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Westinghouse Advanced Reactors Division

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STAINLESS STEEL CLADDING DEVELOPMENT

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING SEPTEMBER 30, 1968

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Submitted to AEC-NY00 in October 1968

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INTRODUCTION

This is the first quarterly progress report and covers the work performed during the first quarter of the fiscal year (FY)-1969.

SUMMARY OF OBJECTIVES

This project is focused on the short term, ending in fiscal year 1972, and is concerned with steps to improve commercially available Type 316 austenitic stainless steels for use as cladding in LMFBR fuel pins. The overall project objective is to determine the influence of structure on mechanical properties of Type 316 austenitic stainless steel that will assure the maximum performance under LMFBR service conditions.

Initially, a survey will be made to determine tubing material property and microstructural variability based upon procurement of tubing under an existing FFTF specification. This specification will be used as a basic starting point. The unirradiated mechanical properties of the material are related to the tubing microstructure. This has been shown experimentally in unirradiated Type 316 austenitic stainless steel, where prestraining and cold working to produce carbide precipitation decreased the minimum creep rate at temperatures of interest to LMFBR by as much as a factor of 250, and increase creep rupture life by as much as a factor of 25.

It is anticipated that this first phase of the cladding program will culminate at the end of FY-1972, with a definition of the most desirable mechanical and microstructural properties in austenitic stainless steel, to maximize the strength and ductility of the material under the most limiting LMFBR service conditions.

SUMMARY OF CURRENT PROGRESS

A summary of current progress is shown below. Detailed progress is reported in the individual task sections of this document.

Under Task SSAA-110, authorization for work in FY-1969 was received from the Commission based on the work program submitted in June. Internal work authorizations and budgets were established based on fiscal year and interim funding.

Under Task SSAA-210, a detailed test plan has been prepared, that has been reviewed for statistical significance. Characterization studies have begun on commercial grade, air-melted, solution-annealed Type 316 Stainless steel tubing to serve as a base point for the reference vacuum melted tubing. Optical microscopy showed normal inclusion precipitation.

Under Task SSAA-310, substructural characterization of commercial grade air-
eluted, solution-annealed Type 316 stainless steel tubing has begun. This
includes grain size, precipitation and inclusion distribution, x-ray
diffraction studies of the precipitates, transmission electron microscopy
of the dislocation arrangement, and electron beam microanalysis of the
precipitated particles. The results to date show that the tubes have a
higher dislocation density than expected, indicating that the tubes have
been subjected to slight deformation after the recrystalline heat treatment.
Also, the outer surfaces of these tubes are heavily cold worked up to a
depth of about one mil due to a final surface grinding operation.

SSAA-110 - PROJECT ADMINISTRATION

A. E. Duval, W. B. Heubel, P. Murray, P. L. Wyzenbeek

OBJECTIVES

The objectives of this task are to assure that the project objectives are accomplished on schedule, within budget, and to the satisfaction of the Atomic Energy Commission; to assure compliance with contracted obligations; and to coordinate this project with other AEC-sponsored and Westinghouse-sponsored LMFBR development projects.

CURRENT PROGRESS

Authorization for work in FY-1969 was received from the Commission based on the work program submitted in June, and contract modifications 9 through 11, which funded work through September, were received and executed. Internal work authorizations and budgets were established based on RDT's directions of July 24. The FY-1969 work program, WARD-3791-22, was revised and issued. Work is proceeding on schedule and within budget.

SSAA-210 - EVALUATION OF AUSTENITIC STAINLESS STEEL CLADDING

R. Ammon, E. C. Bishop, M. G. Cowgill, W. E. Ray, H. J. Snyder, K. C. Thomas

OBJECTIVE

The objective of this task is to characterize, in detail, by microstructural analysis, chemical analysis, and mechanical property testing, thin-wall stainless steel tubing fabricated under carefully controlled commercial practice. This information will be used to:

- a. enhance the understanding of the effect of fabrication processes and resulting structures on the properties of thin-wall tubing; and
- b. provide out-of-reactor data required to predict and improve swelling behavior and strain limits of cladding in LMFBR environment.

CURRENT PROGRESS

Test Program

A detailed test program plan has been prepared and personnel assignments made for the various phases of the program.

