CEND-3742-352

unclass
Kahn 6/10/69

VANADIUM PURIFICATION

NINTH QUARTERLY PROGRESS REPORT

Issued April, 1969

NUCLEAR POWER DEPARTMENT
COMBUSTION ENGINEERING, INC.

P1553

DISCLAIMER

CEND-3742-352
UC-25, Metals, Ceramics and Materials
TID-4500, 53rd Edition

VANADIUM PURIFICATION
NINTH QUARTERLY
PROGRESS REPORT

For Period

October 1, 1968 to March 31, 1969

Prepared by:

J. C. La Vake, CENPD
S. S. Christopher, CENPD
J. R. Stewart

Contract AT(30-1)-3742
U. S. Atomic Energy Commission

Issued April, 1969

Unclassified
Classification

William H. Simon 4/69
Authorized Classifier, date

Approved by

W. P. Chernock
W. P. Chernock, Manager
Nuclear Laboratories

NUCLEAR POWER DEPARTMENT
COMBUSTION ENGINEERING, INC.
WINDSOR, CONNECTICUT

CEND-3742-352
UC-25, Metals, Ceramics
and Materials
TID-4500, 53rd Edition

EXTERNAL DISTRIBUTION	No. of Copies
Mr. J. W. Crawford, Assistant Director Office of Engineering Standards U. S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
Mr. J. Edward Fox Fuels and Materials Branch U. S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	2
Mr. Jules M. Simmons, Chief Fuels and Materials Branch U. S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
Mr. C. E. Weber Fuel Engineering Branch U. S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
Dr. Glen W. Wensch, Chief Liquid Metal Projects Branch U. S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
U. S. Atomic Energy Commission New York Operations Office 376 Hudson Street New York, New York 10014 Attn: Development Contracts Division	1
U. S. Attomic Energy Commission New York Operations Office 376 Hudson Street New York, New York 10014 Attn: NYO Library	1

EXTERNAL DISTRIBUTION (Continued)	No. of Copies
Mr. H. S. Potter, Chief New York Patents Group U. S. Atomic Energy Commission Brookhaven Office Upton, Long Island, New York 11973	1
U. S. Atomic Energy Commission Division of Technical Information Extension Post Office Box 62 Oak Ridge, Tennessee 37830	1
Mr. Leonard S. Hartman, Authorized Representative U. S. Atomic Energy Commission New York Operations Office 376 Hudson Street New York, New York 10014	1
M. L. Kelman Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439	1
Mr. J. H. Kittel Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439	1
Mr. F. L. Yaggee Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439	1
Dr. D. H. Gurinsky Brookhaven National Laboratory Upton, Long Island, New York 11073	1
Mr. R. D. Baker Los Alamos Scientific Laboratory Los Alamos, New Mexico 87544	1
Mr. P. Patriarca Oak Ridge National Laboratory Post Office Box X Oak Ridge, Tennessee 37830	1

EXTERNAL DISTRIBUTION (Continued)	No. of Copies
Mr. W. O. Harms Oak Ridge National Laboratory Post Office Box X Oak Ridge, Tennessee 37830	1
Mr. T. T. Claudson Pacific Northwest Laboratory Battelle Memorial Institute Post Office Box 999 Richland, Washington 99352	1
Mr. S. J. Paprocki Battelle Memorial Institute Columbus, Ohio 43001	1
Mr. O. N. Carlson Iowa State University Institute of Atomic Research Ames, Iowa 500010	1
Mr. D. J. McPherson IIT Research Institute 10 West 35th Street Chicago, Illinois 60616	1
Dr. J. L. Ballif Atomics International, Inc. P. O. Box 309 Canoga Park, California 91304	1
Mr. L. R. Weissert Babcock & Wilcox Company Atomics Energy Division Lynchburg, Virginia 42502	1
Mr. E. L. Zebroski General Electric Company Vallecitos Atomic Laboratory Post Office Box 1131 San Jose, California 95125	1
Mr. J. A. McGurty General Electric Company Cincinnati, Ohio 45215	1

EXTERNAL DISTRIBUTION (Continued)	No. of Copies
Mr. R. C. Werner Mine Safety and Appliance Company 230 North Braddock Avenue Pittsburgh, Pennsylvania 15208	1
Mr. K. Puechl Nuclear Materials and Equipment Corporation Apollo, Pennsylvania 15613	1
Mr. A. Strasser United Nuclear Corporation Fuels Division New Haven, Connecticut 06511	1
Mr. R. T. Begley Westinghouse Electric Corporation Astro Nuclear Laboratory Post Office Box 10864 Pittsburgh, Pennsylvania 15236	1

CEND-3742-352
UC-25, Metals, Ceramics and Materials
TID-4500, 53rd Edition

VANADIUM PURIFICATION

Ninth Quarterly Progress Report

Table of Contents

List of Tables

CEND-3742-352
UC-25, Metals, Ceramics and Materials
TID-4500, 53rd Edition

VANADIUM PURIFICATION

Ninth Quarterly Progress Report

List of Illustrations

ABSTRACT

During this report period, stress-rupture testing was continued on the high purity V-15Cr-5Ti sheet to obtain data on time-to rupture and minimum-creep-rate properties. Five hundred-hour stress-rupture tests have shown contamination; however, modifications to the creep furnace, which have just been completed, are expected to eliminate this problem.

Recrystallized sheet has been electron beam and TIG welded. The TIG welds showed low ductility due to precipitate agglomeration. Heat treatments are being performed in an attempt to increase ductility. Electron beam welds, with their faster cooling rates, showed good ductility.

Twenty-seven pounds of excess V-15Cr-5Ti sheet have been sent to Argonne National Laboratory for use by other laboratories.

