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VANADIUM ALLOY SCREENING STUDIES AND
FABRICATION OF V-15w/oTi-7.5w/oCr TUBING
FOR NUCLEAR FUEL CLADDING

by

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ABSTRACT

Based upon the results of screening tests involving a number of alloys, the vanadium-15 w/o titanium-7.5 w/o chromium alloy has emerged as a promising cladding candidate for sodium-cooled fast reactors. "Scale-up" or pilot-plant production technology is presented for this alloy. Consolidation involved consumable arc-melting of compacted electrodes, followed by arc-remelting. The double-melted ingots were broken down by extrusion, followed by re-extrusion into rod, sheet-bar, and tube-blanks. Rod and sheet products were easily cold-rolled to finished sizes. Extruded tube-blanks were processed by swaging, tube-reducing, and drawing. Some early processing problems were solved, and high yields have been realized in the production of reactor-grade tubing. The results of annealing studies and property tests are presented and discussed.

I. INTRODUCTION

Alloys for fast-reactor cladding applications ideally possess a combination of properties including high-temperature strength, irradiation stability, compatibility with fuel and coolant, low neutron-absorption cross section, good fabricability, and reasonable cost. However, ideal alloys are rarely found. A specific cladding alloy for a well-defined reactor system is generally selected from a list of less than ideal candidates and through compromise so that the surviving choice has the best available combination of desired properties. Since room for improvement always exists, a continuing alloy-development program is needed. This need becomes acute when even the best available alloy has gross shortcomings under a particular set of conditions of current interest.

Since early 1963, the Metallurgy Division has conducted such a continuing alloy-development program. Once compositions were selected for consideration, cast alloy buttons were screened through a battery of tests--fabricability, sodium corrosion, and mechanical properties. Most-promising alloys were selected for more thorough evaluation. "Scale-up" studies were required to enable consolidation and fabrication of a greater amount of alloy material for testing. When an alloy was finally singled out to receive concentrated effort, a fabrication technology was developed to provide large quantities of reactor-grade wrought products--tubing, sheet, and rod. These products were and are being used as specimen material for long-term sodium-corrosion (including in-pile) tests, long- and short-term mechanical-property tests, and irradiation experiments.

Vanadium-base alloys have received primary consideration because of their favorable nuclear characteristics and promising combinations of properties for fuel cladding in a sodium-cooled reactor. Incompatibility between Type 304 stainless steel and a uranium-plutonium-fizzium fuel alloy spurred initial efforts in 1963, which resulted in development of vanadium-20 w/o titanium (TV-20).^{1,2} This alloy has good compatibility with U-Pu-Fz fuel. A large quantity of tubing and other wrought TV-20 products was produced, and the alloy is still undergoing long-term testing. While data indicate that sodium corrosion and strength properties (including creep) may be adequate, work has continued toward development of other vanadium-base alloys having improvements in both areas. Of major importance was the necessity for retaining sufficient fabricability to permit the production of high-quality tubing and wrought products. The improved alloys should be useful for a variety of fuels being considered for fast-reactor applications.

Production development efforts on TV-20 were essentially completed by midyear 1964. Of alloys screened since that time, vanadium-15 w/o titanium-7.5 w/o chromium has emerged as a "second-generation" alloy having significantly improved creep properties and moderately improved sodium-corrosion resistance compared to TV-20. This report summarizes the initial screening of vanadium-base alloys since mid-1964, and "scale-up" studies on two of these alloys--vanadium-40 w/o titanium and vanadium-15 w/o titanium-7.5 w/o chromium. Fabrication development for V-15Ti-7.5Cr wrought products is treated in detail.

Certain annealing studies and property tests were performed during this work to obtain appropriate annealing temperatures, evaluate fabrication methods, and determine end-product quality. Results of more rigorous tests for obtaining design data will be reported elsewhere.

II. ALLOY SCREENING

The selection of suitable alloy compositions for consideration was the first step in the preliminary screening process. Following composition selection, small alloy buttons were arc-cast and evaluated for fabricability by hot-, warm-, and cold-rolling into sheet stock. Further screening of fabricable materials included sodium compatibility and, in some cases, property testing. As a result of this sequence of tests, the most promising alloys were selected for more thorough evaluation, the scale of operations being enlarged to produce the additional quantities of material needed for evaluation.

A. Selection of Compositions

Selection of alloy compositions was based primarily on neutron cross-section considerations, and on the nature of the constitution diagrams of vanadium with the pertinent alloying additions. Complete solid solubility was favored for potential benefits regarding fabricability as well as microstructural (and accompanying mechanical property) stability under irradiation. The alloys were generally devoid of intentional additions of dispersions and/or precipitation-hardening elements. Feedback from tests on sheet specimens prepared from the initial compositions resulted in preparation of additional compositions thought to be promising. Titanium and chromium were the major alloying additions studied.

B. Arc-casting of Buttons

When compositions had been selected, small alloy buttons were arc-cast under an 80 v/o helium-20 v/o argon atmosphere using a non-consumable (tungsten-tip) electrode. The alloy buttons were broken up, and recast several times to promote alloying and homogeneity. As-cast buttons were approximately 38-mm (1.5-in.) square x 13-mm (0.5-in.) thick with rounded corners and crowned tops. The buttons were encapsulated (weld-sealed) within Type 304 SS compacts to avoid atmospheric contamination during hot-rolling.

C. Evaluation of Alloy-button Fabricability

The compacts were hot-rolled (650 to 1200°C) on a 430 x 610-mm (17 x 24-in.)-two-high United mill to a thickness of 3.2 to 4.8 mm (0.125 to 0.187 in.) with single-pass reductions of 10%. Dejacketed materials were then cold-sized to a uniform 3.2-mm (0.125-in.)-thick strip. The sized strip was vacuum ($<10^{-5}$ Torr)-annealed (900°C for 1 hr) and cold-rolled on a 150 x 360 x 300-mm (6 x 14 x 12-in.)-four-high Bliss mill to a 1.6-mm (0.062-in.) thickness, with reductions of 5 to 10% per pass.

Certain compositions were not amenable to cold-rolling after hot breakdown. These alloys were warm-rolled (400 to 550°C) on the four-high Bliss mill to a minimum thickness of 2.4 mm (0.094 in.) with reductions of 2 to 8% per pass. The warm-rolled strip was vacuum-annealed (900°C for 1 hr) and cold-reduced to 1.6-mm (0.062-in.) thickness.

Relative fabricability ratings were assigned to the alloys. The ratings were based on hot- and/or cold-rolling characteristics (i.e., extent of cracking, amount of reduction per given mill setting) and hardness measurements taken at various steps in the reduction schedule. Obviously, an optimized fabrication procedure could not be established for each composition; therefore the relative ratings were taken only as rough guides. However, this rating procedure did cull out compositions that definitely were difficult to fabricate. Among the fabricable alloys, the ratings indicated those that posed the greatest (or least) fabrication problems.

Some of the data gathered during the fabricability rating of 28 vanadium-base alloys are presented in Table I. The alloys fall generally into four categories: V-Ti binaries (Nos. 1-3), V-Cr binaries (Nos. 4-9), V-Ti-X ternaries (Nos. 10-24), and V-Cr-X ternaries (Nos. 25-28).

TABLE I. Vanadium-base Alloy Fabrication Data

Alloy Composition, w/o	Hardness As Cast, RA	Hot- rolling Temp, °C	Hardness after Hot- rolling, RA	Warm- rolling Temp, °C	Hardness after Warm- rolling, RA	Hardness after Cold- rolling 50%, RA	Hardness As Annealed, RA	Fabricability Rating ^a
1. V-30Ti	62-65	1050	62-65			65	62	b
2. V-40Ti	61-62	1050	61-63			64	61-62	a
3. V-50Ti	61-62	1050	62-63			63-64	62	a
4. V-5Cr	52-54	900	48-52	400	60-63	62-63	52-54	a
5. V-10Cr	52-54	850-650	61-63			59-61	54	b
6. V-15Cr	57-58	900-750	60-63					e
7. V-20Cr	61-64	1050-850	62-65					e
8. V-25Cr	65-67	1150						d
9. V-40Cr	66-67	1200						d
10. V-15Ti-5Cr	59-61	1000	57-59.5			62-63.5	57-58	a
11. V-15Ti-7.5Cr	62-62.5	1050	52-58			64-64.5	58-61	b
12. V-30Ti-5Cr	59-62	1000	58-62			65-67	63	c
13. V-30Ti-10Cr	63-66	1000	59-64			66-67	64-65	c
14. V-20Ti-5Cr	61-62	1050	57-61			64-65	58-61	c
15. V-5Ti-15Cr	57-58	900	58-62	450-500	65-67	64-65	59-61	c
16. V-20Ti-2Mo	59.5-60.5	1000	53-59			62.5-63	57-58	a
17. V-20Ti-2Ta	55.5-58.5	1000	58-60			61.5-62	56-58	a
18. V-20Ti-2Nb	57.5-61	1000	59-61			61-61.5	56-58	a
19. V-40Ti-5Cr	63-64	900	61-63			66-68	62-64	c
20. V-40Ti-10Cr	66-67	900	61-66			67-68	64-65	c
21. V-40Ti-10Mo	65-67	900	68-70	500-550	64-66	66	62-64	b
22. V-15Ti-7.5Mo	62-63	900	63-65	500-550	63	62	56	a
23. V-15Ti-7.5Cr-1Y	58-59	1050	47-53			63	57-58	a
24. V-2Ti-18Cr	57-59	1150	51-55					d
25. V-5Cr-10Si								d
26. V-5Cr-15Zr	54-57	1000						d
27. V-5Cr-10Al	60-64	1000						d
28. V-20Cr-10Al	64-68	1000	58-60	500				d

^aa = similar to V-20Ti, b = slightly more difficult, c = considerably more difficult, d = unable to fabricate satisfactorily, e = not completely evaluated.

The V-Ti binary alloys through 50w/oTi proved to be quite similar to V-20Ti in fabricability, with the exception of V-30Ti, which was slightly more difficult to fabricate. In V-Cr binary alloys, increasing chromium content is accompanied by decreasing fabricability. It was possible to fabricate V-5Cr and V-10Cr, but not the V-25Cr and V-40Cr alloys, into sheet. The other two V-Cr alloys listed, containing 15 or 20w/oCr, have not been fully evaluated. V-Ti-Cr (V-Ti-X) ternary alloys became increasingly harder to fabricate with increasing Ti-Cr contents. Combinations of high chromium and low titanium were especially difficult, and one alloy of this type, V-2Ti-18Cr, could not be successfully fabricated into sheet. Additions of 2w/oMo, Ta, or Nb to V-20Ti had no effect on fabricability, and increasing the molybdenum content had less effect than increasing the chromium content in V-Ti-X alloys. Ternary additions of Si, Zr, or Al (V-Cr-X) alloys resulted in alloys that could not be fabricated successfully. The only alloy not covered in the four categories listed above is the quaternary V-15Ti-7.5Cr-1Y alloy (No. 23), which was similar to V-20Ti in its fabrication characteristics.

D. Fabrication of Sheet Specimens

All 19 alloys with ratings of a, b, or c (see Table I) were fabricated into sheet specimens for corrosion and property tests. These specimens were made from 0.8-mm (0.031-in.)-thick sheet stock. The sheet was prepared from 1.6-mm (0.062-in.)-thick strip, which was vacuum-annealed and cold-rolled 50% to final thickness. Specimens were made available in both the cold-worked (50% reduction) and vacuum-annealed (900°C for 1 hr) conditions.

