boundaries and within the lath interiors (Figure 11). Examination of Figure 12 reveals that the net effect of tempering at 650°C instead of 600°C resulted in coarsening of the Fe_3C so that the average carbide particle size had increased from 0.25 μm to 0.4 μm .

3.3.2.2 0.15C - 0.5Mn - 2Cr Alloy: Microstructural examination of the chromium alloy was carried out after tempering at 650°C and 680°C. The

carbon extraction replicas are shown in Figure 13. It can be seen that tempering at 650°C resulted into two alloy carbides being present viz a fine dispersion of acicular carbides, tentatively identified by selected area diffraction as M_7C_3 , and a coarser type of carbide which appeared to be of the $M_{23}C_6$ type. On increasing the tempering temperature by 30°C viz. to 680°C, some coarsening of the $M_{23}C_6$ carbide had occurred with almost no M_7C_3 carbide being present. Thus, subsequent hydrogen attack experiments on this steel for these two treatments will help establish if there exists a correlation between the crystal structure of the carbide and the hydrogen attack resistance of the steel.

3.3.2.3 0.15C-0.5Mn-3.5Mo Alloy: A limited amount of microstructural examination of the Mo alloy has also been carried out on tempering at 650°C. The typical carbide structure observed is shown in Figure 14. and consists of fine dispersed Mo_2C needles which are known to lie along $\{100\}$ habit planes. Examination of Figure 13a and Figure 14a reveals that the acicular carbides in both systems have a similar morphology, and it will be of interest to examine the attack response of the two alloys in these tempered conditions.

Currently microstructural examination is also being carried out of the W modified alloy and the results will be presented when available. Further, electrolytic extraction of the alloy carbides and subsequent EDAX or X-ray fluorescence analysis is also being planned. This will help establish a correspondence between the chemical composition of the carbides and the crystal structures and morphologies observed using transmission electron microscopy.

3.4 Task 4: Hydrogen Attack Evaluation of Binary and Ternary Alloy Systems

Progress in this task has been behind schedule due to the delays in establishing safety requirements outlined in Task 2. Since no actual hydrogen attack data are available, this task will outline the proposed experiments.

As defined in Task 3, the binary and ternary systems chosen for study consist of a 0.15C-0.5Mn binary alloy to which singular additions of Cr, Mo and W have been made. The heat treated specimens which will subsequently be used for hydrogen attack evaluations will therefore consist of ferritic matrices with the following carbides:

- (i) M_3C carbides only in the 0.15C-0.5Mn alloy.
- (ii) M_2C carbides of similar morphologies, but varying chemical compositions in the Mo and W alloys.
- (iii) M_7C_3 and $M_{23}C_6$ carbides in the Cr alloy.

Further, by varying the tempering temperatures, the size and type of carbides can be varied in the binary alloy and the Cr alloy. Thus the variations in alloy compositions will help establish if there exist correlations between:

- (i) Carbide type and hydrogen attack resistance
- (ii) Chemical composition and/or morphology and hydrogen attack resistance of the steel.

3.4.1 Hydrogen Attack Experiments: For hydrogen attack evaluation on the heat treated specimens, it is proposed to hold the specimens outlined in Task 3 in high pressure hydrogen (1500psig) at 480°C for varying periods of time from 10 hours up to 1200 hours. The objective in holding

the heat-treated specimens at a low temperature is to prevent variation in carbide structure and/or morphology due to elevated temperature tempering, since this would certainly affect the observed attack response of the steel. Thus to a good approximation, the only phenomenon that would occur in the elevated temperature high pressure hydrogen atmosphere in the autoclave, would be the process of decarburization and associated methane bubble formation due to reaction of atomic hydrogen with carbon from ferrite, carbon being supplied through the concentration gradient between ferrite and carbides.⁽⁷⁾ Thus if the alloy carbides govern the attack response of the steels, the proposed experiments will help establish whether:

- (i) For a given period of exposure to high pressure-high temperature hydrogen, alloy steels of similar strength but varying chemical compositions of carbides, have identical hydrogen attack susceptibility.
- (ii) Methane bubble formation occurs only in plain carbon, chromium or molybdenum steels; or in other alloy steels such as tungsten steels, for which no Nelson diagrams are known to exist.
- (iii) Examination of fracture surfaces will establish whether bubble formation in alloy steels occurs at carbide-ferrite interfaces, as is believed to occur in plain carbon steels, or only at second phase inclusions such as MnS particles.

Thus a fundamental understanding of the interrelations between hydrogen attack behavior of simple binary and ternary steels and their microstructural parameters, notably the carbides that form in these steels,

will help gain insight into the future design of steels with improved hydrogen attack resistance.