I. INTRODUCTION

This program was initiated to produce a 100-pound, high purity (<500 ppm total interstitial content) vanadium ingot by a process suitable for commercial applications. The process developed by Wah Chang, Albany, Oregon, to produce the ingot is as follows:

1) aluminothermic reduction of V_2O_5;
2) consolidation by electron beam melting the vanadium reductions;
3) double electron beam melting.

The high purity vanadium ingot was then alloyed by:

1) compaction of vanadium, titanium and chromium flakes and chips;
2) double arc melted, first in argon, then in vacuum.

Combustion Engineering is presently evaluating the high purity (~500 ppm interstitial) V-15Cr-5Ti alloy sheet. The purpose of this evaluation is to determine the effect of lower interstitial content on the mechanical properties of this alloy. Argonne National Laboratory is in the process of determining the mechanical properties on the same alloy with an interstitial content of approximately 1200 ppm. The present program will provide comparison of short term tensile and stress-rupture data on both base metal and welded sheet material.

Argonne National Laboratory, in their evaluation of the lower purity material, found that recrystallization occurred after annealing at 900°C for 1 hour with a resulting grain size of ASTM-9 to 10. Heat treating at higher temperatures produced little if any change in grain size up to 1400°C. Above this temperature very rapid grain growth occurred. It is assumed that the abrupt increase in grain size was due to solution of grain boundary precipitates above 1400°C. Argonne National Laboratory chose to anneal their material at 1250°C for 1 hour for optimum stress rupture properties.

Heat treatment studies on the higher purity material showed complete recrystallization after 1 hour at 1050°C. The grain size after this treatment was ASTM-7 to 8. Annealing above 1050°C caused initiation of grain growth. This differed from the Argonne National Laboratory results, and is assumed to be related to insufficient grain boundary impurities in the higher purity material to retard grain growth. Heat treating at 1250°C for 1 hour resulted in a grain size of ASTM-4 to 5, as compared to approximately ASTM-8 for the Argonne National Laboratory material.

Based on the above heat treatment studies, it was decided to test the high purity material in the 1050°C and 1250°C annealed conditions. The majority of the tests will be performed on recrystallized (1050°C) specimens since this would more nearly duplicate the structure and grain size of the Argonne National Laboratory tests. A limited number of tests will be performed at 1250°C to evaluate the effects of grain size and second phase on strength properties.

II EXPERIMENTAL EFFORT AND DISCUSSION

During the past two quarters, stress-rupture testing has continued. Table I presents all the stress-rupture data generated to date, tests Nos. 11, 12, 13, 14 and 16 being performed during this report period. Figure 1 indicates the lack of third stage creep for tests Nos. 11, 12 and 13 run at 650°F for 40 to 60 hours. Other investigators have seen this phenomenon, attributing strain aging as the responsible mechanism. This is further substantiated by serrated-type tensile stress-strain curves previously obtained at this temperature.

As indicated by tests Nos. 14 and 16, we have attempted to run the 500-hour stress-rupture tests. However, due to contamination during the longtime tests, poor data have resulted. Figure 2 presents the creep curves for tests Nos. 14 and 16. As shown, interstitial contamination has resulted in strengthening of the alloy. This is shown by the decrease in the minimum creep rate of the material. Test No. 14 was run prior to an overhaul of the furnace retort; test No. 16 was run after. The linear secondary creep of test No. 16 remained constant for 120 hours, 30 more hours than test No. 14, indicating a somewhat cleaner system.

All precautions are taken to preserve the purity of the vanadium alloy during testing. The elevated stress-rupture tests have been run in static purified argon. The argon is passed through a molecular sieve, then through 1600°F titanium sponge. The V-15Cr-5Ti test samples are further protected by wrapping in either tantalum or columbium foil. The argon atmosphere at approximately 5 psig is established in the furnace after three vacuum pump-downs and argon backfills. The vacuum system, a diffusion pump with liquid nitrogen cold trap, is capable of obtaining vacuums in the system of 10^{-6} torr.

Table I. V-15Cr-5Ti Stress-Rupture Data

Temp (°C)	Stress (ksi)	Time to Rupture (hr)	Time to 3rd Stage (hr)	Min Creep Rate (in./in./hr)	Initial ε (%)	ε_0 Intercept (%)	ε at 3rd Stage (%)	Final ε (%)	Test No.
650	74.0	3.0	1.3	4.6×10^{-2}	11.4	11.4	4.6	25.0	5
650	72.5	5.6	2.7	2.2×10^{-2}	11.2	11.5	14.0	22.0	6
650	65.0	58.8	33.0	1.0×10^{-3}	5.1	5.6	7.1	18.5	7
650	63.0	45.8	44.0	3.1×10^{-4}	4.4	4.9	6.3	6.8	11
650	64.0	49.3	39.3	4.1×10^{-4}	4.6	5.0	7.0	7.0	12
650	64.0	63.0	63.0	3.9×10^{-4}	4.8	5.6	8.0	8.0	13
800	50.0	1.4	0.5	6.1×10^{-2}	1.2	2.4	4.6	34.0	3
800	40.0	28.1	12.0	4.0×10^{-3}	0.2	0.8	3.2	21.0	4
800	37.5	28.2	8.5	1.4×10^{-2}	0.1	0.4	2.0	18.0	8
800	35.0	118.3	28.0	5.8×10^{-4}	0.1	0.6	2.0	16.5	9
800	35.0	72.0	27.0	1.0×10^{-3}	0.1	0.6	4.0	23.5	10
800	32.0	425	--stopped--	2.0×10^{-5}	0.1	0.4	---	---	14
800	32.0	580	--stopped--	2.6×10^{-5}	0.1	0.2	---	---	16