E. Additional Screening Tests

Corrosion test results reported by Ruther and Greenberg³ are given in Table II for 12 of the alloys tested in the cold-worked condition. This group of alloys consisted of the V-Ti binaries and most of the V-Ti-X ternaries; all were fabricated from arc-cast buttons. (Only two V-Cr binaries were successfully fabricated into sheet. No corrosion results have been obtained on these alloys. No V-Cr-X alloys were fabricated into sheet test specimens.)

The corrosion screening tests were performed at 650°C in static-refreshed sodium containing 40 to 50 ppm oxygen. Results for the V-20Ti reference alloy (No. 13) are for an annealed specimen. Each specimen was subjected to these test conditions for 7 days.

The corrosion characteristics of V-Ti binaries improved as the titanium content increased. Results of tests on ternary alloys suggested that the titanium content was most significant in determining the corrosion resistance. Chromium additions aided in the formation of a more tightly adherent surface oxide film and therefore reduced surface losses more effectively than titanium.

TABLE II. Effect of Alloy Composition on Corrosion in 650°C Sodium

Alloy Composition, w/o	External Loss per Side, μ	Depth of Hardening, μ	Total Metal Penetration, μ
1. V-30Ti	52	23-27	75-79
2. V-40Ti	28	13-16	41-44
3. V-50Ti	25	12-18	37-43
4. V-15Ti-5Cr	24	40-45	64-69
5. V-15Ti-7.5Cr	21	34-38	55-59
6. V-30Ti-5Cr	14	20-22	34-36
7. V-30Ti-10Cr	18	15-18	33-36
8. V-20Ti-5Cr	23	32-35	55-58
9. V-5Ti-15Cr	9	60-70	69-79
10. V-20Ti-2Mo	17	40-45	57-62
11. V-20Ti-2Ta	34	35-40	69-74
12. V-20Ti-2Nb	34	40-50	74-84
13. V-20Ti (Reference)	42	30-35	72-77

In addition to these results for cold-worked specimens, corrosion values have been reported for annealed (900°C for 1 hr) specimens of the V-Ti binaries. The annealed specimens had somewhat less corrosion damage than the cold-worked specimens, although the relative ranking was unchanged. Although most of the binary and ternary alloys had improved corrosion resistance, compared to V-20Ti, the V-40Ti alloy (as annealed) offered the largest improvement of the 12 alloys tested.

Fig. 1. Creep of Annealed V-Ti-Cr Alloy Sheet Specimens Tested at 15-kg/mm² Stress and 650°C

Several annealed specimens of V-Ti-Cr alloys were creep-tested for 500 hr at 15 kg/mm² (21,300 psi) and 650°C. Test results reported by Gilbert and Yaggee⁴ are shown in Fig. 1. Results on V-20Ti are included for comparison. Resistance to creep was improved with a decrease in titanium content and/or an increase in chromium content. The creep rates of the V-15w/oTi-7.5w/oCr and V-5w/oTi-

15w/oCr alloys are about an order magnitude lower than that of V-20Ti. Although not included in Fig. 1, the V-15Ti-5Cr alloy has been creep-tested for 100 hr and has a creep rate similar to that of the V-15Ti-7.5Cr alloy.

III. INITIAL SCALE-UP STUDIES

Two vanadium-base alloys--V-40w/oTi and V-15w/oTi-7.5w/oCr--were selected for scale-up from small button melts into larger ingots. The V-40Ti alloy was of interest because of its improved sodium-corrosion resistance (compared to V-20Ti). The V-15Ti-7.5Cr alloy was selected for scale-up based on its greatly improved elevated-temperature creep rate over that of V-20Ti, and to a lesser extent on its improved corrosion resistance.

A. Consolidation and Fabrication of V-40Ti

Scale-up of the V-40Ti alloy began with the consolidation of two 58-mm (2.3-in.)-diam ingots by electron-beam (EB) melting. Typical interstitial levels in the charge materials are shown in Table III. Drip rods for EB melting were prepared by compacting 35-g batches of vanadium chips and titanium sponge into 19-mm (0.75-in.)-diam x 25-mm (1.0-in.)-long briquets in a three-piece split die at 96.0 kg/mm² (68 tsi). After being compacted, the briquets were welded under an inert atmosphere into 635-mm (25-in.)-long rods. Three rods were grouped, welded together, and melted simultaneously as a single drip rod.

TABLE III. Typical Interstitial-element Analyses of Starting Materials for Alloying

Material	Analyses, ppm				
	Carbon	Oxygen	Nitrogen	Hydrogen	Total
Vanadium Chips	200	800	350	50	1400
Titanium Sponge	50	500	300	20	870
Chromium Flakes	300	5	30	5	340

Electron-beam melting incorporated a power setting of 26 to 29 kW and a vacuum of $<10^{-5}$ Torr. A melt rate of ~80 g/min was maintained by proper focus of the beam and positioning of the drip rod. Under these conditions, approximately 3% of the material charged was lost through vaporization and splattering of molten metal from the mold when heavy drops or an occasional solid piece fell from the briquet drip rods. Based on experience with EB melting of V-20Ti, increases in melt rate beyond ~80 g/min do not increase the overall yield because increasing splatter losses overshadow any further reduction of vaporization losses. In general, an overall yield of >96% at melt rates of 50 to 100 g/min is a practical maximum.

Since the EB ingots required a remelt to insure homogeneity, surface quality and internal porosity of the initial ingot were inconsequential.

Surface quality was improved, however, by proper positioning of the molten pool in the mold, with other conditions (beam focus, power setting, and drip-rod position) constant. A molten pool too low in the mold results in excessive cold shuts; if the molten pool is too high in the bell-shaped mold top, surface tearing occurs as the ingot is retracted.

The consumable-electrode arc-remelt conditions were straight polarity (consumable electrode negative), $<10^{-2}$ Torr pressure, and 36.5 kW (27 V and 1350 Amp) of power. A stirring coil setting of 1.5 Amp aided arc collimation, and a hot-topping procedure (reduction of power in successive steps near the end of the melt cycle) was used to minimize secondary piping at the ingot top. A melt rate of about 1 kg/min was maintained, and there was no detectable loss of charge during melting. The resultant arc-cast ingot (AM-49) was 58-mm (2.3-in.) in diameter and 130-mm (5-in.) long.

Results of analyses on AM-49 for titanium and interstitial elements are given in Table IV. The excess titanium stems from charging 41 w/o titanium in the drip-rods for EB melting. It has since been found, however, that at melt rates >50 g/min under 10^{-7} to 10^{-5} Torr pressures, preferential loss of titanium is insignificant.

TABLE IV. Analytical Results on Arc-cast V-40Ti (AM-49) Ingot

Element	Analysis
	<u>w/o</u>
Titanium	
Top	41.5
Bottom	40.6
	<u>ppm</u>
Carbon	244
Oxygen	790
Nitrogen	260
Hydrogen	99
Total Interstitial Content	1393

The arc-cast V-40Ti ingot was conditioned to a 44.2-mm (1.74-in.)-diam canned in Type 304 SS, and extruded (Extrusion No. 461) at 1100°C and a 6.9:1 reduction ratio to yield a 19.6-mm (0.77-in.)-diam extruded rod. After being straightened, the rod was dejacketed by pickling in hot, concentrated HCl. The extruded surface of the dejacketed, 15-mm (0.60-in.)-diam V-40Ti alloy rod exhibited severe longitudinal striations characteristic of V-20Ti ingot breakdown extrusions.

After being conditioned, the rod was cold-rolled to an ~9.6-mm (0.38-in.) diam and vacuum-annealed for 1 hr at 900°C. Sections of the rod were machined into samples for EBR-II in-pile sodium-corrosion testing. The balance of the rod was cross-rolled and long-rolled to 1.5-mm (0.060-in.)-thick sheet for annealing and tensile-test studies and 0.76-mm (0.030-in.) sheet for corrosion studies. No difficulties were encountered in the rod and sheet rolling.

B. Consolidation and Fabrication of V-15Ti-5Cr

Attempts were made to utilize the V-40Ti consolidation procedure in producing the V-15Ti-7.5Cr alloy with the modification of increased chromium in the briquets to compensate for expected losses in melting. Typical impurity levels in the charge materials were shown in Table III.

Drip rods for the first V-Ti-Cr ingot (EB-47) were prepared by compacting 40-g batches of vanadium chips, titanium sponge, and electrolytic chromium flake into 19-mm (0.75-in.)-diam x 25-mm (1.0-in.)-high briquets in a three-piece, split compacting die at 96.0 kg/mm² (68 tsi). The split die, die holder, and compacting rod are shown in Fig. 2. The briquets were welded together into rods, three of which were bundled together to form a drip rod. The drip rod was EB melted (EB-47) at a power setting of 21 to 28 kW and a pressure of $<10^{-5}$ Torr. Although a melt rate of ~80 g/min was maintained, about 7.5 w/o of the charge was lost during melting, primarily because of the high vapor pressure of chromium. Ingot surface quality was good, but a large amount of internal porosity was evident.

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Fig. 2. Three-piece Compacting Die with Die Holder and Compacting Rod

After consumable-arc remelting under conditions similar to those for the V-40Ti, except for a power level of 42 kW (30 V and 1400 Amp), the ingot (AM-50) appeared sound and fully consolidated. No weight loss occurred during remelting. The analytical results of AM-50, shown in Table V, indicate that although the titanium content was 15 w/o, as had been charged, the alloy contained only ~5 w/o chromium. Although an effort had been made to compensate for the expected loss of chromium during vacuum melting, by incorporating 9 to 10 w/o chromium in the drip-rod charges, losses were greater than anticipated. Some nitrogen contamination was evident. This probably occurred during welding of the briquets and electrodes.

Further attempts at melting under vacuum in both the arc and EB furnaces proved

TABLE V. Analytical Results on Arc-cast V-15Ti-5Cr (AM-50) Ingot

Element	Analysis
	<u>w/o</u>
Titanium	
Top	15
Bottom	15
Chromium	
Top	4.8
Bottom	4.9
	<u>ppm</u>
Carbon	262
Oxygen	880
Nitrogen	510
Hydrogen	19
Total Interstitial Content	1671

unsuccessful from the standpoint of controlling chromium losses. Accordingly, the consolidation technique was revised to consumable-electrode arc-melting in a helium-argon atmosphere. This technique proved successful in controlling chromium content, as will be described in more detail in Section IV-A.

To study fabrication characteristics and provide test material, the arc-cast ingot (AM-50) analyzing V-15w/oTi-5w/oCr was conditioned, canned in Type 304 stainless steel, and extruded (Extrusion No. 67) to rod at an extrusion temperature of 1100°C and a 6.9:1 reduction ratio. After being dejacketed and conditioned, the rod was rolled to a 9.6-mm (0.38-in.) diam and then to 1.5-mm (0.060-in.) and 0.76-mm (0.030-in.)-thick sheet in a manner similar to

that described above for V-40Ti. The sheet material was used for annealing, tensile testing, and corrosion testing. As with V-40Ti, no problems were encountered in cold-rolling the V-15Ti-5Cr alloy.