The test program will be based mainly on vacuum-melted material, although selected tests will be carried out on air-melted tubing for comparison. To minimize compositional variables, it is proposed to split an air-melted, Type 316 stainless steel heat four ways and to process as follows:

a. Air Melt	process to tubing
b. Vacuum Induction Remelt	process to tubing
c. Consumable Electrode Vacuum Remelt	process to tubing
d. Vacuum Induction Remelt and
Consumable Electrode Vacuum Remelt	process to tubing

The detailed microstructural and mechanical property characterization studies are shown in Figures 1(a), 1(b), and 1(c). This will enable a precise determination of the effect of type of vacuum melting on the properties of the tubing.

The effect of grain size on the properties of tubing will be investigated by testing two grain sizes. These sizes will be obtained by the proper combinations of cold work (in the final tube passes) and annealing temperature.

WORK AND TESTING FLOW CHART
SSAA - 210

LEGEND		
A - CHEMICAL ANALYSIS OPTICAL METALLOGRAPHY B - GRAIN SIZE C { INCLUSION COUNT MORPHOLOGY OF INCLUSIONS D { CARBIDE PRECIPITATION CONTENT MORPHOLOGY OF CARBIDES E - SIGMA PHASE CONTENT F { TWIN FREQUENCY (LINEAR INTERCEPT METHOD) G - MICROMHARDNESS	ELECTRON MICROSCOPY TRANSMISSION E.M. H { DISLOCATION SUBSTRUCTURE DISLOCATION DENSITY STACKING FAULT ENERGY EXTRACTION E.M. J { SECOND PHASE CONTENT, MORPHOLOGY AND DISTRIBUTION (CARBIDES AND SIGMA PHASE). INCLUSION, IF DE- TERMINED TO BE OF INTEREST, MAY BE INVESTIGATED AT A LATER DATE. SECOND PHASE COMPOSITION	
	X-RAY ANALYSIS K { RESIDUAL STRESS BY X-RAY LINE BROADENING CRYSTALLOGRAPHIC ORIENTATION BY LAUE BACK REFLECTION TECHNIQUE L - FRACTOGRAPHY	

Figure 1(a)

3018-5

Figure 1(c)

Tubing in the annealed, cold worked (25%), and cold worked (25%) and aged condition will be evaluated. The "Garofalo" aging treatment will be used as it has been established previously that this treatment significantly improves the creep performance of austenitic stainless steels by dislocation pinning of the sub-structure[1]. This treatment involves aging the 25% cold-worked structure in the following manner:

900°F for 24 hours, then
1300°F for 216 hours and air cooled,

This test plan has been reviewed by the Westinghouse R&D Center (Mathematics Department) for statistical significance. With minor modification, they are in agreement with the plan.

Procurement

A request for quotation for tubing in the various conditions listed in Figure 1 has been sent to several vendors. It is expected that the quotations will be received during mid-October. The tubing is being ordered to a WARD Specification which encompasses key FFTF driver fuel cladding dimensions:

0.235-inch outside diameter by 0.015-inch wall thickness.

In order to establish a base line for air-melted tubing and to develop testing techniques for subsequent studies on vacuum-melted tubing, a request has been made to PNL for 30 feet of air-melted, Type 316 stainless steel, FFTF tubing. It is expected that this will be shipped in October.

In addition, studies have been initiated using four lots of Type 316 stainless steel tubing currently available at WARD. The dimensions and processing history of these tube lots are shown in Table 1, and the test plan for this study is shown in Figure 2. This test plan is similar to that proposed for the vacuum-melted material (Figure 1). As the test results become available, they will be included in this Figure.

Test Results

A detailed chemical analysis has been carried out on a specimen of tubing from lot #7-248. All the tubing lots are from the same heat, and it is assumed that lot #7-248 is typical of the heat. The chemical composition determined is:

	C	N	Ni	Cr	S	P	O	
wt%	0.054	0.0726	11.66	18.20	0.012	0.022	0.0087	
	B	Mn	Mo	Cu	Nb	Ti	Si	Fe
wt%	0.0003	1.39	2.48	0.06	0.014	0.033	0.64	Balance

Table 1

Dimensions and Processing History of Tubing Produced from Heat No. 20303

Lot # ^a	Wall Thickness (in.)	Outside Diameter (in.)	Rod Drawing		Plug Drawing	
			No. of Draws	Reduction each draw (%)	No. of Draws	Reduction each draw (%)
316727	0.010	0.30	3	34-43	2	30
316727	0.012	0.30	2	43-45	2	34-39
316727	0.014	0.30	2	42-43	2	31-35
7-2489	0.012	0.30	2	43-45	2	34-39

^aAll lots started at a size of 0.738-inch O.D. by 0.041-inch wall. Breakdown annealing performed either in air atmosphere at 2100°F or in dry hydrogen at 1950/2000°F. All final anneals carried out in dry hydrogen.