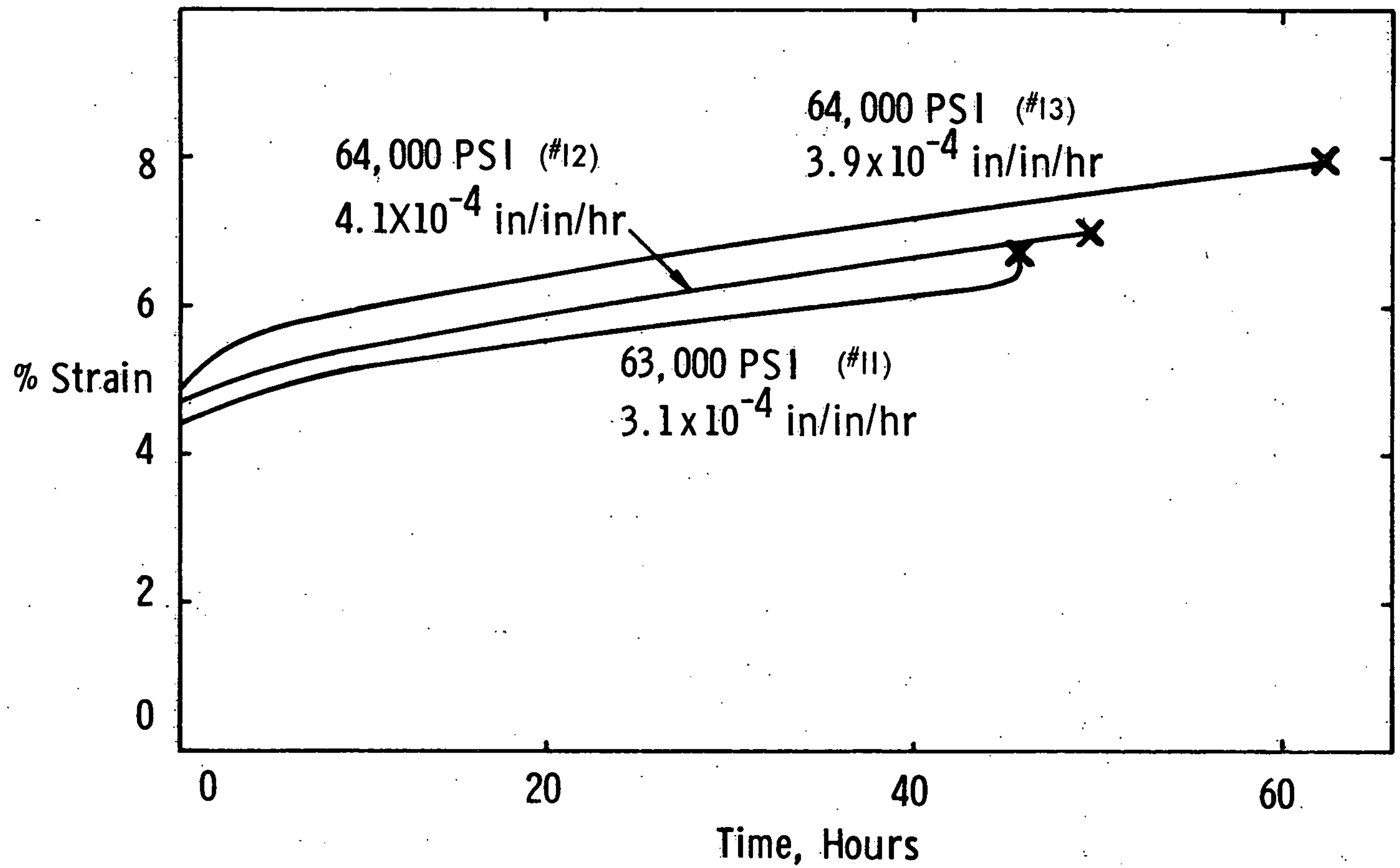


Figure I. 650°C Stress-Rupture Test Results of V-15Cr-5Ti Sheet in Recrystallized Condition (1050°C/1 hr)