C. Effects of Annealing Treatments on the V-40Ti and V-15Ti-5Cr Alloys

1. General Annealing Behavior

An isochronal annealing study was performed on 1.5-mm (0.060-in.)-thick sheet of each alloy to determine parameters for in-process and final anneals on production material. The annealing behavior of each alloy was determined by postanneal hardness measurements and metallographic observations of microstructural changes. Each anneal was performed in a vacuum of 10^{-5} Torr or better for 1 hr at temperature and furnace-cooled.

Diamond-pyramid-hardness (DPH) measurements were taken on the polished and etched surfaces used for metallographic evaluation. The hardness data are shown in Fig. 3. Both alloys have attained the same hardness after being cold-rolled, and both exhibited minimum hardness after being annealed at 700°C. The V-40Ti alloy had a significantly higher minimum hardness than did the V-Ti-Cr alloy, possibly due to an increase in solid-solution hardening brought about by the larger solute content. As the annealing temperature was raised, the hardness for the V-Ti-Cr alloy increased, but the V-40Ti alloy retained its minimum observed hardness up to 1000°C before significant hardening was observed.

42866

150X

42596

150X

42648

850X

(g) Annealed at 1350°C
Hardness: 272 DPH

(h) Annealed at 1500°C
Hardness: 306 DPH

(i) Annealed at 1500°C
Hardness: 306 DPH

Fig. 4. Microstructures of 1.5-mm (0.060-in.)-thick V-40Ti Sheet Annealed for 1 hr at Temperatures Indicated

Fig. 3. Change in Hardness as a Function of 1-hr Anneals for V-40Ti and V-15Ti-5Cr Alloy

The increase in hardness observed for both alloys is not clearly understood, but may have arisen in part from a precipitation-hardening phenomenon. However, from precipitation-hardening theories^{5,6} the hardness values would not be expected to continue to rise as indicated by the V-40Ti curve of Fig. 3, but there would be an inflection point in the curve in the higher temperature range. The bulk of the observed rise in hardness from 1350 to 1500°C for the V-40Ti alloy must result from contamination, as indicated by

the analyses results of Table VI. The interstitial-element content has increased markedly over that for the starting or ingot material. Further studies will be required on this alloy to separate any interstitial contamination effects from those resulting from true precipitation-hardening behaviors.

TABLE VI. Interstitial-element Content for V-40Ti Ingot and Specimen Annealed at 1500°C

Material	Interstitial Content, ppm			
	Carbon	Oxygen	Nitrogen	Hydrogen
Ingot (AM-49) (from Table IV)	244	790	260	99
Annealed Specimen	590	1800	302	26

The cold-worked and annealed microstructures of V-40Ti are shown in Fig. 4. The microstructures indicate that apparent full recrystallization has occurred at 700°C, the higher-temperature anneals resulting in marked grain growth. After heat treatment at 1000°C and higher, a dispersed phase was evident at the grain boundaries and throughout the matrix. The dispersed phase, or precipitate, obtained at the higher annealing temperatures appeared to affect the grain-boundary migration of this material. At present, it is not clear whether the acicular particles were migrating to the grain boundaries or the grain boundaries were sweeping the particles along as they moved through the matrix. The composition of the dispersed phase has not been identified, but a previous investigation on V-20Ti disclosed a similar precipitate, which has been tentatively identified as a TiC(N) complex.¹

42590

150X

(a) As-rolled transverse structure
Hardness: 305 DPH

42591

150X

(b) Annealed at 700°C
Hardness: 248 DPH

42592

150X

(c) Annealed at 800°C
Hardness: 247 DPH

42593

150X

(d) Annealed at 900°C
Hardness: 247 DPH

42594

150X

(e) Annealed at 1000°C
Hardness: 249 DPH

42595

150X

(f) Annealed at 1200°C
Hardness: 259 DPH

The cold-worked and annealed microstructures of V-15Ti-5Cr are shown in Fig. 5. Full recrystallization appeared to have resulted from the 800°C anneal, compared with 700°C for V-40Ti. Because of the fine grain size, full recrystallization was evident at only high magnifications, i.e., Fig. 5d as compared to Fig. 5c.

The V-15Ti-5Cr alloy exhibited a banded structure composed primarily of particles that have not gone into solution. The nature and composition of these particles are not known. The banding persisted up through the 1200°C anneal, and the particles had a peculiar effect on grain-growth behavior. They appeared to represent nucleation sites for new grains, which in turn had a restricted grain-growth behavior. The 1350°C anneal seemed to result in a transitional structure between the 1200 and 1500°C anneals. Most of the banding had been eliminated at 1350°C. However, two types of particles appeared in the matrix. The acicular-shaped particles appeared to be the result of a precipitation process and have not been identified. The nodular-shaped particles appeared as inclusions--possibly resulting from an agglomeration of particles that composed the original banded regions.

Heat treatment of the alloy above 1350°C entirely eliminated the bands (and/or nodular-type particles), and the 1500°C treatment resulted in a heavily precipitated Widmanstätten structure. This latter structure, examined at the higher magnification, showed two acicular precipitates (light and dark colored), which were indicative of two different compounds. The light-colored particles had a marked effect on grain-boundary migration. It appeared that as a grain boundary swept across the matrix, the light particles initially retarded its movement until enough thermal energy had been supplied for continued movement. With sufficient thermal energy the boundary did not appear to break away from the particles, but swept them along with it as it moved.

As a speculation, one might identify the two observed particles as being (1) a TiC(N) complex (dark-colored particles, since these particles are similar to those identified in V-20Ti) and (2) a chromium-interstitial element complex (light-colored particles, which were not observed in the V-Ti binary alloys).

The grain-growth behavior of the two alloys is shown in Fig. 6. Low-temperature grain-growth behavior of V-20Ti is included for comparison. Even though both alloys were consolidated and fabricated in the same manner, the V-15Ti-5Cr alloy possessed a grain size nearly a factor of four smaller than V-40Ti for anneals up to and including 1200°C, and nearly a factor of two smaller than the grain size observed for V-20Ti (although the latter comparison may be affected by differing fabrication schedules and interstitial levels).

42767

150X

(g) Annealed at 1200°C
Hardness: 240 DPH

42868

150X

(h) Annealed at 1350°C
Hardness: 237 DPH

42869

150X

(i) Annealed at 1350°C
Hardness: 237 DPH

42870

850X

(j) Annealed at 1350°C
Hardness: 237 DPH

42597

150X

(k) Annealed at 1500°C
Hardness: 250 DPH

42646

850X

(l) Annealed at 1500°C
Hardness: 250 DPH

Fig. 5. Microstructures of 1.5-mm (0.060-in.)-thick V-15Ti-5Cr Sheet Annealed for 1 hr at Temperatures Indicated

42764

150X

(a) As-rolled structure
Hardness: 303 DPH

42765

150X

(b) Annealed at 700°C
Hardness: 212 DPH

42637

150X

(c) Annealed at 800°C
Hardness: 214 DPH

42647

1000X

(d) Annealed at 800°C
Hardness: 214 DPH

42638

150X

(e) Annealed at 900°C
Hardness: 219 DPH

42639

150X

(f) Annealed at 1000°C
Hardness: 275 DPH

Fig. 6. Effect of 1-hr Anneals on Mean Grain Diameter of Some Vanadium-base Alloys

2. Effect of Annealing Treatments on Room-temperature Tensile Properties

A series of room-temperature tensile tests (strained to rupture) was run on sheet samples of V-40Ti, V-15Ti-5Cr and, for comparison, V-20Ti. All samples were annealed for 1 hr at 700, 900, or 1350°C, the V-15Ti-5Cr also receiving a 1500°C treatment. The tensile results are shown in Table VII.

As mentioned in Section III-C-1 above, the V-40Ti alloy may have been solid-solution hardened by the additional titanium. Its tensile properties likewise reflect the additional strengthening. The yield, ultimate strength, and elongation for V-40Ti are apparently reduced by the 1350°C anneal. For the V-15Ti-5Cr alloy, the yield and ultimate tensile strengths are relatively unaffected by their prior heat treatment. However, the elastic modulus, elongation, type of fracture, and hardness reflect the influence of heat treatment. The 900°C, fully recrystallized structure would be selected

TABLE VII. Room-temperature Tensile Results* for V-20w/oTi, V-40w/oTi, and V-15w/oTi-5w/oCr Annealed at Various Temperatures

Alloy	Annealing Temperature, °C	Elastic Modulus, kg/mm ² × 10 ⁻³ (psi × 10 ⁻⁶)	Yield Stress, kg/mm ² (psi)	Ult. Tensile Stress, kg/mm ² (psi)	Percent Elongation	Type of Fracture
V-20Ti	700	12.35 (17.55)	59.00 (84,000)	67.80 (96,500)	15.6	Ductile
	900	11.30 (16.05)	52.80 (75,100)	61.90 (88,000)	18.7	Ductile
	1350	12.27 (17.45)	52.00 (74,000)	60.50 (96,000)	12.5	Brittle
V-40Ti	900	9.92 (14.10)	42.00 (59,700)	44.30 (63,000)	25.0	Ductile
	1350	9.43 (13.40)	68.50 (97,350)	69.60 (98,900)	8.1	Brittle
V-15Ti-5Cr	700	9.77 (13.90)	60.40 (85,800)	68.90 (97,800)	25.0	Ductile
	900	13.30 (18.90)	56.90 (80,800)	67.80 (96,200)	26.5	Ductile
	1350	13.00 (18.50)	60.50 (86,000)	70.30 (100,000)	10.2	Brittle
	1500	9.85 (14.00)	59.00 (83,900)	64.90 (92,300)	7.8	Brittle

*Tensile tests were run on 1.5-mm (0.060-in.)-thick sheet samples. The strain rate was 0.5 mm/min (0.02 in./min), and the gage length was 25 mm (1 in.).

for optimum short-time, room-temperature, mechanical-property behavior. Unfortunately, no extrapolation to the long-time elevated-temperature, mechanical-property behavior (i.e., creep and creep rupture) can be made from the above data, heat treatments other than 900°C may prove to be better in this area. One might expect that a material containing a structure similar to that shown for the 1500°C anneal would be desirable for increasing the alloy's creep strength, particularly if the dispersed phase was composed of finer particles. However, fabrication was effected in the reverse order, as indicated in Section IV below. (The improved creep strength of the V-15Ti-5Cr and V-15Ti-7.5Cr alloys, both of which were annealed at 900°C, has already been mentioned, and was illustrated in Fig. 1.)

The annealing treatments for V-20Ti had only a moderate effect on the alloy's tensile properties. The 700°C anneal is basically a recovery anneal; i.e., the temperature is not high enough for full recrystallization. As a result, the observed values for the elastic modulus, yield, and ultimate tensile strengths are expected to be higher than those observed for the 900°C annealed specimen, which was in a fully recrystallized condition. The 1350°C anneal resulted in a less ductile material, which exhibited a brittle fracture at rupture. No increase in the ultimate and yield stress over that of the 900°C anneal was observed; however, the hardness did increase. A slight increase in the elastic modulus was also noted.

3. Effect of Annealing Treatments on Fabricability

Preliminary fabrication studies on the ternary alloy annealed at high temperatures have not been encouraging. Attempts to roll sections of the V-15Ti-5Cr alloy after annealing at 1500°C were unsuccessful at room temperature and also at 500°C. Intergranular fracture occurred after approximately a 10% reduction in area. While the annealed grain size was large and penalized fabricability, the apparent brittleness may be attributed to the presence of the particles segregated in the grain boundaries.

