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HIGH STRENGTH VANADIUM ALLOY PROJECT

SIXTH QUARTERLY PROGRESS REPORT

For The Period Ending

June 30, 1966

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W. Pollack
K. C. Thomas

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FOREWORD

This report was prepared by the Westinghouse Electric Corporation under contract AT(30-1)-3487. This work is sponsored by Mr. A. Van Echo of the Fuels and Materials Development Branch of the United States Atomic Energy Commission and administered by Mr. J. J. Dissler of the New York Operations Office of the United States Atomic Energy Commission.

A parallel Westinghouse-funded effort is being conducted to evaluate the resistance of vanadium alloys to corrosion by liquid sodium and to investigate their compatibility with ceramic fuels.

The work is being administered at Westinghouse by K. C. Thomas (WAPD) with W. Pollack (WANL) serving as principal investigator. Other Westinghouse personnel contributing are R. T. Begley (WANL), W. R. Buckman (WANL), and M. Spewock (WRL). This report covers the work performed during the period April 1, 1966 to June 30, 1966.

Work conducted during the previous period is described in WCAP-3487-14.

HIGH STRENGTH VANADIUM ALLOY PROJECT
SIXTH QUARTERLY PROGRESS REPORT
For the Period Ending
June 31, 1966

W. Pollack
K. C. Thomas

ABSTRACT

An investigation is being conducted to develop high strength V-alloys for application as fuel element cladding in a liquid-metal-cooled fast breeder reactor. Parallel efforts are being conducted in the areas of alloy development, creep testing, sodium corrosion and fuel compatibility evaluation, and welding characterization.

During the current report period, all 45 button melted alloys have been processed to sheet and hot hardness and tensile evaluations of them concluded. The bulk of the creep-rupture testing of these alloys has been completed.

Of the six more promising alloys selected for scale-up to 2-1/2 in. diameter ingots, three have been rolled to final sheet, while processing of the remaining three is nearing completion. Evaluation of the former by hot hardness, tensile, and creep rupture testing is in progress.

The corrosion behavior in convection sodium loop tests of an additional 16 alloys, for a total of 32, has been evaluated. All alloys continue to exhibit only weight gains.

The compatibility of selected V-alloys helium bonded to UO_2 fuel has been tested, and the results are being evaluated. Preparations are being made to study the compatibility of these alloys when sodium bonded to carbide fuels.

Welding tests have been performed on all alloys, while ductile-brittle transition temperature evaluation is still in progress.

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I. INTRODUCTION

This is the Sixth Quarterly Report under Contract AT(30-1)-3487, covering activities from April 1 through June 31, 1966. The objective of the program is the development of a vanadium base alloy for potential application as fuel cladding in a liquid-metal-cooled fast breeder reactor. For this application, the alloy must be fabricable into high quality tubing, have sufficient strength to contain the fuel at temperatures up to 800°C, be resistant to corrosion by sodium, be compatible with the fuel, and possess good nuclear characteristics.

The program consists of three concurrent and interdependent phases. Phase I is a systematic investigation of the effects of selected alloying additions on the mechanical properties of vanadium base alloys. Phase II involves the determination of long time creep and stress-rupture data on the promising alloys. Phase III, a Westinghouse-funded effort, will provide preliminary information on the resistance of the alloys to sodium corrosion and evaluate their compatibility with ceramic fuels.

A total of 45 non-consumable arc-melted button compositions produced to date are in various stages of evaluation. During the current period, hot-hardness, tensile, and creep rupture results were obtained on these button compositions. Six of the more promising compositions were selected for scale-up to 2-1/2 inch diameter arc-melted ingots. Three of these alloys have been processed to sheet and the balance have been forged and are being rolled to sheet. Welds have been made in almost all of the alloys and ductile-brittle transition temperatures determined for many of them.

A second series of 13 alloys has been corrosion tested in flowing sodium at 800°C for 300 hours, and a concluding group are now in progress. The first of a series of compatibility tests is also in progress.

II. PROJECT STATUS

A. Processing

During the current report period, processing of non-consumable arc melted button heats to 0.042 inch thick sheet was completed. Conversion of the remaining three consumable electrode-arc-melted ingots to sheet continued.

Non-Consumable Electrode Heats

The nominal composition of the non-consumable button heats produced to date in the program are listed in Table I. The systems studied may be more easily identified by the listing in Table II where the alloys are grouped according to the total solute level and the various compositional variations. During this report period, compositions HSV-41 through 45 were processed to sheet following the standard processing schedule⁽¹⁾. This consists of Dynapak forging the stainless steel encapsulated buttons, which are then processed to sheet by a combination of warm and cold rolling. Observations on the primary and secondary working characteristics of alloys HSV-41 through 45 are summarized in Table III.

The primary working characteristics of these alloys have been excellent. Some of the alloys exhibited marginal secondary working characteristics in rolling to 0.065 inch. However, after conditioning and annealing, the 0.065 inch sheet was rolled at room temperature to 0.042 inch thickness without evidence of edge cracking.

Consumable Electrode Melts

The compositions of the scale-up alloys are listed in Table IV. These compositions, evaluated initially as non-consumable melted ingots,

TABLE I
Nominal Composition of Experimental Alloys
200 Gram Button Melts

<u>Alloy No.</u>	<u>Nominal Composition (w/o)</u>
HSV-3	100V
HSV-4	V-12.2Cr-2.68Zr-.302C
HSV-5	V-12.3Cr-2.70Zr-.124C
HSV-6	V-12.2Cr-5.34Zr-.713C
HSV-7	V-12.1Cr-5.28Zr-.302C
HSV-8	V-20.5Mo-4.85Zr-.597C
HSV-9	V-19.9Cb-4.88Zr-.60C
HSV-10	V-13Fe-5.3Zr-.653C
HSV-11	V-10Ti
HSV-12	V-20Ti
HSV-15	V-6.1Cr-1.33Zr-.123C
HSV-16	V-6.1Cr-1.33Zr-.052C
HSV-17	V-6.1Cr-2.68Zr-.30C
HSV-18	V-6.1Cr-2.68Zr-.141C
HSV-19	V-10.7Mo-1.26Zr-.049C
HSV-20	V-10.4Cb-1.27Zr-.049C
HSV-21	V-6.5Fe-1.32Zr-.051C
HSV-22	V-10W-1.24Zr-.047C
HSV-23	V-9.87Ta-1.24Zr-.047C
HSV-24	V-19.45Cr-4.26Zr-.252C
HSV-25	V-8.48Cr-10W-1.24Zr-.050C
HSV-26	V-8.91Cr-5.48Mo-1.32Zr-.053C
HSV-27	V-9.11Cr-3.27Fe-1.33Zr-.054C
HSV-28	V-9.15Cr-2.82Ti-1.34Zr-.054C
HSV-29	V-8.49Cr-9.85Ta-1.24Zr-.050C
HSV-31	V-12.2Cr-1.34Zr-.055C
HSV-32	V-20.4Mo-1.21Zr-.046C
HSV-33	V-13Fe-1.32Zr-.053C
HSV-34	V-5.64Ti-1.34Zr-.052C
HSV-35	V-12.2Cr-1.33Zr-.044N
HSV-36	V-1.35Zr-.051C
HSV-37	V-10.4Cb-1.28Zr-.03C
HSV-38	V-8.95Ti-1.35Zr-.055C
HSV-39	V-5.95Cr-5.32Cb-1.30Zr-.052C
HSV-40	V-5.67Cr-9.86Ta-1.24Zr-.049C
HSV-41	V-6.36Fe-5.3Cb-1.3Zr-0.050C
HSV-42	V-6.56Fe-1.53Cr-0.8Al-1.34Zr-0.052C
HSV-43	V-6.58Fe-1.06Al-1.34Zr-0.052C
HSV-44	V-6.51Fe-1.52Cr-1.33Zr-0.052C
HSV-45	V-6.5Fe-1.7Ni-1.33Zr-0.052C

