WARD-3791-30
Category UC-25

# VANADIUM ALLOY CLADDING DEVELOPMENT

# QUARTERLY PROGRESS REPORT

# FOR THE PERIOD

# ENDING DECEMBER 31, 1968

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Prepared for the New York Operations Office
U. S. Atomic Energy Commission
Under AEC Contract AT(30-1)-3791

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Submitted to AEC-NYOO in February 1968

## AVAILABILITY NOTICE

Printed in USA. Price ~~$3.00~~. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Virginia 22151.

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# INTRODUCTION

This is the sixth quarterly progress report on Vanadium Alloy Cladding Development Project being performed under AEC Contract AT(30-1)-3791. It covers the work performed during the second quarter of fiscal year 1969, September 30 through December 31, 1968.

## PROJECT OBJECTIVES

The project objectives are to further the development and characterize the properties of vanadium-based alloys that may offer certain advantages over stainless steel for fuel cladding in a liquid-metal-cooled fast breeder reactor (LMFBR). For this application, the alloys must:

a. have sufficient strength to contain the fuel at temperatures up to 800°C;
b. be resistant to liquid-sodium corrosion;
c. be compatible with mixed uranium-plutonium ceramic fuels;
d. be resistant to embrittlement by fast flux irradiation;
e. be readily fabricated into high-quality tubing at reasonable cost; and
f. have acceptable nuclear physics characteristics.

This development project is being accomplished under Commission sponsorship to supplement and extend the favorable data on novel vanadium-based alloys obtained under AEC Contract AT(30-1)-3487. The work is specifically directed to the identification of an alternate LMFBR fuel cladding that has improved mechanical properties and irradiation damage resistance compared to stainless steels.

The project consists of six technical tasks and one administrative task as follows:

| | |
|---|---|
| UPVA-105 | Fuel Element Design Evaluation |
| VCAA-110 | Alloy Selection and Fabrication |
| VCAA-120 | Structural and Mechanical Properties Evaluation |
| VCAA-130 | Sodium Corrosion Evaluation |
| VCAA-140 | Cladding Alloy-Fuel Compatibility Evaluation |
| VCAA-150 | Irradiation Performance Evaluation |
| VCAA-160 | Project Administration |

The objective of each task is summarized below:

UPVA-105 was an assessment of the technical and economic potential of the successful development of an advanced vanadium alloy cladding for a prototypical LMFBR fuel element. This task has been completed.

In VCAA-110, five vanadium alloy compositions are being melted into 4-inch ingots, from which sheet, rod, and tubing are being fabricated. The five compositions are:

| Nominal Composition | Original Designation | New Designation[a] |
|---|---|---|
| V - 9Cr - 3Fe - 1.3Zr - 0.05C | HSV 207 | VANSTAR-7 |
| V - 6Fe - 5Cb - 1.3Zr - 0.05C | HSV 209 | VANSTAR-9 |
| V - 8Cr - 10Ta - 1.3Zr - 0.05C | HSV 208 | VANSTAR-8 |
| V - 15Cr - 5Ti | | |
| V - 20Ti | | |

[a] Agreement was reached on the adoption of VANSTAR as the designation for the family of Westinghouse-developed alloys.

VANSTAR-7, VANSTAR-8, and VANSTAR-9 are Westinghouse compositions developed under AEC Contract AT(30-1)-3487. V - 15Cr - 5Ti and V - 20Ti are alloys developed by the Argonne National Laboratory (ANL).

The alloys VANSTAR-8 and VANSTAR-9 have been selected for the characterization, compatibility, corrosion, and irradiation phases. The original choice of VANSTAR-9 was confirmed in view of the very promising results to date on the mechanical and creep properties of this alloy. VANSTAR-8 has been evaluated in VTL-1 Run 1 of the corrosion work; but, it was impossible to do so in VTL-2 Run 1 due to unavailability of VANSTAR-8 sheet at the time. A limited characterization of the other three alloys (VANSTAR-7, V - 15Cr - 5Ti, and V - 20Ti) is being performed. A stock of all five alloys, in the form of rod, sheet, and tubing, will be made available to other Commission contractors.

VCAA-120 is aimed at thorough characterization of the VANSTAR-8 and VANSTAR-9 alloys, including structure analysis, response to heat treatment, creep in vacuum and in sodium, welding, and thermal stability of welds. In addition, limited characterization will be performed on the other three alloys.

VCAA-130 is an evaluation of corrosion resistance of the VANSTAR-8, VANSTAR-9, and V - 20Ti alloys in pumped sodium loops, investigating the variables of temperature, flow rate, and time.

VCAA-140 is an evaluation of the compatibility of the same alloys with mixed-oxide, single and mixed-carbide fuels, varying temperature, fuel stoichiometry, bonding medium, and time. This has been temporarily suspended.

VCAA-150 is a preliminary examination of the effect of fast flux irradiation on the mechanical and structural properties of the two selected alloys, VANSTAR-8 and VANSTAR-9.

Under VCAA-160, project planning, coordination, and control necessary for timely within-budget completion will be furnished; AEC Contract Administration requirements will be met; and this Vanadium Alloy Cladding Development

project will be coordinated with other Commission-sponsored LMFBR R&D projects.

## PRIOR WORK

All work related to the present investigations and performed prior to the present period has been fully reported in WCAP-3487-16[1] and the previous five quarterly reports on this contract.[2,3,4,5,6]

## SUMMARY OF CURRENT PROGRESS

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

a. The nuclear and economic analysis of vanadium fuel element cladding was completed and fully reported in both a quarterly report[4] and a topical report.[7]

b. All melting, was completed as was the extrusion and tube reduction at ANL.

c. Processing to rod and sheet was successfully accomplished for all the alloys with the exception of the V - 15Cr - 5Ti alloy. V - 20Ti sheet was shipped to AEC contractors.

d. Extrusion at ORNL was completed, although some problems were encountered with the V - 15Cr - 5Ti alloy and VANSTAR-7 and -9. No significant differences in ease of extrusion were noticed between the alloys.

e. Creep rupture tests at 800°C on the VANSTAR alloys and the effects of testing vacuum on creep properties were continued.

f. The effects of 500-hour aging at 700 and 800°C on the microstructure, hardness, and mechanical properties of the VANSTAR alloys were small, although some precipitation was observed.

g. Both sodium corrosion loops ran satisfactorily; VTL-2, the higher velocity system, completed operation after 1500 hours. The corrected oxygen analysis of both systems is now <10 ppm.

h. In conjunction with ANL, unalloyed vanadium wires were exposed in both loops for internal friction evaluation of the loop impurity contents.

i. Parabolic kinetics were assigned to the corrosion processes, and activation energies for VANSTAR-7, VANSTAR-9, and V - 20Ti were calculated.

j. Chemical analyses of a corroded VANSTAR-9 sample revealed that large quantities of the interstitials, nitrogen, carbon, and oxygen, were absorbed during corrosion, resulting in the observed weight gains.

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k. Due to the absorption of the interstitials, considerable reductions in the mechanical properties of a corroded VANSTAR-9 sample, particularly at room temperature, were observed.

l. In the WARD/PNL High-Flux Irradiation Program, six subcapsules containing vanadium alloy tensile/creep specimens were assembled and shipped to EBR-II to await insertion in the reactor.

m. Authorization for the FY-1969 scope of work and full FY-1969 funding were obtained. Formal approval of our FY-1969 work program and formal concurrence with our October request for Government furnished materials and services were also received. A thorough review and updating of program status and plans were conducted for the AEC's mid-year review.

RELATED ACTIVITIES

a. Messrs. Borgstedt, Rühle, and Wincierz (KFK West Germany) visited the Waltz Mill Site for discussions on corrosion in areas of mutual interest.

b. Presentations were made at the AEC Vanadium Alloy Working Group Meeting held at Ames, Iowa in October, 1968.

c. WARD participated in a round-robin analysis program on impurity determination in Vanadium.

d. A paper entitled, "Development of Vanadium Alloys for LMFBR Cladding" by R. T. Begley, E. C. Bishop, R. W. Buckman, R. A. Nadler, and G. A. Whitlow, describing some of the recent results of this contract, was presented at the 1968 winter meeting of the American Nuclear Society in Washington DC.

# UPVA - 105 - FUEL ELEMENT DESIGN EVALUATION

G. E. Edison, R. P. Harrill, I. M. Keyfitz, D. Schwartz, G. A. Whitlow

## OBJECTIVE

The objective of this task is to assess the technical and economic potential of the successful development of an advanced vanadium alloy cladding for a prototypical LMFBR fuel element.

A physics and cost comparison was made of vanadium alloy cladding versus stainless steel cladding in a 1000-MWe LMFBR. The merits of vanadium alloy cladding were evaluated relative to those of stainless steel for nuclear safety and economic incentive. A 1000-MWe design was chosen from the 1000-MWe LMFBR Follow-on Study (Argonne National Laboratory, Contract No. ANL-31-109-38-2000), and three different cladding materials, including stainless steel and two vanadium alloys, were compared.

To take advantage of the high-temperature strength properties of vanadium, different vanadium alloy cladding thicknesses were considered; the possibility of raising the reactor coolant outlet temperature and increasing the temperature gradient across the core was also considered.

## CURRENT PROGRESS

This task was completed in January 1968, and a topical report was issued.[7] A paper summarizing the results of this study was presented at the ANS meeting in Toronto in June 1968.[8] Detailed progress on this task was reported in some of the previous quarterly reports on this contract.[2,3,4,5]

It was demonstrated that sodium void and Doppler coefficients are slightly more favorable when the VANSTAR alloys are substituted for Type 316 stainless steel, while breeding ratio is relatively unaffected. Power costs were estimated to be a few hundredths of a mill/kWh higher than stainless steel at vanadium alloy tubing costs, which appeared to be reasonable in volume production. However, optimization of secondary systems and steam cycles could lead to small cost improvements.

# VCAA - 110 - ALLOY SELECTION AND FABRICATION

R. T. Begley, R. W. Buckman, Jr., R. A. Nadler, G. A Whitlow

## OBJECTIVES

One objective of this task is to furnish material for the mechanical property, sodium corrosion, fuel compatibility, and irradiation evaluations being conducted under the other tasks of this project. A further objective is to supply materials, as directed by the USAEC, for programs in progress at national laboratories and other institutions.

Rod, sheet, and tubing of five vanadium-base alloys are to be produced from a total of 13 ingots, each of which is to weigh 35 to 40 pounds. During this work, appropriate chemical analyses, nondestructive tests, microstructural studies, and evaluations of processing variables will be performed to achieve maximum yields of a final product possessing satisfactory and uniform properties. The distribution of the ingots is to be as listed below.

| Alloy | No. of Ingots |
|---|---|
| V - 20Ti | 1 |
| V - 15Cr - 5Ti | 3 |
| V - 9Cr - 3Fe - 1.3Zr - 0.05C (VANSTAR-7) | 3 |
| V - 6Fe - 5Cb - 1.3Zr - 0.05C (VANSTAR-9) | 3 |
| V - 8Cr - 10Ta - 1.3Zr - 0.05C (VANSTAR-8) | 3 |

## PRIOR WORK

Five hundred pounds of electrolytically-reduced vanadium granules were evaluated and qualified for use as melting stock. Eleven of the 13 ingots were melted, and sheet and rod specimens were prepared for the compatibility, corrosion, and irradiation studies from upset-forged, cast billets. Five billets were machined and shipped to Argonne National Laboratory (ANL) for extrusion and tube reduction. Sheet bars of V - 20Ti and VANSTAR-8 were extruded at ANL and returned to Westinghouse, where the V - 20Ti was rolled to sheet and shipped to AEC evaluating agencies. Tube reduction and rod extrusion were completed for the V - 15Cr - 5Ti alloy at ANL, and similar work was started on the VANSTAR alloys, but none of this material was returned to Westinghouse. Arrangements were also made to extrude ten billets to sheet bar, cylindrical bar, and tube hollows at Oak Ridge National Laboratory (ORNL).

## CURRENT PROGRESS

### Melting

Melting was completed for the last two of the 13 scheduled ingots. Chemical analyses were also completed, and the results are presented in Table 1. Good control was maintained over alloying elements, including carbon, but oxygen contents were rather variable. As previously indicated,[2] the vanadium melting stock consists of long, needle-like, fairly coarse particles of moderate oxygen content (400 to 700 ppm), and relatively equiaxed particles of high oxygen content (approximately 1000 ppm). The particles rich in oxygen, therefore, tend to segregate and promote wide variations in oxygen content.

### Fabrication

#### Westinghouse/ANL Processing

ANL completed the extrusion and tube reduction of the remaining four billets supplied by Westinghouse, and all materials were returned to Westinghouse late in December. Figure 1 shows a general process outline for this material. For primary extrusion, billets were machined to the drawing of Figure 2 and fitted into a 3.5-inch, Schedule 40 (4-inch O.D. x 0.226-inch wall), Type 304 stainless steel pipe with welded end and nose caps. The V - 15Cr - 5Ti billet received a two-hour pre-extrusion heat treatment at 1200°C, which ANL has found beneficial to extruded surface quality. The canned billets were placed in an electrically heated furnace, held for two hours at 1100 to 1125°C, and extruded (3.9:1 reduction ratio) on the 1250-ton-capacity Lake Erie horizontal press with a molybdenum disulfide-graphite mixture as lubricant.

The primary extrusions were then radiographed, dejacketed, sectioned, and machined into billets for secondary extrusion on ANL's 350-ton Lombard vertical press. The O.D. of all vanadium alloy billets for re-extrusion was 1.74 inch, and the I.D. of the tubular billets was 0.75 inch. Both the solid and hollow billets were externally clad with 1.95-inch O.D. x 0.100-inch wall Type 304 stainless steel, while the tubular billets were also clad internally with 0.75-inch O.D. x 0.035-inch wall stainless steel. The solid and tubular billets were induction heated and held at 1100°C for five minutes prior to extrusion. Tube shells were produced by extruding the tubular billets 7.5:1 over a floating mandrel, while the extrusion ratios were 8.6:1 for the rods (exception - 10.5:1 for V - 20Ti) and 13:1 for the sheet bars.

Extrusion constants for the five alloys extruded at ANL are presented in Table 2. No data are given for the primary extrusion (3.9:1) of the V - 20Ti - VANSTAR-8 composite billet, since they did not appear to be representative values and may have been influenced by the unusual billet geometry. The data of Table 2 do not reveal any unusual or consistent differences in ease of extrusion between any of the alloys.

The secondary extrusions were radiographed, dejacketed, and, except for the tube blanks, returned to Westinghouse for further processing. The tube blanks were heat treated (850°C for two hours for V - 15Cr - 5Ti and 1100°C for one hour for the VANSTAR alloys) and tube reduced at 250°C

## Table 1

### Vanadium Alloy Ingot Analyses
(wt%)

| Alloy | Heat No. | Ingot Location | Cr | Fe | Cb | Ta | Ti | Zr | C(ppm) | O(ppm) | N(ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| V - 20Ti | Nominal | Composition | | | | | 20 | | | | |
| | HSV-300 | Top | | | | | 20.1 | | 150 | 820 | 89 |
| | | Middle | | | | | 19.5 | | 150 | | 63 |
| | | Bottom | | | | | 19.5 | | 90 | 840 | 97 |
| V - 15Cr - 5Ti | Nominal | Composition | 15 | | | | 5 | | | | |
| | HSV-303 | Top | 15.1 | | | | 5.2 | | 120 | 710 | 110 |
| | | Middle | 14.6 | | | | 5.3 | | 81 | | 77 |
| | | Bottom | 14.9 | | | | 4.5 | | 180 | 810 | 110 |
| | HSV-307 | Top | 14.9 | | | | 5.0 | | 78 | 960 | 98 |
| | | Middle | | | | | | | | | |
| | | Bottom | 14.9 | | | | 5.0 | | 98 | 820 | 91 |
| | HSV-311 | Top | 15.1 | | | | 4.9 | | 89 | 820 | 92 |
| | | Middle | | | | | | | | | |
| | | Bottom | 14.9 | | | | 4.8 | | 140 | 940 | 92 |
| VANSTAR-7 | Nominal | Composition | 9.0 | 3.3 | | | | 1.3 | 540 | | |
| | HSV-302 | Top | 8.6 | 3.0 | | | | 1.1 | 560 | 690 | 87 |
| | | Middle | 9.0 | 3.0 | | | | 1.3 | 490 | 620 | 73 |
| | | Bottom | 8.5 | 3.4 | | | | 1.3 | 550 | 740 | 92 |
| | HSV-306 | Top | 9.2 | 3.3 | | | | 1.2 | 550 | 670 | 96 |
| | | Middle | 9.3 | 3.2 | | | | 1.2 | 400 | | 89 |
| | | Bottom | 8.8 | 3.3 | | | | 1.2 | 540 | 860 | 87 |
| | HSV-309 | Top | 9.6 | 3.3 | | | | 1.2 | 660 | 650 | 88 |
| | | Middle | | | | | | | | | |
| | | Bottom | 9.2 | 3.3 | | | | 1.2 | 620 | 610 | 88 |
| VANSTAR-8 | Nominal | Composition | 8.5 | | 9.8 | | | 1.25 | 500 | | |
| | HSV-304 | Top | 8.6 | | 10.0 | | | 1.2 | 530 | 740 | 43 |
| | | Middle | 8.7 | | 10.3 | | | 1.1 | 480 | | 93 |
| | | Bottom | 8.9 | | 8.8 | | | 1.0 | 490 | 840 | 100 |
| | HSV-310 | Top | 8.0 | | 9.2 | | | 1.1 | 560 | 650 | 79 |
| | | Middle | 8.0 | | 9.3 | | | 1.0 | 520 | | |
| | | Bottom | 8.2 | | 8.9 | | | 1.1 | 520 | 580 | 77 |
| | HSV-312 | Top | 8.1 | | 9.2 | | | 1.1 | 550 | 600 | 91 |
| | | Middle | | | | | | | | | |
| | | Bottom | 8.7 | | 8.6 | | | 1.1 | 600 | 740 | 92 |
| VANSTAR-9 | Nominal | Composition | | 6.4 | 5.3 | | | 1.3 | 500 | | |
| | HSV-301 | Top | | 6.2 | 5.1 | | | 1.3 | 550 | 790 | 87 |
| | | Middle | | 6.2 | 5.3 | | | 1.2 | 520 | | 80 |
| | | Bottom | | 6.0 | 5.1 | | | 1.3 | 470 | 730 | 99 |
| | HSV-305 | Top | | 6.0 | 5.3 | | | 1.3 | 530 | 760 | 83 |
| | | Middle | | 6.0 | 5.1 | | | 1.1 | 550 | | 95 |
| | | Bottom | | 5.1 | 4.7 | | | 1.1 | 520 | 620 | 81 |
| | HSV-308 | Top | | 6.2 | 5.3 | | | 1.2 | 610 | 960 | 98 |
| | | Middle | | | | | | | | | |
| | | Bottom | | 6.3 | 5.2 | | | 1.2 | 600 | 830 | 92 |