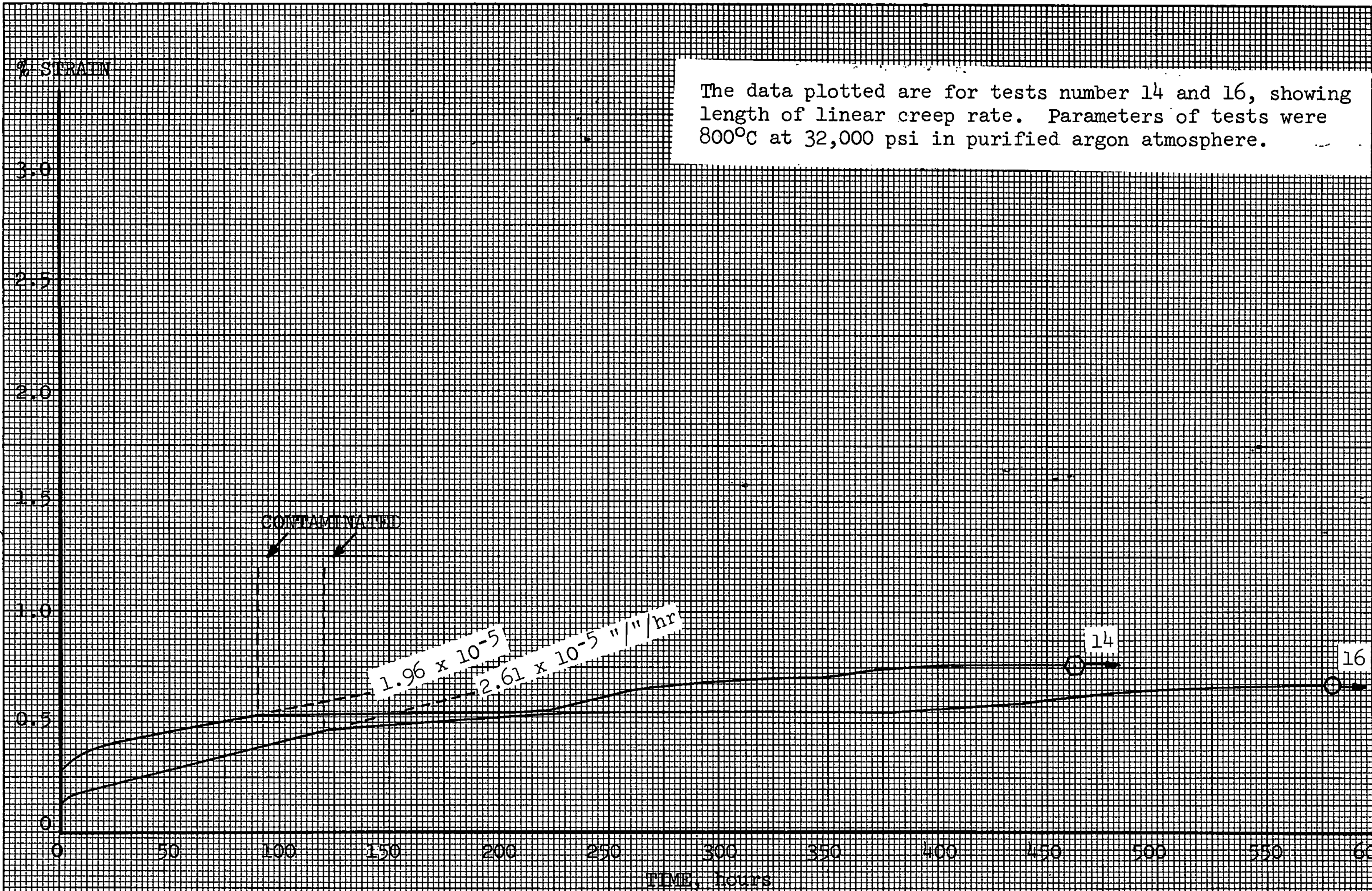


Figure 2. Creep Curves for V-15Cr-5Ti Alloy Tested in Recrystallized Condition (1050°C/1 hr)

The furnace retort has been recently modified to provide additional protection for the test sample. This entails a coil of tantalum wire placed inside the furnace directly above the foil-wrapped sample. Through resistance heating, the coil will be maintained at 1100°C while the sample is tested at 800°C. It is expected that this hot getter will further protect the sample from contamination. Tests have started; however, data will not be available until the next report period.

Other laboratories testing vanadium alloys have also had contamination problems during stress-rupture testing. However, our problem is further aggravated by the high purity of our starting material ($\sim$ 400 ppm total interstitial content). Results of interstitial analyses show that contamination to the extent of 1100 ppm interstitial content (H, C, N and O) is sufficient to alter the creep rate. Most investigators start with material containing 1200 to 1500 ppm interstitials.

A comparison of the linear secondary creep rates of tests Nos. 14 and 16 to those of shorter time tests is plotted in figure 3. The creep rates show excellent agreement to the previous data, indicating the initial minimum creep rates are representative of the uncontaminated material.

The last phase of this program is an evaluation of the TIG and electron beam welds in the high purity V-15Cr-5Ti sheet. The 0.040-inch thick sheet has been welded by both methods with the following schedules:

Electron Beam	Tungsten Inert Gas
80 kilovolts	1/8" dia. thoriated tungsten electrode
2.5 milliamps	90 amp dc
30" per minute travel	10" per minute travel

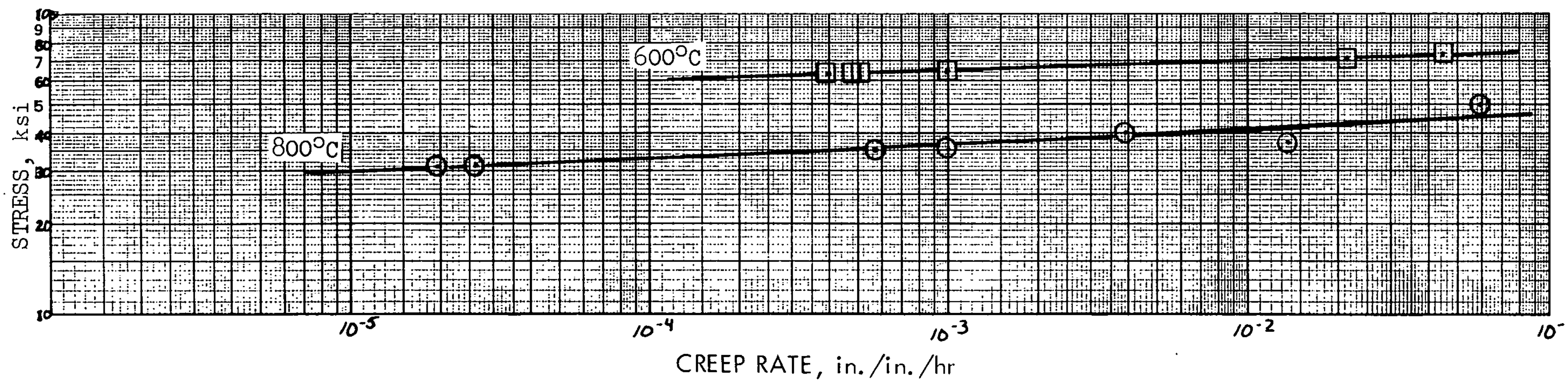


Figure 3. Minimum Creep Rate vs Stress - V-15Cr-5Ti Alloy Tested in Recrystallized Condition (1050°C/1 hr)

All sheets were welded from one side with a "head-on-plate", necessitating no filler metal or shearing. The weld beads were transverse to the rolling direction of the sheet. All material was welded in the recrystallized condition (1050°C/1 hr). After welding, the sheets were bowed due to weld metal shrinkage. Therefore, another 1050°C/1 hour heat treatment was performed to faciliate straightening and machining. Figures 4 and 5 show the head-on-plate welds.