A section of alloy rod annealed at 1500°C was canned in Type 304 stainless steel and extruded at 1100°C and a 4:1 reduction ratio to determine if the structure would be amenable to hot fabrication by extrusion. The alloy broke up into pieces, and only a 76-mm (3-in.) length was recovered. Based upon this brief testing, high-temperature anneals appear to produce a microstructure that severely limits fabricability.

There still remains the problem of particle banding in the alloy. One would expect a heterogeneous deformation from such a structure--which would be considered undesirable. This problem should be minimized, however, in the fabrication of large-size (97-mm-diam) ingots, where double extrusion, cold reduction, and a number of anneals are employed in the further working of the material to the final product size.

IV. PRODUCTION TECHNOLOGY FOR THE V-15Ti-7.5Cr ALLOY

Although both the V-40Ti and the V-15Ti-7.5Cr alloys were scaled-up from arc-cast buttons to 59-mm (2.3-in.)-diam ingots, only the V-15Ti-7.5Cr alloy has undergone further scale-up to 97-mm (3.8-in.)-diam production-size ingots. The consolidation technology developed for V-20Ti was directly applicable to V-40Ti, and no difficulty would be anticipated in scaling up this binary alloy to full production, if required. This same philosophy did not hold for the V-Ti-Cr alloy.

A. Consolidation

A major change was required in the consolidation procedure for production ingots of the V-15Ti-7.5Cr alloy to avoid chromium losses.

The final consolidation procedure involved double arc-melting under a helium-argon atmosphere by a consumable-electrode technique.

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Fig. 7. Rectangular-cavity Compacting Die

walls and the charge material. As a consequence, the green strength of the pressed briquets was inadequate for subsequent handling. Frequent cleaning of galled material from the die cavity was necessary, and more time

To expedite the compaction of briquets for electrode preparation, a die was fabricated having a 25 x 76-mm (1 x 3-in.) rectangular cavity. The die and compacting ram are shown in Fig. 7. Since this die was not split as was the three-piece die used previously, each pressed briquet was removed by pushing it out through the bottom of the cavity. When the die was not lubricated, galling occurred as briquets were removed from the die cavity. After only a few briquets had been compacted, galled-material buildup in the die cavity became excessive, and during subsequent pressings a large redundant pressure was expended in overcoming friction between the cavity

was involved in making briquets using this die than in briquetting the same amount of material in the smaller split die previously used (see Fig. 2).

When a die lubricant, 1% stearic acid in CCl_4 , was applied on the cavity walls before each pressing, no galling occurred, die cleaning was obviated, and the compacted briquets had good green strength with a pressure of 38 kg/mm^2 (27 tsi). This procedure permitted briquet compaction in much less time than was required to press an equivalent weight of material in the split die. Briquets pressed in the lubricated die were vacuum-outgassed at 350°C to ensure that all the lubricant was volatilized.

After the pressing procedure with the new die was established, 20 briquets weighing 260 g each were prepared containing 76.5w/oV, 15w/oTi, and 8.5w/oCr. The briquets were outgassed and welded together into two electrodes each 760 mm (30 in.) long. The electrodes were single arc-melted in two separate operations--one under a 500-Torr atmosphere of argon, the other under a 500-Torr atmosphere of 75 v/o helium-25 v/o argon. Based on analyses of samples from the ingots produced (AM-56 and AM-58), none of the charged chromium was lost.

Since the chromium content could be accurately controlled, electrode preparation proceeded on the basis of a V-15Ti-7.5Cr composition. Figure 8 shows the raw materials before and after being pressed into briquet form. The briquets were welded together in an inert atmosphere to form the consumable electrodes for the first melting operation. To reduce electrical resistance, all four sides of each joint between end-buffed briquets were welded, and, in addition, a continuous-weld bead was applied along two opposite sides of the electrodes from end to end. Briquets and a typical welded electrode are shown in Fig. 9.

Two electrodes (12 to 14 briquets each) were used to make a single 63-mm (2.5-in.)-diam by ~250-mm (10-in.)-long arc-cast ingot. Generally three of the 63-mm-diam cast ingots were welded together to form the electrode for remelting into the final 97-mm (3.8-in.) ingot.

All arc melts were made under straight polarity (consumable electrode negative) conditions. First melts of briquet electrodes were performed at a power setting of ~75 kW (50 V and 1500 Amp) and a stirring-coil setting of 1.5 Amp. Melt rates were 0.4 to 0.5 kg/min. Remelting required ~113 kW (42 V and 2700 Amp) with 3 Amp on the stirring coil. The remelt rate was >1 kg/min. No charge weight was lost during either melting operation.

Surface quality of the first- and second-melt ingots was excellent. Internal porosity was minor in first-melt ingots and was not evidenced in second-melt ingots, except for some fine pores near the ingot sidewall (probably due to solidification characteristics in a water-cooled copper mold). No effort was made to "hot-top" first-melt ingots since they were

Vanadium Chips

Titanium Sponge

Chromium Flake

Pressed Briquet

106-8568

Fig. 8. Raw Materials (Vanadium, Titanium, and Chromium) before and after Being Pressed into Briquet Form

to be remelted, but improved hot-topping procedures used on remelt ingots resulted in a reduced secondary pipe.

106-8567

Fig. 9. Briquets before and after Being Welded into an Electrode Length

To date, four arc-cast production ingots (AM-64, -68, -75, and -92), 97 mm (3.8 in.) in diameter by ~330 mm (13 in.) or more in length, have been produced by using the above developed consolidation technique. The cropped ingots weighed ~12.8 kg (28 lb). Figure 10 shows a typical V-15Ti-7.5Cr ingot (AM-68) after cropping.

Analytical results on the four ingots are given in Table VIII. The alloy content is quite close to the charge composition when consideration is given to the weighing, blending, and pressing techniques employed during preparation of the briquets. A comparison of results on these ingots with the values reported in Table III for the raw materials leads to the conclusion that consolidation procedures had little effect on the interstitial levels.

Since trace amounts of boron and uranium in a fast-reactor cladding may effect reactor physics and irradiation behavior, analyses for these elements were performed on samples from two of the production ingots--AM-64 and AM-68. Results indicated 2.0 ppm boron and 2.0 to 6.0 ppm uranium. (For comparison, similar samples of Type 304 SS contained 4.0 to 6.0 ppm boron and 3.5 ppm uranium.)

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Fig. 10. Arc-cast V-15Ti-7.5Cr Cropped Ingot (AM-68)

TABLE VIII. Analytical Results on Arc-cast V-15Ti-7.5Cr Alloy Ingots (AM-64, -68, -75, and -92)

Element	Ingot and Location											
	AM-64			AM-68			AM-75			AM-92		
	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Titanium, w/o	15.1	14.5	14.8	14.9	14.7	14.6	15.1	14.7	14.7	15.0	14.8	15.2
Chromium, w/o	7.5	7.3	7.8	7.6	7.3	6.9	7.5	7.6	7.5	7.6	7.7	6.7
Carbon, ppm	234	-	265	222	-	226	229	-	187	168	-	286
Oxygen, ppm	772	-	632	810	-	810	660	-	630	580	-	560
Nitrogen, ppm	390	-	410	390	-	440	540	-	360	246	-	300
Hydrogen, ppm	13	-	15	17	-	13	45	-	19	6	-	10
Total Interstitials, ppm	1409	-	1322	1439	-	1489	1474	-	1196	1000	-	1156

The microstructure near the top of ingot AM-64 varied from the edge (sidewall) to the center of the ingot, as shown in Fig. 11. Near the water-cooled copper mold wall, the ingot structure was that of an alloy matrix filled with a fine random precipitate. A cored structure was apparent near the slow-cooled center of the ingot. The microstructures at the top and bottom of the ingot were the same. Rockwell-hardness measurements across the diameter of the ingot ranged from 22 to 24 R_C .

Micro 43000

150X

(a) Microstructure near ingot center

Micro 43005

150X

(b) Microstructure near ingot sidewall

Fig. 11. Transverse Sections through 97-mm (3.8-in.)-diam Arc-cast Ingot of V-15Ti-7.5Cr.
(Etchant: four parts HNO_3 , three parts H_2O , two parts HF.)

B. Primary Fabrication

The procedure for primary fabrication of the V-15Ti-7.5Cr alloy was identical to that for the V-20Ti alloy: namely, a low-ratio, ingot-breakdown extrusion into bar stock, which was machined into billets and re-extruded into rod, sheet-bar, and tube-blanks for secondary fabrication.

1. Ingot Breakdown Extrusion

The 97-mm (3.8-in.)-diam x ~330-mm (13-in.)-long arc-cast ingots were conditioned for extrusion by machining billets 90 mm (3.54 in.) x ~292 mm (11.5 in.) long, weighing approximately 11 kg (24 lb). The billet nose was tapered (120° included angle) to facilitate initial deformation upon entry into the die.

Conditioned ingots (billets) were "canned" in Type 304 SS to prevent contamination of the alloy and permit billet heating in a conventional air-atmosphere furnace. The overall billet diameter was 102 mm (4.0 in.). The billets were heated for a minimum of 2 hr at 1100°C and transferred to a 1250-ton horizontal extrusion press. Transfer times ranged from 22 to 26 sec. A MoS₂:graphite (95:5) and synthetic oil mixture was swabbed on the die and container liner as a lubricant. The nominal 3.7:1 reduction ratio yielded a solid bar approximately 53 mm (2.1 in.) in diameter. Data for the breakdown extrusions are given in Table IX. The average extrusion constant for the three breakdown extrusions was 65.7 kg/mm² (93,500 psi). The breakthrough pressure was approximately 20% higher than the running pressure.

No difficulties were experienced in the breakdown-extrusion operation. When required, the hot extruded bars were easily straightened on a 50-ton press. The V-Ti-Cr alloy extruded surface was severely striated, as was expected from experience with the V-20Ti alloy. These striations apparently are due to the relatively large grain size of the arc-cast material. The steel can surrounding the V-Ti-Cr alloy prevents the extrusion die from "ironing" the alloy surface to provide a uniform surface. This striated surface is removed in machining the bar into billets for re-extrusion. The primary extrusion produces a fine-grained product, which upon re-extrusion yields a good surface having only minor striations.

The V-15Ti-7.5Cr alloy exhibited severe nose bursts (cracking) in the breakdown-extrusion operation, as seen in Fig. 12. This was not encountered in extruding the V-20Ti alloy. Fortunately, the cracks did not propagate to any significant extent, and the defective material was removed by cropping approximately 50 mm (2 in.) from the lead end of the extruded bar.