3.5 Task 5: Metallurgical Characterization of Candidate Commercial Low Alloy Steels and Their Modifications for Hydrogen Attack Studies

The candidate commercial low alloy steels that are studied in this task and which will be considered for hydrogen attack evaluation in Task 6 consist of:

- (i) A533 type (Mn-Mo-Ni) steels
- (ii) A542 type (Cr-Mo) steels

3.5.1 A 533 Type (Mn-Mo-Ni) Steels:

Thick section plates (8" - 12" thick) of A 533 type (Mn-Mo-Ni) steels are popular for nuclear-related applications since these steels meet the requirements of ASME Boiler and Pressure Vessel Code, Section III.⁽⁹⁾ This class of steels appears to have the potential for application in coal gasification/liquefaction processes. However before these steels can be utilized, it is important to assess the hydrogen attack resistance of these steels.

Concurrent with assessment of the environmental behavior of Mn-Mo-Ni steels, it is important to examine the microstructures of thick sections in this group of steels, since it is evident that their environmental behavior will be controlled by microstructural variables. For this purpose, extensive research is being performed at U.C. Berkeley on this class of steels. In particular, thick section simulations have been performed⁽¹⁰⁾ on A533 steel and some of its alloy modifications.

The objective of this research has been to gain an insight into the microstructure for improved mechanical properties and future environmental resistance. The compositions investigated are outlined in Table 3.

Initial developmental work on this system involved establishing base-line data for subsequent research towards mechanical property improvements. The impact properties for 12" spray quenched plate of A533 B, typical of thick sections that would be used in coal gasifiers, are shown in Figure 15. Energy as well as lateral expansion and per cent fibrous fracture are displayed. In addition the tensile properties are tabulated in Table 4.

Concurrent with mechanical property evaluation, detailed microstructural examination was also carried out using optical and TEM techniques. As shown in Figure 16 the interiors of thick plates of the A533 B base alloy consist primarily of bainitic structures. Figure 17 is a carbon extraction replica of 12" plate of A533 B steel at 1/4 T location i.e. within the interior of the plate. The carbides typically observed are spherical in nature with diameters of about $0.35\mu\text{m}$. In addition some elongated carbides with lengths up to $2\mu\text{m}$ can also be seen. The carbide microstructures observed were consistent with those reported for tempered bainitic structures by Hester⁽¹¹⁾. Using selected area electron diffraction it was confirmed that the only carbide present was cementite. No alloy carbides were detected in this system.

3.5.1.1 Alloy Modifications of A-533 B Steel

Alloy modifications of A 533 B were investigated for improved microstructural features leading to superior mechanical properties.

The alloys investigated are tabulated in Table 2, and essentially consisted in modifying A 533 B steel with minor additions of Cr, Mn, Cr+Mn, and Cr+Mn+Si. Each alloy modification will now be discussed individually.

A. Cr Addition: An addition of 1 wt pct Cr to A 533 B showed encouraging improvements in mechanical properties. The improvement in tensile properties can be seen in Table 4 and the impact properties are shown in Figure 18. It can be seen that the Cr addition led to a decrease in the 50 ft-lb transition temperature from 10°C for the base alloy to -5°C (Figure 18). Concomittantly, the FATT decreased from 20°C to 5°C.

Microstructural evaluation revealed that the tempered microstructure was different for the Cr modified alloy. Whereas the tempered bainite in the base alloy had large elongated carbides, those in the Cr modified alloy were fine and spherical in nature (Figure 19a). Analysis of the crystal structure by TEM selected area diffraction and X-ray analysis showed that the carbide was still of the M_3C type and there was no substantial change in lattice parameter. However, subsequent energy dispersive X-ray analysis of the carbides verified that a significant amount of Cr had been incorporated in the M_3C structure - some 10% higher than the base alloy.

A comparison of the hydrogen attack resistance on the base alloy and the Cr modification will help establish the relation between chemical composition and hydrogen attack susceptibility in two commercial alloys which have potential for gasifier type operations.

B. Mn addition: Addition of 0.5% Mn to A 533 B led to improve-

ments in tensile properties (Table 4) and associated improvements in impact properties (Figure 20). However, X-ray analysis revealed that the only type of carbide present was cementite. Thus a comparison of the hydrogen attack resistance of the base alloy and its Mn modification will help assess the importance of microstructural constituents of other than the carbide structure in establishing the hydrogen attack resistance of steels.

C. Cr+Mn additions: Dual additions of 1.0%Cr and 0.7% Mn (Table 3) resulted in the greatest hardenability among the A 533 B type alloys being investigated. This led to vast improvements in tensile and impact properties in comparison to the base alloy (Table 4 and Figure 21 respectively).

Microstructural examination of the tempered bainite in this system revealed that again the only carbide in this system was of the M_3C type (Figure 19b). However the dispersion of carbides in this steel was much finer than in the base alloy, and subsequent EDAX analysis again established a higher Cr content in the M_3C carbides. Thus a comparison of the hydrogen attack resistance of this steel can establish the effect of carbide composition as well as other microstructural variables, such as matrix composition, to the hydrogen attack resistance of the steel.