TABLE III
Composition of Experimental Alloy
Grouped by Solute Concentration

Substitution Solute - a/o	Zr C	Alloy No.	Nominal Composition (w/o)
0	0	HSV-3	100V
0	2	HSV-36	V-135Zr-0.051C
3	2	HSV-22	V-10W-1.24Zr-0.047C
3	2	HSV-23	V-9.8Ta-1.24Zr-0.047C
6	2	HSV-19	V-10.7Mo-1.26Zr-0.049C
12	2	HSV-32	V-20.4Mo-1.21Zr-0.046C
6	1	HSV-15	V-6.1Cr-1.33Zr-0.123C
6	2	HSV-16	V-6.1Cr-1.33Zr-0.052C
6	1	HSV-17	V-6.1Cr-2.68Zr-0.30C
6	2	HSV-18	V-6.1Cr-2.68Zr-0.141C
6+3	2	HSV-39	V-5.95Cr-5.32Cb-1.30Zr-0.052C
6+3	2	HSV-40	V-5.67Cr-9.86Ta-1.24Zr-0.049C
12	2	HSV-31	V-12.2Cr-1.34Zr-0.055C
12	2	HSV-35	V-12.2Cr-1.33Zr-0.044N
12	1	HSV-4	V-12.2Cr-2.68Zr-0.302C
12	2	HSV-5	V-12.3Cr-2.70Zr-0.124C
12	1	HSV-6	V-12.2Cr-5.34Zr-0.713C
12	2	HSV-7	V-12.1Cr-5.28Zr-0.302C
18	2	HSV-24	V-19.45Cr-4.26Zr-0.252C
9+3	2	HSV-25	V-8.48Cr-10W-1.24Zr-0.050C
9+3	2	HSV-26	V-8.9Cr-5.48Mo-1.3Zr-0.053C
9+3	2	HSV-27	V-9.11Cr-3.27Fe-1.33Zr-0.054C
9+3	2	HSV-28	V-9.15Cr-2.82Ti-1.34Zr-0.054C
9+3	2	HSV-29	V-8.49Cr-9.85Ta-1.24Zr-0.050C
6	3	HSV-37	V-10.4Cb-1.28Zr-0.03C
6	2	HSV-20	V-10.4Cb-1.27Zr-0.049C
6	2	HSV-34	V-5.64Ti-1.34Zr-0.052C
9-1/2	0	HSV-11	V-10Ti
9-1/2	2	HSV-38	V-8.95Ti-1.35Zr-0.055C
19	0	HSV-12	V-20Ti
6	2	HSV-21	V-6.5Fe-1.32Zr-0.051C
6+3	2	HSV-41	V-6.36Fe-5.3Cb-1.3Zr-0.050C
6+1-1/2	2	HSV-44	V-6.51Fe-1.52Cr-1.33Zr-0.052C
6+1-1/2	2	HSV-45	V-6.5Fe-1.7Ni-1.33Zr-0.052C
6+1-1/2+1-1/2	2	HSV-42	V-6.56Fe-1.53Cr-.8Al-1.34Zr-0.052C
6+1-1/2	2	HSV-43	V-6.58Fe-1.06Al-1.34Zr-0.052C
12	2	HSV-33	V-13Fe-1.32Zr-0.053C

TABLE III

Processing Results and Hardness Data for Vanadium Alloys

Heat No (e)	<u>Upset Forged (a)</u>			<u>Rolled to 0.065 in. (b)</u>			<u>Rolled to 0.042 in. (c)</u>				
	DPH (d)			DPH (d)			DPH (d)				
	Substitutional Solute Level (atom %)	Zr/C (atom ratio)	As Forged	Annealed	Remarks	As Rolled	Annealed	Remarks	As Rolled	Annealed	Remarks
HSV-43	7	2	236	243	B	268	185	C	249	179	A
HSV-44	7 1/2	2	238	236	A	267	183	C	254	182	A
HSV-45	7 1/2	2	257	244	C	263	215	C	270	193	A
HSV-42	8 1/2	2	236	234	A	281	206	C	254	181	A
HSV-41	9	2	265	253	A	300	200	C	281	206	A

a) Upset forged 50% at 1100°C - Annealed 1 Hr 1000°C

b) Rolled to 0.065 in at 750°C - 70% reduction - Annealed 1 hr 1200°C

c) Rolled to 0.042 in at R. T. - 35% reduction - Annealed 1 hr 1200°C

d) 5 kg load

e) Compositions listed in Table I and II

f) Fabricability index -

A - Excellent - No edge cracks

B - Good - Minor edge cracks

C - Fair - Moderate edge cracks

D - Poor - Severe edge cracks

TABLE IV

Nominal Composition of Scale-up Vanadium Alloys*
(2.5-Inch Diameter Ingots)

Alloy No.

HSV-200	V - 10 Ti*
HSV-202	V - 20 Ti*
HSV-203	V - 10.4 Cb - 1.27 Zr - 0.049 C
HSV-204	V - 6.5 Fe - 1.32 Zr - 0.051 C
HSV-205	V - 12.2 Cr - 2.68 Zr - 0.122 C
HSV-206	V - 8.48 Cr - 10 W - 1.24 Zr - 0.050 C
HSV-207	V - 9.11 Cr - 3.27 Fe - 1.33 Zr - 0.053 C
HSV-208	V - 8.49 Cr - 9.85 Ta - 1.24 Zr - 0.050 C

* Reference alloys

exhibited the most promising combination of creep strength and fabricability.

Electrodes for consumable electrode double arc-melting were fabricated from sheet material of each constituent using the techniques described in Quarterly Report No. 2⁽¹⁾. All of the alloy elements used were readily available in sheet form except Cr. Electroplating Cr onto V strip, using a chromic acid bath, has proved to be a satisfactory technique for adding Cr to the alloy.

First and second melts are made under a partial pressure of argon (1/3 atmosphere) into a water-cooled mold. Melting of all of the scale-up alloys was completed during the current report period. All second melts were made into a 2-1/2 inch diameter mold.

Chemical analyses of sections removed from the top and bottom of the second melt ingots are shown in Table V, which also lists the results obtained on comparable button melts. In general, replication of the button melt compositions was achieved in the consumable electrode arc melts. The largest deviation noted is in alloy HSV-205, which shows a deviation of 15% in the amount of Cr from bottom to center of the ingot. The center and top sections of this ingot, however, show a deviation of less than 1%.

After conditioning, the ingots were plasma sprayed with Mo (0.030 inch thickness) prior to forging. Three billets, 2-3/8 inch diameter by 1-7/8 inch high from each ingot were heated in a muffle furnace in an

TABLE V
Chemical Analyse of Vanadium Alloys

Heat No	Type	Position	Nominal Composition (w/o)	Analysis (w/o)									
				Cb	Cr	Fe	Ta	W	Zr	C	O	N	H
HSV-203	Scale-up	Top	V - 10.4Cb - 1.27 Zr - 0.049C	10.9	-	-	-	-	1.4	0.057	0.095	0.025	-
HSV-203	Scale-up	Bottom		10.6	-	-	-	-	1.4	0.062	-	0.027	-
HSV-20	Button			10.6	-	-	-	-	1.2	0.052	0.083	-	-
HSV-204	Scale-up	Top	V - 6.5Fe - 1.32Zr - 0.051C	-	-	6.9	-	-	1.4	0.060	0.094	0.025	-
HSV-204	Scale-up	Bottom		-	-	6.8	-	-	1.3	-	-	-	-
HSV-21	Button			-	-	6.5	-	-	1.2	0.050	0.088	-	-
HSV-205	Scale-up	Top	V - 12.3Cr - 2.70Zr - 0.124C	-	12.8	-	-	-	2.6	0.178	0.128	0.024	0.0029
HSV-205	Scale-up	Center		-	12.7	-	-	-	2.6	-	0.127	-	-
HSV-205	Scale-up	Bottom		-	11.0	-	-	-	2.4	0.142	0.116	0.024	0.0003
HSV-5	Button			-	12.6	-	-	-	2.7	0.135	0.074	-	-
HSV-206	Scale-up		V-8.48Cr - 10W - 1.24Zr-0.050C	-	8.6	-	-	9.5	1.1	0.061	0.11	0.023	0.0016
HSV-25	Button			-	8.3	-	-	9.9	1.2	0.062	0.098	0.020	-
HSV-207	Scale-up		V-9.11Cr - 3.27Fe-1.33Zr - 0.054C	-	9.2	3.2	-	-	1.2	0.069	0.11	0.024	0.0017
HSV-27	Button			-	9.2	3.5	-	-	1.2	0.064	0.079	0.023	-
HSV-208	Scale-up	Top	V-8.49Cr-9.85Ta - 1.24Zr-0.050C	-	8.6	-	10.1	-	1.3	0.060	0.107	0.022	-
HSV-208	Scale-up	Bottom		-	8.8	-	10.1	-	1.2	0.061	0.098	0.023	-
HSV-29	Button			-	8.6	-	10.3	-	1.2	0.064	0.078	0.022	-