Tensile testing of the TIG and electron beam welds has started. Results from the tests are shown in table II which indicates brittle TIG welds.

Table II. Tensile Tests on Welded Sheet
V-15Cr-5Ti
Preweld and Postweld Anneals of 1050°C/1 hr

Weld	Test Temp	UTS ksi	Y.S. ksi	R.A. %	Elong %	Comments	No.
TIG	R.T.	80.40	73.6	∿ 1%	2.5	Failed in weld	TIG-2
TIG	R.T.	68.5	62.3	16.0	3.0	Failed in weld	TIG-3
EB	R.T.	90.1	74.1	47.0	18.0	Failed in Parent metal	EB -2
EB	R.T.	91.8	75.4	45.6	21.5	Failed in Parent metal	EB -3
none	R.T.	87.5	∿ 75	46.4	26.0	(Control)	-----
TIG	800°C	23.5	17.0	----	∿ 3	Failed in weld	TIG-1
EB	800°C	63.0	41.0	45.6	21.5	Failed in Parent metal	EB -1
EB	800°C	60.0	38.6	15.0	17.0	Failed in weld	EB -4
none	800°C	59.2	39.3	45.9	24.0	(Control)	-----

Similar results were observed by Westinghouse Atomic Power Laboratory in their preliminary survey of vanadium alloys. Cross sections of as-welded and welded and annealed samples are shown in figures 6 and 7. The figures show that the 1050°C anneal caused precipitate agglomeration. The