D. Cr+Mn+Si additions: Additions of Si to the Cr-Mn alloy outlined in the previous paragraph were made because the retarding effect of silicon on carbide-coarsening kinetics is well known. Owen⁽¹²⁾ has suggested that in the presence of silicon, the growth of the carbide interface at high temperatures is controlled by the slower diffusion of

silicon away from the carbide and not the diffusion of carbon.

The Si modified Cr-Mn alloy showed better tensile and impact properties than did the base alloy (Table 3 and Figure 22 respectively). Microstructural examination showed that the carbides, again identified as cementite were extremely fine in nature and therefore this alloy appeared promising on environmental tests since it would help establish whether the surface area of carbides was important in hydrogen attack tests.

3.5.2 A 542/A 387 type (Cr - Mo steels).

2.25Cr - 1Mo steel has enjoyed good resistance to hydrogen attack as gauged from the popularity of this steel in the petrochemical industry. The well known Nelson diagrams⁽¹⁾ outline service conditions for Cr - Mo steels i.e. temperature-pressure defines when the steel would be safe from hydrogen attack. However, the atmosphere in coal-gasifier lead to service conditions that are different from those in petrochemical operations, and therefore it is important to assess the behavior of this steel in gasifier-type atmospheres.

The composition of 2.25Cr - 1Mo steel is given in Table 2. Current use of this steel involves two variants - thick section applications in the normalized condition, (A 387 type) for applications where high strength is not an important parameter; and high strength applications, nominally restricted to thin sections i.e. A 542 type; since quenched and tempered A 542 has inadequate hardenability for thick section applications.

Utilization of 2.25Cr - 1Mo steel in gasifier related operations would involve high strength levels and with this goal in mind, a detailed investigation of the effect of microstructure in controlling

mechanical behavior of thick section quenched and tempered 2.25 Cr-1Mo steel was undertaken by Kar⁽¹³⁾.

3.5.2.1 Microstructural Analysis of 2.25 Cr-1Mo steel:

Before examining the behavior of 2.25Cr-1Mo steel in a hydrogen environment it is important to assess microstructural parameters in this steel. The CCT(continuous cooling transformation) diagram is plotted in Figure 23. As can be seen in this figure, slow cooling typical of thick sections of this steel spray quenched after austenitization, leads to the formation of large amounts of a second phase which has been identified as polygonal ferrite⁽¹³⁾ through microstructural examination (Figure 24). Thus the interiors of thick sections of 2.25Cr-1Mo steel consist of mixtures of bainite and ferrite. It is evident that the initial microstructures formed on slow cooling control the subsequent tempering response of the steel as can be judged from the tensile properties (Table 4) on tempering to two different strength levels. The impact properties are also shown in Figure 25. (The tempering temperatures involved are typical of those used for tempering thick-section action plates).

In order to achieve a better understanding of microstructural features notably the carbide structure and morphology, which probably affect the environmental resistance of this steel, detailed microstructural examination was carried out using transmission electron microscopy. The results of this investigation will now be presented in detail.

Tempering of the steel to a TTP of 34.1 (equivalent to tempering at 650°C for 4 hours) resulted in extensive precipitation

of Widmanstätten carbide within the bainitic laths as is shown in Figure 26 (TTP = Larson-Miller time-tempering parameter). The orientation relationship between the ferrite and carbide which was identified as cementite, is shown in Figure 26 (c) & (d). In addition, extensive carbide precipitation also occurred at ferrite-bainite boundaries, as is shown in Figure 27. Occasional stringers of alloy carbides were also observed on the ferritic side of the boundary, as seen in Figure 27, but these were insufficient for diffraction information. The nature of the carbide indicates these are Mo_2C (M_2C type), but unequivocal identification would need further work.

In contrast, when the tempering parameter was increased to 36.2 (tempering at 700°C for 4 hours), extensive precipitation of alloy carbide occurred both in the bainitic and ferritic phases. This is shown, for the former case, in Figure 28. Examination of Figure 28a, which is representative of 12" plate, shows that the bainitic laths continue to exist despite prolonged elevated temperature tempering. The foil was in the $[100]_\alpha$ orientation and the dark field (Figure 28b) shows the Mo_2C particles reverse contrast when the streak on the (011) matrix spot is imaged. In addition coarse Fe_3C can also be seen at lath boundaries.

Hydrogen attack studies of these two tempered variants will be important because the role of carbide type (M_3C in one case and $\text{M}_3\text{C} + \text{M}_2\text{C}$ in the other case) on the attack behavior can be assessed in a commercial steel.

3.5.2.2 Alloy Modifications of 2.25Cr-1Mo steel

Alloy modifications to 2.25Cr-1Mo steel were made with a

view towards improved thick section properties; since as mentioned earlier, coal gasifier applications demand improved properties. The compositions of the modified Cr-Mo alloys are given in Table 3 and consist of a singular addition of 1 wt% Mn, or a binary addition of 0.5% Ni+0.5%Mn. These alloy additions were made since it has been shown⁽¹³⁾ that Ni or Mn additions are effective in retarding polygonal ferrite formation in thick-sections of 2.25 Cr-1Mo steel.