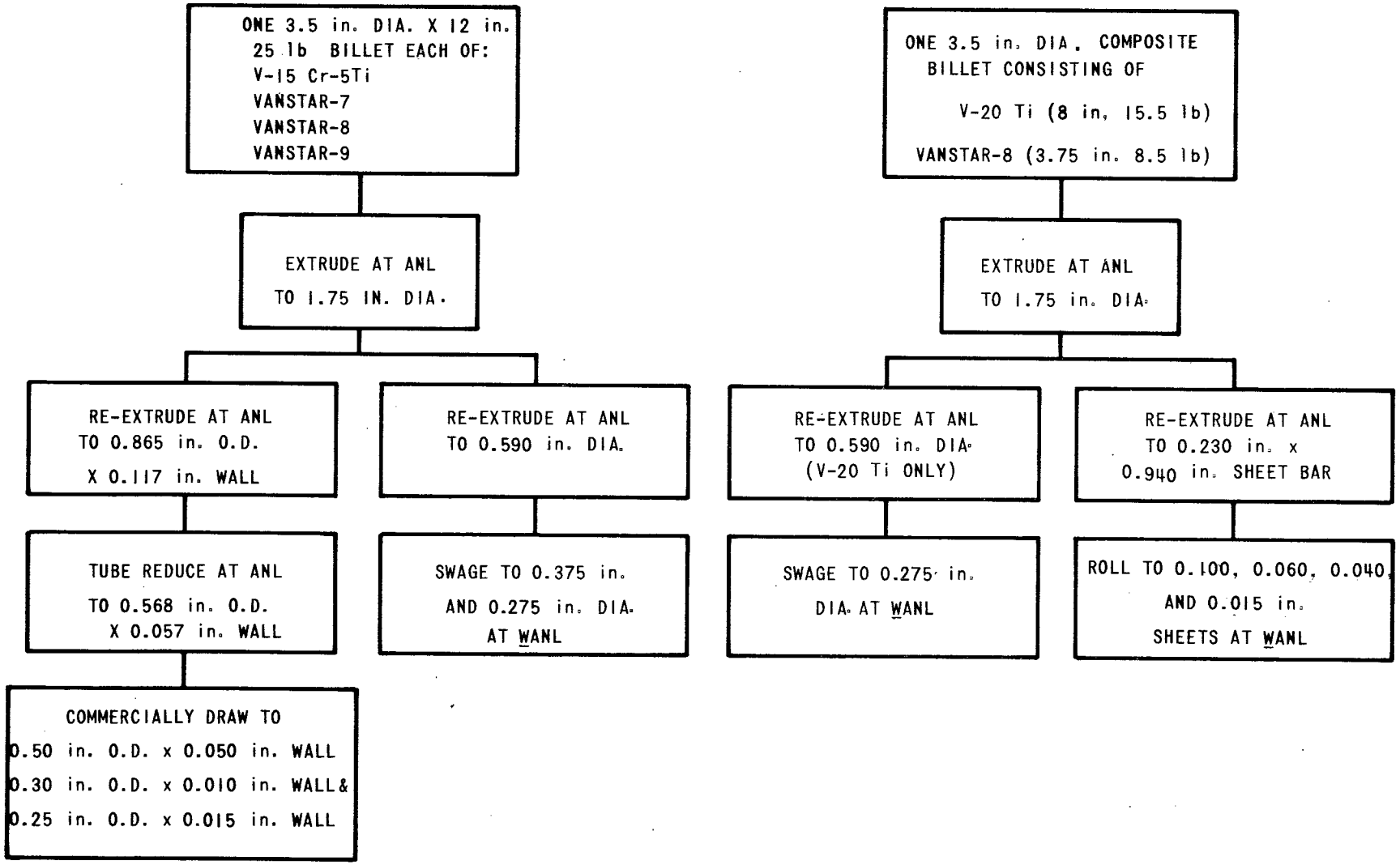


Figure 1 Process Outline for Vanadium Alloy Billets via Argonne National Laboratory

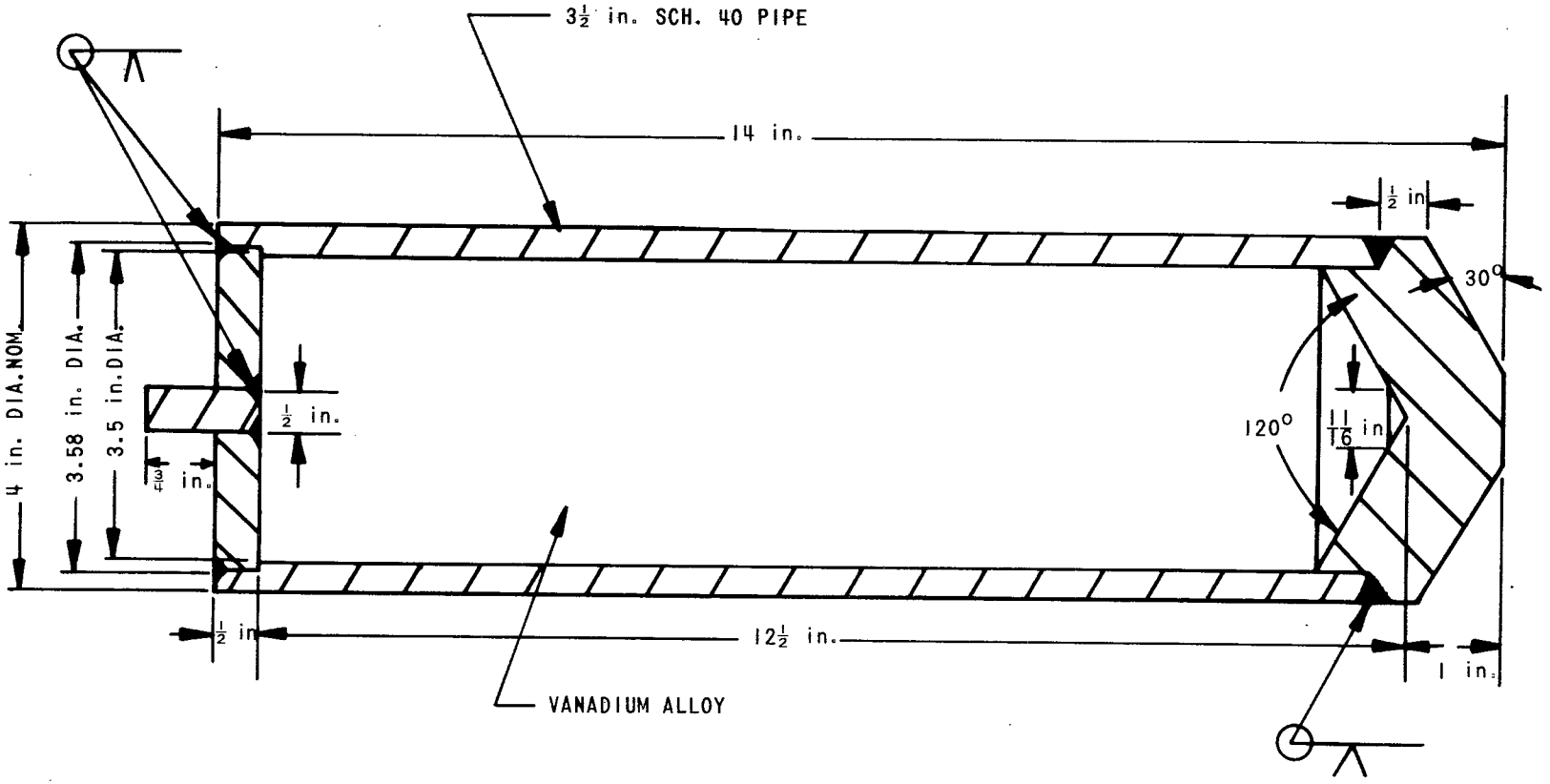


Figure 2 Vanadium Alloy Extrusion Billet and Type 304 Stainless Steel Can. (Argonne National Laboratory)

Table 2

Extrusion Constants for Vanadium Billets Processed at ANL[a]

| Product | Extrusion Ratio | Extrusion Constant (ksi)[b] | | | | |
|---|---|---|---|---|---|---|
| | | V - 20Ti | V - 15Cr - 5Ti | VANSTAR-7 | VANSTAR-8 | VANSTAR-9 |
| 1.75-in. dia bar | 3.9:1 | -- | 81.6 | 77.9 | 82.3 | 85.2 |
| 0.59-in. dia re-extruded rod | 8.6:1 | 54.3[c] | 58.4-62.2 | 46.7-51.9 | 54.4-59.5 | 53.6-54.0 |
| 0.865-in. O.D. x 0.117-in. wall re-extruded tube blank | 7.5:1 | -- | 64.8-66.6 | 51.7-54.7 | 50.7-57.7 | 52.2-59.7 |
| 0.23-in. x 0.94-in. re-extruded sheet bar | | 46.0-54.6 | -- | -- | 50.7-53.4 | -- |

[a]Billets heated to 1100°C for extrusion.

[b]Extrusion constant, $K = \frac{P}{\ln R}$, where P is the average running pressure on the stem of the extrusion press and R is the extrusion ratio.

[c]10.5:1 extrusion ratio

to approximately 0.568-inch O.D. x 0.057-inch wall. As an additional service, ANL annealed the finished V - 15Cr - 5Ti tubing in preparation for tube drawing. Details of the ANL equipment and shop practices are available in the literature.[9,10,11]

The status of the ANL-processed material is as follows:

a. The extruded rods were straightened and lathe-conditioned at Westinghouse Astronuclear Laboratory (WANL). The rods were then annealed at 1200°C for one hour (VANSTAR alloys) 900°C for one hour (V-20 Ti), or 850° for two hours (V - 15Cr - 5 Ti), and swaged to 0.375-inch diameter (approximately 50% reduction of area). Except for V - 15Cr - 5Ti which was heated to 500°C for swaging, the alloys were swaged at room temperature. Processing of the V - 20Ti and VANSTAR alloy rods was accomplished with relative ease; but, serious longitudinal splitting and transverse cracking of V - 15Cr - 5Ti was encountered, although the available processing information for this alloy indicated that 50% reductions were possible. It was subsequently learned from ANL that such reductions may be taken in rolling, but that swaging reductions should be limited to about 20% in the early stages. Unfortunately, the defects were not detectable until the 0.375-inch-diameter rods were sandblasted and/or etched in acid to relieve surface stresses, causing a slight shortage of material for shipment to AEC evaluating agencies. However, the yield of sound material from the four other alloys now appears certain to exceed earlier estimates, so that some material can be substituted where necessary.

b. As indicated earlier,[6] the V - 20Ti sheet bar was fully converted to sheet and shipped to AEC contractors. Extrusion of the VANSTAR-8 sheet bar was mainly intended to give ANL experience in processing a typical Westinghouse-developed alloy. Further processing of this material has been deferred since the available stock is not sufficient to complete the evaluators' requirements and because it is important to provide the various laboratories with material processed by a single method from a single ingot to make meaningful data comparisons. As will be described in a later section, sufficient supplies of sheet will be available from ingots extruded at ORNL.

c. Preparations are being made to anneal the VANSTAR alloy tube blanks at WANL. Quotations have been requested from commercial sources to draw this material to the sizes shown in Figure 1. It is expected that an order will be placed in January, 1969.

Westinghouse/ORNL Processing

Ten billets (two from each of five ingots) were scheduled for extrusion at ORNL. Process outlines and billet and can configurations are shown in Figures 3 and 4, respectively. In contrast to the design of the ANL primary billet (Figure 2) that requires the ingot to be machined to the can I.D., the ORNL can is machined to fit the cast, rough-turned ingot. The wall thickness of the ORNL can is, therefore, approximately 0.14 inch as opposed to 0.23 inch for an ANL can. This relatively thin wall

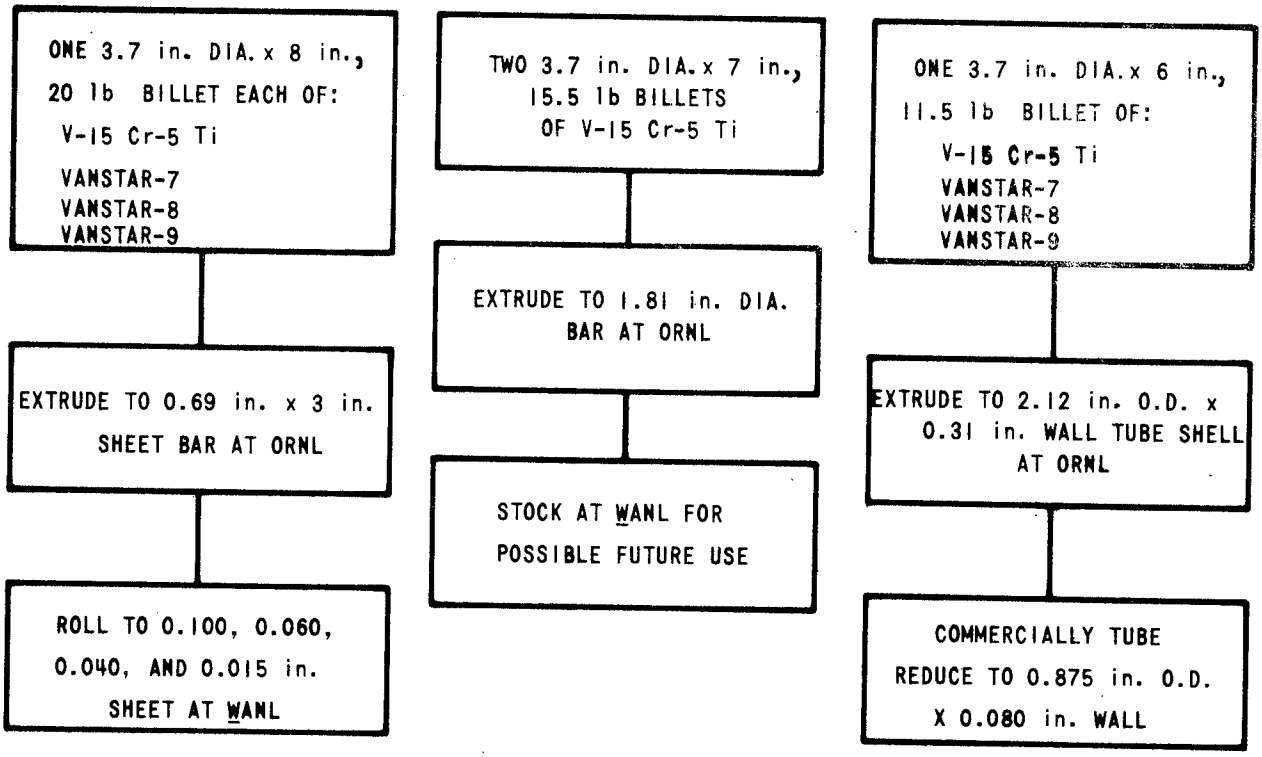


Figure 3 Process Outline for Vanadium Alloy Billets via Oak Ridge National Laboratory

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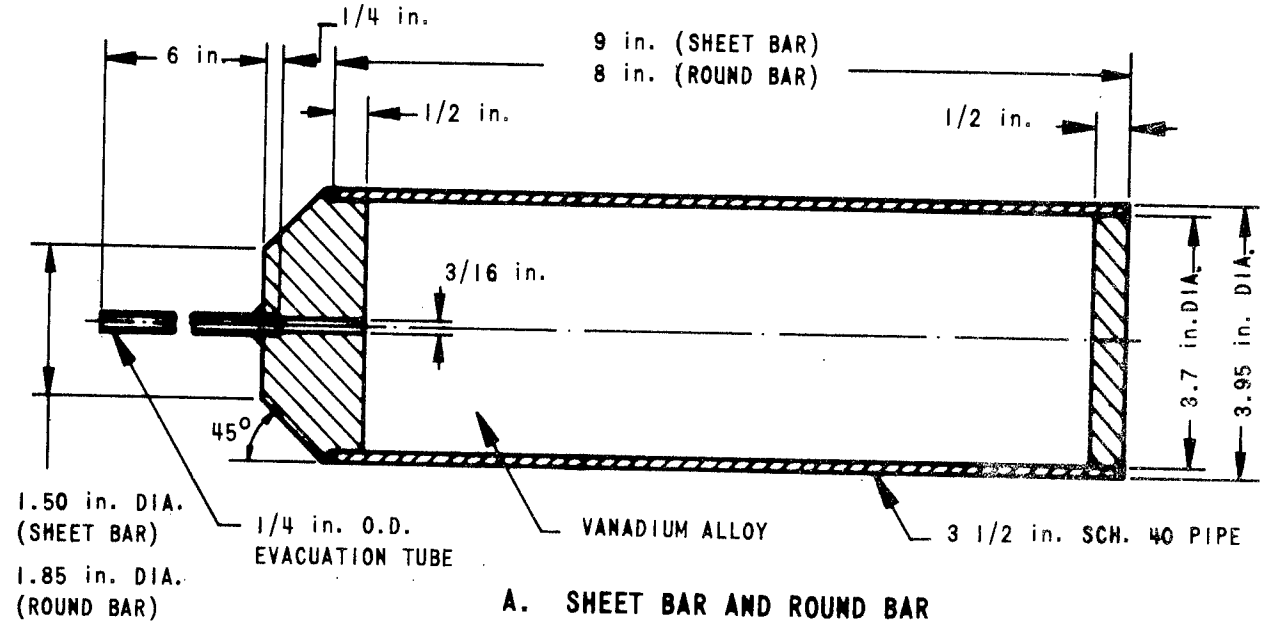
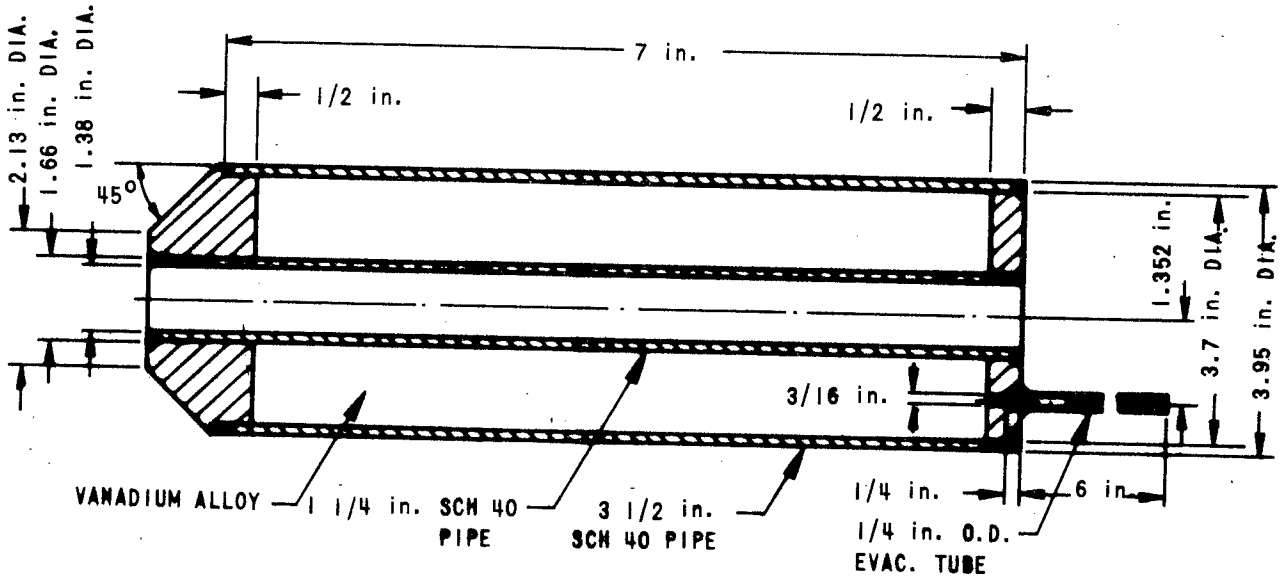



A. SHEET BAR AND ROUND BAR




B. TUBE HOLLOW

Figure 4 Vanadium Alloy Extrusion Billets and Type 304 Stainless Steel Cans. (Oak Ridge National Laboratory)

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did not present any problems in the extrusion of sheet and round bar at ORNL; but, the outer can on the hollow billets did separate from the nose and was pushed backward, thus exposing and oxidizing about six inches of the tube hollow O.D. However, sufficient material is available to complete AEC contractor requirements, assuming that no unusual problems are encountered in subsequent fabrication. Since little of the ingot O.D. was removed and no nose was machined on the ORNL extrusion billets, the yield of useable material should be somewhat higher than that of the billets machined for extrusion at ANL.