argon atmosphere to 1100°C (15 minutes soak) and then upset forged to a thickness of 1/2 inch on a Model 1220C Dynapak. A steel spacer plate was used to limit final thickness to 1/2 inch. Since the ram bottomed on the spacer plate on all forgings, a forging constant for the alloys could not be computed. All of the forgings exhibited shallow edge cracks (1/8 inch deep). Some of the forged billets are shown in Figure 1.

The schedule used to reduce the forged billets to sheet is shown in Figure 2. At the time of report preparation alloys HSV-203, 204, and 205 were successfully reduced to 0.042 inch sheet. Alloys HSV-206, 207, and 208 were rolled to 0.18 inch thickness and are being conditioned for annealing.

Response to Heat Treatment

The one hour recrystallization behavior of the scale-up alloys is being determined on the 0.04 inch sheet which has been cold reduced about 38% from the last anneal. The effect of one hour anneals at temperatures from 700 to 1500°C on the hardness of scale-up alloys HSV-203 and 204 is shown in Table VI and Figure 3. At 900°C, some recrystallized grains were observed in the microstructure of both alloys. At this temperature both alloys have decreased in hardness by approximately 60% of the total hardness change observed. Minimum hardness for HSV-203 and HSV-204 is attained at 1200°C and 1050°C respectively. Increasing the annealing temperature to 1500°C results in an increase in hardness which is

FIGURE 1 - Dynapak Upset Forging of Arc Melt Billets, 2-3/8 Inch Diameter x 1-7/8 Inches

FIGURE 2 - Fabrication Schedule of Scale-Up Alloys

TABLE VI
Effect of Annealing on the Hardness of Vanadium Alloys *
0.042 in. Thickness - (40% Reduction)

<u>Alloy</u>	<u>Annealing Temperature (a) (°C)</u>	<u>Hardness</u> <u>VHN - 5 kg Load</u>	
		<u>Avg.</u>	<u>Range</u>
HSV-203	As-Rolled	214	210-221
V-10.4Cb-1.27Zr-0.049C	700	214	212-216
	800	208	206-208
	900	174	172-177
	1050	160	156-165
	1200	151	148-153
	1200 (HQ)	159	150-167
	1350	161	153-168
	1500	182	177-190
	1500 (HQ)	183	177-190
HSV-204	As-Rolled	244	241-249
V-6.5Fe-1.32Zr-0.051C	700	237	234-249
	800	225	221-229
	900	202	199-204
	1050	170	169-172
	1200	175	171-180
	1200 (HQ)	181	180-183
	1350	178	174-182
	1500	185	182-187
	1500 (HQ)	195	182-210

* One-hour Anneal

(a) Specimens furnace cooled except Helium Quench (HQ)

FIGURE 3 - Hardness of Scale-Up Alloys at 0.042 Inch After 1 Hour Anneal (Reduced 38% from Preceding Anneal)

attributed to resolution of interstitials. No significant increase in hardness was found when the specimens were helium quenched instead of radiation cooled from the annealing temperature. The microstructures of HSV-203 and HSV-204 for the various heat treatments are shown in Figures 4 and 5.

In addition to the one hour annealing treatments, sheet material annealed for one hour at 1200°C and 1500°C is being aged for 500 hours at 700°C and 800°C to evaluate long time thermal stability. Thus, the effect of time at temperature can be evaluated on similar material which has been creep-rupture tested or exposed to a liquid sodium environment under equivalent time-temperature conditions.

B. Mechanical Property Evaluation

Hot Hardness

Hot hardness values for alloys HSV-27 through 29, HSV-31 through 35, and HSV-41 through 45, determined over the temperature range 400 to 850°C, are tabulated in Table VII, and plotted as a function of temperature in Figures 6a, 7a, and 8a. Room temperature hardness values, determined after each elevated temperature test, are shown in Table VIII. All of the alloys except HSV-33 (V-13Fe-1.32Zr-0.053C) and HSV-41 (V-6.36Fe-5.3Cb-1.3Zr-0.050C) exhibited a hardness level less than 100 VHN at 850°C.

Hardness variation with temperature appears to provide some indication of relative alloy stability and thereby a rough approximation of creep resistance. No correlation, however, has been found between absolute

900°C
(13,349)

1050°C
(13,350)

1200°C
(13,351)

1350°C
(13,353)

1500°C
(13,354)

FIGURE 4 - Microstructure of Scale-Up Alloy V-10. 4Cb-1. 27Zr-0.049C
(HSV-203) 0.042 inch Sheet (Reduced Cold - 35%) 200X

900°C
(13341)

1050°C
(13342)

1200°C
(13343)

1350°C
(13345)

1500°C
(13346)

FIGURE 5 - Microstructure of Scale-Up Alloy V-6. 5Fe-1.32Zr-0.051C
(HSV-204)0.042 inch Sheet (Reduced, Cold - 35%) 200X

TABLE VII

Hot Hardness of Vanadium Alloys - (a)

DPH - 2 1/2 Kg Load

<u>Heat No.</u>	<u>Composition</u>	<u>Rm Temp</u>	<u>Test Temperature - °C</u>			
			<u>400</u>	<u>550</u>	<u>700</u>	<u>850</u>
HSV-27	V-9.11Cr-3.27Fe-1.33Zr-.054C	180	116	111	108	85.5
HSV-28	V-9.15Cr-2.82Ti-1.34Zr-.054C	158	125	108	111	90.3
HSV-29	V-8.49Cr-9.85Ta-1.24Zr-.050C	191	123	117	117	84.4
HSV-31	V-12.2Cr-1.34Zr-.055C	154	93.2	90.0	85	69.8
HSV-32	V-20.4Mo-1.21Zr-.046C	207	118	100	97.6	81.6
HSV-33	V-13Fe-1.32Zr-.053C	262	165	150	149	105
HSV-34	V-5.64Ti-1.34Zr-.052C	150	106	97.6	109	87.6
HSV-35	V-12.2Cr-1.33Zr-.044N	169	98	88.5	85.4	75.7
HSV-41	V-6.36Fe-5.3Cb-1.3Zr-.050C		153	148	142	127
HSV-42	V-6.56Fe-1.53Cr-0.8Al-1.34Zr-.052C	201	132	115	119	84
HSV-43	V-6.58Fe-1.06Al-1.34Zr-.052C	204	127	124	114	84.3
HSV-44	V-6.51Fe-1.52Cr-1.33Zr-.052C		197	121	113	81.5
HSV-45	V-6.5Fe-1.7Ni-1.33Zr-.052C	206	129	145	123	73.6

(a) Specimens Annealed 1Hr - 1200°C prior to testing

FIGURE 6 - Hot Hardness of Experimental Vanadium Alloys

FIGURE 7 - Hot Hardness of Experimental Vanadium Alloys

FIGURE 8 - Hot Hardness of Experimental Vanadium Alloys

TABLE VIII

Room Temperature Hardness of Vanadium Alloys after Hot Hardness Test
DPH 2-1/2 Kg Load