The tensile properties of thick-section Cr-Mo modified alloys are tabulated in Table 5 corresponding to tempering to the same TTP's as the base alloy. In addition the impact properties of the modified alloys are shown in Figures 29 and 30.

Microstructural examination of the Mn and Ni-Mn modified Cr-Mo steels was also carried out. Typical microstructures observed are shown in Figure 31. It can be seen that the effect of alloy modification was to eliminate second phase formation on slow cooling after austenitization, as is typical within the interiors of thick plates. The elimination of the second phase would probably affect the environmental response of the modified steels.

To further understand the effect of carbide structures on environmental resistance of the modified steels, high resolution transmission electron microscopy was utilized. The results are shown in Figures 32-35 and can be summarized as follows:

1. Tempering at 650°C (TTP = 34.1) resulted in partial recovery in the bainitic laths (Figure 32) and coarsening of the cementite (1200Å) for the 1 Mn modified alloy. In addition fine alloy carbides could also be seen on imaging streaks that occurred

on matrix spots. The alloy carbides appeared to be completely or partially coherent with the matrix as judged by the streaking and were tentatively identified as Mo_2C .

Examination of the 0.5Ni - 0.5Mn variant of 2.25Cr - 1Mo steel revealed a similar occurrence of Fe_3C and Mo_2C in a lath structure, as is shown in Figure 33. Precipitation of fine needles of Mo_2C occurred on dislocations rather than in-situ on M_3C carbides. The M_3C carbide was fairly coarse and was visible in dark field (Figure 33). The selected area diffraction and its analysis is given in Figure 33c and d.

2. On tempering at 700°C, carbide strengthening in the 1 Mn and 0.5Ni - 0.5Mn modified alloys was primarily due to Mo_2C precipitation. This feature can clearly be seen in Figures 34 and 35 which are transmission electron micrographs of the modified Cr - Mo alloys. The 1 Mn alloy was characterized by extensive recovery (Figure 34) since the substructure consisted of cellular grains, rather than a lath structure. The M_3C carbides had spheroidized ($2500\text{\AA}$) and did not appear to contribute to the strength in the alloy. In addition, the Mo_2C carbide ($700\text{\AA}$ long) could clearly be seen in the light and dark fields (Figure 34a and b). The foil was in the $[100]_\alpha$ orientation and the dark field was formed using the (TT.0) spot of the Mo_2C precipitate. The Mo_2C lies close to the $[100]_\alpha$ habit plane and appears to follow an orientation relationship suggested by Pitsch et al (14,15).

Figure 35 is a typical series of micrographs as the 0.5Ni-0.5Mn modified alloy. It is evident that there was extensive precipitation in Mo_2C which contributed towards improved tensile properties (see Table 5). The weak beam image (Figure 35b) clearly shows that the alloy

carbide precipitation occurred on dislocations.

In summary, detailed microstructural examination of thick sections of the 2.25 Cr-1Mo alloy established that the interiors on thick plates consisted of mixtures of ferrite and bainite. On tempering to two typical TTP's it was determined that for the lower TTP, the carbide precipitated was M_3C , while on increasing the TTP, primary contribution came from alloy carbide precipitation in both phases.

In contrast, alloy modification of 2.25Cr-1Mo through minor additions of Ni, Mn resulted in elimination of the polygonal ferrite. The other major effect of alloy modification was to alter the tempering response of the bainite that formed on slow cooling. Tempering at the lower TTP resulted in precipitation of alloy carbides, whereas no alloy carbide precipitation was observed in the base alloy. Tempering at the higher temperature resulted in extensive precipitation in both the base as well as the modified alloys.

Having evaluated the microstructure in detail the observed hydrogen attack response of the Cr-Mo steels can now be assessed, as will be discussed in the next task.

3.6 Task 6: Hydrogen Attack Evaluation of Candidate Commercial Low Alloy Steels and Their Modifications

Having established microstructural parameters in low alloy steels which appear to have potential for gasifier related applications, it is important to assess their response to hydrogen at elevated temperatures and pressures - as would be typical in coal gasifiers. Thus, the objective of Task 6 is to establish guidelines for the typical

behavior of Mn-Mo-Ni steels and Cr-Mo steels in hydrogenous environments.

Progress in this task has been slow due to the delays in establishing safety guidelines for experimental techniques, as was discussed in Task 2. Therefore, this task will outline the proposed experiments planned on the steels discussed in Task 5.

3.6.1 Hydrogen Attack of Mn-Mo-Ni steels: Currently, specimens of A 533 B steel and its Mn, Cr, Mn+Cr and Mn+Cr+Si modifications have been heat treated for long term exposures to elevated temperature, high pressure hydrogen. Plate simulations have been carried out to represent 12" plate which has been spray quenched after austenitization, and subsequently tempered at 675°C for 8 hours (TTP = 35.2). It is initially proposed to expose the heat treated specimens at 500°C to 1500 psig hydrogen for a period of 1000 hours. The degree of hydrogen attack will be monitored by performing tensile tests on the exposed specimens and evaluating the change in reduction of area, which has been considered to be a sensitive index of the phenomenon of hydrogen attack. Based on the results of the 1000 hour exposure, further tests will be planned where the time of exposure or temperature may be varied.