Another feature of the ORNL can is the 1/4-inch O.D. evacuation tube. Each billet was evacuated in an electron beam welder to $5 \times 10^{-5}$ torr and sealed by melting the tips of the stainless steel welding wires that were placed in the tube. The ANL billets were not evacuated; however, ANL experience has been that the small volume of air in a closely-mated billet assembly can be tolerated.

Of the ten extrusions to be made at ORNL, only one (a V - 15Cr - 5Ti round bar) has not been processed. Inspection of the hollow billets revealed cracks on the I.D. surfaces of the V - 15Cr - 5Ti, VANSTAR-7, and VANSTAR-9 pieces. The defects are thought to be related to the melting process since they are present only in the interdendritic regions, which are the last portions to solidify. Since the cracks were not previously observed in radiographs of solid ingots of the same compositions both prior and subsequent to extrusion, or in finished sheet and rod, they must have been quite narrow in the castings, and/or may have healed during extrusion. Because the chances of healing the cracks appeared to be good, the hollow billets were extruded. The remaining V - 15Cr - 5Ti billet to be extruded at ORNL is being retained at WANL pending evaluation of the hollow extrusions. This last billet is not committed to an AEC program and can be diverted if the V - 15Cr - 5Ti tube hollow, that contained the most severe defects of the three cracked billets, is not of sound quality.

The billets were preheated to 1200°C in an electrically heated furnace for about an hour, and then transferred to a barium chloride salt bath (E.F. Houghton & Co. #1560), that also operated at 1200°C, for approximately one additional hour. The V - 15Cr - 5Ti billets were heated for one to two additional hours to accomplish the heat treatment required for optimum extruded surface quality. Extrusion was initiated approximately 30 seconds after billet removal from the salt bath, so that actual billet temperature was somewhat less than 1200°C. In these operations, the residual salt layer (0.005-inch thick) was used as the billet lubricant.

Extrusion constants for the nine billets are presented in Table 3. Extrusion constants are lower than those reported in Table 2 for the ANL primary extrusions, but this is not unusual since the billet temperature was higher at ORNL. Other conditions (lubrication practice, for example) may also have contributed to the differences in extrusion constants. However, as observed previously at ANL, none of these alloys is significantly easier or more difficult to extrude than another.

Table 3

Extrusion Constants for Vanadium Billets Processed at ORNL[a]

| Product | Extrusion Ratio | Extrusion Constant, (ksi)[b] | | | |
|---|---|---|---|---|---|
| | | V - 15Cr - 5Ti | VANSTAR-7 | VANSTAR-8 | VANSTAR-9 |
| 1.81-in. dia bar | 4.9:1 | 70.0 | -- | -- | -- |
| 0.69-in. x 3-in. sheet bar | 5.7:1 | 71.0 | 68.0 | 57.0 | 74.6 |
| 2.12-in. O.D. x 0.31-in. wall tube shell | 5.8:1 | 63.0 | 49.0 | 55.0 | 63.0 |

[a]Billets heated to 1200°C for extrusion.

[b]Extrusion constant, $K, = \frac{P}{\ln R}$ , where P is the breakthrough pressure on the stem of the extrusion press and R is the extrusion ratio.

The major portion of the ORNL extrusions was received at the end of the reporting period; therefore, little work on this was accomplished at WANL. However, preliminary rolling was performed on the sheet bars, and this indicated that the VANSTAR alloys could be rolled to sheet with little difficulty. The V - 15Cr - 5Ti sheet bar exhibited a pronounced tendency to alligator, i.e., to split transversely at mid-thickness. Metallographic examination showed that very little work was performed at the center of the sheet bar, which is the classic cause of alligatoring. In attempts to correct this situation, rolling was performed at 500°C, the reduction per pass was increased, and the reduction between anneals was reduced. These efforts were only partially successful, and rolling of samples from 750°C, which will be graphite coated for oxidation protection, will be attempted in the near future. Break down of extruded or forged V - 15Cr - 5Ti sheet bar appears to be best accomplished in the hot-working range. In semi-commercial practice, for example,[12] ingots are forged to 1.5-inch thick from 1050°C, and rolled to about 0.25 inch from 1050°C; final thickness is attained by warm rolling at 300°C.

# VCAA-120 STRUCTURAL AND MECHANICAL PROPERTIES EVALUATION

R. T. Begley, R. W. Buckman, Jr., R. A. Nadler, G. A. Whitlow

## OBJECTIVES

In this task, the properties of two Westinghouse-developed candidate alloys for LMFBR fuel cladding,

VANSTAR-8: V - 8Cr - 10Ta - 1.3Zr - 0.05C and

VANSTAR-9: V - 6Fe - 5Cb - 1.3Zr - 0.05C

will be determined in detail; the three other alloys being produced under VCAA-110 will be characterized primarily through tensile and creep tests. The detailed evaluations of the candidate alloys will include:

a. tensile testing up to 1000°C;

b. 2000-hour creep tests in vacuum and 1000-hour creep tests in liquid sodium, at temperatures up to 800°C;

c. welding studies, including the determination of aging behavior of weldments in the range of 600 to 800°C for periods up to 5000 hours; and

d. explorations of the effects of heat treatment on strength, fabricability, and thermal stability.

## PRIOR WORK

Creep tests performed on VANSTAR-9 and VANSTAR-7 sheet showed that the minimum creep rate at 700°C was exceptionally low at stresses that exceeded the short time yield strength by as much as 10,000 psi. One-hour recrystallization and grain growth studies were completed for the VANSTAR alloys. Bend transition and elevated temperature tensile tests were completed for the VANSTAR alloys as well as for V - 20Ti. Preliminary aging data were obtained for the VANSTAR alloys, and densities and solidus temperatures were obtained for the five alloys.

## CURRENT PROGRESS

### Creep Properties

Since the creep rates obtained during tests at 700°C were very low,[6] additional tests were initiated at 800°C to assess the VANSTAR alloys'

load-bearing capabilities at the latter temperature. The results of this work (Figure 5) show that while secondary creep rates were two or three orders of magnitude greater than those obtained at 700°C, the rupture time was remarkably long in some instances--particularly if the temperature (0.50Tm of vanadium and 0.53 of the alloys' absolute solidus temperatures) and the magnitude of the imposed stresses are considered.

During the earlier work which produced the VANSTAR alloys[1] it was demonstrated, on the basis of the analysis of gross section samples, that the gage section of tantalum-wrapped creep specimens did not pick up carbon during creep tests, but that oxygen content did increase from 150 to 300 ppm, depending on the temperature and duration of the test. Although the creep data emanating from the present investigation in general confirm those previously obtained[1], analyses of the gross gage section of a creep specimen (VANSTAR-8, 37,500 psi, 800°C, 212 hours) and the same section with 0.0025 inch removed from both surfaces by machining, showed that the removed layers contained 1650 ppm oxygen,which is approximately double that of unexposed material. Analyses for carbon using the same method were inconclusive. Contamination during creep testing may, therefore, result in anomalously low creep rates, when tests are conducted in the $10^{-6}$ torr range in polymer sealed, oil-diffusion pumped systems.

Although mass transport of interstitials to the vanadium fuel cladding may be expected in liquid-metal-cooled reactors, the extent of the problem is not yet known. Further, it is important that base-line creep data be generated under uniformly good vacuum conditions to maximize the usefulness of the data reported by various laboratories. Therefore, some work is in progress to establish the effect of test environment on creep data. In one test, a direct comparison is made between a VANSTAR-7 specimen exposed to the "conventional" atmosphere ($10^{-6}$ torr) at 700°C and a similar specimen exposed to ultra-high vacuum ($\leq 10^{-8}$ torr) both at a stress of 40,000 psi. The former specimen exhibited a secondary creep rate of $5.6 \times 10^{-4}$/hour, and was still in second stage creep when the test was discontinued (500 hours). A third test will consist of reloading the VANSTAR-7 specimen, previously tested at $10^{-6}$ torr, to the same stress and temperature as before, but in ultra-high vacuum.

## Thermal Stability

The hardness response of the VANSTAR alloys to one-hour thermal treatments is shown in Figure 6. VANSTAR-7 and VANSTAR-9 are reasonably stable, although the cause of the high hardness of VANSTAR-7 annealed at 1350°C, which has been observed on several occasions, is not presently understood. The peak in hardness observed for VANSTAR-8 annealed at 1500°C is a result of aging effects that were observable in the microstructure. At 600 and 800°C (Figure 7) some grain boundary precipitates are noticeable. Overaging was detected by softening as well as by the presence, within grains, of fine and coarse precipitates after the 1000 and 1200°C treatments, respectively.

The effects of 500-hour aging treatments at 700 and 800°C were also examined during this period. Aging was performed in ion-pumped systems operating in

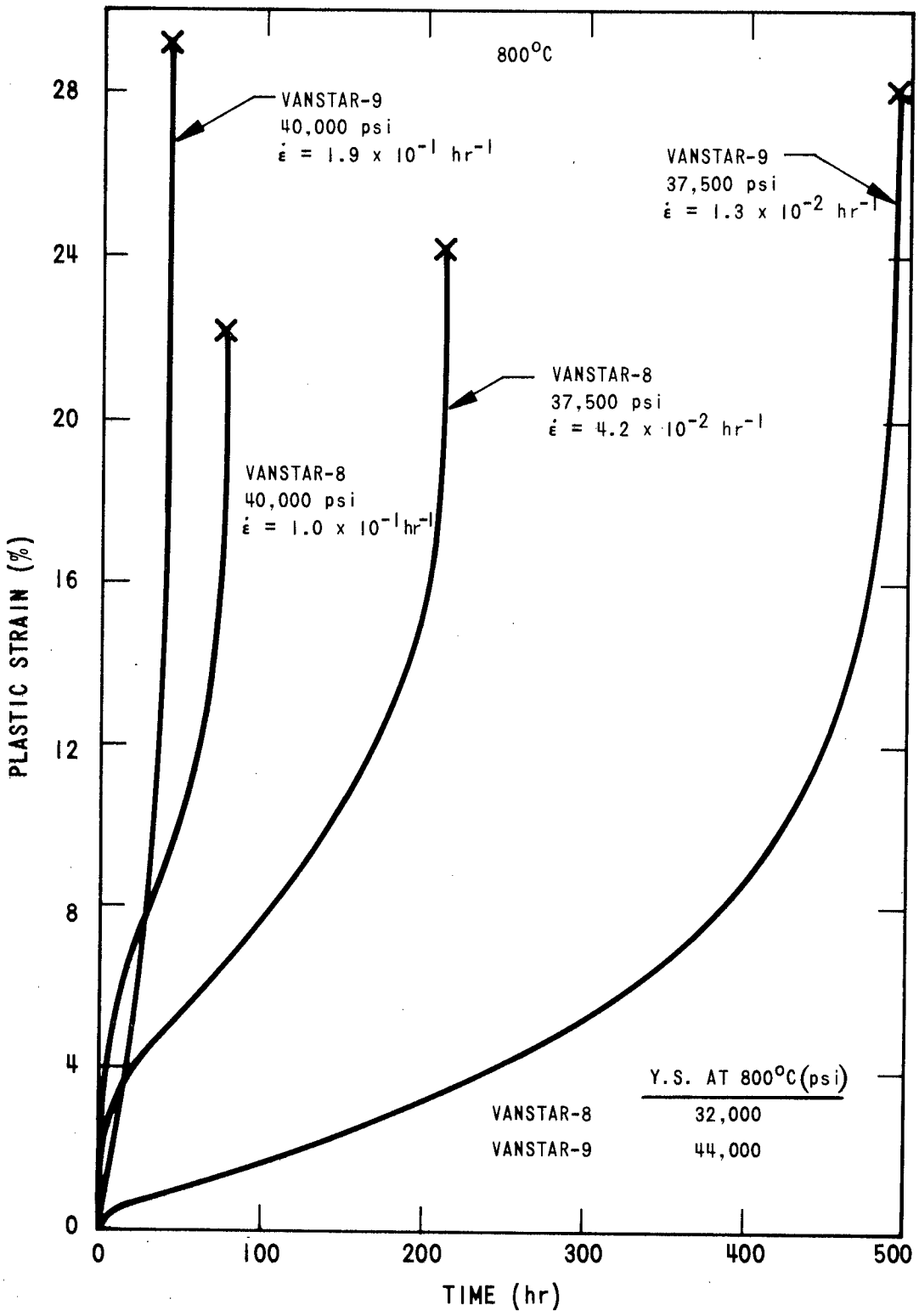



Figure 5 800°C Creep Curves for VANSTAR-8 and VANSTAR-9 Sheet Annealed at 1200°C Tests Conducted at $10^{-6}$ torr.

3122-5

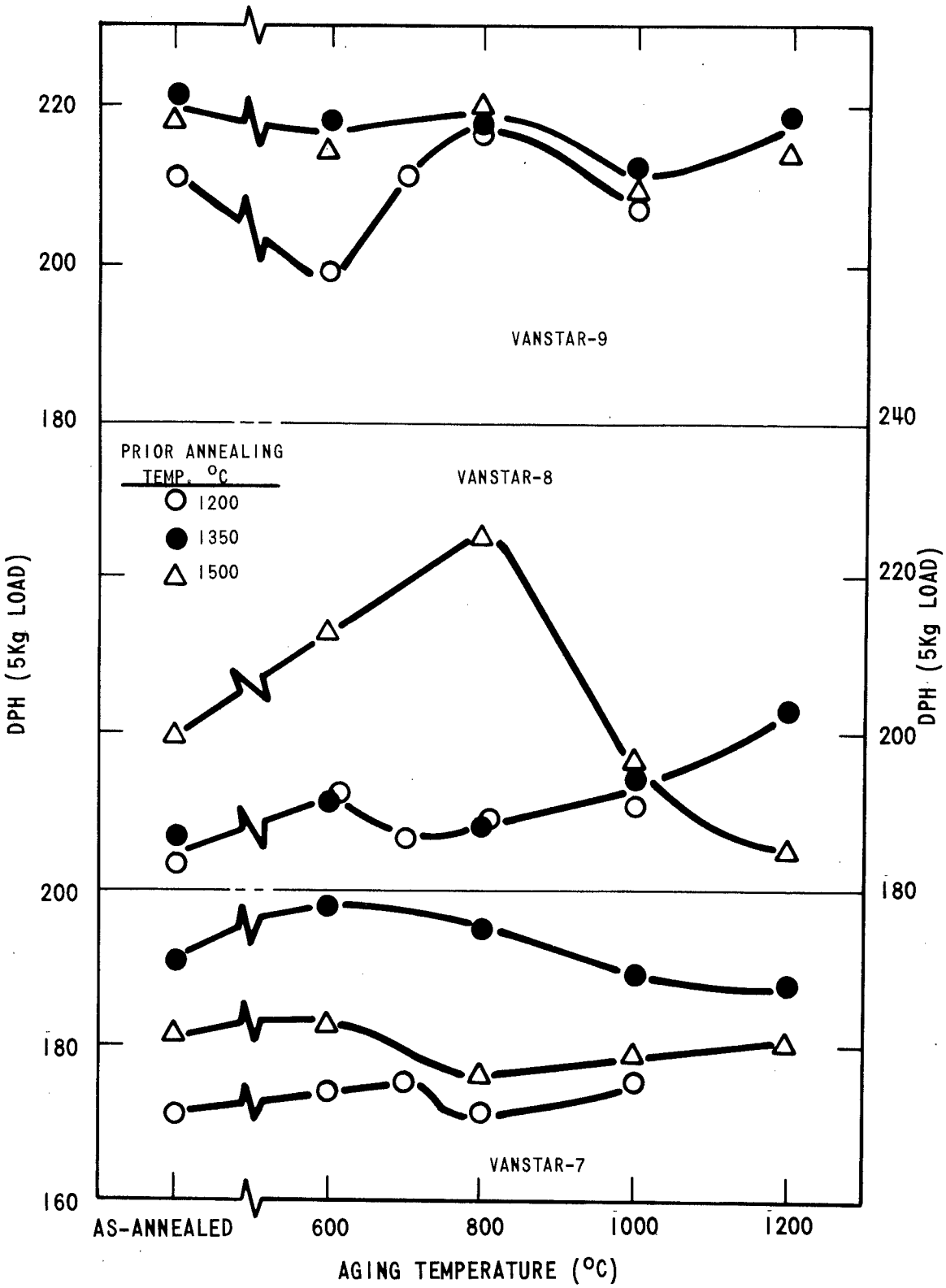
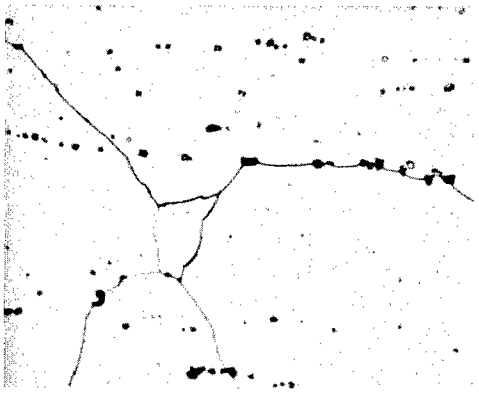
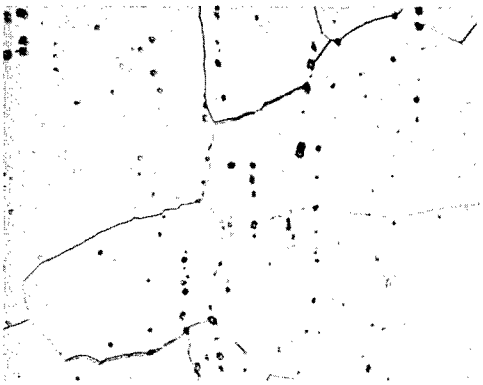



Figure 6 One-Hour Aging Response of VANSTAR Alloy Previously Annealed at 1200, 1350, or 1500°C

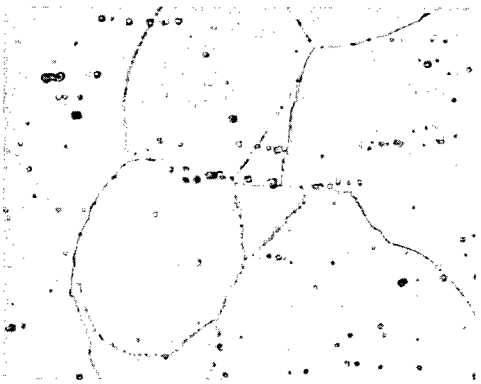
3122-6



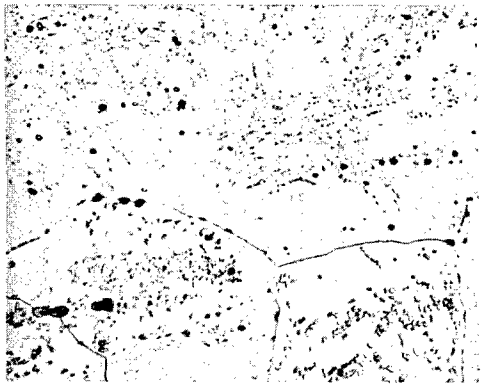
AS ANNEALED (1500°C-1hr)



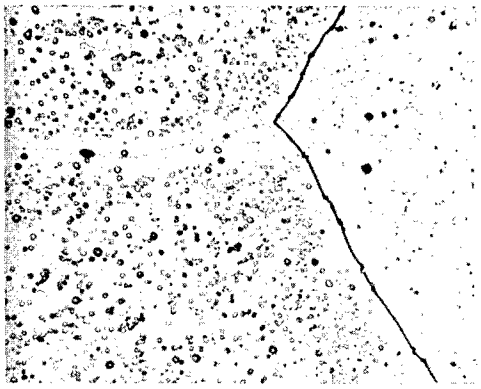
AGED AT 600°C-1hr



AGED AT 800°C-1hr



AGED AT 1000°C-1hr



AGED AT 1200°C-1hr

50 μ

Figure 7 Effect of Thermal Exposure on Microstructure of VANSTAR-8 Originally Annealed at 1500°C