<u>Heat No</u>	<u>Composition</u>	<u>As-annealed</u> ^(a)	<u>400°C</u>	<u>550°C</u>	<u>700°C</u>	<u>850°C</u>
HSV-27	V-9.11Cr-3.27Fe-1.33Zr-.054C	180	182	182	164	167
HSV-28	V-9.15Cr-2.82Ti-1.34Zr-.054C	158	151	149	153	160
HSV-29	V-8.49Cr-9.85Ta-1.24Zr-.050C	191	187	179	185	175
HSV-31	V-12.2Cr-1.34Zr-.055C	154	149	139	135	133
HSV-32	V-20.4Mo-1.21Zr-.046C	207	185	185	181	
HSV-33	V-13Fe-1.32Zr-.053C	262	225	230	237	
HSV-34	V-5.64Ti-1.34Zr-.052C	150	143	136	136	
HSV-35	V-12.2Cr-1.33Zr-.044N	169	147	138	140	
HSV-41	V-6.36Fe-5.3Cb-1.3Zr-.050C		219	205	213	229
HSV-42	V-6.56Fe-1.53Cr-0.8Al-1.34Zr-.052C	201	191	175	178	178
HSV-43	V-6.58Fe-1.06Al-1.34Zr-.052C	204	200	177	175	175
HSV-44	V-6.51Fe-1.52Cr-1.33Zr-.052C		181	176	170	170
HSV-45	V-6.5Fe-1.7Ni-1.33Zr-.052C	206	195	185	186	188

(a) One hour @ 1200°C

hardness values and creep rupture behavior at 700°C. The hardness values at elevated temperature were normalized with respect to the hardness at 400°C using the relationship:

$$\frac{H_T - H_{400}}{H_{400}}$$

where H_T is the hardness at temperature and H_{400} is the hardness at 400°C. The data for these alloys is plotted in Figures 6b, 7b, and 8b. Perturbations in the temperature dependence of hot hardness noted at 550°C or 700°C may arise from strain aging or other structural change. Room temperature hardness changes noted after hot hardness tests appear to be a further indication of a structural change occurring during the hot hardness test.

A plot of the minimum creep rate at 700°C (at constant stress) vs. the absolute hot hardness values at 700°C is shown in Figure 9a and for the normalized hardness values at 700°C in Figure 9b. A correlation was observed for alloys in the V-Cr-Zr-C system to which various additional substitutional solutes have been added. However, it is found that different substitutional solutes added to the V-Fe-Zr-C system produce materials of equivalent hot hardness (or normalized hardness values) but with minimum creep rates differing by a factor of 3 or 4. Studies of the relationship between the temperature dependence of hot hardness and creep behavior will be carried out on the scale-up compositions. Studies of the aging response of these alloys are in progress.

FIGURE 9 (a,b) - Hot Hardness vs. Minimum Creep Rate (30,000 psi) of Experimental Alloys at 700°C

Tensile Properties

Tensile properties of selected experimental and scale-up alloys are listed in Table IX. All specimens were tested in the fully recrystallized condition (annealed one hour at 1200°C). The addition of 3/4 a/o Zr and 3/8 a/o C increases the 700°C yield of unalloyed vanadium from 8,500 to 11,800 psi and the tensile strength from 15,200 to 25,900 psi. However, the addition of substitutional solutes to V-Zr-C alloys results in a greater increase in tensile properties. The addition of 6 a/o Ti (HSV-34) and 9 a/o Ti (HSV-38) increases the 700°C yield strength to 30,700 psi and 43,400 psi respectively. On the other hand, V-9-1/2 a/o Ti has a tensile strength of 73,600 psi. and a yield strength of 39,900 psi. It appears that the creep properties of the V-Ti alloys do not bear any relationship to the short time tensile properties. In the section which follows, it will be shown that the creep properties are dependent on the dispersed phases ZrC and Zr(C,N) as well as the substitutional solutes. Thus, the difference in creep rates between the V-Ti-Zr-C alloys is not as great as between these alloys and the solid solution V-Ti alloys.

The effect of temperature on the tensile properties of the two of the scale-up alloys is shown in Table IX. The decrease in tensile strength or yield strength with increasing temperature for HSV-203 (V-Cb-Zr-C) is less than for HSV-204 (V-Fe-Zr-C). Both alloys, however, have approximately the same creep properties. Tensile elongation is satisfactory at both room and elevated temperature.

TABLE IX

Elevated Temperature Tensile Properties of Vanadium Alloys (a)

<u>Alloy</u>	<u>Nominal Composition (w/o)</u>	<u>Test Temp (°C)</u>	<u>Ultimate Tensile Strength (Psi)</u>	<u>0.2% Yield Strength (Psi)</u>	<u>Elong (%)</u>
HSV-32	V-20.4Mo-1.21Zr-0.046C	700	46,800	24,200	18
HSV-34	V-5.6Ti-1.34Zr-0.052C	700	58,400	30,700	18
HSV-35	V-12.2Cr-1.33Zr-0.044N	700	45,300	21,800	19
HSV-36	V-1.35Zr-0.051C	700	25,900	11,800	18
HSV-37	V-10.4Cb-1.28Zr-0.03C	700	59,000	31,400	18
HSV-38	V-8.95Ti-1.35Zr-0.055C	700	71,600	43,400	24
HSV-39	V-5.95Cr-5.32Cb-1.3Zr-0.052C	700	55,100	28,800	18
HSV-40	V-5.67Cr-9.86Ta-1.24Zr-0.049C	700	54,200	27,900	17
HSV-203	V-10.4Cb-1.27Zr-0.049C	Rm T	67,100	42,800	35
HSV-203		700	60,400	31,200	18
HSV-203		800	50,500	29,900	32
HSV-204	V-6.5Fe-1.32Zr-0.051C	Rm T	70,400	45,100	35
HSV-204		700	55,900	23,300	21
HSV-204		800	46,200	27,700	35
HSV-21	V-6.5Fe-1.32Zr-0.051C	Rm T	70,300	45,200	28
HSV-21		700	55,000	28,200	20

(a) Specimens Annealed 1 hr - 1200°C prior to test

Creep Rupture Properties

Experimental Alloys

For short-time screen tests of the various experimental alloys, specimens are loaded to a stress of 30,000 psi at 700°C and 10,000 psi at 800°C. These stresses produced failure of the V-10Ti reference alloy in approximately 100 hours at 700°C and 800°C. If the alloys are still in the second stage of creep (which is the region of interest) after 100 hours, the stress level is increased by 5,000 psi and continued for an additional 100 hours or to failure.

The creep rupture data for the experimental alloys tested at 700°C during this report period are summarized in Table X and Figure 10. All of the alloys in the V-Fe, V-Cr, V-Ti, or V-Cb system (except as noted) contain 3/4 a/o Zr+3/8 a/o C. In the V-Fe-Zr-C system it was previously found that increasing the iron from 6 to 12 a/o results in a decrease in the secondary creep rate from 0.0055 to 0.002%/hour. The addition of Ni to a V-6 a/o Fe matrix (HSV-45) does not result in any improvement in creep resistance at 700°C (Figure 10). Addition of Cr to a V-6 a/o Fe matrix (HSV-44), however, decreased the creep rate to 0.0034%/hour, while Al (HSV-43) decreased the creep rate to 0.0024%/hour. However, when both Al and Cr were added to the V-6 a/o Fe matrix (HSV-42), the creep rate did not change. The addition of 3 a/o Cb to V-6 a/o Fe (HSV-41) reduced the minimum creep rate to 0.0009%/hour. However, when the stress on the V-Fe-Cb-Zr-C alloy was increased by 5,000 psi (to 35,000 psi), the minimum creep rate after 68 hours did not show an increase as normally expected. The stress, therefore, was decreased to

TABLE X
Preliminary Creep Rupture Data for Button Melt Vanadium Alloys
Test Temperature - 700°C