7627

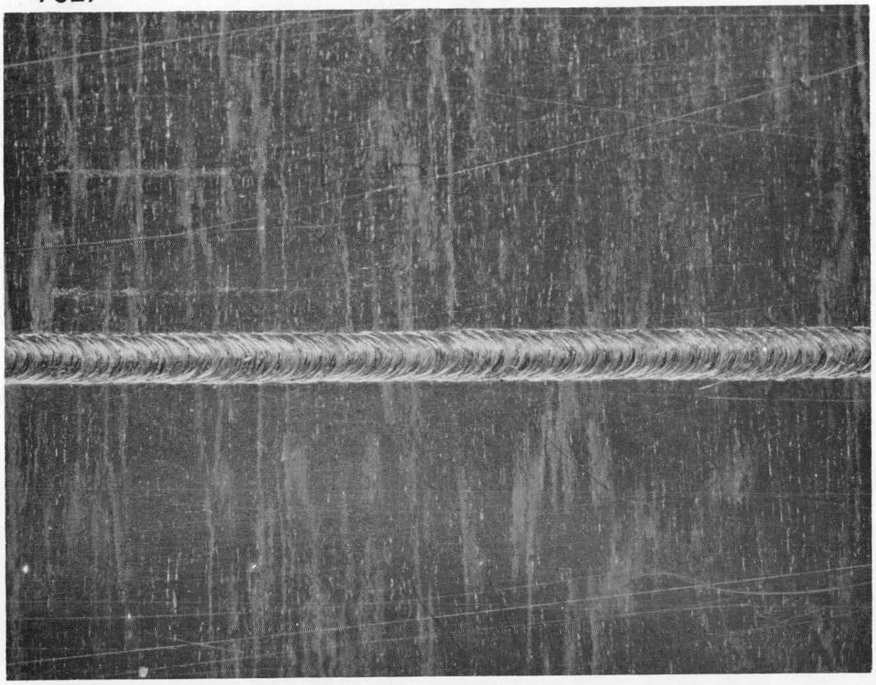


Figure 4. TIG Weld Bead on V-15Cr-5Ti Sheet

7628

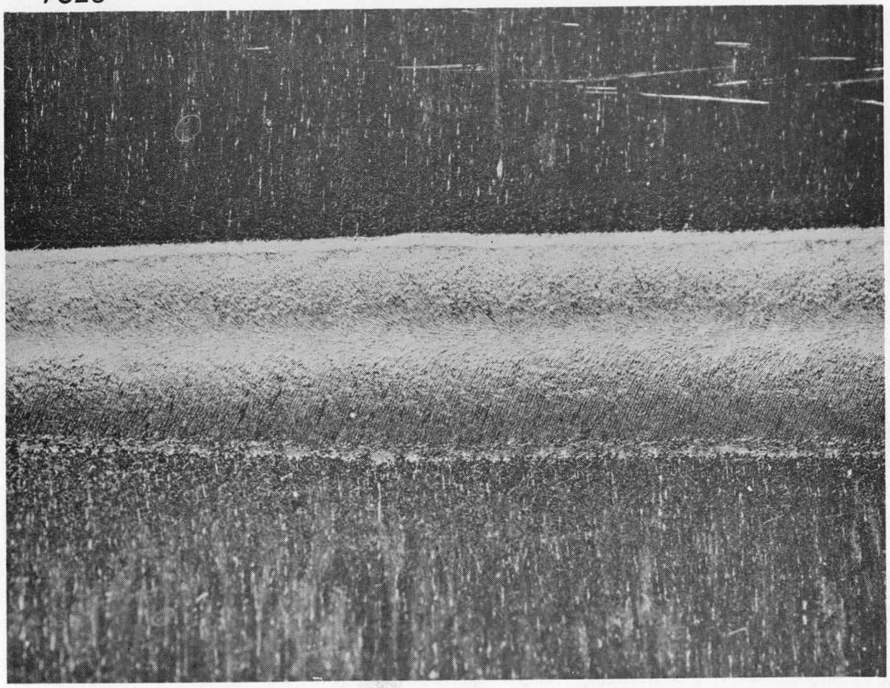
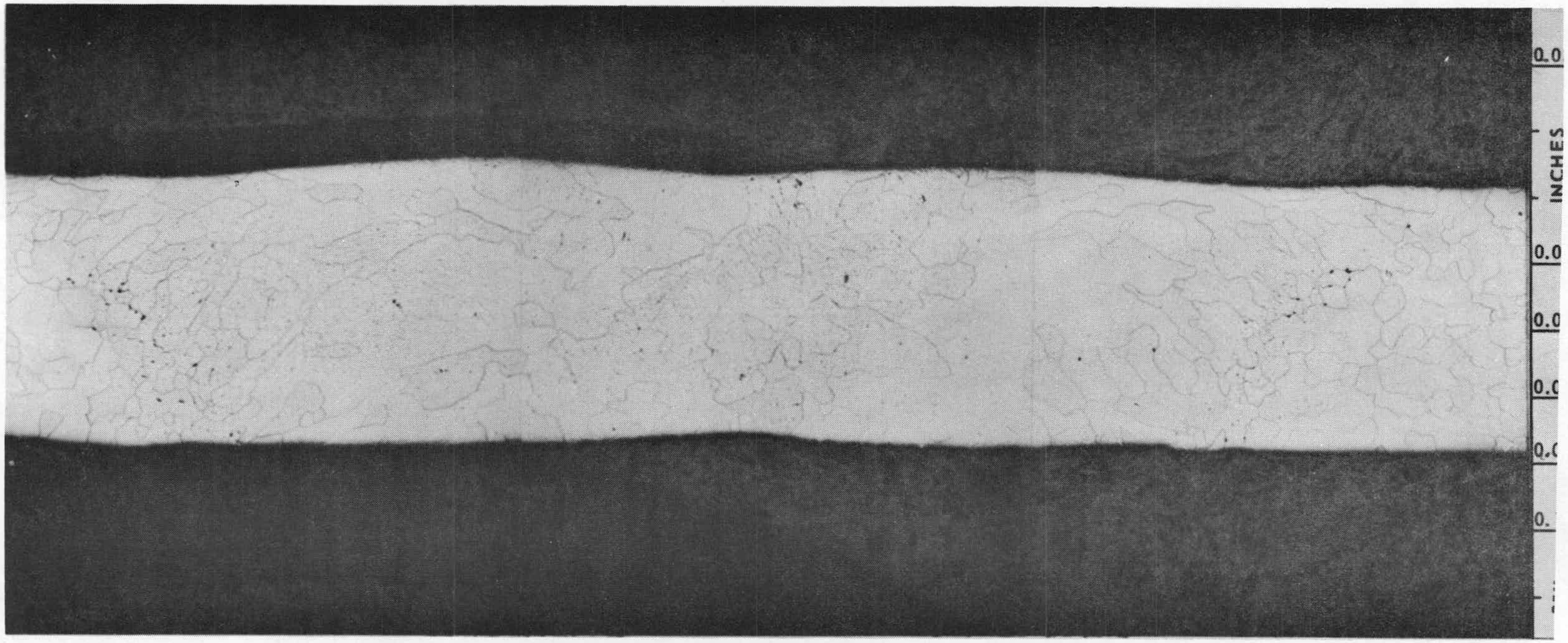