After extrusion, the bar was radiographed, and the lead- and tail-end defects were cut off. The stainless-steel jacket and striated surface of

TABLE IX. Extrusion Data for Ingot Breakdown and Re-extrusion of V-15Ti-7.5Cr

Extrusion No. and Type	Extrusion Product	Billet Temp, °C	Reduction Ratio	Extrusion Speed mm/sec (in./sec)	Extrusion Pressure, kg/mm ² (psi)		Extrusion ^a Constant, K, kg/mm ² (psi)
					Breakthrough	Running	
535 (Ingot Breakdown)	Bar	1100	3.7:1	300 (12)	105 (150,000)	88 (125,000)	67 (96,000)
550 (Ingot Breakdown)	Bar	1090	3.8:1	200 (8)	102 (145,000)	88 (125,000)	66 (94,500)
560 (Ingot Breakdown)	Bar	1100	3.7:1	100 (4)	103 (147,000)	85 (119,000)	63 (90,000)
536 (Re-extrusion)	Rod	1075	7.1:1	100 (4)	117 (166,000)	109 (155,000)	55 (79,000)
538 (Re-extrusion)	Rod	1100	4.1:1	150 (6)	72 (103,000)	63 (90,000)	45 (64,000)
539 (Re-extrusion)	Rod	1100	6.8:1	130 (5)	95 (135,000)	84 (120,000)	44 (62,500)
570 (Re-extrusion)	Rod	1100	9.0:1	150 (6)	111 (158,000)	104 (148,000)	47 (67,500)
571 (Re-extrusion)	Rod	1100	8.9:1	130 (5)	106 (151,000)	98 (140,000)	45 (63,800)
572 (Re-extrusion)	Rod	1100	8.9:1	130 (5)	108 (153,000)	98 (140,000)	45 (63,800)
573 (Re-extrusion)	Rod	1100	8.9:1	130 (5)	112 (160,000)	101 (144,000)	46 (65,800)
574 (Re-extrusion)	Rod	1100	8.9:1	150 (6)	106 (151,000)	98 (140,000)	45 (63,800)
537 (Re-extrusion)	Sheet-bar	1150	13.0:1	80 (3)	132 (188,000)	119 (169,000)	46 (66,000)
569 (Re-extrusion)	Sheet-bar	1150	13.0:1	100 (4)	124 (176,000)	112 (160,000)	44 (62,400)
540 (Re-extrusion)	Tube-blank	1150	8.1:1	130 (5)	102 (145,000)	87 (124,000)	42 (59,500)
541 (Re-extrusion)	Tube-blank	1100	8.2:1	130 (5)	107 (152,000)	91 (129,000)	43 (61,500)
542 (Re-extrusion)	Tube-blank	1100	8.3:1	100 (4)	119 (170,000)	98 (140,000)	46 (66,000)
543 (Re-extrusion)	Tube-blank	1100	5.9:1	150 (6)	80 (114,000)	70 (100,000)	40 (56,500)
561 (Re-extrusion)	Tube-blank	1100	8.6:1	130 (5)	111 (158,000)	100 (143,000)	47 (66,500)
562 (Re-extrusion)	Tube-blank	1100	8.0:1	130 (5)	109 (155,000)	99 (141,000)	47 (67,500)
563 (Re-extrusion)	Tube-blank	1100	7.9:1	130 (5)	106 (151,000)	97 (138,000)	47 (66,500)
564 (Re-extrusion)	Tube-blank	1100	8.0:1	130 (5)	122 (173,000)	98 (140,000)	47 (67,500)
566 (Re-extrusion)	Tube-blank	1100	8.0:1	130 (5)	136 (194,000)	92 (131,000)	42 (59,600)
567 (Re-extrusion)	Tube-blank	1100	8.0:1	150 (6)	108 (153,000)	98 (140,000)	45 (63,700)
568 (Re-extrusion)	Tube-blank	1100	8.0:1	150 (6)	108 (153,000)	100 (143,000)	46 (65,000)

^aFrom $P = K \ln A_0/A$, where P is the running extrusion pressure, A_0/A is the reduction ratio, and K is the extrusion constant.

Fig. 12. Typical Nose Burst (cracking) on Lead End of V-15Ti-7.5Cr Alloy after Arc-cast Ingot Breakdown Extrusion

the vanadium alloy were removed in machining the alloy to a 44.2-mm (1.74-in.) diam for re-extrusion billets. The machined bar was sectioned into billets 114 to 140 mm (4.5 to 5.5 in.) long.

As mentioned earlier, the billet noses were initially chamfered (120° included angle) to minimize breakthrough pressures and nose cracking on re-extrusion. A subsequent trial with a flat-nosed billet indicated that the tapered nose was of little benefit and most of the re-extrusion billets were of the flat-nose design, which improved material recovery from the extruded bar. A 19.1-mm (0.75-in.)-diam axial hole was drilled in billets for re-extrusion into tube-blanks to allow passage of the tool-steel mandrel employed in tube-blank extrusion.

Based on the original machined arc-cast ingot weight before breakdown extrusion, approximately 70% of the V-Ti-Cr alloy was recovered as machined billets for re-extrusion. The data are shown in Table X. Since the extruded bars were machined into varying numbers of

TABLE X. Yield of V-15Ti-7.5Cr Billets for Re-extrusion Based on Starting Billet Weight

Extrusion No.	Arc-cast Ingot Number	Component Weights, kg			Yield as Percent of Starting Primary Billet Weight	
		Primary Extrusion Billet	Actual Re-extrusion Billets	Corrected Re-extrusion Billets*	Actual Billets	Corrected Billets*
535	AM-64	10.77	7.35	8.14	68.2	75.6
550	AM-68	11.13	7.16	8.78	64.3	78.9
560	AM-75	10.89	8.65	8.65	79.4	79.4
Total		32.79	23.16	25.57	70.6	78.0

*Weight of hollow billets for tube-blank extrusions recalculated as solid billets to correct for varying numbers of hollow billets machined from the different extrusions.

billets for tube-blank extrusion, the actual yield varies. The corrected yield shown represents the yield if the bar had been machined completely into solid billets for re-extrusion. The corrected yield is 78% meaning 22% of the original conditioned arc-cast billet weight was lost in cropping the lead- and tail-end extrusion defects and in removing the striated surface by machining to the 44.2-mm (1.74-in.)-diam for re-extrusion. All billets from the extruded bar from Extrusion No. 550 were machined into billets with an axial hole for tube-blank extrusion, and the yield in this case was about 64%. By difference from the corrected yield (based on all solid billets), approximately 14% of the starting weight is lost in drilling the axial hole, which is required for extruding over a mandrel.

2. Re-extrusion

As with the V-20Ti alloy, the V-Ti-Cr ternary alloy billets were "canned" in Type 304 SS for re-extrusion into rod, sheet-bar, and tube-blanks for secondary fabrication. For tube-blank extrusion, the axial hole in the billet was clad with a thin liner tube of Type 304 SS to prevent contamination of the internal surface. A typical billet for tube-blank extrusion is shown in Fig. 13.

For the most part, billets were re-extruded at 1100°C, although the two sheet-bar billets were extruded at 1150°C to compensate for the increased reduction ratio of 13:1. The initial tube-blank extrusion was performed at 1150°C, subsequent extrusions being made at 1100°C after the initial extrusion indicated that press and tooling limits would not be exceeded. Billets were induction-heated by a 30-kW, 10-kc MG set. The heat time was approximately 5 to 6 min, and the billets were "soaked" at temperature for 5 min. Extrusion speeds ranged from 80 to 150 mm/sec (3 to 6 in./sec), the billet transfer time (from coil to extrude) being roughly 10 sec. Standard hot-work tool-steel (H-12) dies hardened to 47-52 R_C were employed. The dies were designed with a 120° included approach angle and an approximate 3-mm (0.12-in.) land or bearing length. The extrusion lubricant, MoS₂:graphite (95:5) mixture in a synthetic oil, was swabbed on the container and die before extrusion. In tube-blank extrusion, the hardened (58-62 R_C), high-speed, tool-steel (T-1) mandrel was coated with a 0.25-mm (0.010-in.) layer of Corning 7052 (borosilicate) glass powder applied as a slurry and dried before extrusion. The glass served as a lubricant between the billet and mandrel and eliminated internal surface tearing, which resulted when the MoS₂:graphite:oil mixture was employed as the mandrel lubricant.

Twenty-one billets have been re-extruded to date, eight being rod extrusions, two being sheet-bar, and eleven being tube-blanks. Pertinent extrusion data are given in Table IX. No difficulties were encountered in re-extrusion. In regards to tube-blank extrusion, the average extrusion constant was 45.0 kg/mm² (64,000 psi). This contrasts with an average constant of 41.0 kg/mm² (58,000 psi) and 37.0 kg/mm² (53,000 psi) for V-20Ti and Type 304 SS, respectively, all extruded under similar conditions at

1100°C. The breakthrough pressure was about 17% higher than the running pressure of 94.5 kg-mm^{-2} (134,500 psi) for tube-blank extrusion at a nominal 8:1 reduction ratio. Although no specific material yield data were generated for re-extrusion, the yield of extruded material acceptable for secondary fabrication was 95+% for rod and sheet-bar, the loss resulting from cropping the lead- and tail-end defects. The latter constituted the bulk of the cropped material. In tube-blank extrusion, approximately 90% of the extruded blank was suitable for secondary fabrication. Again, lead- and tail-end defects accounted for most of the scrap, but occasionally the tube-blank did not clear the mandrel after extrusion. In these cases, approximately 75 mm (3 in.) of alloy tube-blank remained on the mandrel after sectioning to free the extrusion.

Fig. 13. Typical Billet Design for Extruding V-15w/oTi-7.5w/oCr Tube-blanks

Following extrusion, the products were straightened and the protective stainless-steel jacket removed. On rods, sheet-bar, and the outer surface of tube-blanks, the steel was removed by mechanical peeling. The steel jacket was removed from the internal surface of tube-blanks by pickling in concentrated (40 to 50 v/o) hydrochloric acid heated to 50 to 70°C. After dejacketing, extruded V-Ti-Cr tube-blanks were approximately 21.6-mm OD x 16.1-mm ID (0.850-in. OD x 0.63-in. ID). The length of extruded tube-blanks varied as a function of the original billet length and the reduction ratio, most tube-blanks being about 920 mm (36 in.) long.

The typical microstructure of the V-15Ti-7.5Cr alloy after re-extrusion (Extrusion No. 537: sheet-bar extruded at 1150°C and a 13:1 reduction ratio) is shown in Fig. 14. The as-extruded hardness was approximately 21 R_C.

43069

150X

Etchant: 50 ml H₂SO₄, 50 ml HF, 2 ml HNO₃, 50 ml H₂O

Fig. 14. Typical Microstructure of V-15Ti-7.5Cr after Re-extrusion.
(Extrusion No. 537: Sheet-bar extruded at 1150°C and a
13:1 reduction ratio.)

C. Secondary Fabrication of Rod and Sheet

Extruded rod and sheet-bar were converted into finished products by cold-rolling. The dejacketed product sizes were approximately 14.7-mm (0.580-in.) diam for the rod stock and approximately 5.6 mm thick x 25.2 mm wide (0.22 in. thick by 0.99 in. wide) for the sheet-bar. The final product sizes were 6.6- to 7.4-mm (0.260- to 290-in.) diam for the rod stock and a 1.5-mm (0.060-in.) thickness for sheet.

Initial attempts to cold-roll the rod and sheet-bar resulted in serious cracking after an approximate 10% reduction. The cracks were longitudinal and propagated rapidly. Unlike the V-20Ti alloy, which was easily cold-rolled from the as-extruded condition, the V-15Ti-7.5Cr ternary alloy required a 900°C anneal after extrusion even though the alloy was in a fully recrystallized condition with an as-extruded hardness of approximately 21 R_C. After annealing, the alloy was easily cold-rolled to final sizes. In-process annealing (1 hr at 850 or 900°C) was required after an approximate 60% reduction in area.

D. Secondary Fabrication of Tubing

Extruded tube-blanks were converted into finished tubing by processing procedures similar to those developed for the V-20Ti alloy, namely, a light swaging of the de jacketed tube blank followed by drawing to final size.