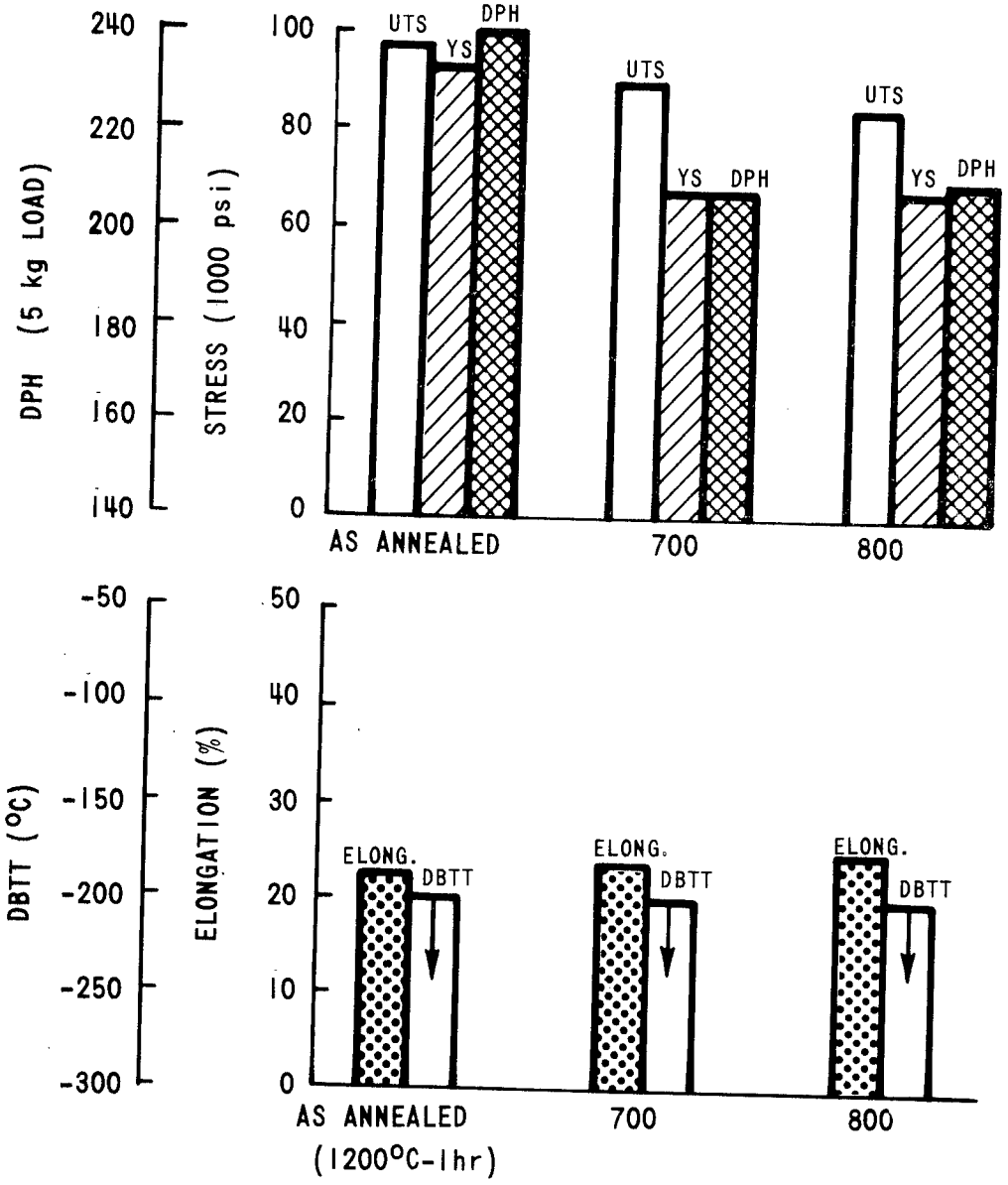
3122-7

the $10^{-8}$ torr range. All specimens were acid etched and wrapped in clean tantalum foil prior to thermal exposure. Changes in ductile-brittle bend transition temperature (DBTT) and in room temperature hardness and tensile properties are shown in Figure 8. Of the four alloys tested, V - 20Ti was most severely affected. Yield strength and hardness reductions of about 20,000 psi and 30 DPH, respectively, were observed for the alloy; however, ductility was not impaired and tensile elongation actually increased slightly. VANSTAR-9 properties were apparently unaffected by the 500-hour treatments, but slight progressive increases in hardness and decreases in tensile elongation were observed for VANSTAR-7. VANSTAR-8, aged at 800°C exhibited slightly higher hardness than unaged material, and the bend transition temperature increased from <-196°C to about -150°C, but these changes in properties are not judged indicative of gross instability.

The elevated temperature tensile properties of the four alloys, prior to and subsequent to thermal exposure, are given in Figure 9. As for the 20°C data (Figure 8), the most significant effect was the reduction in strength for the V - 20Ti alloy. The properties of the VANSTAR alloys were not greatly changed by the heat treatments, although some reduction of tensile ductility was observed for VANSTAR-8 aged and tested at 800°C.

Although the thermal treatments sometimes had no apparent effect on mechanical properties, some structural instability was observed for each alloy. The V - 20Ti alloy was particularly affected, and typical microstructures are shown in Figure 10. The annealed sheet of this alloy contains precipitates, presumably titanium carbides and/or carbonitrides, that are uniformly dispersed throughout the structure. During the 700 and 800°C heat treatments, additional precipitation, and overaging, occurred. In addition, diffusion of elements to the grain boundaries resulted in the creation of a new phase and in the denudation of precipitates in the areas adjacent to the new phase. It is also apparent that there is a large difference in the solubility of the precipitating elements at 700 and 800°C. The annealing temperature of 1200°C, it may be argued, is high in view of the grain size it produces. This is true, but it is also true that the 900°C annealing temperature frequently used for the alloy does not always fully recrystallize the structure, particularly when the amount of prior cold reduction is low. Furthermore, the aging data for 1200°C-annealed material may be indicative of the stability of welds at the test temperature since welding will produce large-grained structures and should be an effective solution treatment. Nevertheless, some evaluation of 900°C-annealed material will be performed as schedules and material availability permit.

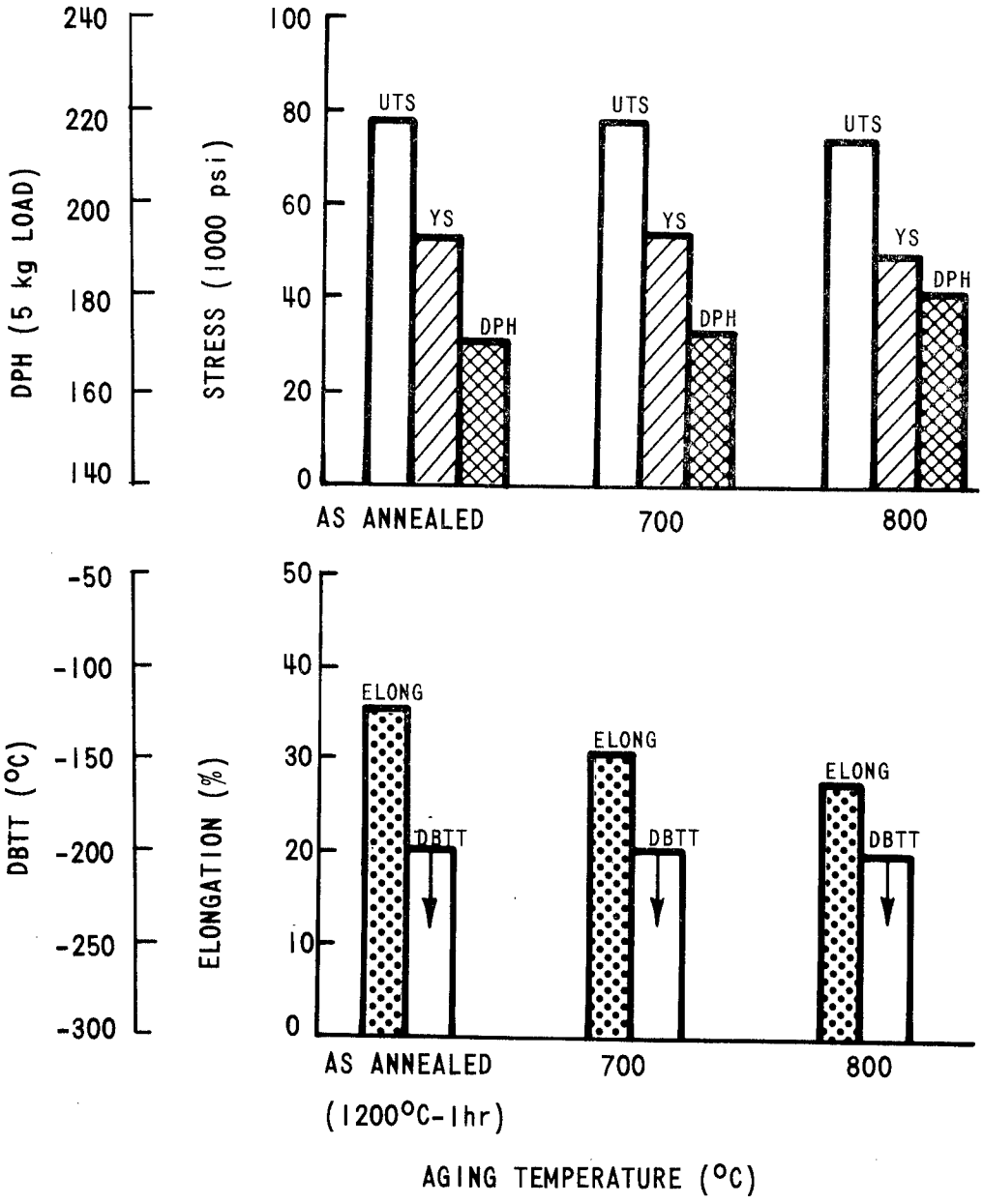
Additional precipitates were also observed in the structures of the VANSTAR alloys exposed at 800°C (Figure 11). VANSTAR-8 so treated contains blocky grain boundary precipitates that are the apparent cause for the somewhat higher transition temperature, since the fractures in bend specimens were intergranular. The precipitates seen in VANSTAR-7 and -9 appear similar, yet altered mechanical properties were observed only for VANSTAR-7. The composition of the new precipitates is unknown. However, work is under way to establish their identity by means of x-ray analysis of extracted residues and, for V - 20Ti, electron microprobe study.




a. V-20 Ti

Figure 8 (a) Effect of 500-hour Thermal Exposure on the Bend Transition Temperature, Hardness, and 20°C Tensile Properties of Vanadium Alloys

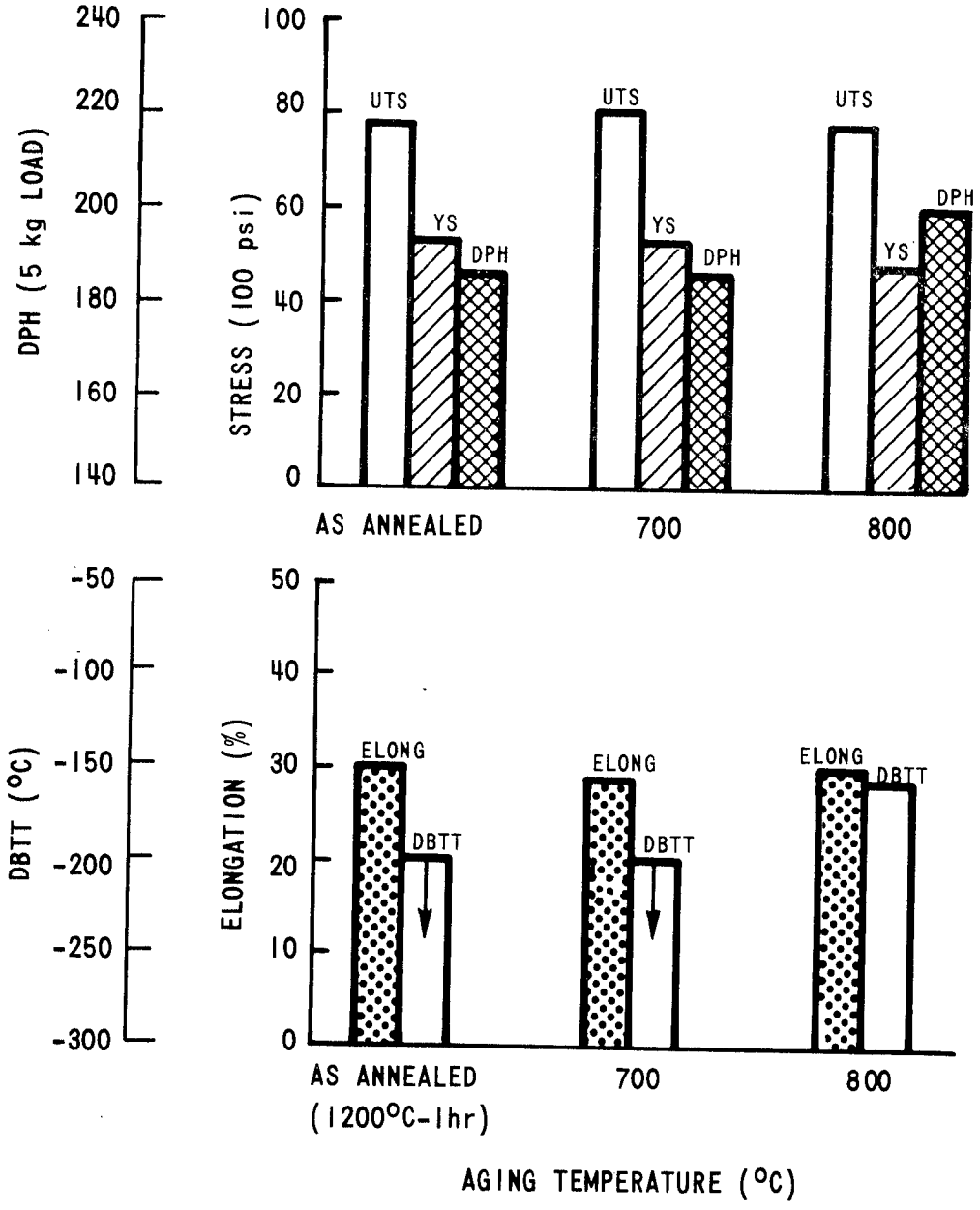
3122-8




b. VANSTAR-7

Figure 8 (b)

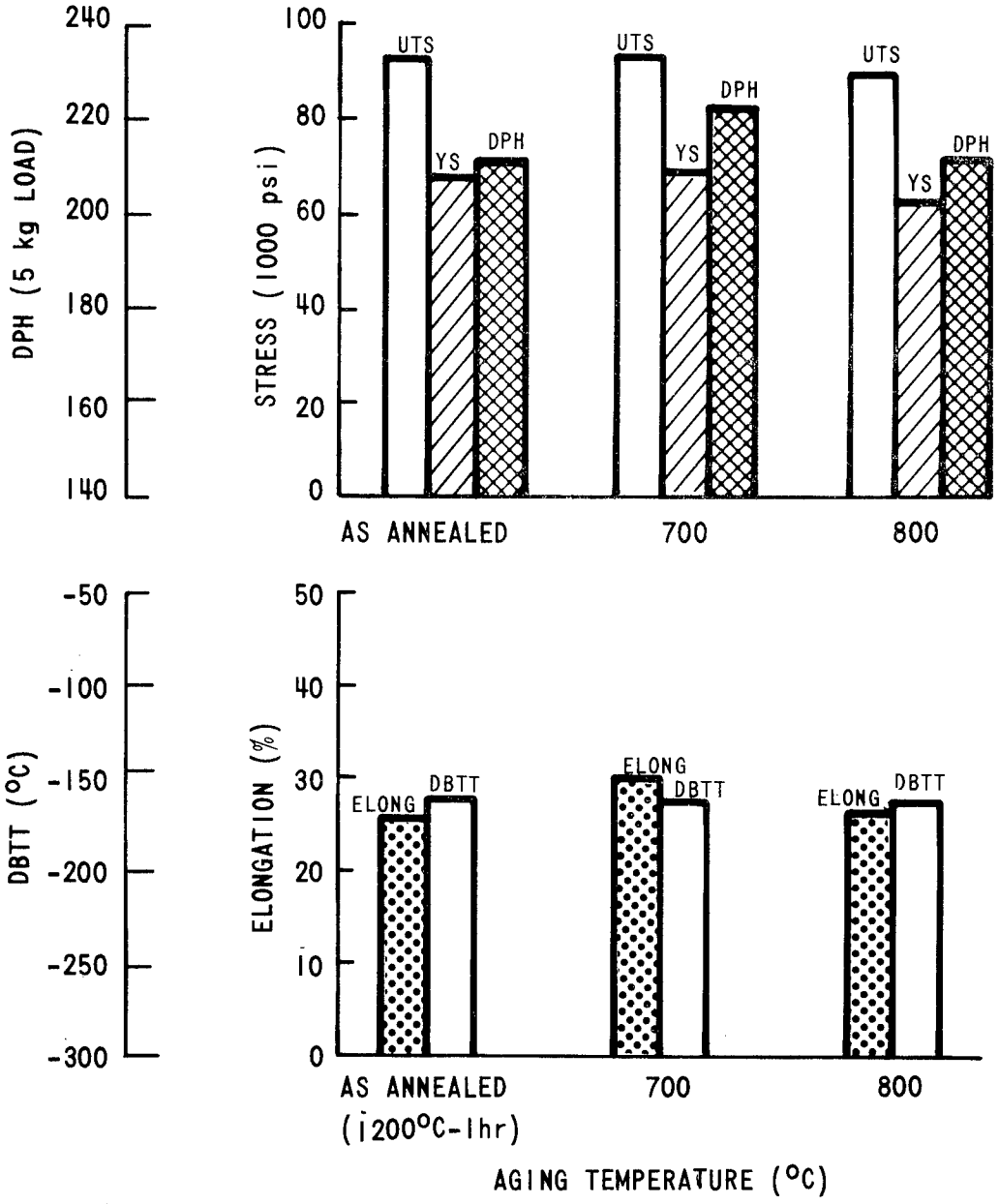
3122-9




c. VANSTAR-8

Figure 8 (c)