Figure 5. Electron Beam Weld Bead on V-15Cr-5Ti Sheet

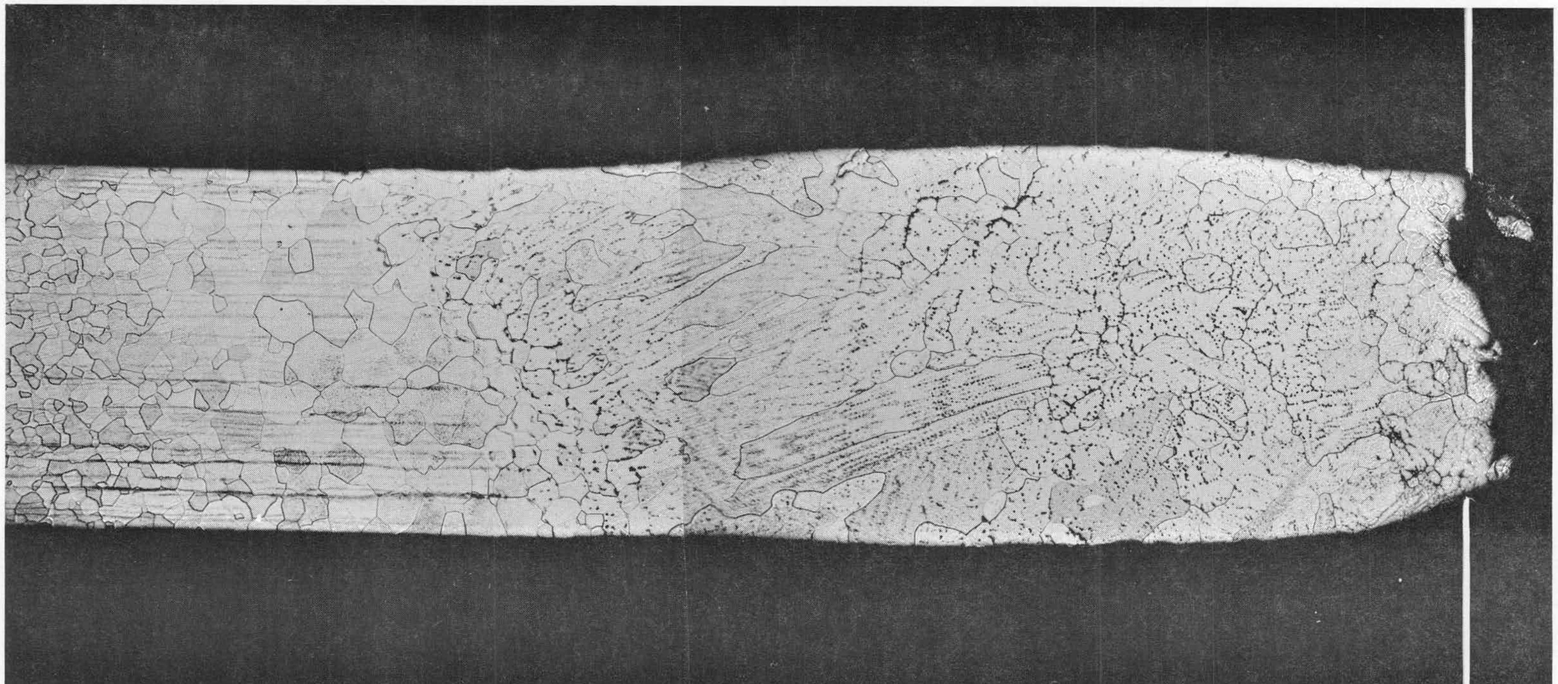
7820



35X

Figure 6. As-Welded TIG Weld. Preweld Heat Treatment of 1050°C/1 hr

7648, 7649



50X

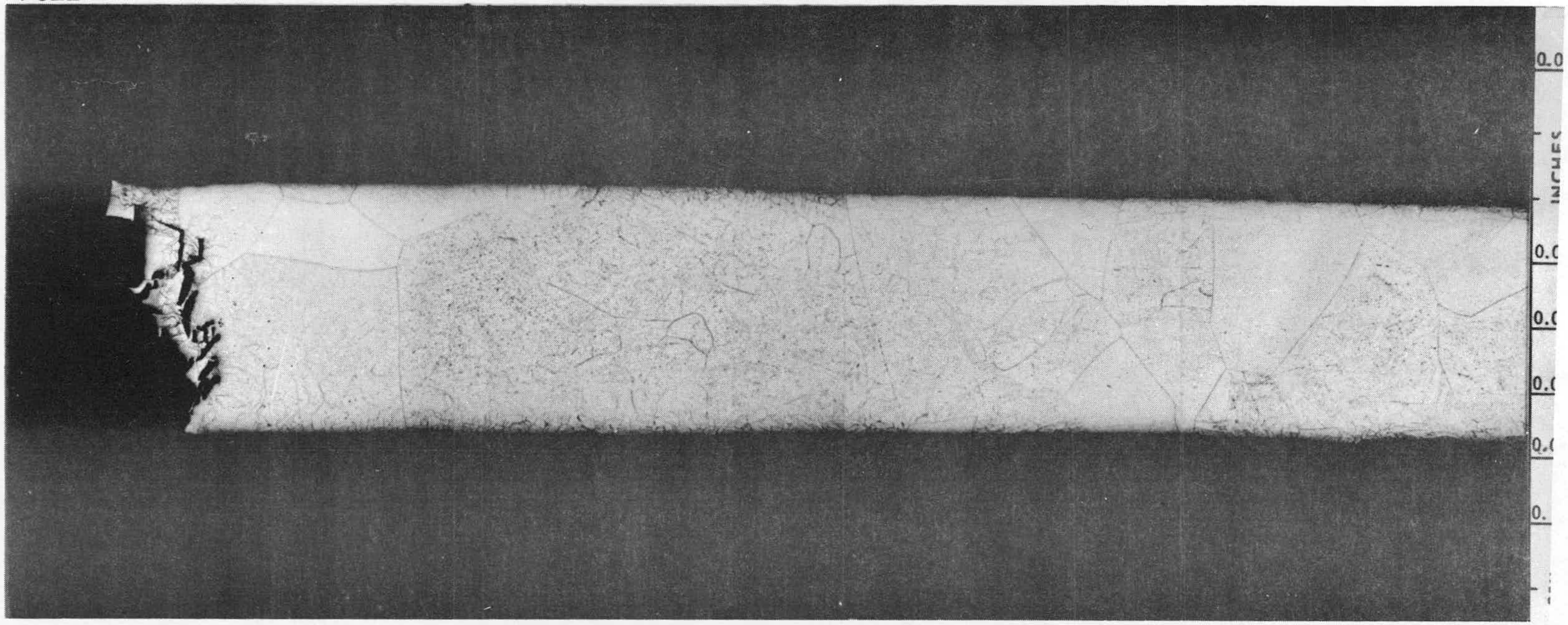
centerline of weld

Figure 7. Fractured TIG Weld with a Postweld Heat Treatment of 1050°C/1 hr. Note Severe Agglomeration of Precipitate

agglomeration in the TIG welds is analogous to "coring" in ingots. The second phase is concentrated due to differences in solubility on cooling. In an effort to more uniformly distribute the agglomerated second phase, fractured samples of annealed welds were heat treated at 1500°C for 4 hours, then cooled at 700°C per hour. Figure 8 shows the results. As seen, the precipitate went into solution and precipitated in a more uniform distribution. Of course, this does not offer a solution to the problem since the grains are grossly oversize as a result of the 1500°C heat treatment. It would appear from these preliminary tests that welding procedures which do not lead to agglomeration should be evaluated. One method appears to be electron beam welding. Due to the rapid cooling after welding, agglomeration cannot occur, as can be seen in figure 9. It can be noted, however, that one centrally located grain shows agglomeration. This grain would be one of the last to solidify. Ductility of the electron beam welds has been shown to be good by the results of table II. Figure 10, a cross section of an 800°C electron beam welded tensile test, shows a ductile, transgranular fracture even though the failure occurred in the weld.