The results of the tests on the Mn-Mo-Ni alloys will help establish the following:

1. Determination of whether Mn-Mo-Ni steels are susceptible to carburization and methane bubble formation, and whether the degree of attack is similar to plain carbon steels, since the only carbide observed is M_3C , similar to the cementite in plain carbon steels.
2. The relative effects of alloying elements viz Cr, Mn and Si additions, either alone or in combination, in affecting the

susceptibility of Mn-Mo-Ni steel to hydrogen attack.

3. The importance of carbide stability in determining the amount of attack in commercial steels. As discussed in Task 5, the alloy additions made to A 533 B do not appear to change the carbide crystal structure for the tempering treatment studied. However, with greater amount of Cr (and Mn) in the carbides of the modified alloys, the attack resistance of these steels should be notably different if the chemical composition of the carbide viz M_3C in this case, plays a role in determining the stability of the steel to hydrogen attack.

3.6.2 Hydrogen Attack of Cr-Mo Steels: Heat treatments of 2.25 Cr-1Mo steel (A542) and its Mn and Ni, Mn modifications have been carried out to simulate 12 inch plates tempered to two different TTP's viz 650°C and 700°C. As discussed in Task 5, this results in the following microstructural features:

1. Occurrence of duplex structures in the base alloy which have a varied tempering response. Tempering at 650°C results in the majority of carbide being present as M_3C in the bainitic phase, with little or no alloy carbides present. Tempering at a higher temperature viz 700°C results in large amounts of M_2C being present in both phases, with small amounts of coarse M_3C persisting in the bainitic regions. A comparison of the attack resistance of the steel subjected to these two different tempering treatments will help establish whether alloy carbides govern the attack resistance of Cr-Mo steels, as has been suggested by Geiger and Angeles⁽⁷⁾.

2. Alloy modifications of Mn, Ni lead to improved microstructural constituents, as has been discussed in Task 5. Moreover,

the other major effect of alloy addition is to vary the tempering response of the steel so that on tempering at 650°C, precipitation of M_2C occurred in the modified alloys. Therefore, a 1000 hour exposure of the modified alloys and the base steel will help establish if the modified alloys, which have better strength and toughness than the base steel, also exhibit superior resistance to hydrogen attack.

3. A comparison of the attack susceptibilities of the modified alloys will help in examining the role of alloying elements which are either weak or non-carbide formers, in governing the attack resistance of Cr-Mo steels, Ni is not a carbide former, and Mn is a weak carbide former, and the effect of these alloy additions was to alter tempering kinetics in 2.25Cr-1Mo steel, as was discussed in Task 5. Examination of the attack resistance of the Mn modified and Ni, Mn modified steels will help assess if these elements do play a role in hydrogen attack.

4. WORK FORECAST

4.1 Task 1: Design Criteria for Hydrogen Attack Studies:

Efforts will be made to constantly update design criteria for hydrogen attack studies viz., through interaction with other DOE contractors, it is planned to upgrade the experimental techniques used to include methods for attack initiation such as incorporating high temperature transducers in the vessels.

4.2 Task 3: Metallurgical Characterization of Binary and Ternary Alloy Systems

Microstructural characterization of the W alloy will be completed to establish the carbide structure and morphology for the tempering temperatures used. Further X-ray fluorescence and EDAX analysis will be carried out to establish the chemical composition of the carbides of the alloys studied in Task 3.

4.3 Task 4: Hydrogen Attack Evaluation of Binary and Ternary Alloy Systems

Heat treated specimens of the alloys discussed in Task 3 will be exposed to high pressure hydrogen (1500 psi) at 480°C for varying periods of time from 10 hours up to 1200 hours and the degree of hydrogen attack will be measured through tensile tests, microscopic and fractographic examination.

4.5 Task 6. Hydrogen Attack Evaluation of Candidate Commercial Low Alloy Steels and Their Modifications

12" thick plate simulations of Mn-Mo-Ni and Cr-Mo steels, and their alloy modifications will be exposed for 1000 hours to 1500 psig hydrogen at 500°C. The degree of attack in the individual steels

will be measured by the change in reduction of area during tensile tests that will be carried out on the exposed specimens. A limited amount of microscopic and fractographic examination will also be performed.