Alloy	1 Hour Anneal (°C)	Stress (Psi)	Time of Test (Hours)	Strain (%)	Time to 1% Strain (Hr)	Plastic Loading Strain (%)	Minimum Creep Rate-%-Hr ⁻¹
HSV-15	1500	25,000	236	1.01	236	0.15	0.00038
V-6.1Cr-1.33Zr-.123C		30,000 (a)	202 (b)	.08	>202	0.0	0.00072
HSV-31	1500	30,000	218	2.49	0.0	1.17	0.0025
V-12.2Cr-1.34Zr-.055C		35,000 (a)	165	0.58	>165	0.12	0.0037
		40,000 (a)	77 (b)	4.0	36	0.0	0.014
HSV-36	1200	8,500	119	0.9	>120	0.0	0.0018
V-1.35Zr-.051C		11,000 (a)	47	0.47	-	0.19	0.002
		13,500 (a)	96	0.78	-	0.31	0.0028
		16,000 (a)	70	0.58	-	0.16	0.0035
		20,000 (a)	143	1.99	0.0	1.09	0.0055
		22,500 (a)	33	6.98	0.1	0.82	0.046
HSV-37	1200	30,000	119	1.56	10	0.23	0.0035
V-10.4Cb-1.28Zr-.03C		35,000 (a)	139	1.29	53	0.39	0.0032
		40,000 (a)	27 (b)	1.40	10	0.31	0.025
HSV-38	1200	30,000	119	1.17	53	0.0	0.0021
V-8.95Ti-1.35Zr-.055C		35,000 (a)	166 (b)	3.97	77	0.0	0.0102
HSV-39	1200	30,000 (c)	165	6.75	2	0.47	0.0019
V-5.95Cr-5.32Cb-1.30Zr-.052C		35,000 (a)	148 (b)	0.39	-	0.0	0.0014
HSV-40	1200	30,000	92	1.91	0.8	0.47	0.0031
V-5.67Cr-9.86Ta-1.24Zr-.049C		35,000 (a)	171 (b)	0.98	>171	0.31	0.0016
HSV-45	1200	30,000	98 (b)	1.60	12	0.0	0.006
V-6.5Fe-1.7Ni-1.33Zr-.055C							
HSV-42	1200	30,000	145	1.52	52	0.0	0.0051
V-6.56Fe-1.53Cr-0.8Al-1.34Zr-.052C		35,000 (a)	122 (b)	6.1	1.2	0.55	0.026
HSV-43	1200	30,000	162	1.33	55	0.0	0.0024
V-6.56Fe-1.06Al-1.34Zr-.052C		35,000 (a)	150	0.82	>150	0.0	0.0049
		40,000 (a)	59	10.5	12	0.0	0.071
HSV-44	1200	30,000	143	2.1	0.8	0.62	0.0034
V-6.51Fe-1.52Cr-1.33Zr-.052C		35,000 (a)	268	16.7	37	0.0	0.011
HSV-41	1200	30,000	144	0.94	150	0.0	0.0009
V-6.36Fe-5.3Cb-1.3Zr-.050C		35,000 (a)	68	0.12	> 68	0.0	0.0008
		30,000 (a)	95	0.43	> 95	0.0	0.0011
		35,000 (a)	141(b)	0.19	>200	0.0	0.00036

(a) Increased from previous stress

(b) Test stopped

(c) Sample overloaded to 45,000 psi,
at lower temperature for ~10 hours.

FIGURE 10 - Minimum Creep Rate of Experimental Vanadium Alloys at 700°C

30,000 psi, and after 95 hours it was verified that the creep rate increased slightly (0.0011%/hour) and was probably due to an increase in the recovery rate upon relaxation of the specimen. When the stress was again raised to 35,000 psi. the minimum creep had decreased to 0.00036%/hour. The creep curve for this alloy is shown in Figure 11. After 450 hours this specimen has strained about 1.5%. This test is still in progress and the stress will be increased by increments of 5,000 psi every 100 hours until the specimen ruptures. A creep test at 800°C also is to be run on this alloy. Examination by metallographic and x-ray diffraction procedures of the matrix and extracted phases will be made in an attempt to explain the high creep resistance of this alloy. It is likely that precipitation during creep straining accounts for the low stress dependence of creep rate.

The effect of Zr+C additions on the creep resistance of vanadium is illustrated in Figure 12. Whereas unalloyed vanadium failed at 8,500 psi in 4.2 hours, vanadium containing $3/4$ a/o Zr and $3/8$ a/o C (HSV-36) had much superior creep properties. After 119 hours the specimen had strained only 0.9%. Subsequent incremental loadings increased to 20,000 psi, however, resulted in rupture after 33 hours with an additional strain of 6.98%. It is to be recalled that the unalloyed vanadium had a yield strength at 700°C of 8,500 psi. while the V-Zr-C alloy had a yield strength of 11,800 psi. This experiment demonstrates that the creep properties of vanadium are significantly improved by addition of Zr+C which provides

FIGURE 11 - Effect of Stress on Creep of Experimental Alloy HSV-41 (V-6.36Fe-5.3Cb-1.3Zr-0.05C)

FIGURE 12 - Effect of Zr-C Addition on Creep Rate of Vanadium

dispersed phase strengthening in the alloy. Addition of substitutional solutes to the alloy matrix results in additional strengthening of the matrix and also considerable improvement in creep properties (primary and secondary creep rates). The long time creep properties of such alloys, however, are dependent on the stability of the structure at the temperature of test.

The secondary creep rate of V-6 a/o % Ti+ 3/4 a/o Zr+3/8 a/o C (HSV-34) was reported⁽²⁾ to be lower than that obtained on the V-9-1/2 a/o Ti (HSV-11) reference alloy at 700°C and 30,000 psi by a factor of 3. Creep tests performed during the current report period (Table X) on a V-9-1/2 a/o Ti+3/4 a/o Zr+3/8 a/o C alloy (HSV-38) resulted in a creep rate which is lower than the reference alloy by a factor of 3 (Figure 13). It is concluded, therefore, that the reduction in the creep rate of vanadium-titanium is primarily due to the addition of Zr+C, or some dispersed phase strengthening, and not in the reduction of Ti.* It was observed in these tests that a reduction in the amount of Ti in the V-Ti-Zr-C system results in a change in the transient creep. Decreasing the Ti from 9-1/2 to 6 a/o results in a plastic loading strain of 0.3% and also reduces the time to produce a strain of 1% from 60 to 3 hours.

Addition of 3 a/o substitution solutes Cb (HSV-39) or Ta (HSV-40) to a V-6 a/o Cr-3/4 a/o Zr-3/8 a/o C alloy resulted in a significant decrease in the minimum creep rate at 700°C and 30,000 psi (Figure 13). Transient

* Lowering the amount of Ti in V probably results in an increase in the recovery and recrystallization temperature of the alloy.

FIGURE 13 - Minimum Creep Rate of Experimental Alloys at 700°C

creep of these alloys likewise was reduced by the addition of Cb or Ta. When the stress on these alloys was increased from 30,000 to 35,000 psi, the minimum creep rate decreased from approximately 0.002-0.003%/hour to 0.0015%/hour. After approximately 150 hours at the higher stress level, the tests were stopped in order that the specimens might be examined to determine the reason for this behavior.

An alloy containing V-6 a/o Cb-3/4 a/o Zr was produced with only that carbon residual found in the vanadium base material (340 ppm) in order to determine the effect of a slightly higher ratio of Zr/C. Creep tests on alloy HSV-37 (Figure 13) at 700°C show an increase in the minimum creep rate as compared to alloy HSV-20 (V+6 a/o Cb+3/4 a/o Zr+3/8 a/o C) and very similar results in scale-up alloy HSV-203. This would indicate that increasing the volume fraction of dispersoid is effective in promoting improved creep resistance. Two V-Cr alloys (HSV-15 and HSV-31) were heat treated for one hour at 1500°C (helium quenched) instead of one hour at 1200°C prior to creep testing, which resulted in significant improvement in creep resistance. HSV-15 annealed at the lower temperature failed in 1.5 hours on loading to 29,700 psi, whereas the specimen annealed at 1500°C, after 236 hours at 25,000 psi strained only 1.01% and 202 hours at 30,000 psi strained only an additional 0.08%. Creep tests of HSV-31 showed an improvement in creep resistance* as a result of the higher anneal temperature level but not to the same extent as with HSV-15 (Figure 14). The creep curves for these alloys are shown in Figure 15. The increase in

*HSV-31 annealed 1 hr./1200°C failed in 145 hours at 35,000 psi after 136 hours at 30,000 psi.