The above results indicate that the V-15Cr-5Ti alloy can be joined successfully by electron beam welding. On the other hand, TIG welds tend to be brittle. Based on these results, tests on welds will be performed using the EB welded samples. In addition, a small heat treatment study will be performed on TIG welded specimens in an effort to determine if ductility can be restored.

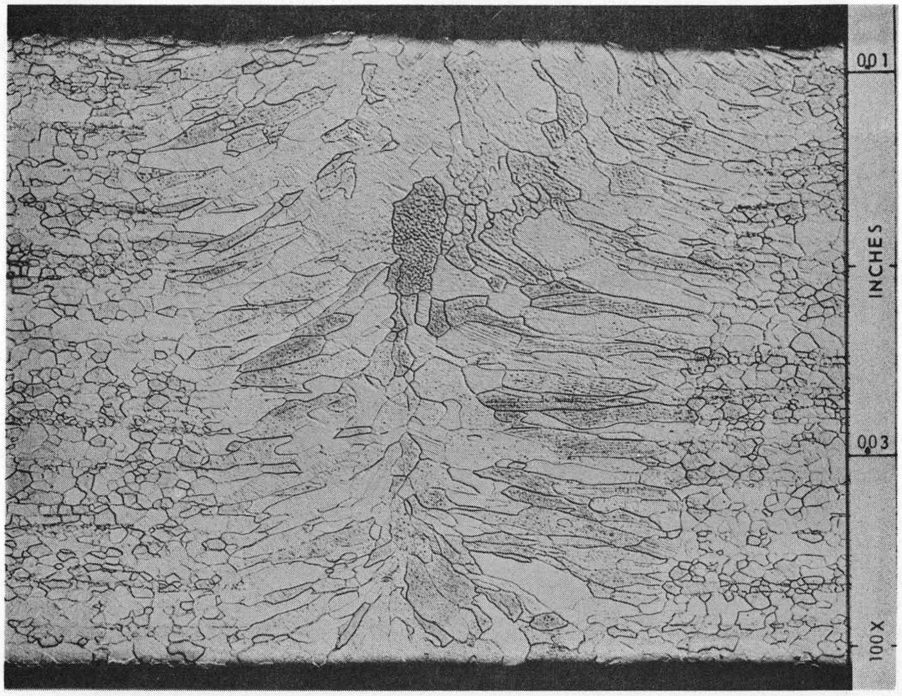
7822



35X

Figure 8. Fractured TIG Weld after Heat Treating at 1050°C/1 hr and 1500°C/4 hr. The Second Phase is Redistributed

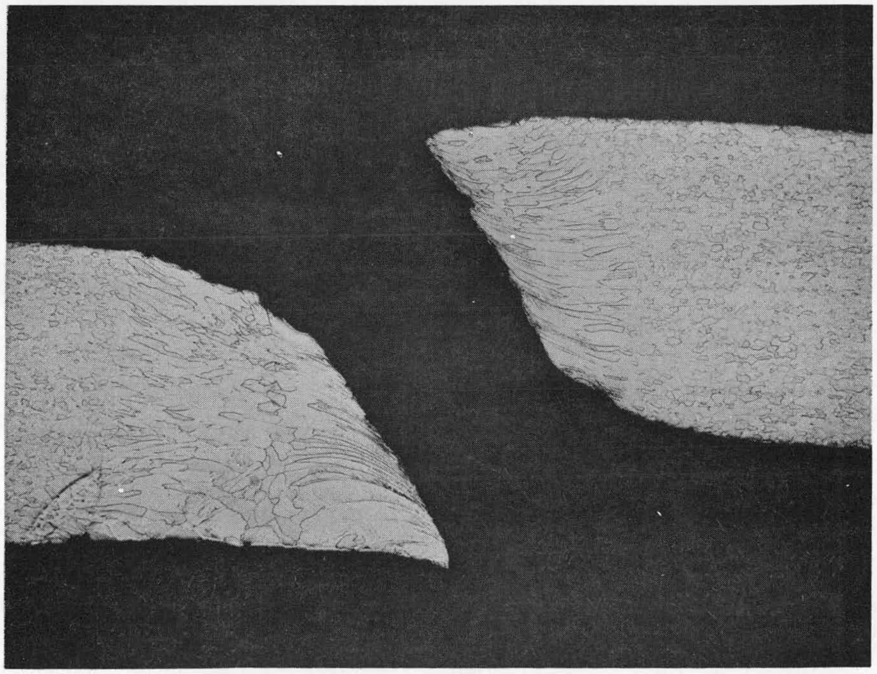
7727



100X

Figure 9. Cross Section of Electron Beam-Welded V-15Cr-5Ti Sheet. Note Lack of Agglomerated Precipitate. The Weld had Preweld and Postweld Heat Treatments of 1050°C/1 hr

69-133



50X

Figure 10. Cross Section of V-15Cr-5Ti Fractured Tensile Sample Tested at 800°C. Sample Failed in Weld with a Ductile Time Fracture

III FUTURE WORK

Long time stress-rupture tests will continue in the modified creep rig.

Electron beam-welded specimens will be stress-rupture tested. A limited aging study will be performed on TIG-welded samples to determine if heat treating can restore ductility of the welds.