5. CONCLUSIONS

Based on the results of this investigation, the following conclusions were established:

1. Task 1: A detailed review of published literature established that the phenomenon of hydrogen attack could be investigated by experimental techniques such as tensile tests coupled with microscopic and fractographic examination.
2. Task 2: High pressure elevated temperature reaction vessels were fabricated to expose heat treated samples to high pressure hydrogen at 500°C for time periods of up to 1200 hours.
3. Task 3: Microstructural examination of a series of plain carbon and ternary steels established the following:
 - (a) Austenitization of 0.15-0.5Mn steel at 1000°C followed by quenching resulted in microstructure free of undissolved carbides. The prior austenite grain size was ASTM 3-4. Further, austenitization of the Chromium modified steel at 1050°C and the molybdenum and tungsten modified steels at 1150°C, followed by quenching resulted in microstructures having similar grain sizes and free from undissolved carbides.
 - (b) On subsequent tempering of the as-quenched steels, it was determined that the molybdenum and tungsten modified steels exhibited secondary hardening peaks, whereas the chromium modified steel and the base alloy did not reveal secondary hardening peaks.
 - (c) Tempering of the 0.15C-0.5Mn base steel at 600°C and 650°C resulted in M_3C carbides of average sizes 0.25 μ m and 0.4 μ m respectively.

In contrast tempering of the Cr modified steel at 650°C resulted in precipitation of M_7C_3 and $M_{23}C_6$ carbides. On increasing the tempering temperature to 680°C, only coarse $M_{23}C_6$ carbides could be observed. Tempering of the Mo modified steel at 650°C resulted in a fine dispersion of M_2C carbides.

4. Task 5: Microstructural and mechanical property evaluation of Mn-Mo-Ni steels and Cr-Mo steels and some of their modifications established the following:

(a) The carbides observed in A 533B on tempering to a TTP of 35.2 were primarily M_3C of average diameter 0.35 μ m. Further, modifications of A 533B with Cr, Mn or Si, either alone or in combination resulted in finer dispersions of M_3C being present. Subsequent energy dispersive X-ray analysis of the carbides revealed that higher amounts of Cr were incorporated in the M_3C carbides of the modified steels.

(b) Tempering of 2.25Cr-1Mo steel (A 542 type) at a TTP of 34.1 resulted in the formation of Widmanstätten M_3C in the bainitic regions and minor precipitation of M_2C in the ferritic areas. Tempering to a higher TTP, viz. 36.2 resulted in extensive precipitation of M_2C in both phases, and coarsening of the M_3C carbides.

(c) The effect of alloy additions of Mn or Ni, Mn was to alter the tempering response of the steel in that precipitation of M_2C was observed on tempering to a lower temperature viz. TTP = 34.1 whereas M_2C was observed in the base alloy only on tempering at much higher temperatures.

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- Figure 2 : Schematic diagram illustrating operation of hydrogen attack reaction vessels,
- Figure 3 : Tempering response of 0.15C-0.5Mn Base alloy after austenitization at 900°C, 1000°C and 100°C for 1 hour.
- Figure 4 : As quenched microstructures of 0.15C-0.5Mn Base after austenitization at various temperatures:
(a) Austenitized at 900°C (b) Austenitized at 1000°C
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- Figure 5 : Tempering response of 0.15C-0.5Mn-2Cr alloy after austenitization at 900°C, 1000°C and 1050°C for 1 hour,
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- Figure 11: Transmission electron micrograph of 0.15C-0.5Mn base alloy after tempering at 600°C shows M_3C carbide precipitation within ferritic laths and at lath boundaries.
- Figure 12: Transmission electron micrograph of 0.15C-0.5Mn base alloy after tempering at 650°C shows coarser Fe_3C carbides (average size 0.4 μ m).

Figure 13: Transmission electron micrographs of carbon extraction replicas of 0.15-0.5Mn-2Cr alloy after tempering for 1 hour:

(a) Tempered 650°C

(b) Tempered 680°C

Figure 14: Transmission electron micrograph of 0.15C-0.5Mn-3.5Mo alloy tempered at 650°C shows fine dispersed Mo_2C needles.

Figure 15: Impact properties of A533B steel for simulated 12" spray quenched plate tested at 1/4T location.

Figure 16: Optical micrograph of A533 steel shows that the as quenched microstructure consists of bainite with no polygonal ferrite present.

Figure 17: Transmission electron micrograph of A533 steel tempered at 675°C shows spherical M_3C carbides of average diameter = 0.35 μm . Some elongated carbides with lengths up to 2 μm can also be seen.

Figure 18: Impact properties of A533 steel modified with 1%Cr. (The impact properties of the base steel are superimposed in dotted lines).

Figure 19: Transmission electron micrographs of modified A533 steel and tempered at 675°C:

(a) Cr modified

(b) Cr+Mn modified

Figure 20: Impact properties of A533 steel modified with 0.5%Mn. (The impact properties of the base steel are superimposed in dotted lines).

Figure 21: Impact properties of A533 steel modified with a dual addition of Cr + Mn. (The impact properties of the base steel are superimposed in dotted lines).

Figure 22: Impact properties of A533 steel modified with Si, Mn and Cr additions.

Figure 23: CCT diagram of 2.25Cr, 1Mo steel.

Figure 24: Optical micrographs of 2.25Cr-1Mo steel cooled at various cooling rates ranging from rapid quenching (characteristic of the surface) to slow cooling (typical of 12" thick plate).