FIGURE 14 - Effect of Heat Treatment on Creep Rate of V-Cr-Zr-C Alloys at 700°C

FIGURE 15 - Effect of Anneal Temperature on the Creep Curve of Experimental Alloys

creep resistance in this experiment is attributed to an increase in solubility of carbon at the higher temperature and subsequent precipitation on dislocations. An increase in hardness was found as a result of the higher anneal temperature. Examination by light microscopy did not, however, indicate any difference in dispersed phase morphology, although an increase in grain size resulted from the anneal at the higher temperature. Examination of these specimens by electron microscopy is in progress, but preliminary examination of replicas has not shown any difference in dispersoid morphology. A modification of the polishing and etching technique is being made to insure that the very fine particles, which are more than likely responsible for improved creep resistance, are not being removed in preparation of the replicas.

Scale-Up Alloys

Creep tests of scale-up alloys were performed on specimens which were given one hour recrystallization anneals prior to testing at 1200 or 1500°C. Specimens were tested at 700 and 800°C at different stress conditions. The initial stress selected for these alloys was either 30,000 psi or 35,000 psi, depending on the lowest stress level used in the evaluation of the experimental alloys (button melts).

The creep properties of HSV-203, 204, and 205 at 700°C and 800°C are summarized in Table XI. Plots of stress vs. the minimum creep rate are shown in Figures 16 and 17 for tests at 700°C and Figure 18 for tests at 800°C. In these plots, the effect of the prior anneal condition, i.e., one hour at 1200°C (furnace cool) or 1500°C (helium quench) are also

TABLE XI

Preliminary Creep Results of Scale-up Vanadium Alloys

<u>Alloy</u>	<u>1 Hr Anneal Temperature (°C)</u>	<u>Temp of test (°C)</u>	<u>Stress (psi)</u>	<u>Time at Temp (Hours)</u>	<u>Strain (%)</u>	<u>Time to 1% Strain (Hours)</u>	<u>Plastic Loading Strain (%)</u>	<u>Min Creep Rate %-Hr⁻¹</u>
HSV-203 V-10.4Cb-1.27Zr-0.049C								
-1	1200	700	35,000	285	2.5	0.5	0.78	.0042
-2	1200	700	20,000	143	0.98	>143	0.0	0.0029
-3	1500 (FC)	700	30,000	142	1.05	87	0.0	0.0022
-4	1200	800	10,000	139	1.01	135	0.0	0.0025
-5	1500 (HQ)	700	30,000	260	1.56	45	0.0	.0019
HSV-204 V-6.5Fe-1.32Zr-0.051C								
-1	1200	700	30,000	268	2.69	0.9	0.31	.0029
-2	1200	700	20,000	263	1.05	240	0.0	.0019
-3	1500 (FC)	700	30,000	143	1.40	35	0.0	.0033
-4	1200	800	10,000	141	1.09	114	0.0	.0026
-5	1500 (HQ)	700	30,000	258	1.4	138	0.0	.0018
-6	1200/1500 HQ	700	30,000	120	1.33	20	0.23	.0022
HSV-205 V-12.3Cr-2.70Zr-0.124								
-1	1200	700	30,000	226	3.94	0.0	1.25	.0036

FIGURE 16 - Minimum Creep Rate of Scale-Up Alloy (HSV-203) at 700°C

FIGURE 17 - Minimum Creep Rate of Scale-Up Alloy (HSV-204) at 700°C

FIGURE 18 - Minimum Creep Rate of Scale-Up Alloys at 800°C

shown. The minimum creep rate of HSV-203 (V-Cb-Zr-C) (0.0042%/hour) at 35,000 psi and 700°C is found to be higher than that exhibited by the comparable alloy HSV-20 (0.0007%/hour) produced by non-consumable electrode melting. On the other hand, HSV-204 (V-Fe-Zr-C) has a lower creep rate (0.0029%/hour) than the non-consumable melted alloy HSV-21 (0.0054%/hour) tested at 30,000 psi at 700°C. HSV-205 (V-Cr-Zr-C) also has a lower creep rate (0.0036%/hour) at 30,000 psi, 700°C than the button melt HSV-5 (0.006%/hour). The transient creep properties of the scale-up alloys were not very different from the values recorded for the comparable button melts.

When the stress was reduced to 20,000 psi at 700°C, the minimum creep rate was reduced except for HSV-205, which exhibited a slight increase over that recorded at 30,000 psi. No plastic loading strain was recorded for this alloy. However, at the time of this writing the specimen was at temperature only 66 hours and the steady state creep value reported may be somewhat on the high side.

At a stress of 10,000 psi at 800°C the creep properties of HSV-203 and 204 appear to be quite similar with respect to transient as well as second stage creep. (The creep rate of HSV-203 and the button melt HSV-20 are identical). HSV-205, although only tested 68 hours, appears to have a higher primary creep rate. The higher creep rate for HSV-205 at 700 and 800°C is attributed to a higher recovery rate or lower strain hardening (or both) than alloys HSV-203 and 204. The creep specimens are being metallographically examined to relate microstructure with behavior at

elevated temperature and at different stress levels. When the one hour annealing temperature was increased from 1200 to 1500°C, the minimum creep rate of HSV-203 decreased by almost a factor of 2. A slightly lower creep rate was recorded for the helium quenched sample than for the furnace cooled sample annealed for one hour at 1500°C. Increasing the one hour anneal temperature from 1200 to 1500°C for HSV-204 resulted in a reduction in the minimum creep rate by almost a factor of 2 when the annealed sample was helium quenched. A creep rate slightly higher than that recorded for the sample annealed at 1200°C is found when the specimen annealed at 1500°C is furnace cooled (Table XI). The time to 1% strain increases from 35 to 138 hours as a result of the higher quenching rate at 1500°C. Room temperature hardness values of HSV-203 creep specimens, taken in the head section, increase from 153 to 188 to 220 VHN for one hour anneals at 1200°C (furnace cooled), 1500°C (furnace cooled), and 1500°C (helium quenched) respectively. Room temperature hardness values of HSV-204 creep specimens increase from 166 to 184 to 178 VHN for one hour anneals at 1200°C (furnace cooled), 1500°C (furnace cooled), and 1500°C (helium quenched) respectively. On the other hand, room temperature hardness values for HSV-205 creep specimens range from 146 to 158 for a one-hour anneal at 1200°C (furnace cooled) and 156 to 161 for a one hour anneal at 1500°C (helium quenched). Hardness readings taken in the head section after creep testing are generally found to be higher than before the test except for those tests performed at 800°C. However, these hardness values may be higher than normal since the head section is not covered with tantalum foil as is the gauge section and small amounts of oxygen and carbon pick up are possible⁽²⁾.

The improvement in creep resistance of the experimental (and scale-up) alloys produced in this program over that of the reference alloys V-10Ti or V-20Ti is shown in Figures 19 and 20. Included in the 700°C plot is a curve estimated from data reported in ANL-7230. The initial portion of this curve may not be correct but the V-15Ti-7.5Cr alloy nevertheless failed in less than 400 hours with a plastic strain of over 50%. This is in contrast to many of the current alloys which contain ZrC(N) dispersoids and exhibit a total strain of less than 4% after exposure times up to 600 hours at stresses of 30,000 psi or higher at 700°C.

Phase Identification Studies

Phase identification studies are continuing in an attempt to develop a better understanding of the effects of the dispersed phase composition and stability vs. the creep behavior of the experimental alloys. The procedure followed to extract the dispersed phases is described in the Fourth Quarterly Report⁽³⁾.