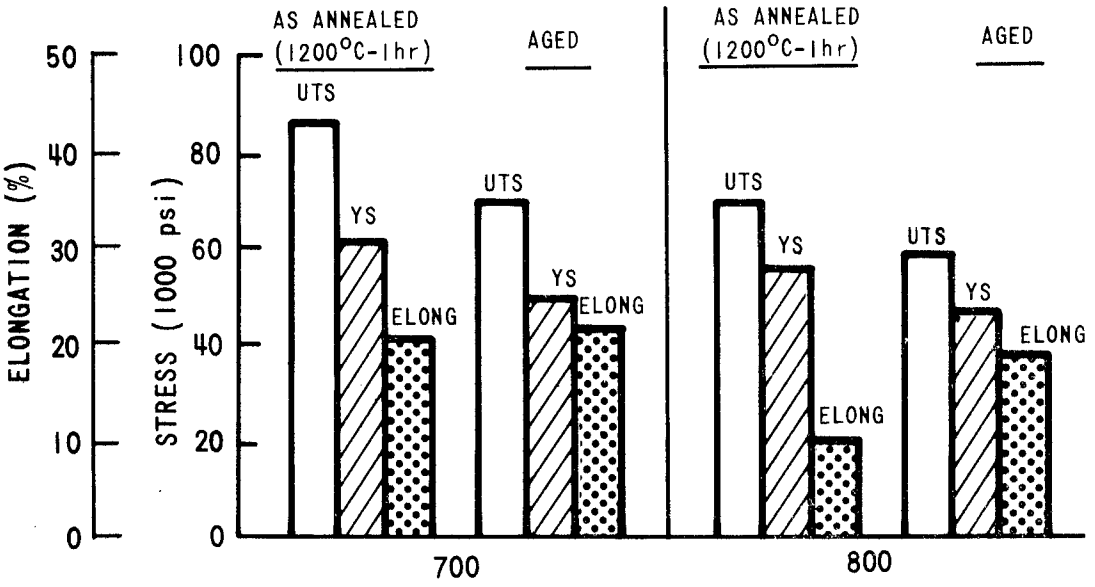
3122-10



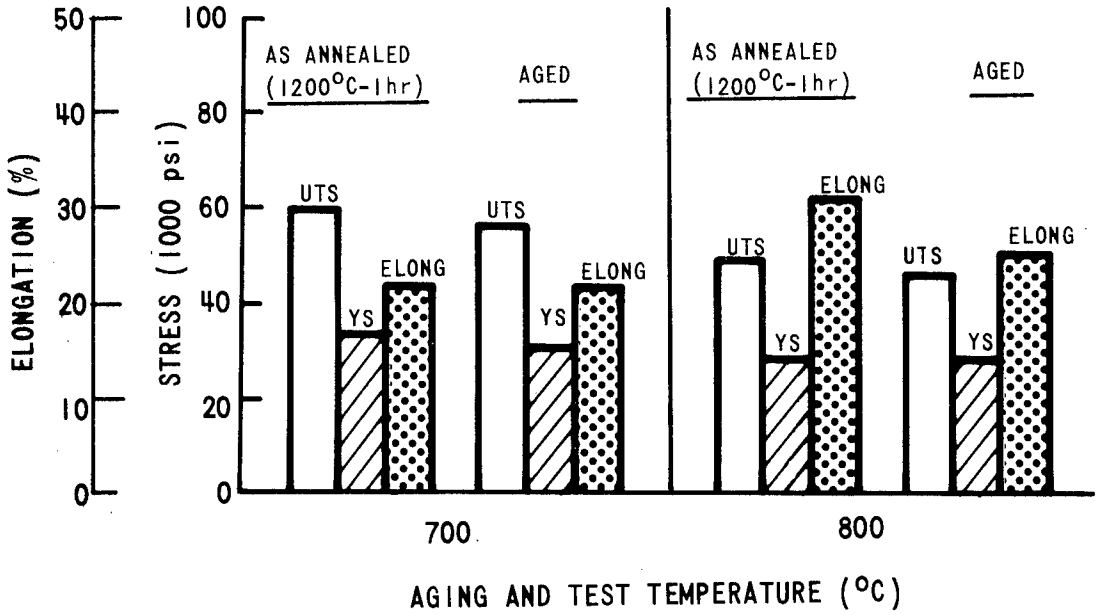

d. VANSTAR-9

Figure 8 (d)

3122-11



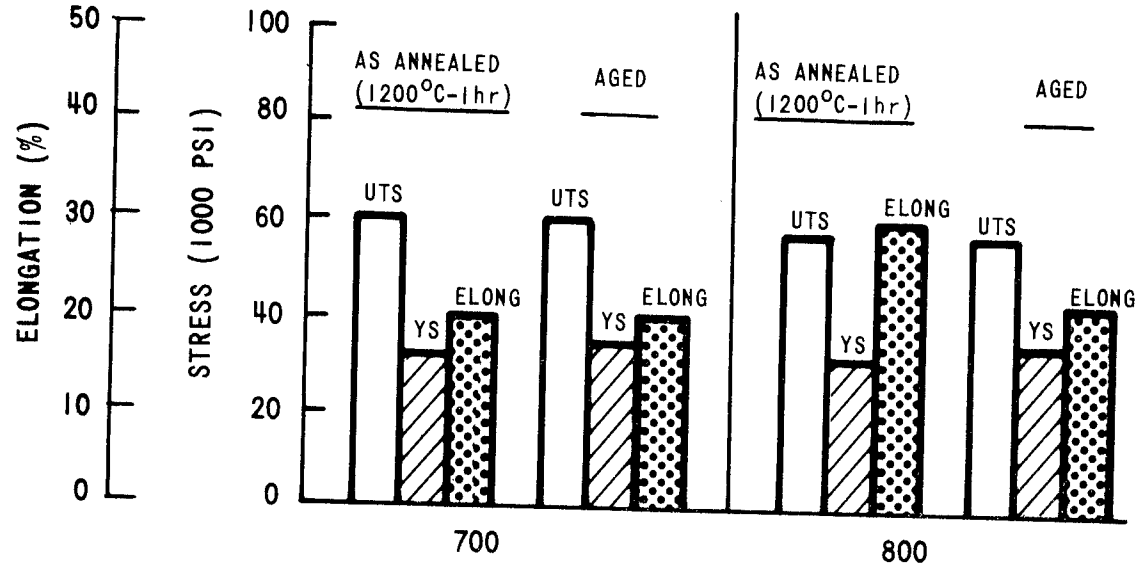

a. V-20 Ti



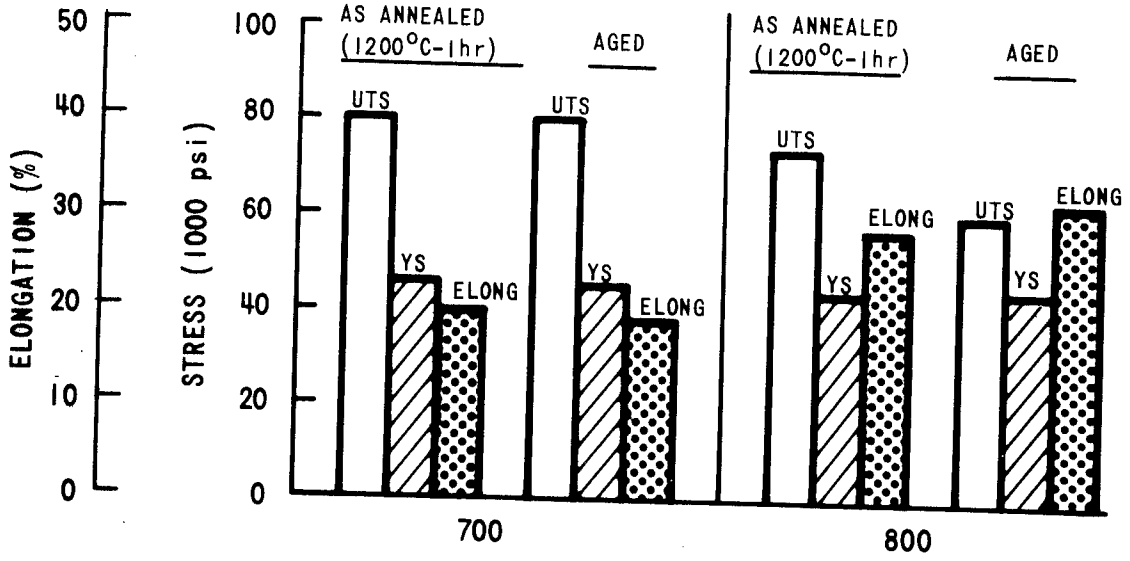

b. VANSTAR-7

Figure 9 Effect of 500-hour Thermal Exposure on the Elevated Temperature Tensile Properties of Vanadium Alloys

3122-12




c. VANSTAR-8




d. VANSTAR-9

Figure 9 (Continued)

3122-13

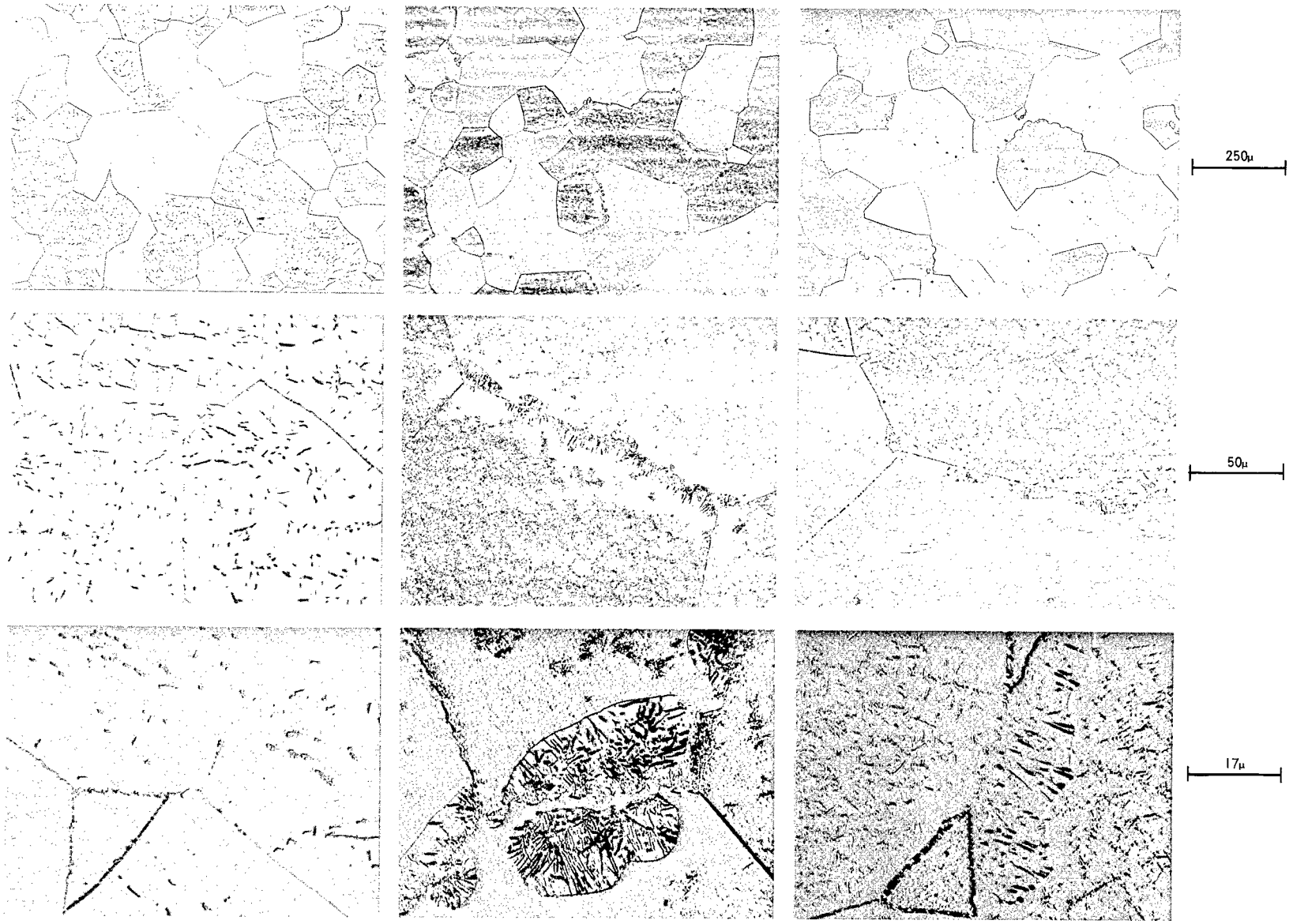
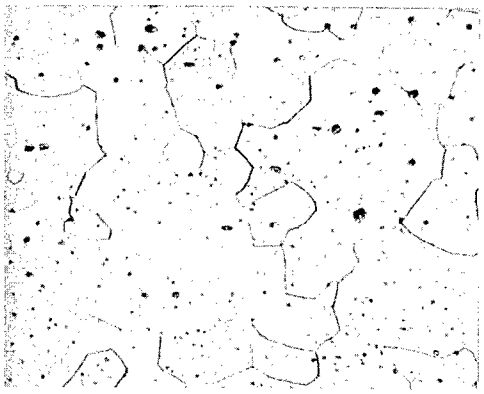
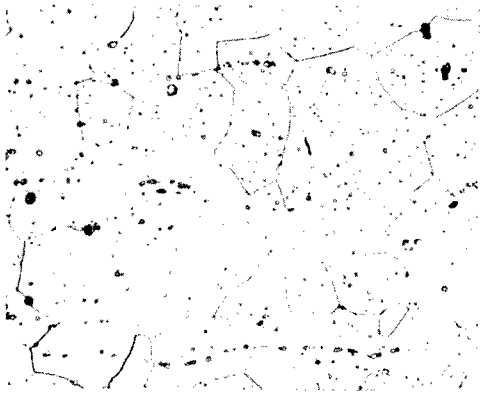


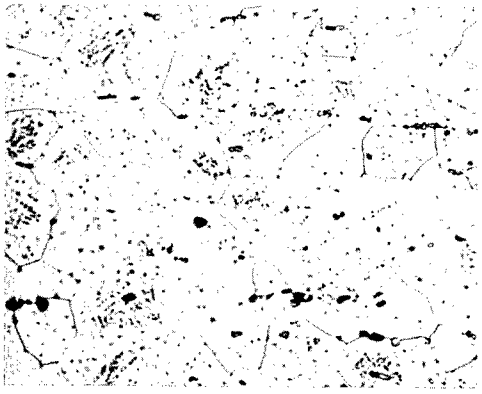

Figure 10 Effect of Thermal Exposure on Microstructure of V-20 Ti




AS ANNEALED (1200°C-1hr)




700°C-500hr



800°C-500hr




800°C-500hr

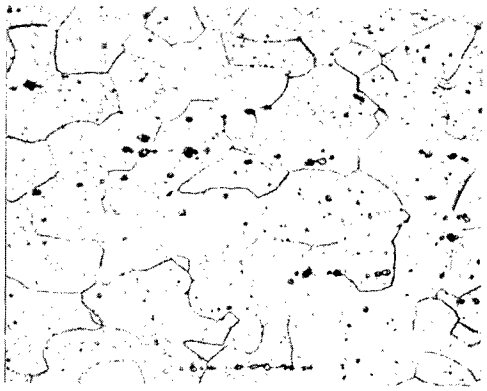



OBLIQUE LIGHTING

a. VANSTAR-7

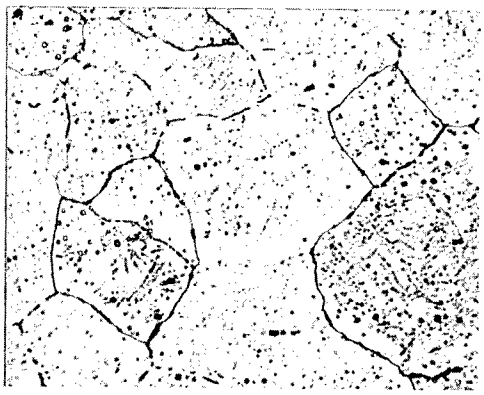
Figure 11 (a) Effect of Thermal Exposure on Microstructure of Vanadium Alloys

3122-15




AS ANNEALED (1200°C-1hr)


700°C-500hr




800°C-500hr

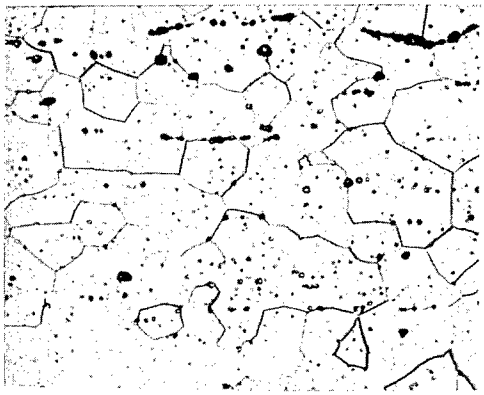

800°C-500hr

OBLIQUE LIGHTING

b. VANSTAR-8

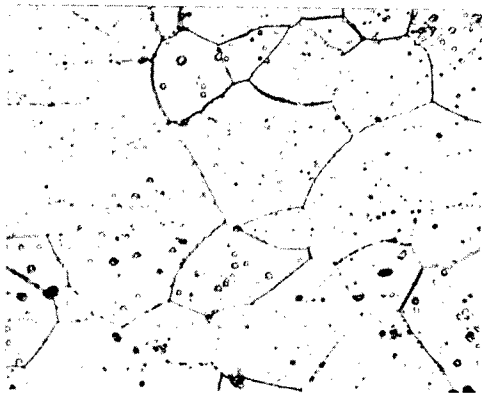
Figure 11 (b)

3122-16



50 μ

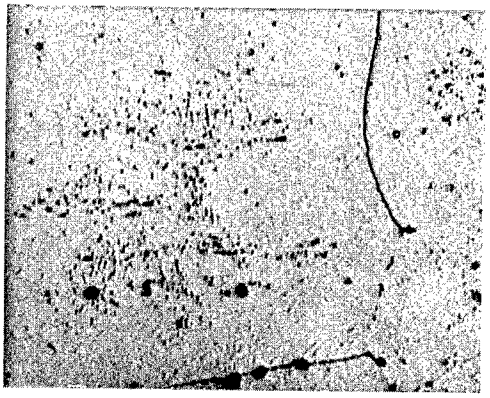
AS ANNEALED (1200°C-1hr)



50 μ

700°C-500hr

800°C-500hr 50 μ



800°C-500hr 17μ

OBLIQUE LIGHTING

c. VANSTAR-9

Figure 11 (c)

3122-17

# VCAA-130 - SODIUM CORROSION EVALUATION

R. J. Hornak, S. L. Schrock, G. A. Whitlow

## OBJECTIVES

The objectives of this task are to evaluate the effects of flowing sodium in the temperature range of 700 to 800°C on the corrosion and mechanical properties of the two selected vanadium-base alloys (VANSTAR-8 and VANSTAR-9) and the V - 20Ti alloy, and to gain some understanding of the mechanism of the corrosion process. The study is being conducted in two pumped loops, investigating the variables of temperature, flow rate, and time.

## PRIOR WORK

All work related to the present investigation and performed prior to the present period was fully reported in previous Vanadium Alloy Cladding Development Quarterly Progress Reports[2,3,4,5,6].

It was found that when exposed in VTL-1 to sodium @ 675 to 800°C, flowing at 5 fps and containing ∿10 ppm oxygen, samples of the VANSTAR-7, VANSTAR-9, and the V - 20Ti alloys gained weight. The increases in weight were accompanied by microstructural changes and hardness increases, both resulting from the absorption of interstitials by the alloy. The ductile-brittle bend transition behavior of all three alloys was adversely affected after 500-hours exposure. Some reduction was observed in the elevated temperature tensile properties of the VANSTAR-7 and VANSTAR-9 alloys.

## CURRENT PROGRESS

### Loop Operation

The low-velocity (5 fps) loop system has now accumulated 2650 hours at operating temperature. Previous analyses for oxygen content of the sodium in this loop have indicated an average value of ∿15 ppm. However, some work was recently completed on the determination of the "bias" in the result introduced by the oxygen content of the stainless steel tube which contains the sodium sample, and which is carried through with the sodium in the amalgamation step. In addition, the interference of hydrogen in the oxygen analytical process has been examined. The results of these two investigations indicate that there is a 'blank' associated with the oxygen in sodium determination of 5 to 8 ppm. Therefore, the corrected oxygen analyses of

both VTL-1 and VTL-2 are now described as < 10 ppm. All results presented in previous quarterly reports on this contract should be amended accordingly.

The higher-velocity (14 fps) loop system, VTL-2, has now completed operation after 1500 hours at temperature. Although VTL-2 was originally a three-time-leg loop system, one leg was lost due to failure of a clamshell heater and subsequent tubing collapse; hence the effect of velocity on these vanadium alloys may be compared at only two times, viz. 500 and 1500 hours.

During this quarter, WARD has participated in an ANL-organized program designed to compare the oxygen levels of the experimental loop systems of the laboratories in this country and those in Karlsruhe, West Germany working in the field of vanadium alloy sodium corrosion. ANL submitted samples of 0.010-inch-diameter unalloyed vanadium wire for insertion in the respective loop systems. The operation of VTL-1 and VTL-2 has therefore been interrupted to allow for this insertion. After 48 hours exposure, the samples were removed from the loop systems and cleaned in methanol. Two lengths of four inches each were returned to ANL for analysis by an internal friction technique. At the same time, conventional analyses of the remainder of the inserted material are being conducted by WARD.