Figure 2 Evaluation of Air-Melted Superior Tubing Heat No. 20203

Detailed optical metallographic examination of tubing specimens from each lot is almost complete. The results indicate that the tubing is very clean with respect to non-metallic inclusions. Inclusion counts were determined in accordance with ASTM-45-63 Method A modified for thin-wall tubing. The inclusions were mostly D type (thin), which are globular oxide type. The Field numbers associated with the various tube lots are:

<u>Tube Lot Number</u>	<u>Field Number</u>
#7-2489	1.5 average
#316727	1.6 average
#316728	1.2 average
#316726	1.1 average

There were some angular yellow-pink colored inclusions, mostly in stringer form, associated with the D type inclusions. These are presumed to be titanium carbo-nitride inclusions. Examples of the inclusion types are shown in Figure 3 along with the grain structure.

Mechanical testing of tubing, under biaxial conditions in air, has been initiated. When the inert gas test chamber becomes available, the tests will be carried out in argon. Tensile tests have been completed on 0.010- and 0.014-inch-wall tubing at 850 and 1000°F, and stress rupture tests at 1000°F are in progress. The test results to date appear in Tables 2 and 3. The yield strength of the 0.010-inch-wall tubing is about 18% higher than that of the 0.014-inch-wall tubing at 850°F, whereas it is only about 8% higher at 1000°F. The ultimate tensile strengths and elongation values of the two wall thicknesses are not significantly different at these two temperatures.

Testing of the four tubing lots will continue according to the test plan shown in Figure 2.

UNETCHED

X500

(a) GLOBULAR AND ANGULAR INCLUSIONS

UNETCHED

X1000

(b) ANGULAR TITANIUM CARBIDE TYPE
INCLUSIONS

ETCHED IN AQUA REGIA

X250

(c) GRAIN STRUCTURE

FIG. 3 Inclusion Types and Grain Structure of Type 316 Stainless Steel Tubing -
Longitudinal sections, Lot 7-2489

Table 2
Tensile Properties of 0.010-, 0.012-, and 0.014-Inch
Wall Tubing at 850 and 1000°F

Test Temperature (°F)	Lot #	Wall Thickness (in.)	0.2% Offset Yield Strength (psi) ^a	Ultimate Tensile Strength (psi)	Total Diametral Elongation (%)
850	316727	0.010	31,175	60,900	19.3
	7-2489	0.012	28,500	61,440	17.7
	316728	0.014	26,046	59,243	18.6
1000	316727	0.010	30,450	59,813	20
	316728	0.014	25,025	58,017	20

^aBased on mean tube diameter

Table 3
Stress Rupture Properties of 0.010-, 0.012-, and 0.014-Inch
Wall Tubing at 1000°F

Test Temperature (°F)	Tube Lot #	Wall Thickness (in.)	Initial Hoop Stress (psi) ^a	Time To Failure (hr)
1000	316727	0.010	66,700	Burst on Loading
	7-2489	0.012	55,200	Burst on Loading
	7-2489	0.012	48,000	308.1
	31627	0.014	49,029	356 - Test in Progress

^aBased on mean tube diameter

SSAA-310 - ELECTRON MICROSCOPIC ANALYSIS OF AUSTENITIC STAINLESS STEEL CLADDING

W. K. Appleby, M. L. Bleiberg, R. Stickler*, and B. Weiss*

OBJECTIVES

The objectives of this task are to augment the level of understanding of microstructure on deformation mechanisms of Type 316 stainless steel cladding over that obtained in Task SSAA-210. This program will provide information on sub-structural features such as dislocation network density, dislocation distribution, and subgrain size. Also, the cladding will be examined by Laue back-reflection techniques to determine whether any preferred orientation effects, such as preferential precipitation of second phases, occur. These features will be correlated with the test variables described in Task SSAA-210 and will provide a more fundamental basis for examining the influence of microstructure on the mechanical properties of Type 316 stainless steel cladding.

CURRENT PROGRESS

This progress report describes the experimental progress made during this working period and also includes a summary of the pertinent literature available on Type 316 stainless steel.