The phases identified in tensile or creep specimens are summarized in Table XII. In all of these alloys a fcc phase was identified as ZrC(N), with lattice constants ranging from 4.615 to 4.659 Å. A plot of the lattice parameters of the dispersed phase for all of the alloys examined to date (Quarterly Report Five)⁽²⁾ shows a correlation with the carbon or nitrogen content (Figure 21). Those alloys to which carbon was added to produce an atom ratio of $Zr/C = 1$ have a lattice parameter higher than those alloys to which carbon is added in the ratio of $Zr/C = 2$. As

FIGURE 19 - Creep Curves at 700°C of Westinghouse and Reference Alloys

FIGURE 20 - Creep Curves at 800°C of Westinghouse and Reference Alloys

TABLE XII

Identification of Dispersed Phases in Vanadium Alloys

<u>Alloy</u>	<u>Nominal Composition (w/o)</u>	<u>1 Hr Anneal °C</u>	<u>Test Temperature °C</u>	<u>Phases Identified and Lattices Parameters in Angstroms</u>
HSV-15	V-6.1Cr-1.33Zr-0.123C	1200	700	ZrC(N), $a_o = 4.659$, ZrO ₂ , V, $a_o = 3.015$
HSV-15		1500	700	ZrC(N), $a_o = 4.657$, ZrO ₂
HSV-31	V-12.2Cr-1.34Zr-0.055C	1200	700	ZrC(N), $a_o = 4.638$, ZrO ₂ , V, $a_o = 3.008$
HSV-31		1200	RT	ZrC(N), $a_o = 4.638$, ZrO ₂ , V, $a_o = 3.008$
HSV-35	V-12.2Cr-1.33Zr-0.44N	1200	700	ZrN(C), $a_o = 4.614$, ZrO ₂ , V, $a_o = 3.008$
HSV-27	V-9.11Cr-3.27Fe-1.33Zr-0.054C	1200	700	ZrC(N), $a_o = 4.638$, ZrO ₂ , V, $a_o = 3.004$
HSV-27		1200	800	ZrC(N), $a_o = 4.638$, ZrO ₂ , V, $a_o = 3.008$
HSV-28	V-9.15Cr-2.82Ti-1.34Zr-0.054C	1200	700	ZrC(N), $a_o = 4.632$, ZrO ₂ , V, $a_o = 3.021$
HSV-204	V-6.5Fe-1.32Zr-0.051C	1200	700	ZrC(N), $a_o = 4.636$, ZrO ₂

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FIGURE 21 - Lattice Parameter of Dispersed Phases in Vanadium Alloys
(Numbers Refer to Compositions - Table 3)

expected, alloy HSV-35, which contains nitrogen in place of carbon, exhibited a dispersed phase with a lattice parameter considerably lower than the alloys containing an atom ratio $Zr/C = 2$.

A monoclinic phase identified as ZrO_2 was found in all of the residues except alloys HSV-4, 5, and 18. It was thought that (5th Quarterly)⁽²⁾ the reason for the absence of the ZrO_2 phase in these alloys was due to an increase in the solubility of O_2 due to the chromium, which is common in the three alloys. However, more recent results show that other alloys containing 6 and 12 atom percent Cr do contain a ZrO_2 phase, although the lines are weak.

In some of the residues examined by x-ray diffraction a bcc phase is observed in the film. This phase is identified as the matrix $V-M_x$; however, the lattice constant reported in Table XII for the bcc phase is affected by the solution of some Zr in those alloys where the atom ratio of $Zr/C = 2$ is used.

Sodium Corrosion Testing

Four thermal convection loop tests (#1, #2, #3, and #4) on V-alloys have been completed. the results of loop tests #1 and #2 were reported and discussed in detail in the 5th Quarterly Report⁽²⁾. The test conditions in loop tests #3 and #4 were similar to those in loop tests #1 and #2.

Temperature of hot leg	740 - 815°C
Temperature of cold leg	500 - 600°C
Oxygen in sodium (before and after test)	< 10 ppm

Flow rate

7 cms/sec.

Specimen size

1.5 x 0.5 x 0.040-in.

After test the weight change in each specimen was determined. Both loop tests contained specimens of the same alloy. In loop test #3 the V-alloy specimens were placed in the hot leg in the following order:

Bottom of leg 740°C

Top of leg 815°C

HSV-40, -39, -38, -37, -36, -35B, -35A, -34, -33, -32, -31B,
-31A, -29, -28, -27, -27.

In the loop test #4 the order was reversed and an additional alloy, HSV-200, included.

Bottom of leg 740°C

Top of leg 815°C

HSV-200, -27, -27, -28, -29, -31A, -32, -33, -34, -35A, -35B,
-36, -37, -38, -39, -40, -200.

Each alloy, therefore, had two specimens subjected to two temperatures within the 740°C to 815°C range. Assuming a linear relationship between weight change and temperature, an interpolation was made to obtain the weight change at a temperature of 790°C. This allowed a valid comparison of the alloys to be made.

The results of loop tests #3 and #4 are given in Table XIII. In all cases but one, weight gains were observed. In contrast to the results on loop tests #1 and #2, careful visual examination revealed that tarnishing occurred on all specimens. However, there was no indication

TABLE XIII

WEIGHT GAIN DATA FOR V-ALLOYS TESTED IN
A SODIUM THERMAL CONVECTION LOOP FOR 500 HOURS

Alloy	Loop #3		Loop #4		Interpolated ΔW at 790°C mg/dm ²	Integrated Hardness VPN- $\times 10^2$		Integrated Hardness VPN- $\times 10^2$ Interpolated at 790°C
	Temperature °C	ΔW , mg/dm ²	Temperature °C	ΔW , mg/dm ²		Loop #3	Loop #4	
HSV-27	815	15	742	0	10	435	0	290
HSV-28	815	28	746	3	19	0	0	0
HSV-29	814	19	748	1	12	640	170	470
HSV-31A	812	16	756	0	10	825	250	600
HSV-32	806	15	761	11	13	663	190	500
HSV-33	801	15	767	7	8	-525	100	-310
HSV-34	786	23	774	28	--	150	150	150
HSV-35A	778	11	794	3	--	210	460	400
HSV-35B	770	10	800	0	--	--	--	--
HSV-36	764	13	805	13	13	525	1250	940
HSV-37	754	11	810	29	22	185	785	570
HSV-38	750	11	812	45	33	600	70	250
HSV-39	744	8	815	14	12	0	605	390
HSV-40	740	8	815	3	5	550	0	190
HSV-200	750	12	815	55	38	--	--	--

of sub-surface precipitates in the microstructure. In alloys HSV-34, -35, and -40 it was noted that the weight gain at higher temperature was less than that exhibited at the lower test temperature. This could be due to inaccuracy in weighing the specimens or to loss of metal occurring at higher temperatures. At present the reason for these anomalous results is not clear. However, since weight changes of only about 1/10% are being recorded, it seems probable that errors in weighing could account for the results.

The interpolated weight changes at 790°C are given in Table XIII and Figure 22. In Figure 22 the results for loop tests #1 and #2 are also included and the alloys are grouped according to total solute level and composition variation. (See Table II for explanation of the grouping.) Although it is not possible to definitely establish the role of each alloy element in determining the behavior of V-alloys in liquid sodium, some trends are evident. For example the Cr alloys generally exhibit less weight gain than the reference V-Ti alloys (HSV-11, -12). However, additions of W and Mo even at a high Cr level, viz. HSV-25, -26, give comparatively high weight gains. Additions of Cb and Ta to Cr containing alloys (HSV-39, -40 respectively) and alloys with Fe additions, viz. HSV-21, -23, exhibit low weight gains.