## Data Evaluation

The first batch of samples removed from VTL-2 after 515 hours exposure to sodium, flowing at 14 fps, containing <10 ppm oxygen, over the temperature range 675 to 800°C, were all found to exhibit weight gains. In this loop system, the VANSTAR-8 was substituted for VANSTAR-7 for reasons detailed in a previous report. The weight gains observed in this run, which are plotted as average corrosion rates over the 500-hour time period against the reciprocal of the absolute temperature (Figure 12), were slightly greater for VANSTAR-8 than for VANSTAR-9. As observed previously at the lower velocity, the V - 20Ti alloy again exhibited weight gains or average corrosion rates three times the magnitudes of those of the VANSTAR alloys. In all cases, weight gains increased with an increase in sample temperature.

If the data in Figure 12 are compared with those obtained from the first run in VTL-1 (the lower-velocity system) (Figure 13), it can perhaps be inferred that at 500 hours, VANSTAR-8 has a higher average corrosion rate than the other two VANSTAR alloys when allowances are made for the velocity difference. When the 1500-hour data of Figure 13 are examined, it is seen that VANSTAR-7 has a lower corrosion rate than VANSTAR-9. When the data from the 1500-hour exposure in VTL-2 are available, it should be possible to make a more definitive comparison of the respective corrosion rates of the VANSTAR alloys.

Figure 14 illustrates the dependence of average 500-hour corrosion rate on velocity for VANSTAR-9 and the V - 20Ti alloy. The increase in rate with velocity increase appears to be constant over the temperature range 675 to 800°C. There would appear to be a parabolic dependence of weight change on the velocity, as shown in Figures 15 and 16, for these two alloys.

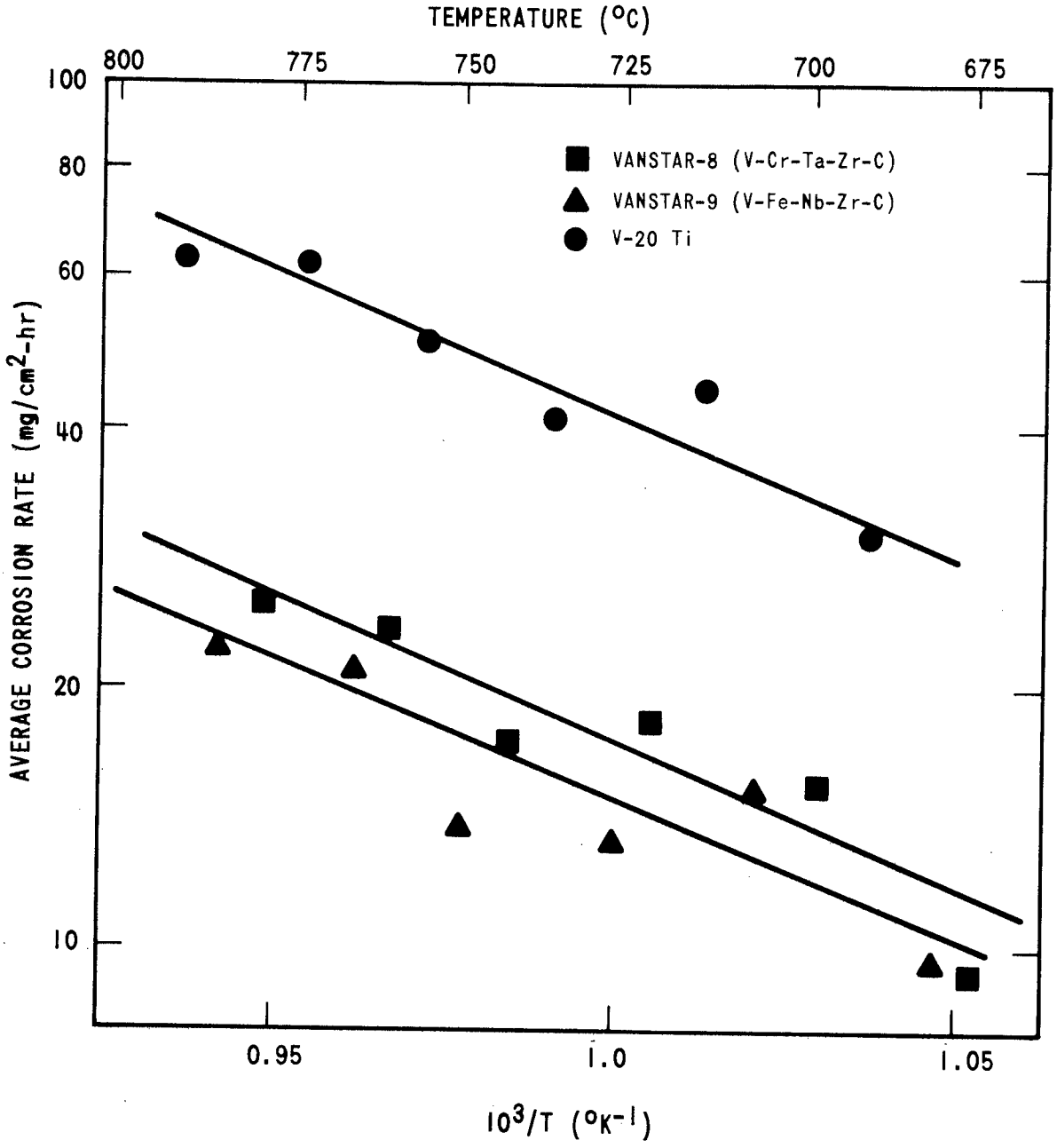



Figure 12 Dependence of Average Corrosion Rate over 500 Hours on Temperature for three Vanadium Alloys Exposed to Sodium Containing < 10 ppm Oxygen and Flowing at 14 fps (VTL-2 Run 1)

3122-18

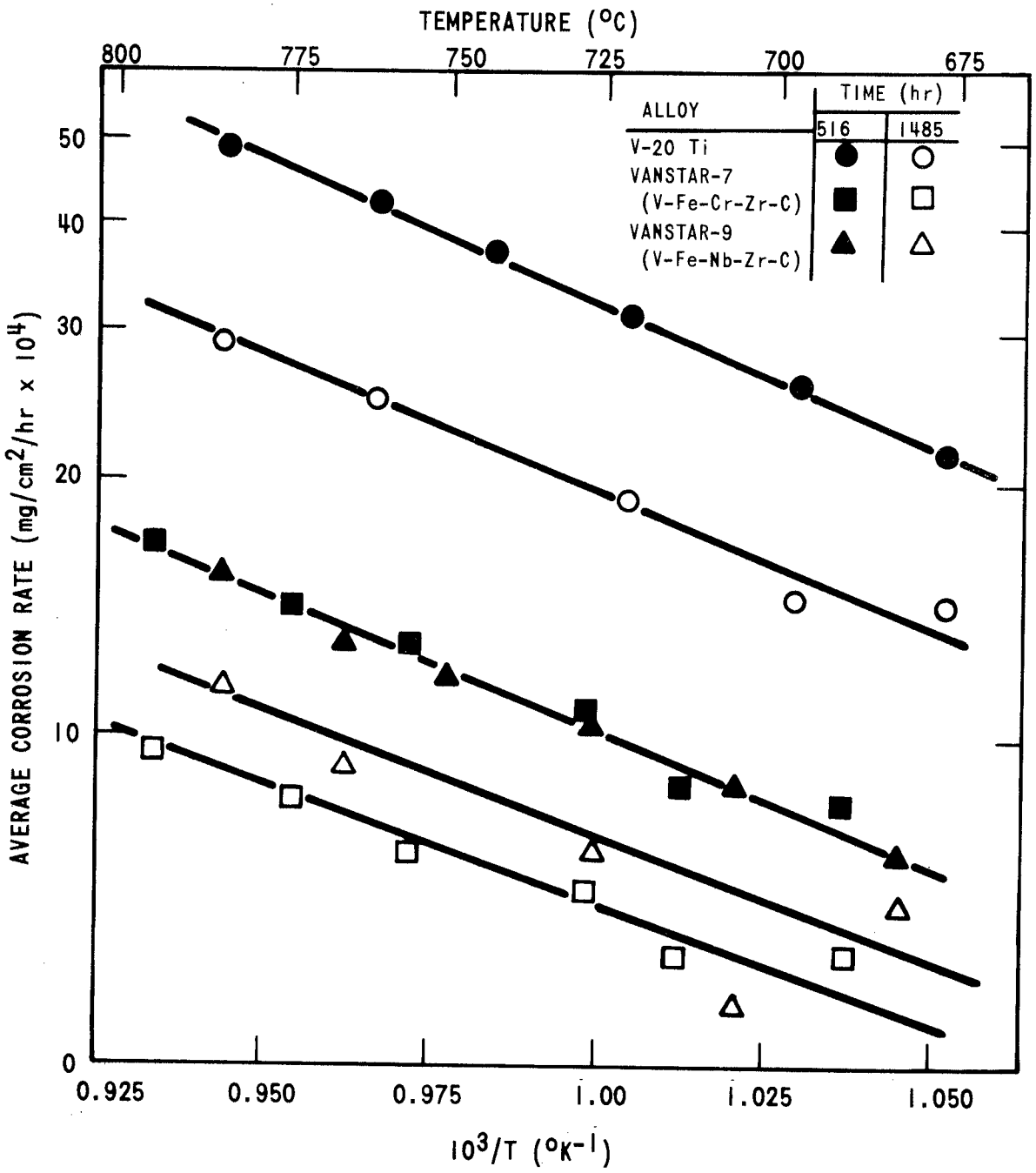



Figure 13 Effect of Time and Temperature on the Corrosion Rate of Vanadium Alloys in Sodium Containing < 10 ppm Oxygen and Flowing at 5 fps (VTL-1 Run 1)

3122-19

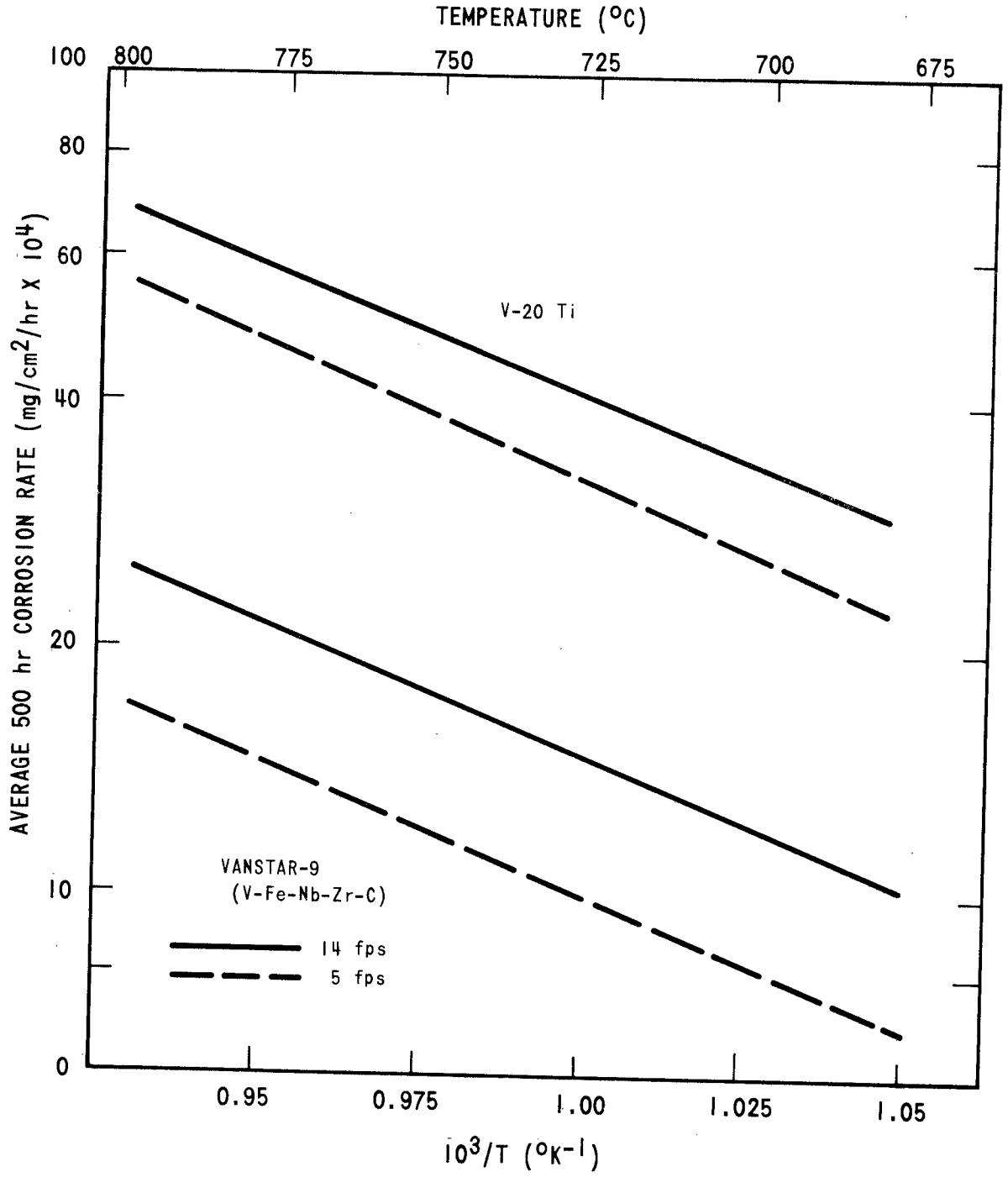



Figure 14 The Effect of Velocity on the Dependence of Average Corrosion Rate over 500 Hours on Temperature for two Vanadium Alloys Exposed to Sodium Containing < 10 ppm Oxygen

3122-20

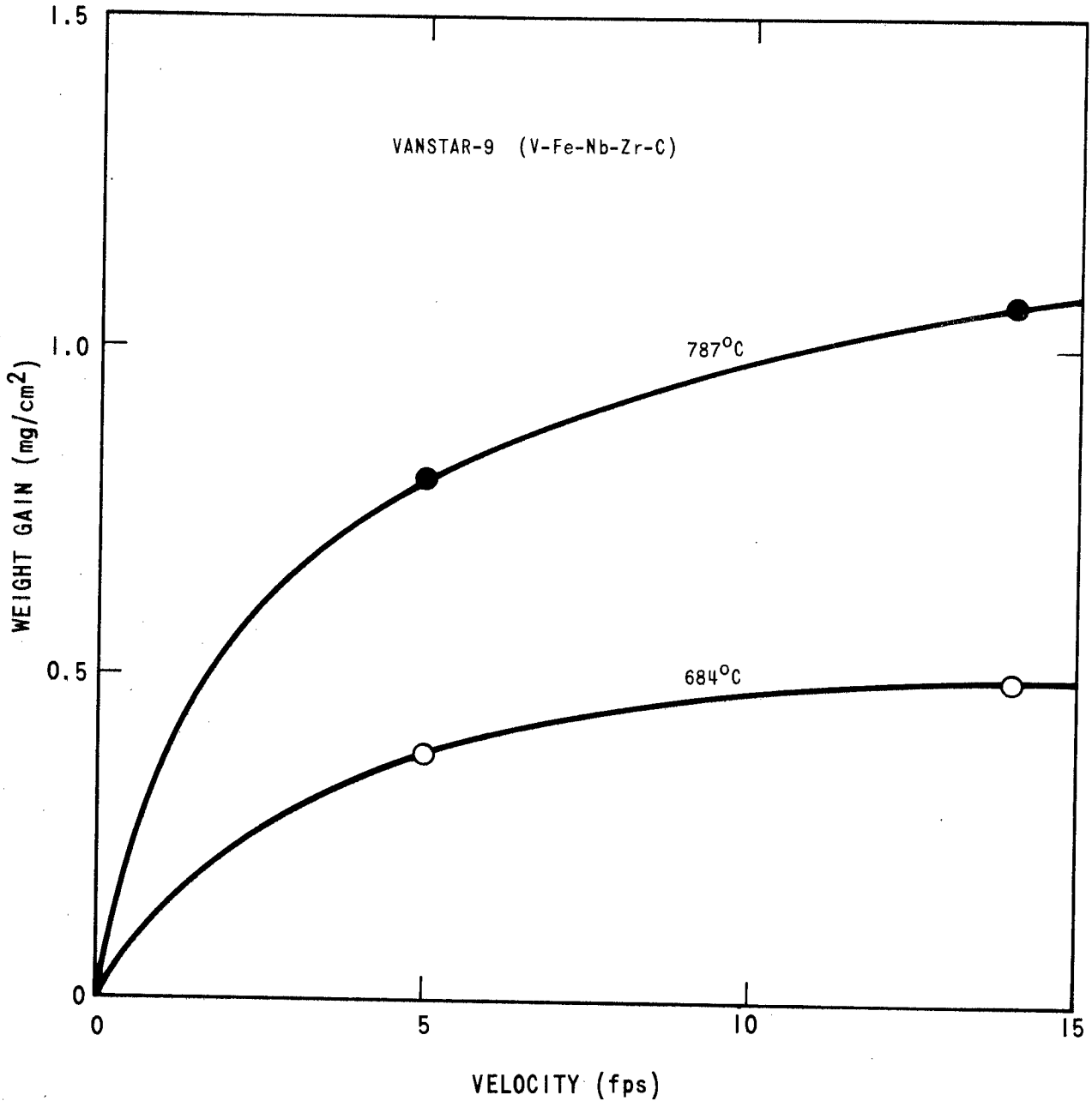



Figure 15 Dependence of Weight Change on Velocity for the VANSTAR-9 (V-Fe-Nb-Zr-C) Alloy after 500-hour Exposure to Sodium Containing < 10 ppm Oxygen at Two Temperatures