Starting Extruded Blank Size 22.2-mm OD x 16.1-mm ID x ~1000 mm long
(0.875-in. OD x 0.635-in. ID x ~40 in. long)

Fig. 15. Typical Tube-production Flow Sheet

Recently, tube reducing on an experimental machine designed and built at ANL has replaced part of the drawing schedule. The tubing fabrication procedures are described below; a flow sheet of the operations is shown in Fig. 15.

Annealed tube-blanks (900°C for 1 hr), 22.2-mm OD x 16.1-mm ID x ~1 m long (0.875-in. OD x 0.635-in. ID x ~40 in. long), were swaged over a 15.1-mm (0.595-in.)-diam hardened tool-steel mandrel to a final size of 20.3-mm OD x 15.2-mm ID (0.800-in. OD x 0.600-in. ID). The mandrel was coated with a chlorinated wax lubricant (Aldraw J-1) before insertion in the tube-blank. The cross-sectional area was reduced ~17%. This swaging operation was sufficient to provide a good surface and a uniform wall thickness.

Only minor conditioning of the extruded tube-blanks was necessary before swaging, as current extrusion practice supplied a blank devoid of heavy striations or tears. The light surface striations were readily ironed out without lap-over during swaging, and little if any postswaging conditioning was

necessary. Swaged tube-blanks were vacuum-annealed (850°C for 1 hr), followed by tube-reduction to an intermediate size.

Tube-reduction was the preferred fabrication route as greater reductions could be achieved with less effort. Also, the large size of the swaged tube-blanks limited the draw speed and maximum reduction due to limitations in drawbench capacity. Further, when mandrel drawing was performed, an intermediate anneal was necessary before obtaining a tube size equivalent to that produced by tube-reduction.

The ANL-designed tube-reducer* is based upon an early model by Krause,⁷ later modified by Nosal.⁸ Schematic details of the tube-reducer are shown in Figs. 16 and 17. During operation, the three rolls converge on the tube, ultimately ironing the wall over a hardened mandrel or plug.** Tube-reduction occurs with each forward (work) stroke of the rolls and housing. The tube-feed (advance) and -indexing (rotation) operations occur after the return stroke.

The tube-reducer--while still in the development stage--has been successfully used for reducing the V-15Ti-7.5Cr alloy in two passes as outlined in Table XI. In the two passes the tube-blank underwent an approximate 60% total reduction in area. Ultrasonic inspection of the reduced tube revealed no cracks or other discontinuities.

Before tube-reduction, the swaged tube-blanks received only limited surface conditioning followed by a light vapor blast. The conditioned tubes were wiped with acetone, lubricated on the interior with a chlorinated-wax lubricant (Aldraw J-2), slipped over the mandrel, and mounted in the tube-reducing machine. After the first pass, the mandrel was easily removed on a drawbench. The tubes were then cleaned, visually examined, vapor blasted, and lubricated, and the new mandrel was inserted for the second pass. After the final reduction, the mandrel was removed as before.

Although both the external and internal surfaces of the tube-reduced product were quite satisfactory, some evidence--albeit inconclusive--was gathered which indicated that slight imperfections present on the starting tube-blank surface could lead to an exaggerated surface defect after tube-reduction. Problems were encountered with surface flaking and pitting during reduction of certain of the tube-blanks. This flaking condition and the related surface problems associated with certain tube-blanks are believed to result from a grain-boundary carbide network formed during annealing of the swaged tube-blanks at 950°C before tube-reducing.

*The experimental tube-reducer will accept a 1-in. maximum tube diameter. The minimum size tube that can be processed has not yet been determined.

**Initial trials have been made with a plug replacing the mandrel. Thus, the need for mandrel removal after each pass is eliminated. Results of reducing over a plug and additional information on machine capabilities, reduction schedules, etc., will be the subject of a separate report.

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Fig. 16. Schematic Arrangement of ANL Three-roll Tube-reducer

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Fig. 17. Roller Arrangement and Operational Details of ANL Three-roll Tube-reducer

TABLE XI. Tube-reduction Data for V-15Ti-7.5Cr Tube-blanks
(Starting size ~0.800 OD x 0.600 ID x ~38 to 44 in. long)

Reducer Pass Schedule	Roll Diameter, mm (in.)	Mandrel Diameter, mm (in.)	Reduced Tube Size		Reduction, % (Total Reduction)		Final ~D/t
			OD, mm (in.)	ID, mm (in.)	~Area	~Wall	
1	22.2 to 19.1 (0.875 to 0.750)	14.7 (0.581)	19.5 (0.766)	14.7 (0.581)	11.0	7.5	8.3:1
2	19.1 to 15.9 (0.750 to 0.625)	13.8 (0.543)	16.2 (0.637)	13.8 (0.543)	55.5	49.0	13:1

Metallographic examination of a tube-blank after annealing at 950°C revealed evidence of a grain-boundary precipitate. (The structure appeared similar to that of material annealed at 1000°C shown later in Fig. 20.) Since annealing studies indicated that full recrystallization was obtained at 800°C, the annealing temperature for the swaged tube-blanks was lowered from 950 to 850°C to eliminate the troublesome grain-boundary network. This change in annealing temperatures resulted in marked improvement in the quality of the tube-reduced product.

From the tube-reduced size of 16.2-mm OD x 13.8-mm ID (0.636-in. OD x 0.543-in. ID), the tubes were mandrel-drawn to near final size according to the schedule shown in Fig. 15, using intermediate anneals of 1 hr at 850°C at the sizes indicated. The tubes were finished by plug-drawing to the final size. The microstructure of a finished piece of 7.4-mm-OD x 0.38-mm-wall (0.290-in.-OD x 0.015-in.-wall) tubing is shown in Fig. 18. The hardness of the as-drawn (40% cold reduction) tube was 274 DPH (26 R_C), dropping to 197 DPH (91 R_B) after annealing at 850°C for 1 hr.

In all drawing operations, mandrel or plug, lubrication was critical because of the galling characteristics of the vanadium alloy. The outer surface of the tubing was coated with a plastic base-coat (Hangsterfer No. 5 PC, diluted to 50% with No. 7 thinner), which was allowed to dry before drawing. The drawing lubricant was a chlorinated wax (Aldraw J-1), which was also applied to the mandrels before insertion into the tubes. Several draws could be made before the plastic base-coat required renewing. Before plug-drawing, the internal surface of the tube was swabbed with the plastic base-coat. The tube was filled with the chlorinated-wax lubricant before the plug was inserted. The lubricant and base-coat were removed by immersion in chloroethene.

During the tubing production, area reductions of up to approximately 33% per pass were achieved in mandrel-drawing, although reductions generally were lighter. Draw speeds up to the maximum bench capacity of 4.5 meters/min (15 ft/min) were achieved. During plug-drawing, draw speeds and reductions were kept low to minimize strain on the tubing and plug holder. Dies and plugs were carbide, and mandrels were hardened Latrobe "mandrel steel."

(a) As-drawn tubing; Hardness: 274 DPH (26 R_C)

(b) Annealed tubing (850°C for 1 hr); Hardness: 197 DPH (91 R_B)

Fig. 18. Typical Microstructure of 7.4-mm-OD x 0.38-mm-wall (0.290-in.-OD x 0.015-in.-wall) V-15w/oTi-7.5w/oCr Tubing in the As-drawn and Annealed Conditions.
(Etchant: Creighton's, followed by six parts H_2O , three parts HNO_3 , and one part HF.)

Following the final plug-draw, the tubing was cleaned, straightened, annealed* (as required), and nondestructively inspected by a pulsed eddy-current technique. In general, tubing quality was excellent except for some of the initial tubing that had been annealed at 950°C in the early stages of processing. Limiting the maximum annealing temperature to 850°C resulted in markedly improved tubing quality. Yields of high-quality tubing were excellent.

* Much of the tubing (including the tube-reduced blanks) was too long to be accommodated in existing annealing facilities. Lengths up to approximately 12 ft were zone-annealed in a specially constructed "Long John" vacuum furnace previously described.² An induction coil is moved over the tubing, and some adjustment in temperature is generally required to compensate for the reduced time at temperature of the tubing in contrast to the 1 hr or more holding time (at temperature) in the more conventional batch-type vacuum-annealing furnaces.

V. PROPERTY STUDIES ON THE V-15Ti-7.5Cr ALLOY

A. Annealing Behavior

The annealing behavior of the V-15Ti-7.5Cr alloy was determined by post-anneal hardness measurements and metallographic observations of microstructural changes in much the same manner as for the V-40Ti and V-15Ti-Cr alloys (see Section III-C).

The annealing study was performed on coupons cut from cold-rolled sheet. The sheet material originated from a double-extruded product in which the second extrusion (Extrusion No. 536) was a conversion to sheet-bar approximately 25 mm (1 in.) wide x 6.1 mm (0.24 in.) thick. The extruded sheet-bar was annealed for 1 hr at 900°C and cold-rolled to a 1.5-mm (0.060-in.) thickness representing a reduction of 75%. The annealing specimens, in the form of 12.7-mm (0.50-in.)-square coupons, were cut from the 1.5-mm (0.060-in.)-sheet stock.

The coupons were annealed at various temperatures for 1 hr each in vacuums of $\sim 10^{-6}$ Torr. At the higher temperatures, the specimens were wrapped in tantalum foil to minimize chromium loss and potential contamination.

Diamond-pyramid-hardness measurements were taken on the polished and etched surfaces used for metallographic evaluation. The resulting hardness values are plotted as a function of the annealing temperature in Fig. 19.

Fig. 19. Change in Hardness as a Function of 1-hr Anneals for V-15Ti-7.5Cr Alloy

Annealing treatments ranging in temperature from 700 to 1000°C produced minimum hardness values. Annealing at temperatures greater than 1000°C resulted in an increase in hardness, which became more pronounced with increasing temperature. To determine the extent of hardness increase that might be attributable to contamination, the specimen annealed at 1500°C was analyzed for interstitials and chromium content. The results are shown in Table XII.

The chemical analysis of the annealed specimen is, for all practical purposes, the same as that obtained for the ingot. (There at least appears to be no gross change in total interstitial composition.) The bulk of the rise in hardness could be more reasonably attributed to precipitation hardening.