Sample Designation and Summary of Requested Investigations

The submitted samples consisted of four groups of six approximately 1/4-inch O.D. These four groups were identified as follows:

- Group 1: Lot 316727 (Superior Tube Company Order 7-165)
Nominal 0.010-inch wall thickness
- Group 2: Lot 316726 (Superior Tube Company Order 7-164)
Nominal 0.012-inch wall thickness
- Group 3: Lot 316728 (Superior Tube Company Order 7-166)
Nominal 0.014-inch wall thickness
- Group 4: Lot (not available) (Superior Tube Company 7-2489)
Nominal 0.012-inch wall thickness

All samples of these groups were made from Type 316 stainless steel, Heat #20303.

The experimental investigations on these samples will include:

- a. the determination of microstructure, second phase content (morphology, distribution, nature) by light microscopic (LM), electron microscopic

*Westinghouse R&D Center

(EM), x-ray diffraction (XD), electron diffraction (ED), and electron beam microanalytical (EMA) techniques;

- b. the determination of stacking fault energies, dislocation arrangements, and densities by direct transmission electron microscopic techniques (TEM); and
- c. the determination of crystallographic orientations, textures, and residual stresses by x-ray diffraction techniques (XD).

Any plastic deformation of the tube samples was avoided during handling and specimen preparation in order to insure determination of the exact microstructure in the as-received tubes.

Summary of Literature on Microstructure of Type 316 Stainless Steel

Molybdenum-stabilized Type 316 stainless steel is widely used in steam generators and turbines as piping and superheater tube material due to its good mechanical properties at temperatures up to 650°C. [3] A vast number of publications deal with the mechanical properties of Type 316 stainless steels that are not subject to present investigations. The microstructure of Type 316 stainless steel, the effects of fabrication processes (melting practices, heat treatments, cold work) on microstructure and mechanical properties (e.g. creep), and the microstructural and property changes occurring during exposure to steam plant environments have been studied by several investigators [3, 4, 5, 6, 7, 8]. Discrepancies between the data reported by the various investigators indicate that minor variations in composition, mechanical or thermal pretreatment can cause significant variations in properties.

Aging in the temperature range of 600 to 800°C results in the precipitation of various phases [7,8,9], listed in Table 4. The effect of time and temperature of heat treatment on the appearance of the major precipitated phases ($M_{23}C_6$, σ , chi) is summarized in Figure 4. Considerable differences are obvious between the data from two different investigators. The effect of solution treatment temperature on σ -phase formation was studied by Wiegand and Doruk [7], who found that increasing solution treatment temperatures enhance the formation of intermetallic phases such as σ .

Blenkinsop and Nutting [8], also studied the influence of cold work on σ -phase formation. Samples solution treated at 1300°C and then subjected to 5% deformation at room temperature do not exhibit microstructures after aging substantially different from undeformed specimens. Cold work between 5 and 40% prior to aging resulted in considerable changes in microstructure, especially in precipitation of the intragranular σ -phase.

Barnby [6] investigated the effect of strain aging on the creep behavior of Type 316 stainless steel in comparison with microstructural changes. The creep rate of material in which $(Fe,Cr)_{23}C_6$ was removed from solution

Table 4

Detected Phases in Annealed Type 316 Austenitic Stainless

Steel after Long-Time, High-Temperature Exposure

Phase	Crystal Structure and Lattice Parameters	Temperature (°C)	Remarks	Reference
$M_{23}C_6$	fcc; $a = 10.6 \text{ \AA}$	600-800	containing also Mo	6
Sigma (σ)	tetragonal; $a = 9.21 \text{ \AA}$ $c = 4.78 \text{ \AA}$	600-850		6
X ($F_{36}Cr_{12}Mo_{10}$)	bcc; α -manganese structure; $a = 8.920 \text{ \AA}$	600-800	structure similar to σ -phase	7,5
Ferrite (α)	bcc $a = 2.86 \text{ \AA}$		after solution treatment at 1400°C	10
η (Fe_2Mo)	hex $a = 4.73 \text{ \AA}$ $c = 7.72 \text{ \AA}$	650-750 (after 10,000 hr)		7,5,11

Figure 4 Time-Temperature-Precipitation Diagram of $M_{23}C_6$, σ and chi (X) in Type 316 Stainless Steel

by prior precipitation was found to be increased considerably compared to solution-treated material in the temperature range of 600 to 800°C for a stress of 8 tsi.

The most extensive studies of the effects of pretreatments on properties of Type 316 stainless steel were performed by Garofalo, et al, [10] who found that considerably increased creep resistance is connected with microstructural changes produced by a thermomechanical pretreatment. The optimum creep properties were obtained by a treatment consisting of 25 to 30% deformation followed by a precipitation treatment (24 hours at 900°F and 216 hours at 1300°F). Dislocation arrangement of annealed material was not studied in great detail. The dislocations in annealed material Type 316 stainless steel showed a random distribution with no tendency to be aligned.