Figure 25: Impact properties of 2.25Cr-1Mo steel.

Figure 26: Transmission electron micrographs of 12" spray quenched plate of 2.25Cr-1Mo steel tempered at 650°C for 4 hours.

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- Figure 35; Transmission electron micrographs of the 0.5Ni-0.5Mn modified 2,25Cr-1Mo steel tempered at 700°C.

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TABLE 1: COMPOSITIONS OF STEELS FOR FUNDAMENTAL STUDIES

Steel Description	Weight Percent					
	C	Mn	W	Mo	Cr	S
Base	0.14	0.5	-	-	-	0.004
Base + Cr	0.16	0.5	>0.005	0.01	1.98	0.006
Base + Mo	0.15	0.5	>0.005	3.43	>0.005	0.002
Base + W	0.18	0.5	6.36	0.01	>0.005	0.002

TABLE 2: COMPOSITIONS OF COMMERCIAL STEELS INVESTIGATED

Steel Designation	Weight Percent										
	C	Mn	Mo	Ni	Cr	Si	S	P	V	Al	Cu
A 533 B (Mn-Mo-Ni Base)	0.22	1.32	0.57	0.65	-	0.20	0.007	0.009	-	0.036	0.07
Base + 1Cr	0.20	1.27	0.52	0.60	1.00	0.27	0.009	0.008	0.02	0.025	0.08
Base + 0.7Mn	0.22	1.92	0.57	0.62	0.16	0.26	0.009	0.010	0.016	0.026	0.08
Base + 1Cr + 0.7Mn	0.20	1.96	0.58	0.61	0.97	0.25	0.010	0.007	0.023	0.034	0.09
Base + 1Cr + 0.7 Mn + 0.7Si	0.20	1.89	0.56	0.61	0.95	0.94	0.009	0.010	0.014	0.029	0.09
A 542 (2.25Cr - 1Mo Base)	0.15	0.42	0.91	0.10	2.18	0.30	0.009	0.015	-	0.019	0.08
Base + 1Mn	0.15	1.50	0.96	0.13	2.25	0.33	0.007	0.009	-	0.021	0.09
Base + 0.5Ni + 0.5Mn	0.15	0.92	1.03	0.51	2.27	0.28	0.008	0.013	-	0.021	0.09

TABLE 3: TENSILE PROPERTIES OF Mn-Mo-Ni STEELS INVESTIGATED

Alloy	YS (ksi)	UTS (ksi)	Elongation (%)	RA (%)
A 533 B Base	63.8	87.2	23.6	65.0
Base + Cr*	78.8	96.4	26.9	65.2
Base + Mn*	77.6	102.7	26.1	61.6
Base + Cr, Mn*	81.9	105.9	27.0	64.0
Base + Cr, Mn, Si	85.6	109.2	22.2	62.1

Austenitized 925°C - 1 hr

12" - 1/4 T Spray Quenched

Tempered 675°C, 8 hours (TTP = 35.2)

*Grain Refined

TABLE 4: TENSILE PROPERTIES OF CR-MO STEELS INVESTIGATED

Alloy	YS (ksi)	UTS (ksi)	Elongation %	RA (%)
2.25Cr-1Mo* Base	59.4	102.4	21.5	69.5
Base + 1Mn*	86.8	103.5	24.8	72.9
Base + 0.5Ni* to .5Mn	90.2	108.8	24.1	69.2
2.25Cr-1Mo** Base	72.4	92.8	24.9	71.9
Base + 1Mn**	72.2	93.3	22.8	64.3
Base + 0.5Ni** to .5Mn	70.4	91.6	23.8	69.9

Austenitized 1000°C - 1 hour

* Tempered 650°C, 4 hours - TTP = 34.1

**Tempered 700°C, 4 hours - TTP = 36.2

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Figure 1. Overall view of high temperature-high pressure autoclave equipment used for hydrogen attack studies.

SCHEMATIC DIAGRAM OF HYDROGEN ATTACK EXPOSURE EQUIPMENT

NOTES:

- GAS LINE CONNECTION
- ON-OFF GAS VALVE
- PRESSURE GAUGE

XBL 7910-7220

Figure 2. Schematic diagram illustrating operation of hydrogen attack reaction vessels.

Figure 3. Tempering response of 0.15C-0.5Mn Base alloy after austenitization at 900°C, 1000°C and 100°C for 1 hour.

XBB804-4228

Figure 4. As quenched microstructures of 0.15C-0.5Mn Base after austenitization at various temperatures:
 (a) Austenitized at 900°C (b) Austenitized at 1000°C
 (c) Austenitized at 1100°C

Figure 5. Tempering response of 0.15C-0.5Mn-2Cr alloy after austenitization at 900°C, 1000°C and 1050°C for 1 hour.