43360

(g) Annealed at 900°C
Hardness: 216 DPH

43361

(h) Annealed at 900°C
Hardness: 216 DPH

43362

(i) Annealed at 1000°C
Hardness: 218 DPH

43989

(j) Annealed at 1000°C
Hardness: 218 DPH

43364

(k) Annealed at 1100°C
Hardness: 224 DPH

43365

(l) Annealed at 1100°C
Hardness: 224 DPH

150X

850X

150X

850X

150X

850X

43355

150X

(a) As-rolled
Hardness: 245 DPH

43356

150X

(b) Annealed at 600°C
Hardness: 225 DPH

43357

150X

(c) Annealed at 700°C
Hardness: 218 DPH

43358

850X

(d) Annealed at 700°C
Hardness: 218 DPH

43359

150X

(e) Annealed at 800°C
Hardness: 215 DPH

43963

850X

(f) Annealed at 800°C
Hardness: 215 DPH

43366

150X

(m) Annealed at 1250°C
Hardness: 241 DPH

43367

850X

(n) Annealed at 1250°C
Hardness: 241 DPH

43368

150X

(o) Annealed at 1400°C
Hardness: 243 DPH

43370

850X

(p) Annealed at 1400°C
Hardness: 243 DPH

43371

150X

(q) Annealed at 1500°C
Hardness: 245 DPH

43372

850X

(r) Annealed at 1500°C
Hardness: 245 DPH

Fig. 20. Microstructures of 1.5-mm-thick V-15Ti-7.5Cr Sheet Cold-rolled (75%) and Annealed for 1 hr at Temperatures Indicated

TABLE XII. Analyses Results for V-15Ti-7.5Cr Ingot
and Specimen Annealed at 1500°C for 1 hr

Material	Chromium, w/o	Interstitials			
		C	O	N	H
Ingot AM-64 (Top)	7.5	234	772	390	13
Annealed Specimen	7.52	123	950	320	7

The cold-worked and annealed microstructures for the V-15Ti-7.5Cr alloy are shown in Fig. 20. The 600°C anneal resulted in a partially recrystallized structure. The 700°C anneal produced a grain morphology which is characteristic of a fully recrystallized structure; however, the 800°C anneal may be the ascribed recrystallization temperature because of the slightly lower hardness without any significant grain growth.

Annealing at temperatures greater than 900°C produced characteristic structures. At 1000°C the nodular particles (present in the lower-temperature anneals) became partially localized in the grain boundaries, which probably tended to retard grain-boundary migration of selected grains, producing a duplex structure more noticeable after the 1100°C anneal. It is not clear whether the nodular particles were migrating to the grain boundaries or the grain boundaries were sweeping the particles along as they moved through the matrix.

Anneals at 1250°C and higher produced an acicular-shaped Widmanstätten-type precipitate whose intensity increased with temperature. The microstructures for the 1400 and 1500°C anneals showed evidence of a sharp interaction between the grain boundaries and the precipitate. The nodular precipitate, earlier noticed at the grain boundaries, appeared to become less distinct with increasing temperature--suggesting that it probably was going into solution.

The grain size was determined for each specimen annealed at temperatures from 700°C. The resulting grain-growth behavior is shown in Fig. 21, where the mean grain diameter is plotted as a function of temperature. Above 900°C, grain-growth behavior began to accelerate. This may have resulted from the nodular particles going into solution, thus allowing a portion of the grain to grow. The inflection point occurred near 1400°C, where the grain growth decelerates. (The V-15Ti-5Cr grain-growth behavior of Fig. 6 showed a similar relationship; however, a larger grain size at the lower temperatures was evident.) One may attribute this latter observation to either an influence of the acicular precipitate on slowing the grain boundary migration and/or to the mean grain diameter approaching the specimen thickness.

In accordance with theories on precipitation strengthening,^{5,6} the temperature at which the precipitates have grown to a given size and

Fig. 21. Effect of 1-hr Anneals on Mean Grain Size of V-15Ti-7.5Cr Alloy

distribution to serve as effective barriers for dislocation movement would represent the optimum annealing temperature for the best creep properties.* Higher-temperature anneals would result in larger precipitates, which would be less effective in retarding dislocation mobility. A more extensive annealing study on the V-15Ti-7.5Cr alloy is now under way.

B. Tensile Properties

1. Room-temperature Tensile Properties of Sheet Material

Several tensile tests were run on V-15Ti-7.5Cr sheet stock in both the longitudinal and transverse directions (relative to the rolling direction) to determine if any marked anisotropic behavior resulted from

the rolling operation. Fabrication of the sheet stock was similar to that outlined for the annealing studies (see Section V-A above).

The results shown in Table XIII indicate little difference in ultimate strength, the strength in the transverse direction being slightly higher. The yield-strength behavior, although not recorded, showed a similar relationship.

TABLE XIII. Results of Room-temperature Tensile Tests on V-15Ti-7.5Cr Sheet

Material and Condition	Average Ultimate Tensile Strength, [†] kg/mm ² (psi)	
	Longitudinal (Parallel to rolling direction)	Transverse (Perpendicular to rolling direction)
V-15Ti-7.5Cr sheet (Annealed at 900°C for 1 hr)	74.7 (106,300)	77.0 (109,600)

[†]Average of four tests.

*Early indications are that a 1250°C, 1-hr anneal of the as-wrought V-15Ti-7.5Cr alloy markedly improves the creep resistance.⁹

2. Results of Room-temperature and 650°C Tensile Tests on V-15Ti-7.5Cr Tubing

Tensile tests were run on 7.4-mm-OD x 4.0-mm-wall (0.292-in.-OD x 0.016-in.-wall) tubing of V-15Ti-7.5Cr and, for comparison purposes, Type 304 stainless steel. At both test temperatures, the ternary alloy tubes were tested in the as-drawn condition (~40% cold work) and in two annealed conditions: 850° for 1 hr and 1250°C for 1 hr. At both room temperature and 650°C, the 304 SS was tested in the as-drawn condition (~40% cold work) and in an annealed condition (1090°C for 15 min, followed by a rapid cool).

The results of the tensile tests are summarized in Table XIV and the bar chart of Fig. 22. With both materials in an as-drawn condition, the 304 SS had a higher (~20%) ultimate tensile strength (UTS) at room temperature than the ternary alloy. However, the V-15Ti-7.5Cr alloy had a higher UTS (~15%) than the stainless steel when both were in the fully annealed condition. Annealing the V-15Ti-7.5Cr alloy at 1250°C resulted in an insignificant drop in the room-temperature UTS.

TABLE XIV. Results of Room-temperature and 650°C Tensile Tests on V-15Ti-7.5Cr and Type 304 SS Tubing
(Nominal tube size is 0.292-in. OD x 0.016-in. wall thickness)

Material and Condition	Average Ultimate Tensile Strength,* kg/mm ² (psi)	
	Room Temperature	650°C
V-15Ti-7.5Cr, As drawn	100.7 (143,200)	82.0 (116,600)
V-15Ti-7.5Cr, 850°C Anneal	76.4 (108,600)	64.7 (92,000)
V-15Ti-7.5Cr, 1250°C Anneal	75.6 (107,500)	60.4 (85,900)
Type 304 SS, As drawn	118.6 (168,700)	69.0 (98,100)
Type 304 SS, Annealed	66.0 (93,800)	41.7 (59,300)

*Average of three tests, except for V-15Ti-7.5Cr, 850°C anneal, tested at 650°C, which is an average of two tests.

Fig. 22
Bar Chart of Tensile Test
Results on Tubing

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In the 650°C tests, the ternary alloy was stronger (~20%) than the Type 304 SS in the as-drawn condition and half again as strong as the Type 304 SS in the annealed condition. Annealing the V-15Ti-7.5Cr alloy at 1250°C resulted in a slight drop in strength compared with the values obtained on material annealed at 850°C. Between room temperature and 650°C, there was a much more marked decrease in strength (~40%) for the annealed 304 SS than for the annealed ternary alloy (~20%).

The tests at 650°C employed flowing argon both inside and outside the tubing. Since the time at temperature was relatively short (~15 min), little or no surface contamination was expected. Generally, three tubes were tested at each set of conditions.

C. Room-temperature and 650°C Tube-burst Test Results

Tube-burst tests were run on 7.4-mm-OD x 0.4-mm-wall (0.292-in.-OD x 0.016-in.-wall) tubing of V-15Ti-7.5Cr and, for comparison purposes, on Type 304 SS. The ternary alloy tubes were tested at room temperature in the as-drawn condition (~40% cold work) and in the annealed condition (1 hr at 850°C). At 650°C, the alloy was tested in an as-drawn condition and two annealed conditions: the standard anneal of 1 hr at 850°C, and a higher-temperature anneal of 1 hr at 1250°C. At room temperature and 650°C, the 304 SS was tested in an as-drawn condition (~40% cold work) and in an annealed condition (15 min at 1090°C, followed by a rapid cool).

For the room-temperature tests, the tubes were pressurized with oil. For tests at 650°C, the tubes were heated in a flowing-helium atmosphere and pressurized with argon. Since the tubes were heated for a relatively short time (~15 min), the helium atmosphere provided adequate protection against contamination at the test temperature of 650°C. Three tubes were tested for each set of conditions.

Hoop-stress calculations were based on the thick-wall tube formula using pretest tube dimensions. After rupture, an average tube diameter

was measured at a location near the failure to obtain a rough measure of the deformation just before failure. Comparison of the tube diameters before and after testing yielded an approximation of the expansion of the tubes before rupture.

The results of the tube-burst tests are summarized in Table XV, which gives the burst pressures, calculated hoop stress, and approximate elongation. Photographs of tubes ruptured in the room-temperature tests are shown in Fig. 23. Photographs of tubes ruptured at 650°C have not been included since the use of gas as a pressurizing medium resulted in severe deformation which, in many cases, fragmented the tube. This characteristic type of failure made visual comparison of little benefit.

TABLE XV. Results of Tube-burst Tests at Room Temperature and 650°C on Type 304 SS and V-15w/oTi-7.5w/oCr Tubing
(Nominal tube size is 0.292-in. OD x 0.016-in. wall thickness)

Material and Condition	Room Temperature			650°C		
	Average Burst Pressure, kg/mm ² (psi)	Average Calculated Hoop Stress, kg/mm ² (psi)	Average Radial Expansion, %	Average Burst Pressure, kg/mm ² (psi)	Average Calculated Hoop Stress, kg/mm ² (psi)	Average Radial Expansion, %
V-15Ti-7.5Cr, As drawn	13.4 (19,000)	118.2 (168,000)	1.2	10.0 (14,300)	88.4 (125,800)	3.0
V-15Ti-7.5Cr, 850°C Anneal	10.0 (14,200)	87.7 (124,800)	8.6	7.6 (10,800)	66.9 (95,100)	6.9
V-15Ti-7.5Cr, 1250°C Anneal	-	-	-	7.5 (10,700)	66.0 (93,800)	5.7
Type 304 SS, As drawn	15.2 (21,600)	132.3 (188,200)	1.6	8.2 (11,600)	71.2 (101,300)	1.6
Type 304 SS, Annealed	6.5 (9,200)	56.2 (80,000)	24.4	3.7 (5,330)	32.7 (46,500)	16.4

The results of Table XV are plotted as a bar chart in Fig. 24 for comparison. The V-15Ti-7.5Cr alloy proved significantly stronger than the Type 304 SS for all cases, except the room-temperature tests with the materials in an as-drawn condition. In this case, the stainless steel was about 10% stronger. In the annealed condition, however, the vanadium alloy was about 50% stronger than Type 304 SS in the room-temperature tests. In the tube-burst tests at 650°C, the vanadium alloy was about 25% stronger than Type 304 SS in the as-drawn condition, and about twice as strong as Type 304 SS in the annealed condition. Annealing of the V-15Ti-7.5Cr alloy at 1250°C, as opposed to the 850°C standard anneal, resulted in an insignificant drop in hoop stress and a slight drop in expansion. Expansion, as measured by diameter increase, was roughly comparable between the two materials in the as-drawn condition, but the stainless steel showed much more radial expansion than the vanadium alloy in the annealed condition. The Type 304 SS suffered significantly more degradation of strength in going from room temperature at 650°C than did the vanadium alloy. Calculated hoop stresses at failure dropped approximately 40% for annealed Type 304 SS but only about 25% for the annealed V-15Ti-7.5Cr alloy.