The influence of stacking fault energy on the properties of austenitic steels is not known at the moment. It has been proposed that there should be a considerable effect of stacking fault energy on the mechanical properties, precipitation behavior, etc. Silcock, et al [11] and Honeycombe et al [12] measured the stacking fault energies of various austenitic steels, not including Type 316 stainless steel. No relationship could be found to their chemical analysis. From these data, we might expect a low stacking fault energy. In Reference 9, the value for Type 316 stainless steel was listed 11 erg/cm².

It should be pointed out that most of the published investigations are concerned with microstructural and property changes under temperature conditions prevailing in fossil steam power plants (600 to 800°C), and invariably, the experiments have been performed on pieces with relatively large cross-sections. This is in strong contrast to LMFBR conditions where thin-walled tubes will be exposed to temperatures ranging from 300 to 700°C. Little information is available on the effects of neutron irradiation on microstructural changes (dislocation structure) in Type 316 stainless steel; in contrast, numerous investigations were performed on this steel concerning the mechanical properties. Most of the irradiation tests were performed in a temperature range of 50 to 350°C and resulted in embrittlement of the material due to radiation damage and small bubbles filled with inert gases (He) produced by neutron reactions [15,16,17]. Far less is known on structural changes during higher-temperature irradiation in fast neutron spectra conditions that prevail in LMFBR.

Recently, Holmes, et al, [19] reported a rather sophisticated change in dislocation structure in Type 304 stainless steel after irradiation at 532°C with 1.4×10^{22} n/cm², $E > 0.18$ Mev, resulting in numerous voids and Frank sessile loops. An increase in yield stress was obtained. Furthermore, the annealing behavior of this steel was studied with the result that full recovery of the yield strength was observed at 816°C, where both the voids and dislocations were annihilated.

Pfeil and Arkell^[21] and Cawthorne, et al^[18], studied the influence of irradiation on Type 316 stainless steel at approximately 550°C with a dose up to 7×10^{22} n/cm², resulting in swelling of the material due to void information. Annealing experiments indicated that these voids were not filled with gas at equilibrium pressure.

EXPERIMENTAL WORK

Methods of Examination

a. Light Microscopy (LM)

The tubes were examined in the as-received condition to obtain information about the outer-surface roughness. The depth of the grooves was determined by focussing to different positions of the grooves. To obtain information on changes in microstructure, grain size, and precipitates, the specimens were mounted in Bakelite, metallographically polished, and etched in a mixture of 10% Br₂ in anhydrous methanol. The grain size was determined according to the ASTM scale.

b. Electron Microscopy (EM)

Extraction replicas (Replica Technique) of the various tubes were examined in the EM in order to determine the nature and distribution of precipitates and inclusions. Direct-carbon extraction replicas were prepared as follows: The tubes were longitudinally sectioned to remove the outer surface layer, the samples were electropolished in a solution of 10% perchloric acid and 90% acetic acid at temperatures between 0 and 20°C at 30 volts and 400 to 500 milliamperes. To remove a possible passivating layer, the sample was slightly mechanically polished, thoroughly cleaned, etched for 1 to 2 seconds in a mixture of 10% Br₂ in anhydrous methanol, and washed in methanol. The etchant is known to attack the matrix only, while most of the carbides remain unattacked. A carbon film was vapor deposited onto the etched surface. The carbon film was detached by a second etch in the Br₂-methanol solution, washed in methanol, floated onto a water surface and mounted on EM specimen grids. Most of the precipitated particles and most of the inclusions in the surface of the etched specimen remained attached to the carbon film in an almost undisturbed position.

Examination of the portions of these C-extraction replicas in the electron microscope gave information on the morphology, size, and distribution of the particles, while selected-area-electron-diffraction allowed identification of particles by comparison of the measured d-values with those reported on the ASTM Card File. [13]

c. Transmission Electron Microscopy (TEM)