XBB804-4227

Figure 6. As quenched microstructures of 0.15C-0.5Mn-2Cr alloy after austenitization at various temperatures:
 (a) Austenitized at 900°C (b) Austenitized at 1000°C
 (c) Austenitized at 1050°C

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Figure 7. As quenched microstructures of 0.15C-0.5Mn-3.5Mo alloy after austenitization at various temperatures:
 (a) Austenitized at 1050°C (b) Austenitized at 1100°C
 (c) Austenitized at 1150°C

Figure 8. Tempering response of 0.15C-0.5Mn-3.5Mo alloy after austenitization at 1000°C, 1050°C and 1150°C for 1 hour.

XBB804-4229

Figure 9. As quenched microstructures of 0.15C-0.5Mn-6.3W alloy after austenitization at various temperatures:
(a) 1050°C (b) 1100°C
(c) 1150°C

Figure 10. Tempering response of 0.15C-0.5Mn-6.3W alloy after austenitization at 1000°C, 1050°C, 1100°C and 1150°C for 1 hour.

XBB804-4226

Figure 11. Transmission electron micrograph of 0.15C-0.5Mn base alloy after tempering at 600°C shows M₃C carbide precipitation within ferritic laths and at lath boundaries.

XBB804-4231

Figure 12. Transmission electron micrograph of 0.15C-0.5Mn base alloy after tempering at 650°C shows coarser Fe₃C carbides (average size 0.4μm).

XBB804-4232

Figure 13. Transmission electron micrographs of carbon extraction replicas of 0.15-0.5Mn-2Cr alloy after tempering for 1 hour:
 (a) Tempered 650°C (b) Tempered 680°C

XBB804-4225

Figure 14. Transmission electron micrograph of 0.15C-0.5Mn-3.5Mo alloy tempered at 650°C shows fine dispersed Mo_2C needles.

XBL 792-5749

Figure 15. Impact properties of A533B steel for simulated 12" spray quenched plate tested at 1/4T location.

XBB777-7151

Figure 16. Optical micrograph of A533 steel shows that the as quenched microstructure consists of bainite with no polygonal ferrite present.

XBB782-2068

Figure 17. Transmission electron micrograph of A533 steel tempered at 675°C shows spherical M_3C carbides of average diameter = 0.35 μm. Some elongated carbides with lengths up to 2 μm can also be seen.

XBL7 92 5752

Figure 18. Impact properties of A533 steel modified with 1%Cr. (The impact properties of the base steel are superimposed in dotted lines).

XBB791-1055

Figure 19. Transmission electron micrographs of modified A533 steel and tempered at 675°C:
 (a) Cr modified (b) Cr+Mn modified

XBL 792-5754

Figure 20. Impact properties of A533 steel modified with 0.5%Mn. (The impact properties of the base steel are superimposed in dotted lines).

XBL 792-57 53

Figure 21. Impact properties of A533 steel modified with a dual addition of Cr + Mn. (The impact properties of the base steel are superimposed in dotted lines).

XBL 792 5750

Figure 22. Impact properties of A533 steel modified with Si, Mn and Cr additions.

XBL 795-6313

Figure 23. CCT diagram of 2.25Cr, 1Mo steel.

XBB771-161

Figure 24. Optical micrographs of 2.25Cr-1Mo steel cooled at various cooling rates ranging from rapid quenching (characteristic of the surface) to slow cooling (typical of 12" thick plate).

XBL795-6314

Figure 25. Impact properties of 2.25Cr-1Mo steel.

Figure 26. Transmission electron micrographs of 12" spray quenched plate of 2.25Cr-1Mo steel tempered at 650°C for 4 hours.

XBB795-7177

Figure 27. Transmission electron micrographs of 2.25Cr-1Mo steel tempered at 650°C shows carbide precipitation within bainitic laths and at bainite-ferrite boundaries.

XBB796-7677

Figure 28. Transmission electron micrographs of 2.25Cr-1Mc steel tempered at 700°C for 4 hours.

XBL 792-5759

Figure 29. Impact properties of 2.25Cr-1Mo steel modified with Ni, Mn additions.

XBL 792-5756

Figure 30. Impact properties of 2.25Cr-1Mo steel modified with Ni, Mn additions.

XBB795-7424

Figure 31. Optical micrographs of Ni, Mn modified 2.25Cr-1Mo steel show absence of polygonal ferrite in slow cooled thick sections.

XBB795-7175

Figure 32. Transmission electron micrographs of 2.25Cr-1Mo-1Mn steel tempered at 650°C.

- - α spots [011] orientation
- - Fe₃C spots [011] orientation

XBB792-1674

Figure 33. Transmission electron micrographs of 2.25Cr-1Mo+0.5Ni, 0.5Mn steel tempered at 650°C.

XBB795-7184 XBB795-7431

Figure 34. Transmission electron micrographs of the 1Mn modified Cr-Mo steel tempered at 700°C.

XBB795-7185

Figure 35. Transmission electron micrographs of the 0.5Ni-0.5Mn modified 2.25Cr-1Mo steel tempered at 700°C.