Of all the alloys tested to date in this program, the following exhibited greater weight gains than the reference alloys:

FIGURE 22 - Interpolated Weight Gain at 790°C in V-Alloys After Exposure to Liquid Sodium for 500 Hours

HSV-22	V - 10 W - 1.24 Zr - 0.47 C
HSV-23	V - 9.87 Ta - 1.24 Zr - .047 C
HSV-24	V - 19.45 Cr - 4.26 Zr - .252 C
HSV-25	V - 8.48 Cr - 10 W - 1.24 Zr - 0.50 C
HSV-26	V - 8.91 Cr - 5.48 Mo - 1.3 Zr - .053 C
HSV-34	V - 5.64 Ti - 1.34 Zr - .052 C
HSV-37	V - 10.4 Cb - 1.28 Zr - .03 C
HSV-38	V - 8.95 Ti - 1.35 Zr - .055 C

After test the specimens were sectioned, metallographically polished, and a micro-hardness traverse made across the thickness using a 500 gm. load. The results of these tests are shown in Figures 23, 24, 25, and 26. Virtually all specimens increased in hardness during test. As in the case of loop tests #1 and #2, two types of hardness/distance profiles were observed.⁽²⁾ The first type shows a relatively constant hardness from the surface to the center--such an alloy is HSV-34. This might be indicative of a fairly rapid diffusion of interstitials (oxygen, carbon, or nitrogen) from the surface to the interior. The second type of profile, e.g. HSV-31, shows a high surface hardness which decreases towards the center, although this center hardness is higher than that of the specimen prior to test. In this case it appears that the diffusion of interstitials is slower, or that the amount of interstitials taken into solution in the surface region is high. From the high surface hardness of some of the specimens, it is likely that the interstitial absorption is large. In the series of alloys tested no correlation between type of curve and alloy composition is apparent.

→ Micro-Hardness Prior to Test

FIGURE 23 - Micro-Hardness Traverse Across Thickness of V-Alloy Specimens Tested in Liquid Sodium for 500 Hours.

→ Micro-Hardness Prior to Test

FIGURE 24 - Micro-Hardness Traverse Across Thickness of V-Alloy Specimens Tested in Liquid Sodium for 500 Hours.

→ Micro-Hardness Prior to Test

FIGURE 25 - Micro-Hardness Traverse Across Thickness of V-Alloy Specimens Tested in Liquid Sodium For 500 Hours.

→ Micro-Hardness Prior To Test

FIGURE 26 - Micro-Hardness Traverse Across Thickness of V-Alloy Specimens Tested in Liquid Sodium for 500 Hours.

In the discussion⁽²⁾ of the results for loop tests #1 and #2, it was suggested that the hardness increase may be reasonably assumed to be due to solution of interstitials in the alloy matrix. Consequently, the area between the pre- and post-test curves in Figures 23 to 26 is a measure of the total amount of interstitials taken into solution. The integrated hardness would then be expected to be proportional to the weight gain in the specimen. In Figure 27 is shown the integrated hardness as a function of weight gain for loop tests #1 and #2 and for loop tests #3 and #4. In the first two tests a reasonable correlation exists between the integrated hardness and the weight gain. Two curves can be fitted through the data points. It appears that all the high carbon alloys ($\sim 0.3\%$) lie on the lower curve, whereas 7 out of 11 low carbon alloys ($\sim 0.1\%$) lie on the upper curve. However, the data points for loop tests #3 and #4 (Figure 27) show no correlation between integrated hardness and weight gain. This may be due to several reasons:

- (1) The variation in the weight gain data for the pair of specimens may be too large to give an accurate correlation;
- (2) errors in integrated hardness values may also contribute to lack of correlation;
- (3) hardening may be due to a combination of interstitial absorption, age hardening, or interactions between absorbed interstitials and solute elements. The contribution of each of these would be expected to be different for the various alloys.

FIGURE 27 - Integrated Hardness (Interpolated at 790°C) versus Weight Gain for Experimental V Alloys

At this stage it is not possible to explain the data obtained to date. However, it is probable that the results can be accounted for by age-hardening and interstitial absorption. In order to determine the contribution of each of these mechanisms, detailed chemical analyses of specimens exposed to sodium are being carried out. In addition, specimens are being aged in vacuum so that the extent of age-hardening can be determined.

A fifth sodium thermal convection loop test containing specimens of the remaining alloys is now in progress and will be followed by a sixth loop test, reversing the order of the specimens.

Compatibility Studies

Studies are now in progress to determine the compatibility of selected V-alloys with ceramic fuels. The following combinations of fuel and bond are to be tested:

- (1) UO_2 with helium bonding,
- (2) chromium carbide stabilized hyperstoichiometric UC with sodium and helium bonding,
- (3) iron stabilized hypostoichiometric UC with sodium and helium bonding.

The V-alloy specimens in future compatibility tests will be run in a manner slightly modified from that of the first test using UO_2 and helium bonding. Figure 28 illustrates that one specimen will be sandwiched between the ceramic fuel pellets, with one surface in

FIGURE 28 - Schematic Diagram for V-Alloy/Fuel
Compatibility Studies

contact with a pellet and the other separated from a pellet by a vanadium wire spacer. In this way it will be possible to study both alloy/fuel and alloy/bond/fuel interactions.

The capsules will be maintained at 800°C for periods of up to 1,000 hours. After exposure the V-alloy specimens will be sectioned and examined metallographically to determine the extent of alloy/fuel interaction. These tests will be supplemented with hardness change determinations and selected analyses for interstitials.

A series of V-alloys tested with UO_2 in a helium bond has been removed after 2,000 hours at 800°C and is now being examined metallographically. Carbide fuel pellets are now being fabricated for the remaining studies.

Welding Evaluation

Experiments to determine the weldability of V-base alloys were continued during this report period. Samples of annealed 0.042-inch thick sheet were TIG welded in a vacuum-purged, He-filled weld chamber. The He atmosphere is maintained at ~ 1 ppm O_2 and 0.3 ppm H_2O during welding. A longitudinal bead-on-plate weld is made at 15-inch per minute welding speed, with welding currents varying from 60-90 amps, resulting in 100% penetration through the sheet.

The results of the welding tests completed in this period are shown in Table XIV. Scale-up alloys HSV-200, -202 through -208 were successfully

TABLE XIV.
EFFECT OF WELDING CURRENT ON THE
BEAD-ON-PLATE WELDING OF V-ALLOYS

<u>Alloy</u>	<u>Welding</u>	
	<u>90</u>	<u>65</u>
HSV-36		C
HSV-37		C
HSV-38		S
HSV-39		C
HSV-40		C
HSV-41		C
HSV-42		S
HSV-43		C
HSV-44		S
HSV-45		C
HSV-200	S	
HSV-202	S	
HSV-203	S	
HSV-204	S	
HSV-205	S	

S - Satisfactory crack-free welds
C - Cracked along weld

welded at the high current of 90 amps. Of the experimental alloys only HSV-38 (8.95Ti-1.35Zr-.055C), HSV-42 (6.56Fe-1.53Cr-0.8Al-1.34Zr-0.52C) and HSV-44 (6.51Fe-1.52Cr-1.33Zr-0.052C) could be welded without cracking at 65 amps. However, it is likely that bowing of the relatively narrow specimens used may have been principally responsible for cracking in the other alloys. Additional welds are being made to verify this possibility.

Sections 1-in. x 1/2 in. with the weld bead in the long direction were machined from the welded strip. These specimens were tested in a slow bend test according to MAB specifications, using a punch having a 1t (0.052-in.) radius.⁽³⁾ The punch extension and load were autographically recorded during test. The specimens were evaluated for cracking at X250 magnification and by examination of the load/punch extension curve. A cleavage type fracture is evidenced by a sharp drop in the load/punch extension curve.

The results of tests carried out on the two scaled-up reference alloys and unalloyed V are shown in Table XV. The results indicate that the ductile-brittle transition temperature for these alloys is below -100°F.

Other tests are underway to determine the ductile-brittle behavior of the remaining alloys in the series.

TABLE XV

SLOW BEND DATA ON V-ALLOY WELD SPECIMENS 90° BEND

<u>Alloy</u>	<u>Test Temperature °F</u>		
	<u>-100</u>	<u>+70</u>	<u>+125</u>
HSV-200	N.C.*	N.C.	
HSV-202	N.C.	N.C.	
2406-2 (100V)	N.C.	N.C.	N.C.

*N.C. - No cracks.

III. FUTURE WORK

During the next period the following work will be performed:

1. Fabrication of alloys for scale-up into 2-1/2-in. diameter arc melted ingots will be completed and evaluation continued.
2. Work will continue on the identification of precipitates in vanadium alloys.
3. Corrosion testing of the alloys in sodium thermal convection loops will be completed.
4. Welding evaluation and slow-bend testing of the experimental alloys will be completed.
5. Compatibility testing of the V-alloys with UO_2 and UC fuel will be continued.

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