V-15w/oTi-7.5w/oCr

As drawn ($\sim 40\%$ cold work)

44027 1X
Average hoop stress = 118.2 kg/mm^2 (168,100 psi)

Annealed (1 hr at 850°C)

44028 1X
Average hoop stress = 87.7 kg/mm^2 (124,800 psi)

Type 304 Stainless Steel

As drawn ($\sim 40\%$ cold work)

44029 1X
Average hoop stress = 132.3 kg/mm^2 (188,200 psi)

Annealed (15 min at 1090°C)

44030 1X
Average hoop stress = 56.6 kg/mm^2 (80,000 psi)

Fig. 23. Photographs of V-15Ti-7.5Cr and Type 304 SS Tubes
after Pressurizing to Failure at Room Temperature

Fig. 24

Bar Chart of Tube-burst Test Results

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The above results were based on short-time tests with the tubes under pressurization for less than 5 min. The results of these tests may not be indicative of the behavior of tubing in longer-time tests of the same nature--this remains to be determined.

D. Welding Studies

Two types of weld tests on V-15w/oTi-7.5w/oCr indicated that the alloy possessed a high degree of weldability and, in fact, exhibited a more controllable fusion zone than Type 304 SS. Gas tungsten-arc (TIG) welding was employed to seal end plugs into short sections of tubing via a girth weld. Dimensional data on the end plugs and tubing are shown in Fig. 25. The tubes and endplugs were matched to provide three types of fit: loose, matched, and press. The welds were made with direct current, straight polarity, and an argon cover gas. Welding amperage was approximately 40 Amp.

The second type of weld test was an electron-beam (EB) butt weld of 1.5-mm (0.060 in.)-thick annealed sheet. The first test incorporated two passes, one on each side of the sheet. The weld speed was 635 mm/min (25 in./min), and the beam was oscillated to provide a wide weld. A second butt weld was made with a sharp focus

Fig. 25. Nominal Dimensions of V-15w/oTi-7.5w/oCr End Plug and Tube for TIG End-closure Weld

beam to provide penetration and a rapid 1.52-m/min (60 in./min) weld speed. The weld was made in a single pass on one side only, the sharp focus beam producing complete penetration.

All welds appeared excellent in visual examination. The TIG weld bead was uniform and clean with good "feathering" characteristics at the end of the pass. The TIG girth welds (end plug to tube) were relatively insensitive to fit. The EB welds also appeared uniform and clean. Some undercutting occurred in the high-speed weld. Low-magnification photographs of the welds are shown in Fig. 26.

(b) EB butt welds

Fig. 26. Photographs of EB Butt Welds and TIG Girth Welds on V-15w/oTi-7.5w/oCr

The welds were sectioned for metallographic examination of the cross section. Photomicrographs of the TIG and EB welds are shown in Figs. 27-30. The press-fit and loose-fit TIG welds showed porosity; the matched-fit TIG weld showed no indication of porosity in the one plane of the metallographic sample. The welds appeared excellent, with no visible cracks or nonbond at the juncture between the weld metal and base material. The heat-affected zone did not show any unusual structure, and the region of grain growth was relatively short. Grain growth was not excessively large. Both EB welds exhibited porosity. As with the TIG welds, the welds appeared excellent with a relatively small heat-affected zone. No abnormal behavior was observed.

44364

50X

44131

50X

Fig. 27. Photomicrographs of TIG Girth Weld of End Plug into V-15w/oTi-7.5w/oCr Tubing, When Plug Was a Matched Fit into the Tube. (Etchant: Creighton's followed by 5% KOH, 5% $K_3Fe(CN)_6$, 90% H_2O).

44133

44134

44130

44129

Fig. 28. Photomicrographs of TIG Girth Weld of End Plug into V-15w/oTi-7.5w/oCr Tubing, When Plug Was a Loose Fit with the Tube. (Etchant: Creighton's followed by 5% KOH, 5% $K_3Fe(CN)_6$, 90% H_2O).

Fig. 29. Photomicrographs of TIG Girth Weld of End Plug into V-15w/oTi-7.5w/oCr Tubing, When Plug Was a Press Fit into the Tube. (Etchant: Creighton's followed by 5% KOH, 5% $K_3Fe(CN)_6$, 90% H_2O).

44135

50X

(a) Oscillating beam, 6,350-mm/min (25-in./min) weld speed, two passes

44136

50X

(b) Sharp-focus beam, 15,240-mm/min (60-in./min) weld speed, single pass with complete penetration

Fig. 30. Photomicrographs of EB Butt Welds in V-15w/oTi-7.5w/oCr.
(Etchant: Creighton's followed by 5% KOH, 5% $K_3Fe(CN)_6$, 90% H_2O).

A strip was cut from each of the two EB butt-welded samples and machined into a tensile test specimen. A 25.4-mm (1-in.) gage length was used. The tensile-test results shown in Table XVI indicate a slight loss in strength from welding. As-annealed V-15Ti-7.5Cr has a UTS of approximately 73.8 kg/mm² (105,000 psi).

TABLE XVI. Tensile Evaluation of EB Butt Welds

Weld Type	UTS, kg/mm ² (psi)	Elongation, %	Distance of Fracture from Weld Center, mm/(in.)
Single-pass, full penetration	68.3 (97,100)	14.7	7.9 (0.31)
Two-pass weld, one per side	68.1 (96,800)	15.8	6.4 (0.25)

The fractures were ductile and well away from the weld and heat-affected zones.

In general, the welds were excellent when one considers that no attempt was made to optimize welding parameters. Although slight porosity was evident, sound welds were achieved. No microstructural abnormalities were evident.

VI. INDUSTRIAL PARTICIPATION

To date, industrial participation in fabrication of V-15w/oTi-7.5w/oCr has been limited to a single order for redraw of tube-blanks. The Superior Tube Company, Norristown, Pennsylvania, converted nine tube-blanks produced at ANL into finished tubing 5.6-mm OD x 0.4-mm wall thickness (0.220-in. OD x 0.016-in. wall thickness) on ANL Purchase Order No. 522432. The tube-blanks supplied by ANL were 16.3-mm OD x 13.7-mm ID x ~1.27 m long (0.640-in. OD x 0.540-in. ID x ~50 in. long), the total weight being 3.78 kg (8.32 lb). The tube-blanks were produced at ANL in a manner similar to that previously described in Section IV-B-2; i.e., double extrusion followed by a light swaging operation and tube-reducing to the 16.3-mm-OD x 13.7-mm-ID size. The tube-reduced product was conditioned to remove surface defects--if present--and vacuum-annealed at 850°C before shipment. Although specific details on the redraw history at Superior Tube Company were not supplied, the tube-blanks were reduced by mandrel drawing with intermediate anneals when required. Finished tubing was annealed for 1 hr at 850°C in a vacuum of 3×10^{-4} Torr or better.

The amount of tube-blanks shipped to Superior Tube Company-- 3.78 kg (8.32 lb)--was predicated on obtaining 52 m (170 ft) of finished tubing in 915-mm (36-in.) lengths or multiples thereof. In reality, a total of 66 m (216 ft) was received whose weight of 2.40 kg (5.28 lb) represented a yield of 63.5% on the amount of material supplied for redraw.

The finished tubing was inspected by a pulsed-eddy-current non-destructive inspection technique. The reject level was set at the standard defect depth of 10% of the wall thickness. Only one small defect about 25 mm (1 in.) long was found in the total batch (66 m) of tubing.

The vendor experienced no difficulty in processing the tubing. The alloy behaved in a similar manner as the V-20Ti alloy that they had processed before. These results were quite encouraging, especially since about two-thirds of the tube-blanks furnished for redraw had received a high-temperature (950°C) anneal after swaging. Although the tube-blanks were nondestructively inspected and carefully conditioned before shipment, it was felt that these tube-blanks might prove troublesome in further working based on problems encountered at ANL in processing material annealed at 950°C (see Section IV-D).

VII. DISCUSSION

As a result of extensive alloy-screening studies, the V-15Ti-7.5Cr alloy has emerged as a strong candidate for fuel-cladding applications in sodium-cooled fast reactors. Although comprehensive testing is incomplete at this time, early results (fabricability, strength, creep, and sodium corrosion) have been sufficiently encouraging to warrant larger-scale production of this second-generation vanadium-base alloy into the wrought finished products required for more complete evaluation.

This report documents the integrated procedures for processing the V-15Ti-7.5Cr alloy (as well as some other alloys of lesser interest) from raw material to high-quality finished products in the form of sheet, rod, and tubing. The alloy is amenable to conventional consolidation and fabrication methods, and little difficulty is anticipated in commercial processing of this alloy.

Consolidation, by means of consumable double arc-melting under a helium-argon atmosphere (near-ambient pressure), produces controllable chromium contents in the finished ingot. Thus, the alloy can be consolidated on a broader industrial base than might be the case if EB melting were a required operation.

The V-15Ti-7.5Cr alloy is adaptable to primary fabrication by double-extrusion: breakdown extrusion of the arc-cast ingot, followed by re-extrusion into shapes such as rod, sheet-bar, and tube-blanks suitable for secondary fabrication.

Based on studies carried out at ANL on a three-roll, experimental tube-reducer, the alloy is easily tube-reduced. There is no reason to expect that the alloy could not be tube-reduced on commercial, two-roll (Rockrite) tube-reducers.

The galling tendency of the alloy is suitably handled with proper lubricants, and carbide drawing dies can be used without difficulty. Mandrel or plug-drawing can be utilized--the latter operation usually being restricted in use to near the final tube size.

The annealing characteristics, tube-burst properties, welding behavior, and tensile results on sheet and tubing, compared with Type 304 SS in certain instances, have all received a preliminary appraisal, and the results are presented in this report. A more comprehensive evaluation of the alloy is now under-way at ANL and elsewhere. As would be expected with a new material, industrial participation has not been extensive. Several ANL tube-reduced blanks have been commercially processed into high-quality tubing with no apparent difficulties. More extensive industrial assistance is expected to be in direct proportion to the continued interest in the vanadium-base alloy.

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REFERENCES

1. W. R. Burt, Jr., *et al.*, *Consolidation and Fabrication Techniques for Vanadium-20 w/o Titanium (TV-20)*, ANL-6928 (Feb 1965).
2. W. R. Burt, Jr., *et al.*, *Improvements in Consolidation and Fabrication of Vanadium-20 w/o Titanium (TV-20)*, ANL-7127 (May 1966).
3. W. E. Ruther and S. Greenberg, private communication (Dec 29, 1965).
4. E. R. Gilbert and F. L. Yaggee, private communication (Jan 13, 1966).
5. A. Kelly and R. B. Nicholson, *Precipitation Hardening*, Progress in Materials Science, Editor, Bruce Chalmers, Macmillan, Vol. 10, No. 3 (1963).
6. A. Guinier, *Heterogeneties in Solid Solution*, Solid State Physics, Vol. 9, p. 294, Academic Press, New York (1959).
7. Frank R. Krause, *A New Metal Rolling Process ... Its Theory and Operation*, Iron and Steel Engineer, Vol. 15, No. 8 (Aug 1938), pp. 16-29.
8. A. I. Tselikov, *TsKBMM Mills for New Rolling Processes*, Contemporary Problems of Metallurgy (edited by A. M. Samarin), Consultants Bureau, New York (1960), pp. 392-396.
9. E. R. Gilbert and F. L. Yaggee, private communication (June 20, 1966).