TEM was used to determine dislocation arrangement, precipitate distribution, dislocation density, and stacking fault energy. A special

technique was developed to prepare thin foils from the as-received tube samples. Therefore, preparation of thin foils suitable for examination was carried out using a two-stage electrochemical polishing technique. Pre-thinning of the tube sections was achieved by use of a 10% perchloric acid and 90% acetic acid solution. To protect the edges, they were coated with lacquer. The polishing conditions were 30 volts, 400 to 500 milliamperes, and a solution temperature of 0 to 20°C. The cathode consisted of stainless steel. After polishing, the tubes had to be washed carefully in methanol and acetic acid/methanol, and dried in hot air. To determine the polishing rate, the wall thickness was measured with a pointed micrometer after every 5 minutes of polishing. The polishing rate was found to be approximately 10 $\mu\text{m}/\text{minute}$ (Figure 5). The polishing was stopped at a tube thickness of 4 to 5 mils. With a specially-designed punch, the specimens discs were carefully punched out to avoid deformation. The discs had a diameter of 3 mm. For final thinning, these discs were mounted into a twin-jet electropolishing setup, shown schematically in Figure 6. This compact Teflon-apparatus consists of a small centrifugal pump connected to two opposing jet nozzles approximately one centimeter apart and submerged in the electrolyte. Pt-contacts inside the nozzles act as anodes. The specimen, of the diameter to fit directly in the electron microscope specimen holder, is held in a ring-shaped Teflon holder. The cathode contacts are connected to the specimen with a thin Pt-ring. This final polishing was carried out in a 10% perchloric acid and 90% acetic acid solution at 30 volts and 50 milliamperes. Immediately after the first hole appeared, the current was disconnected. The foil was washed thoroughly in methanol and acetic acid/methanol, and dried in hot air. All specimens were examined in a 100-kv Siemens Elmiskop electron microscope.

Dislocation densities were determined by two methods, [20] : (a) the number of intersections of dislocations with the foil surface was counted, and (b) the number (n) of dislocations crossing a line (length = ℓ) drawn on the electron micrograph was counted, and the density was calculated as $p = n/(\ell \cdot t)$, where t is the foil thickness calculated by slip trace analysis.

d. X-Ray Diffraction Studies (XD)

XD studies were carried out to determine the texture of the as-received tube samples. A back-reflection technique was used ($\text{CrK}\alpha$ with V-filter, distance between sample and camera of 3 centimeters). XD-patterns were taken from three different regions: from the as-received inner and outer tube surfaces, from the outer surface, and after removal of 25 μm^* by electropolishing.

e. Electron Beam Microanalysis (EMA)

EMA provides information on the chemical composition or changes in chemical composition of areas as small as 1- μm diameter.

*25 μm = 1 mil

Figure 5 Polishing Rate of Type 316 Stainless Steel in a Solution of 10% Perchloric Acid and 90% Acetic Acid

3039-11

Figure 6 Twin-jet Electropolishing Apparatus Schematic
(Arrows Indicate Electrolyte Flow)

3039-13

In the EMA, a fine beam (less than 1- μ m diameter) of high-energy electron (10 to 30 kev) is focussed on the specimen surface. The fraction of beam-electrons penetrating the specimen is a function of specimen composition (atomic number) and surface topography, so that the absorbed current can be used as a qualitative analytical signal. The penetrating electrons interact with the atoms in the irradiated volume (approximately 3 μ m³) and produce characteristic x-rays. Spectroscopic analysis of this x-ray radiation yields information of qualitative and quantitative composition in the specimen volume.

In addition to the point analysis, the electron beam can be scanned over areas on the specimen surface (up to 400 μ m x 400 μ m) in a TV-type pattern. The respective monitored signals (absorbed electron current or x-ray intensities) are used to modulate the beam intensities of oscilloscopes which are synchronous with the electron beam in the microanalyzer. Photographic recording of the oscilloscope images provides the scanning electron micrographs or scanning X-ray micrographs, respectively. A rapid qualitative and semi-qualitative survey of the distribution of elements in an approximately 1- μ m thick surface layer of the specimen is obtained with the aid of these scanning micrographs.

For this investigation, EMA was used to characterize the chemical composition of inclusions or precipitates. The tube sections were electropolished, flattened, metallographically mounted, and finally polished with 0.35 μ m diamond powder.

Results

All the specimens were examined in the as-received condition. In Figure 7, an LM is shown of the surface of Tube No. 316726. The surface was ground with circumferential grooves. The roughness was measured to be approximately 6 to 10 μ m. All samples had the same surface roughness.

After removing 25 μ m of the surface layer by electropolishing, the unetched surface showed small inclusions (Figure 8), which were aligned parallel to the tube axis. The particle size was in the range of 1 μ m or less. In addition, some larger particles could be detected clustered together in stringers. The grain size of all four samples was ASTM 7 to 8. Occasionally, larger grains were detected.