3122-27

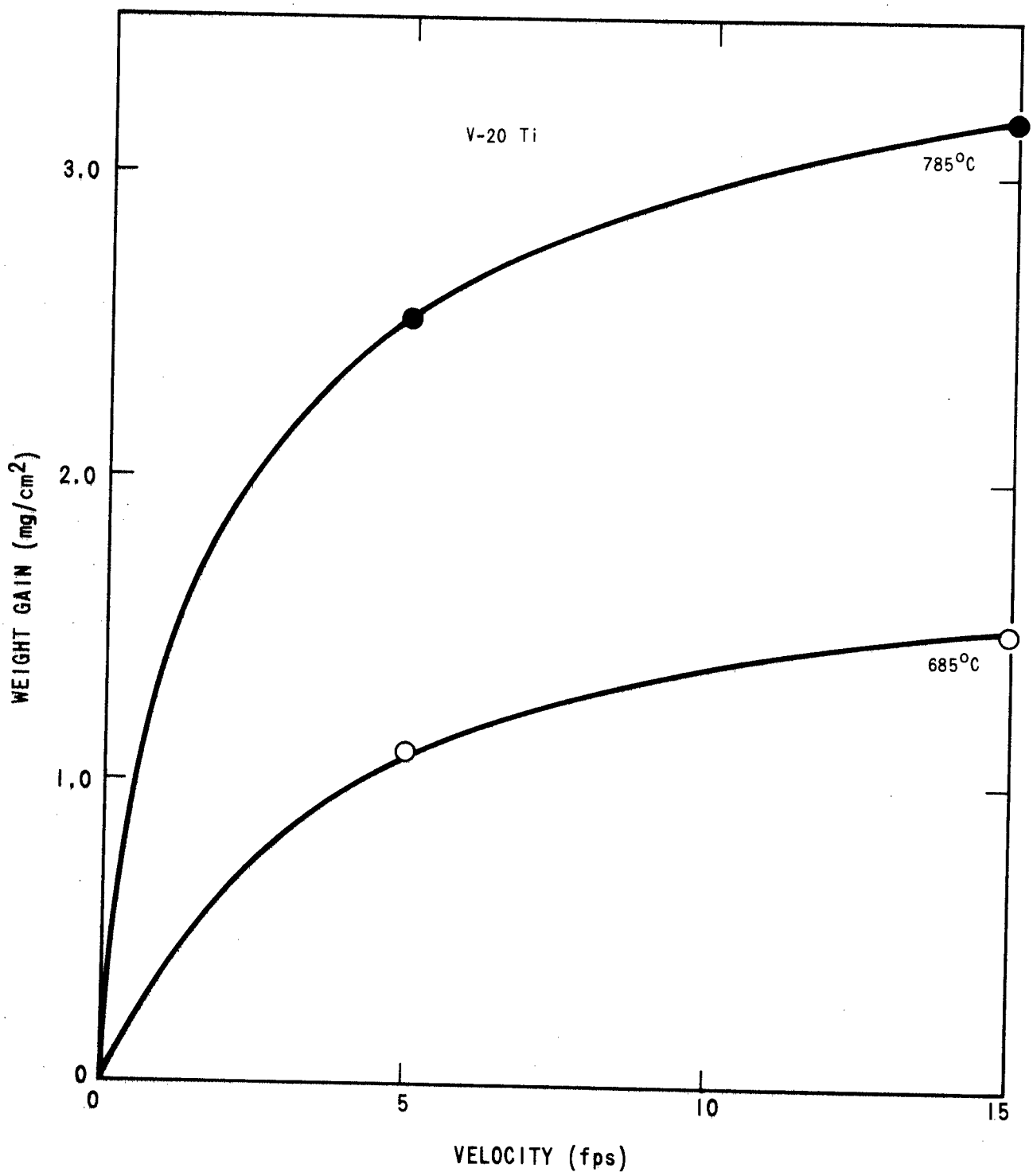



Figure 16 Dependence of Weight Change on Velocity for the V-20 Ti Alloy after 500-hour Exposure to Sodium Containing < 10 ppm Oxygen at Two Temperatures

3122-22

Further analysis of the corrosion results obtained in the low-velocity system has been progressing. In corrosion studies of a V - 20Ti alloy at ANL, Greenburg et al[13] reported that the weight gains in sodium containing less than 10 to 15 ppm oxygen increased parabolically with time. Since data are available only at two time periods, it is impossible to definitely assign parabolic kinetics to the corrosion processes in this WARD study. However, parabolic corrosion behavior may be inferred, since a double logarithmic plot of weight change against time has a slope of two. In addition, a plot of the square of the weight change ($\Delta w^2$) against exposure time (t), converges at or very near the origin (Figure 17). A relationship of the type, $\Delta w^2 = K_p t$, where $K_p$ = parabolic rate constant ($mg^2/cm^4/hr$), may therefore represent the corrosion kinetics. Values of the parabolic rate constant were calculated from the slope of $\Delta w^2$ against t, and the dependence of $K_p$ on temperature is shown in Figure 18 for the three vanadium alloys examined.

Values of the activation energy for corrosion, calculated from the slope of a least-squares fit of this data are:

V - 20Ti: 25,800 cals/mole

VANSTAR-9: 28,000 cals/mole

VANSTAR-7: 21,400 cals/mole

Comparative data are limited to that Greenburg et al[13] who reported an activation energy of 22,800 cals/mole for the V - 20Ti alloy in sodium, oxygen concentrations of 1 to 6 ppm. The excellent agreement between the present data and the above referenced work tends to suggest that the activation energy for corrosion in a V - 20Ti alloy is not as dependent on system operating variables as was originally thought to be the case. As will be seen later in this report, these activation energies probably are composite values for corrosion, since the corrosion process would appear to be the result of the combined diffusion of nitrogen, carbon, and oxygen into the alloy lattice.

## Metallurgical Evaluation

Preliminary microhardness data on the 1500-hour samples exposed in VTL-1 to sodium containing <10 ppm oxygen, flowing at 5 fps, over the temperature range 675 to 800°C indicated, as anticipated, that the depth of the hardened zone has increased with exposure time. Further support for the viewpoint that the corrosion kinetics are parabolic was provided by the linear relationship between the square of the depth of the hardened layer and exposure time for the V - 20Ti alloy (Figure 19).

Investigation of the absorption of interstitials by a VANSTAR-9 sample exposed to sodium at 785°C for 1500 hours has continued. Results for nitrogen and oxygen, together with the carbon figures previously reported, are indicated in Figure 20. Surface concentrations have reached a high level, particularly for nitrogen. At a depth of 0.001 inch, the following analyses were obtained:

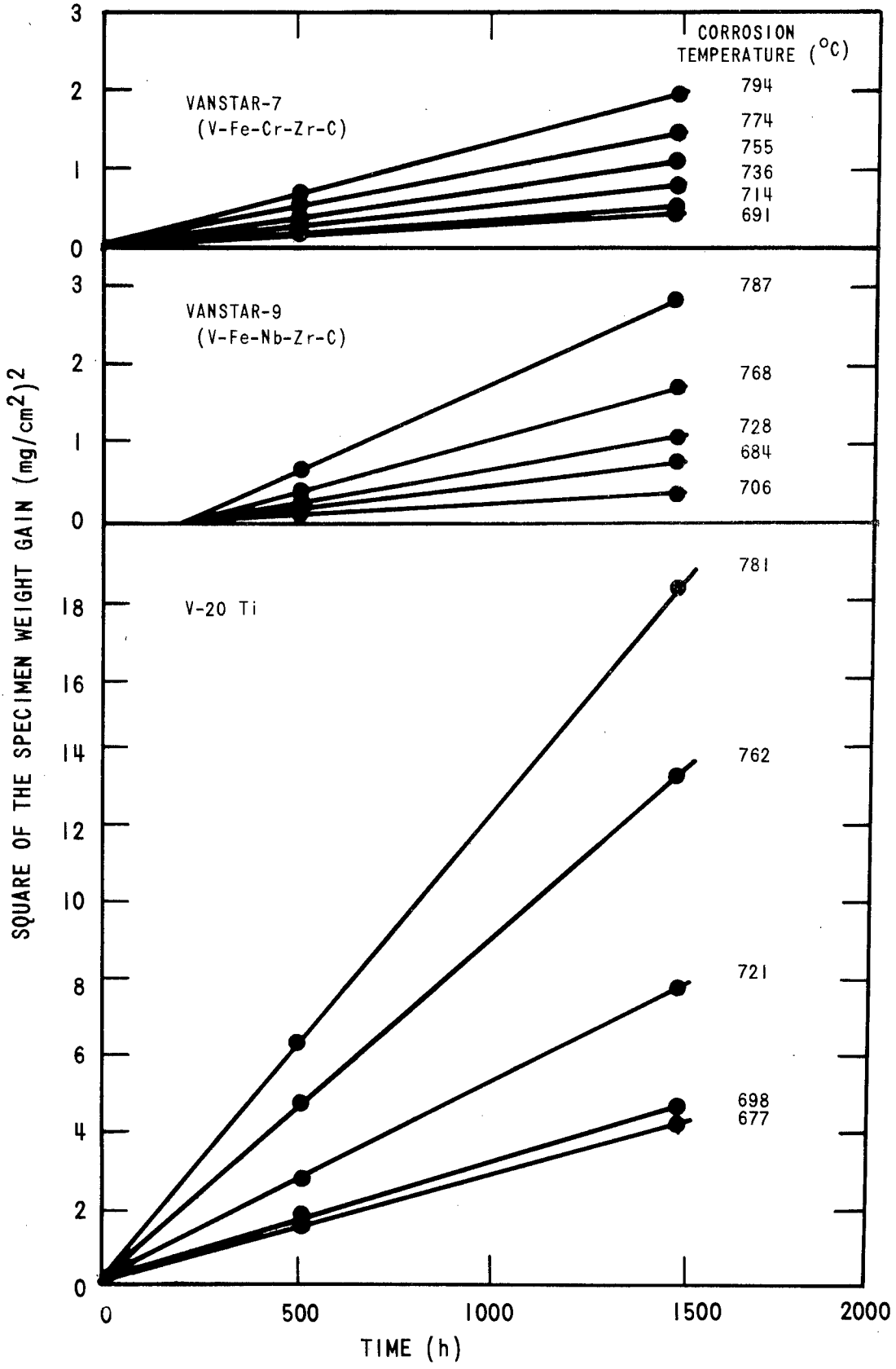



Figure 17 Dependence of Weight Change on Sodium Exposure Time, over the Temperature Range 675 to 800°C, for Three Vanadium Alloys

3122-23

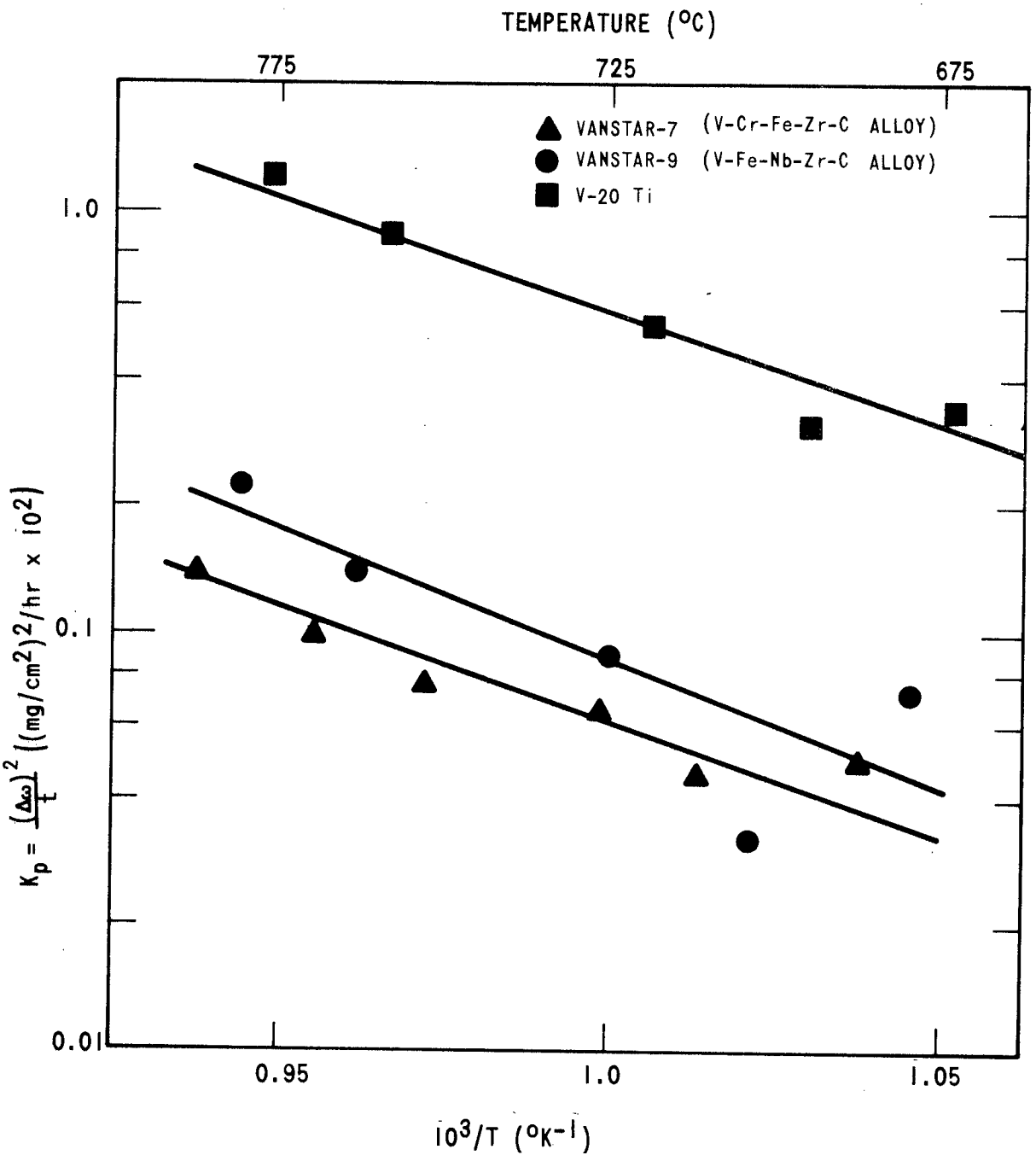



Figure 18 Dependence of Parabolic Rate Constant $K_p$ on Temperature for the Three Vanadium Alloys

3122-24

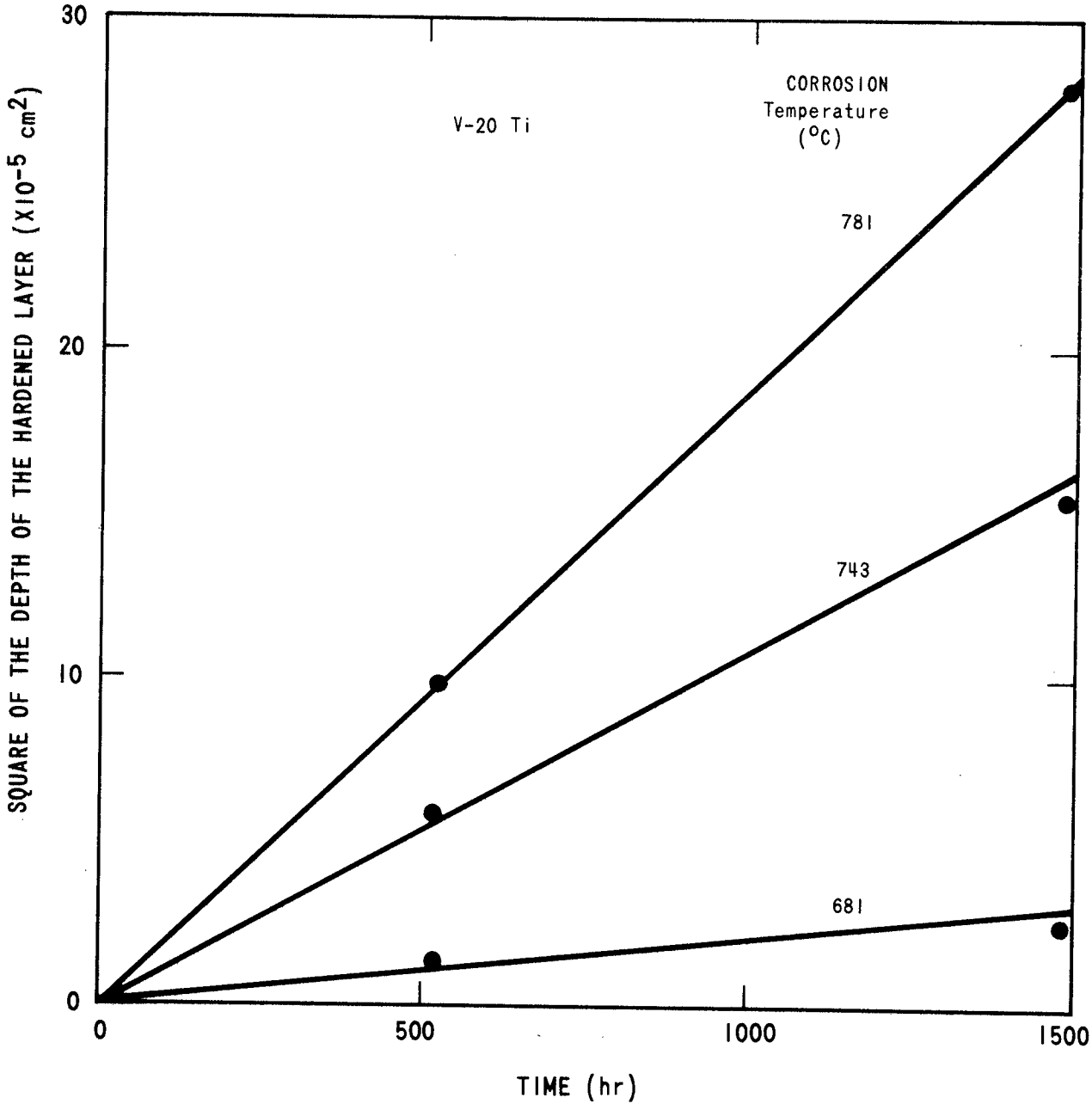



Figure 19 Dependence of the Square of the Hardened Layer Depth on Time of Exposure to Sodium for the V-20 Ti Alloy

3122-25

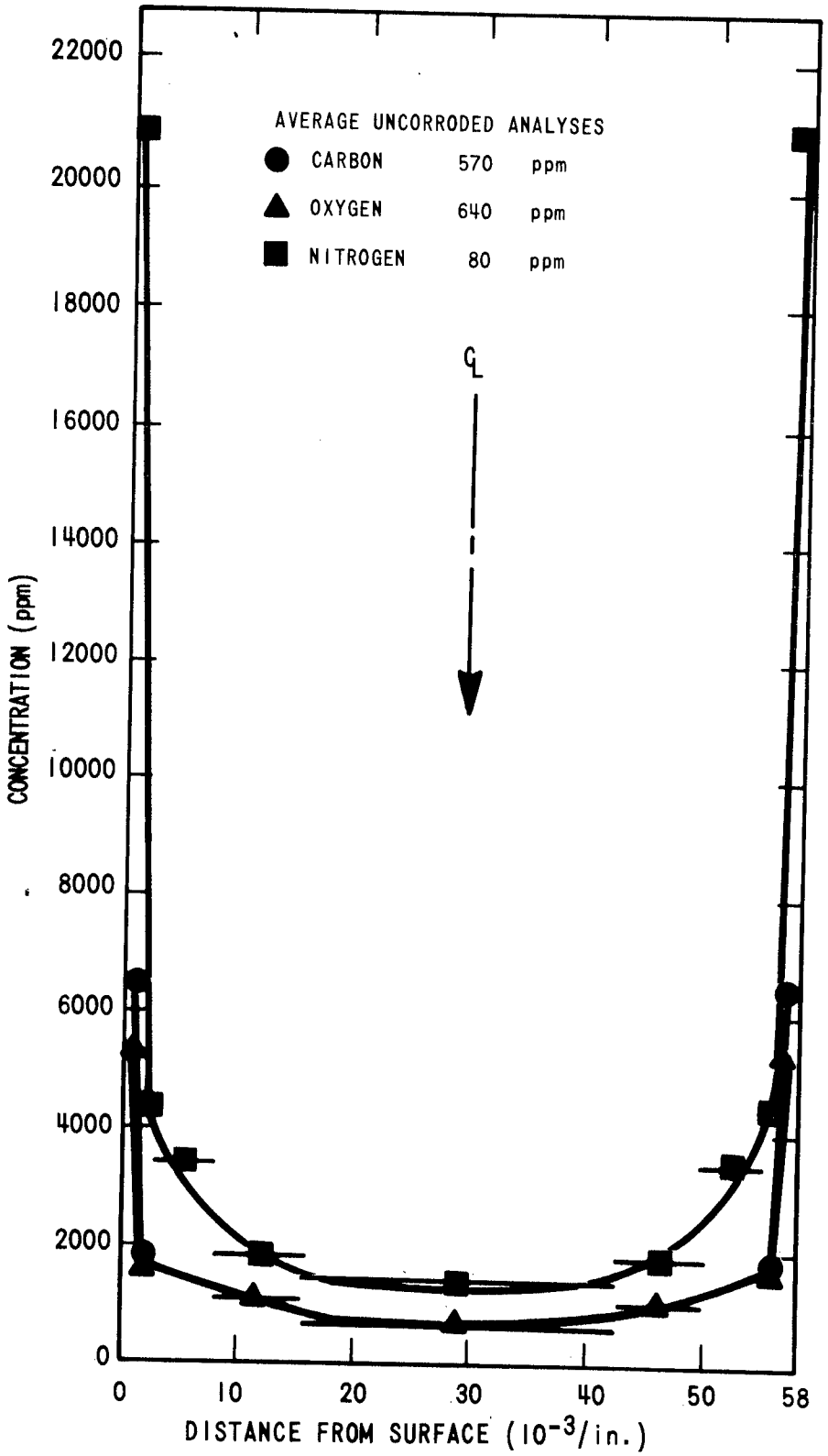



Figure 20 Interstitial Concentration Gradients in a VANSTAR-9 (V-Fe-Nb-Zr-C) Alloy after 1500-hour Exposure to Sodium at 785° Containing < 10 ppm Oxygen and Flowing at 5 fps (VTL-1 Run 1)

3122-26

| | After Corrosion (ppm) | Before Corrosion (ppm) |
|---|---|---|
| Nitrogen | 22,000 | 79 |
| Carbon | 6,500 | 570 |
| Oxygen | 5,800 | 640 |

These results are single values, and further analyses are in progress to establish their reproducibility. Analyses of the stainless steel sample holder immediately adjacent to this specimen revealed that the average nitrogen, carbon, and oxygen contents had decreased by 200, 250, and 120 ppm, respectively. Since these holders are at the same high temperature as the vanadium alloys, it is not at all surprising that a transport of interstitials from the stainless through the sodium to the vanadium alloys appears to have occurred.