Figure 9 shows the microstructure of a longitudinal section. Figure 10 shows the microstructure of a transverse section. No characteristic changes could be detected between the various samples.

Ring patterns in Laue x-ray back-reflection diagrams indicated that the outer surfaces of all tubes are heavily cold worked. A Laue back-reflection

3039-7

500X

Figure 7 Optical Micrograph of Representative Area - As Received (Tube No. 316726)

500X

Figure 8 Optical Micrographs of Representative Area - Electropolished (25 μ m) (Tube No. 316726)

500X

Figure 9 General View of the Microstructure of the Longitudinal Section (Tube No. 316726)

500X

Figure 10 Equiaxed Grains in a Transversed Sectioned Area (Tube No. 316726)

pattern of the as-received sample No. 316726 is shown in Figure 11(a); 25 μm had to be removed to obtain a spot pattern indicating a strain-free material [Figure 11(b)]. The small inclusions were too fine for identification by EMA. Furthermore, the identification by TEM was impossible because these small particles were removed during the process of polishing and thinning. Replicas, which were taken from the polished surface, showed no grain boundary precipitation (Figure 12).

Some larger particles were detected. Figures 13 and 14 show a bright field and dark field EM of these particles. Selected area ED pattern of these inclusions show several ring and spot systems. The measured d-values are listed in Table 5. The inclusions are FCC with a value of $4.33\text{\AA}$ and according to ASTM Card No. 6-0614 are TiC. With EMA some of these particles could be analyzed. Scanning x-ray micrographs of the larger inclusions show (Figures 15 and 16) an enrichment in Ti, and also indicate that the particles have a lower atomic number than the matrix. Figure 16 also shows the scanning micrograph of a small inclusion, which is enriched in Mn and S.

TEM showed no significant difference in the dislocation arrangement in all tube samples. Figure 17(a) shows the dislocation arrangement in tube No. 316726. Figure 17(b) shows the dislocation arrangement in Tube No. 7-2489; most of the dislocations are arranged in rows.

The calculated dislocation densities are listed below:

Tube No.	Dislocation Lines/ cm^2	Intercept Method
		t (foil thickness $\approx 2200\text{ \AA}$)
316726	$(3 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$
316727	$(3 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$
712489	$(3 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$
316728	$(3 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$

SUMMARY AND CONCLUSIONS:

The results of the described investigations are summarized in Table 6. As indicated, some examinations will be completed during the next working period.

The results of the investigations to date did not reveal any measurable differences between the four submitted tube samples. Thus, the following observations and conclusions apply equally to all four samples.

- The outer surfaces of the tubes are heavily cold worked up to a depth of approximately 25 μm (1 mil). The cold work was introduced by a circumferential grinding or abrasion treatment.

(a) OUTSIDE; COLDWORKED

(b) 25 μm REMOVED, INSIDE; STRAINFREE

Figure II X-ray Back Reflection of the Outside and Inside of the Tubes

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Figure 12 Electron Micrograph of Direct-C Extraction Replica
(Tube No. 316726)

3039-1

Figure 13 Electron Micrograph of Direct-C Extraction Replica
(Bright Field)

3039-2

Figure 14 Electron Micrograph of Direct-C Extraction Replica
(Dark Field; (002) Reflex)

3039-3

Table 5

Evaluation of ED Patterns of Extraction

Replicas of Tube No. 316726

$d_{\text{observed}} (\text{\AA})$	$d_{\text{TiC}} (\text{\AA})$, ASTM Card No. 6-0614
2.51	2.508
2.17	2.179
1.52	1.535
1.298	1.311
1.27	1.255
1.065	1.086
0.998	0.997
0.96	0.971

ABSORBED ELECTRONS

Ti K α

Figure 15 Scanning-electron and Scanning-X-ray Micrographs
(Tube No. 316726)

3039-5

Ti K α

S K α

Mn K α

Figure 16 Scanning X-ray Micrographs (Tube No. 316726)

3039-4

Figure 17a Transmission Electron Micrograph, Dislocations
are Arranged in Rows (Lot No. 7-2489)

3039-8

Figure 17b Transmission Electron Micrograph, Dislocations
are Arranged in Rows (Tube No. 316726)