If the calculated weight gain due to interstitial pick up is compared to the measured weight gain for this particular sample:

Calculated weight gain = 0.0320 gm

Measured weight gain = 0.0253 gm

there is a difference of only 20%. If this difference is significant, it may be due to loss of metallic elements from the corrosion sample. No increase in metallic contents have been detected in the sodium analyses conducted, and no data are available on possible deposition in the colder sections of the loop system.

X-ray-diffraction patterns and x-ray-fluorescence identification of the insoluble residues obtained after a bromine extraction procedure are being run on a corroded VANSTAR-9 sample.

As a rule, high-temperature parabolic corrosion kinetics which appear to be the case here, signify that the rate-determining mechanism is diffusion. Since the specimen weight changes appear to be controlled by interstitial transport, their diffusion coefficients can be calculated by solution of Fick's 2nd Law of Diffusion:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

For diffusion into a slab, from both sides, the solution of Fick's Law[14] yields

$$\frac{\pi^2}{8}\left(\frac{C_f - \bar{C}}{C_f - C_i}\right) = \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left[-\left(\frac{(2n-1)}{h}\right)^2 Dt\right]$$

where:

$\bar{C}$ = average concentration of diffusing element over thickness h, after corrosion

$C_f$ = equilibrium final concentration

$C_i$ = initial average concentration over thickness, h.

h = thickness of slab

t = time

D = diffusion coefficient of element into the slab

Using the above analytical data for a VANSTAR-9 sample exposed to flowing sodium at ∿790°C for 1500 hours, the following values for the diffusion coefficients were obtained:

Nitrogen : $1.1 \times 10^{-11}$ $cm^2/sec$

Carbon : $2.5 \times 10^{-12}$ $cm^2/sec$

Oxygen : $2.5 \times 10^{-12}$ $cm^2/sec$

Extrapolation of the data of Borgstedt and Frees to a temperature of 790°C produces a diffusion coefficient for oxygen in a V-20Ti alloy of $4.2 \times 10^{-11}$ $cm^2/sec$. However, their data were obtained using microhardness-oxygen content relationships for unalloyed vanadium. Hence, its validity when applied to their V-20Ti alloy microhardness data may be open to question.

The results obtained in this investigation demonstrate quite clearly that the weight gains, metallographic and hardness changes are most definitely due to the absorption of these interstitials elements and theri reaction with the zirconium or titanium in the alloy. For this set of conditions, hardening is due to the high affinity of VANSTAR-9 for nitrogen and to a lesser degree for carbon and oxygen.

Mechanical Property Evaluation

The work on the effect of prior exposure to flowing sodium on the tensile properties of the vanadium alloys continued. Full details of the testing procedure etc., were given in the previous quarterly report.[5]

Table 4 summarizes the results obtained on some VANSTAR samples which were exposed in VTL-1 Run 1. The general effects of exposure to sodium are seen as increases in strength and reduction in ductility. Room temperature ductility has been reduced to low levels; but, at a tensile test temperature of 800°C, both alloys still retain more than 20% elongation, and have exhibited only minor decreases in reduction area. Metallography of these fractured tensile specimens and of some of the fractured bend test specimens, which will establish failure modes, is in progress. Further tests on the V-20Ti alloy and samples from the high-velocity run are planned.

FUTURE WORK

It is apparent that when tested under the experimental conditions in this investigation, the mechanical properties of the vanadium alloys are seriously affected by sodium corrosion. There are several ways in which the problem

Table 4

Effect of Exposure to Sodium Flowing at 5 fps and Containing < 10 ppm Oxygen on the Mechanical Properties of the VANSTAR Alloys (Strain Rate = 0.05 $min^{-1}$).

| Condition of Sodium Exposure[a] | Tensile Test Temperature[b] (°C) | Ultimate Tensile Strength ($10^3$ psi) | Yield Strength ($10^3$ psi) | Elongation (%) | Reduction of Area (%) |
|---|---|---|---|---|---|
| VANSTAR-9 | | | | | |
| Uncorroded | R.T. | 98.7 | 69.5 | 30 | 27 |
| 1500 hr @ 690°C | | 97.7 | 97.6 | 2 | 0.2 |
| Uncorroded | 800 | 68.6 | 43.8 | 45 | 72 |
| 500 hr @ 690°C | | 76.8 | 52 | 38 | 70 |
| 1500 hr @ 690°C | | 72.2 | 65.5 | 24.4 | 62 |
| VANSTAR-7 | | | | | |
| Uncorroded | R.T. | 73.5 | 49 | 31 | 45 |
| 1500 hr @ 690°C | | 85.8 | 74.4 | 5.7 | 4 |
| Uncorroded | 800 | 52.5 | 31 | 32 | 74 |
| 1500 hr @ 690°C | | 58.5 | 46.7 | 24.4 | 64 |

[a] All samples annealed 1 hr @ 1200°C prior to corrosion.

[b] All tests at 800°C conducted in a dynamic vacuum of $10^{-6}$ torr, room temperature tests in air.

of interstitial transfer can be studied and hence, consideration is being given to modifications of this corrosion program plan. It is now planned to rebuild VTL-2 as a stabilized stainless steel one-leg loop system to operate at ∿14 fps for ∿1500 hours. This system should limit the interstitial transfer from the stainless steel to the vanadium alloys. Operation of the other system (VTL-1) will be terminated before completion of its scheduled 5000-hour run in order that rebuilding may commence. In this rebuild, the operating parameters will be the same as that for the VTL-2 rebuild, but the test section sample holders will be made of vanadium alloy. By this means, the test samples will be at higher temperatures than the stainless steel in the remainder of the loop; the rate of interstitial diffusion out of the stainless steel will be much lower.

# VCAA-140 - CLADDING ALLOY-FUEL COMPATIBILITY EVALUATION

R. C. DeKlever and G. A. Whitlow

## OBJECTIVE

The objective of this task is to assess the compatibility of the VANSTAR-8, VANSTAR-9, and V - 20Ti alloys with mixed uranium-plutonium oxide fuels, with mixed uranium-plutonium carbide fuels, and with uranium carbide fuel, both gas-bonded and sodium-bonded, for times up to 5000 hours. The V-20Ti alloy has been selected as a reference type alloy in order that these results may be compared with prior ANL work in this field.

## PRIOR WORK

Two compatibility capsules were under test, one having accumulated approximately 1000 hours @ 800°C. This capsule contains both unstabilized UC and (U,Pu)C fuel pellets, in contact with VANSTAR-8, VANSTAR-9, and V-20Ti alloy discs. The second capsule, which had only recently been bonded and raised to operating temperature, contains $Cr_{23}C_6$-modified hypostoichiometric (U,Pu)C fuel.

These capsules will not be evaluated until the start of fiscal year 1970, due to funding limitations. Further capsules will be assembled and tested in fiscal year 1970.

## CURRENT PROGRESS

The above two capsules, apart from a short period when the furnace was not operational, have continued to accumulate time at test temperature.

# VCAA-150 - IRRADIATION PERFORMANCE EVALUATION

R. W. Barker*, P. J. Levine, K. R. Wheeler* and G. A. Whitlow

## OBJECTIVE

The objective of this task is to examine the effects of fast flux irradiation on the mechanical properties and structures of the alloys VANSTAR-8 and VANSTAR-9. Exposures of 1 to 2 x $10^{22}$ n/cm$^2$ above 0.1 Mev will be achieved in EBR-II.

## PRIOR WORK

All work related to this phase of the investigation was reviewed and fully reported in previous Vanadium Alloy Cladding Development Quarterly Progress Reports. [2,3,4,5,6]

The irradiation program on this contract, was finalized and consists of three parts:

The WARD Low-Flux Program - designed to study the effects of fast flux irradiation on the mechanical properties of two vanadium alloys

V - 8Cr - 10Ta - 1.3Zr - 0.05C (VANSTAR-8), and

V - 6Fe - 5Cb - 1.3Zr - 0.05C (VANSTAR-9)

at two irradiation temperatures (650°C and 800°C) under the following variable conditions: two pre-irradiation heat treatments of materials (1200°C for one hour, and 1500°C for one hour), one irradiation environment (helium or argon), and three post-irradiation test temperatures (room temperature, 700°C, and 800°C). This program, planned for EBR-II, Row 7, was statistically designed to include 44 tensile/creep samples and six silicon-carbide temperature monitors in 12 specimen holders equally divided between two standard EBR-II Mk-B-7 capsules. In addition, four tubular specimen holders each containing three specimens were scheduled for each capsule. Preparation of design drawings was initiated. Arrangements were made with ORNL to perform the design analysis of these capsules as well as provide silicon carbide to WARD for manufacture of temperature sensors. Capsule hardware was received from ANL.

The WARD/PNL High-Flux Program - planned for Row 2 of EBR-II in conjunction with PNL, was redesigned because of a change in available subcapsule positions and the unavailability of vanadium alloy tubing in time for the capsule assembly.

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* Pacific Northwest Laboratory (PNL)

The anticipated total fluence was $10^{22}$ nvt (E > 0.1 Mev).

The reorganized plan included six subcapsules of which four were to operate at 650°C and two at 800°C. Each subcapsule would contain eight specimens for a total of 45 tensile/creep specimens and three bar specimens for determination of radiation-induced swelling. The latter three specimens were one each of VANSTAR-8 and VANSTAR-9, and one of commercially pure unalloyed vanadium. The arrangement of the eight specimens within a subcapsule included two tantalum holders, the mass of which should provide additional gamma heating to attain the irradiation temperatures (650 and 800°C). Thus, in any subcapsule there were two axially stacked holders each containing four specimens located in longitudinal holes equispaced about the centerline. A small hole was to be drilled on the centerline. A small hole was to be drilled on the centerline of each holder for a 0.100-inch-diameter x 0.500-inch-long SiC temperature sensor. A total of 12 SiC pins in six subcapsules provide a statistical interpretation of irradiation temperature throughout the capsules.

The CDAA 500, EBR-II Program (formerly UPC 500, EBR-II) - the third section of this task, a total of ten vanadium alloy tensile specimens (one per capsule) was contained in the bottom of each Phase I - EBR-II fuel capsule under Task CDAA 500.* These specimens were contained in stainless steel capsules filled with sodium and were to be irradiated at reactor ambient temperature (approximately 360°C).

Two capsules were assembled, and shipped to EBR-II during the last quarter.

## CURRENT PROGRESS

### WARD Low-Flux Program

Little progress has been made on this task due to lack of funding. Higher priority work at ORNL has delayed the completion of their design analysis.

### WARD/PNL High-Flux Program

The revised program content is shown in Table 5 and in addition to the 45 tensile/creep specimens, three swelling samples have also been included.

During this quarter, discussions were held between WARD and PNL at Richland on the planned irradiations in EBR-II, Row 2 to a total design fluence of 1 x $10^{22}$ nvt (E > 0.1 Mev). Of the total of 48 specimens, 16 are to be irradiated at 800°C, the remainder at 650°C. These temperatures will be obtained utilizing the gamma heating produced in the specimens and in the tantalum holders and collets around the specimen gage length. Figure 21 illustrates the specimen flux, and temperature monitor arrangements within any one specimen holder.

*CDAA-500 Task of Uranium Plutonium Carbide Development portion of Fast Reactor Fuel Element Program.

Table 5

Revised WARD/PNL High-Flux Irradiation Plan

| Alloy | Prior Heat Treatment | Number of Tensile/Creep Specimens to be Irradiated at: 650°C | 800°C |
|---|---|---|---|
| VANSTAR-9 | 1200°C/1 hr | 15 | 10 |
| | 1500°C/1 hr | 5 | 4 |
| VANSTAR-8 | 1200°C/1 hr | 9 | 2 |

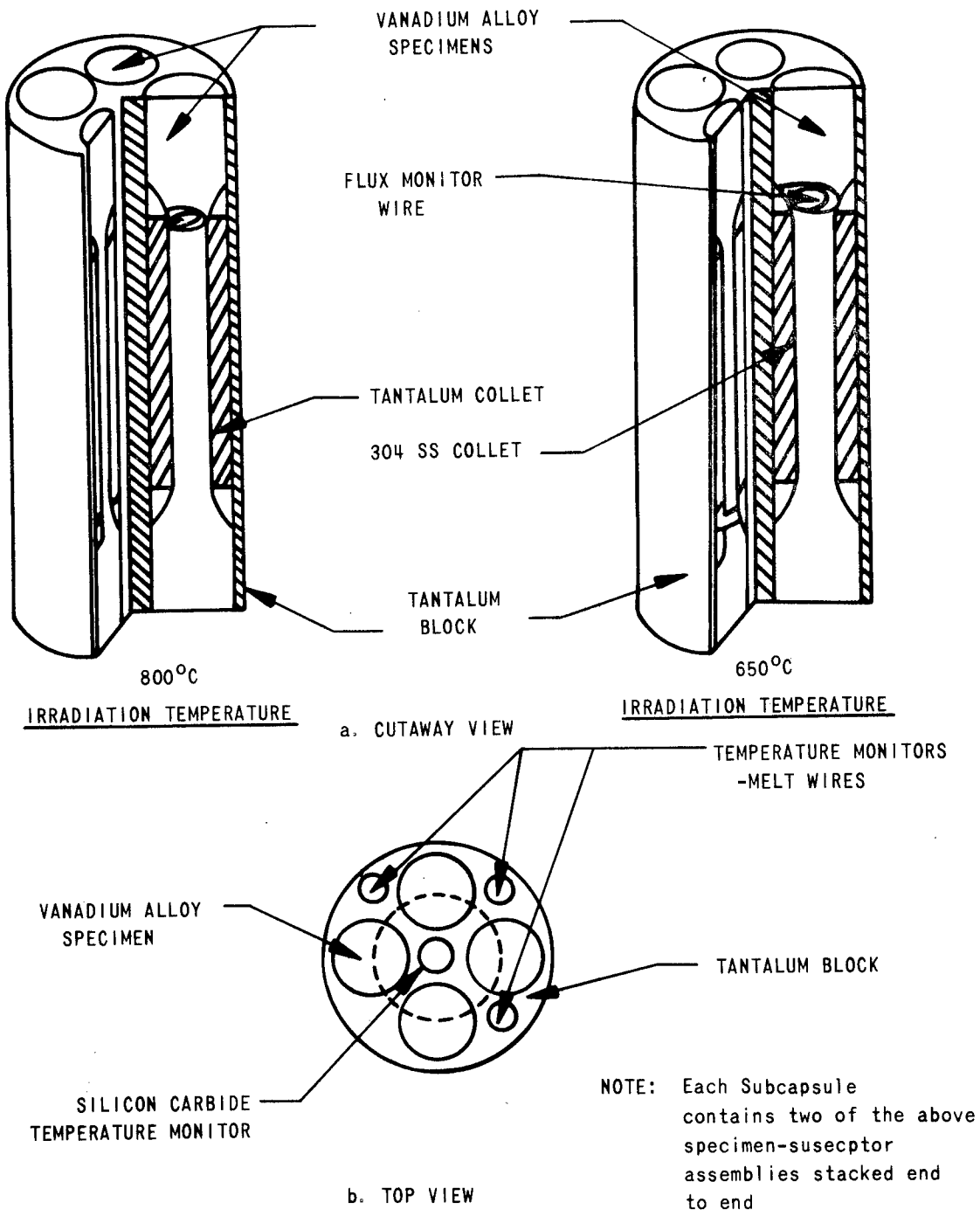


Figure 21 Irradiation Specimen Holder showing Gamma Heat Susceptors and Vanadium Alloy Specimens

3122-21

The subcapsule assembly was conducted as follows:

a. Identification of all components (stamped reference numbers);

b. Density and dimensional data determination and recording;

c. Ultrasonic cleaning of all components using methanol;

d. Preparation of temperature monitors (three melt wires and one silicon carbide rod inserted in tantalum holder) and flux monitors (two iron wires and one copper wire per subcapsule wrapped around a specimen radius);

e. Assembly of specimens and appropriate collets around gauge length and insertion in tantalum holder; (Some galling was experienced here, and reaming of the holes in the tantalum holders was necessary).

f. Evacuation of assembled holders and other subcapsule components in glove box chamber, followed by insertion of components into subcapsule in good argon atmosphere in a glove box.

g. TIG welding of end cap to subcapsule. Some modifications, particularly with regard to tolerances on the holes in the tantalum specimen holders were necessary before the assembly of the subcapsules was completed.

The assembled irradiation pin, containing these six subcapsules containing vanadium alloys, was shipped to EBR-II in December, and is now awaiting insertion.

In order to anticipate possible problems in the remote disassembly of the "hot" subcapsules, it was decided to remotely disassemble two thermally aged subcapsules. In addition, thermal aging control tests are to be initiated at WARD.

Copies of the following have been received from PNL:

a. Request to ANL for approval in principle,

b. Gamma heat calculations for gas gap optimization,

c. Drawing of pin layout and flux profile along the length of the pin,

d. Tantalum holder chemistry, density, and dimensional data, and

e. Design and hazards report.

A detailed layout indicating the positions of the specimens and temperature monitors in the respective subvapsules was prepared.

CDAA - 500, EBR-II Program

The two fueled pins (each containing a vanadium alloy sample) in the CDAA-500 Program, that were shipped to EBR-II in September 1968, are still awaiting reactor insertion. Progress on the assembly, etc., of the remaining pins in this program is dependent on the production of acceptable fuel by WARD at the Carbide Fabrication Laboratory.

# VCAA 160 - 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.

Under this task, overall project direction and day-to-day administration will be provided. Plans and controls will be established and maintained; periodic reviews will be held with the Commission; correspondence and reports will be coordinated; day-to-day technical and administrative liaison with the Commission will be provided.

## PRIOR WORK

Scope of work was defined and incorporated into Contract AT (30-1)-3791. The work program for FY-1968, WCAP-3791-7, was prepared and approved by the Commission. The work was planned in detail; schedules and budgets were established; shop orders and IWRs were issued; progress was closely followed and all aspects coordinated. Day-to-day liaison with the Commission was provided. Quarterly progress reports (WCAP-3791-9, WARD-3791-13, and WARD-3791-17) and a topical report (WARD-3791-19) were prepared, edited, and distributed.

## CURRENT PROGRESS

Contract modifications 12 through 14 were received and executed. Modification No 14 authorized the FY-1969 scope of work and provided full FY-1969 funding. Formal approval of our FY-1969 work program and formal concurrence with our October request for Government furnished materials and services were also received. At the end of the period, program status and plans were thoroughly reviewed and updated in preparation for the AEC mid-year review.

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