3039-9

Table 6

Summary of Results

	Sample Number			
	316726	316727	316728	7-2489
Roughness of surface (μm)	6-10	6-10	6-10	6-10
Microstructure: Grain Size according to ASTM Precipitation & inclusion arrangement	7-8 small inclusions ($<1 \mu\text{m}$) aligned into stringers; some larger inclusions; no grain boundary precipitation	7-8 same as 316726	7-8 same as 316726	7-8 same as 316726
Amount of cold work (Method: x-ray back reflection) Outer surface layer + 25 unremoved and inside of tube	cold worked strain free	cold worked strain free	cold worked strain free	cold worked strain free
EM (replica technique) Grain boundary precipitation Intragranular precipitation + ED of precipitates	none few fcc, $\alpha_0 = 8.35 \text{ \AA}$	*	*	*
TEM Dislocation arrangement	some random, majority are arranged in rows	same as 316726	same as 316726	same as 316726
Dislocation density (lines/ cm^2)	$(3 + 2) \times 10^8$	$(3 + 2) \times 10^8$	$(3 + 2) \times 10^8$	$(3 + 2) \times 10^8$
Intercept method (P)	$(8 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$	$(8 \pm 2) \times 10^8$
Stacking fault energy (erg/ cm^2)	*	*	*	*
EMA Particles identified	Ti-enriched particles Mn and S-enriched particles	*	*	*

* Examination will be completed during the following period.

- b. The inner surfaces of the tubes consist of recrystallized material.
- c. With the exception of the outer surface layer, the tubes consist of equiaxed recrystallized grains of ASTM grain size 7 to 8. Occasionally, isolated larger grains could be found (grain size 5 to 6).
- d. The tubes consist of solution-treated material; no grain boundary precipitates could be observed.
- e. Small particles of Ti (C,N) are present in the tubes, aligned in rows parallel to the tube axes.
- f. Massive inclusions are present in relatively high amounts, aligned in rows parallel to the tube axis. These inclusions are enriched in Ti or Mn and S, and have a lower atomic number than the matrix (probably oxides or carbonitrides).
- g. The measured dislocation density (higher than $10^8/\text{cm}^2$) is higher than to be expected for recrystallized material ($10^7/\text{cm}^2$). Most of the dislocations are arranged in rows. The dislocation density and arrangement indicate that the tubes have been subjected to slight deformation after the recrystallization heat treatment.

REFERENCES

1. R. Garafalo, R. Von Gemmingen, and W. F. Domes, "Creep Behavior of Austenitic Stainless as Affected by Carbides Precipitated on Dislocations," Trans. ASM, V54, 1961, pp 430-444
2. Personal Communciation, J. Simmons USAEC, to P. Murray, Westinghouse Electric Corporation.
3. H. S. Blumberg, "Type 316 Stainless Steel for Elevated Temperature Power Plant Applications," Climax Molybdenum Co., 1965.
4. Hr. R. Dautz and H. Gerlach, Arch. f. d. Eisenhw. H.2, Jg. 39, 1968, 151.
5. J. H. Harlow, ASM-Joint Intern. Conf. on Creep, New York, 1963.
6. J. Barnby, J. of the Iron & Steel Inst., 1966, 23.
7. H. Wiegand, A. M. Doruk, Arch. f. d. Eisenhw. H.8, Aug. 1962, 559.
8. P. A. Blenkinsop and J. Nutting, J. of the Iron & Steel Inst., Sept. 1967, 953.
9. H. Gerlach, E. Schmidtman, Arch. f. d. Eisenhw., H.2, Feb. 1968, 139.
10. F. Garofalo, R. U. Gemmingen and W. Domus, Trans. of the ASM, Vol. 54, 1961, 430.
11. J. Silcock, R. W. Rookes and J. Barford, J. of the Iron & Steel Inst., June 1960, 623.
12. Metals Handbook.
13. ASTM Card 6-0622.
14. R. S. Barnes, Nature, 1965, June, No. 499, p. 1307.
15. P. C. Pfeil and D. R. Harries, "Flow and Fracture of Metals and Alloys in Nuclear Environments", ASTM STP-380 (1964) 202.
16. D. R. Harries, J. Brit, Nucl. Engrg. Soc. (1966) 74.
17. H. Böhm, H. Hauck and G. Hess, J. of Nucl. Matls. 24 (1967) 198.
18. C. Cawthorne, et al, TRG Memo 4345 D; Dounreay Exp. Reactor Establishment.

REFERENCES (CONTINUED)

19. J. J. Holmes, et al, Acta Met., Vol. 16, July 1968, 955.
20. P. B. Hirsch, et al, "Electron Microscopy of Thin Crystals,"
1965 Butterworth, London.
21. P. C. Pfeil and D. R. Arkell, FRPC/FEWP (67) p. 435, AERE Harwell.

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