JUN 29 1964

64-7

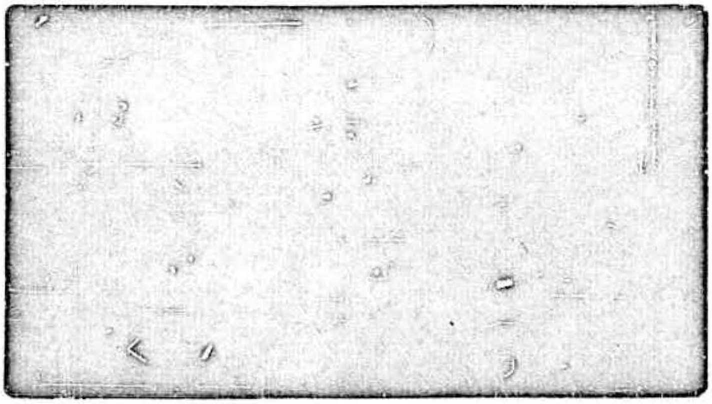
CATALOGED BY DDC
AS AD No. 427343

MASTER

NO RESTRICTIONS FOR ASTIA DISTRIBUTION

IIT RESEARCH INSTITUTE

formerly Armour Research Foundation of Illinois Institute of Technology



Technology Center Chicago, Illinois 60616

427343

DDC
JAN 22 1964

DISPERSION-STRENGTHENED VANADIUM ALLOYS

ABSTRACT

Vanadium-columbium base alloys containing additions of titanium, zirconium, or hafnium in combination with up to 0.2w/o carbon were prepared by arc-melting and fabricated to sheet for elevated temperature creep tests. Compositions based on V-60Cb and containing titanium or zirconium with carbon had good fabricability, but V-60Cb-1Hf-C and V-40Cb-30Ta-C alloys were difficult to work. Creep tests conducted on siliconized specimens in 2000°F air showed that large carbon additions (0.1 and 0.2w/o) produced increased creep rates in V-60Cb base alloys. The most creep resistant composition was V-60Cb-10Ta-1Zr-0.075C which exhibited 1.25 per cent creep in 2.5 hours under a stress of 11,200 psi. This alloy and other materials which elongated less than 2 per cent during the 2000°F air exposure were found to retain most of their original strength and ductility when subsequently tested at or near room temperature. Electron microscope studies revealed that the more creep resistant alloys contained a fine (< 0.2 micron) spheroidal dispersed phase within the grains, whereas alloys with higher creep rates contained grain boundary precipitates.

A series of powder metallurgy alloys based on V-60Cb-1Ti and containing oxide or carbide dispersants was prepared to evaluate the compatibility of various dispersants with the vanadium-columbium alloy matrix. The hydride process was used to prepare the alloy powders which were blended with the dispersant powders, compacted, sintered, then annealed at 2000 and 2400°F. On the basis of microhardness tests of the alloy matrix, hafnium and zirconium carbides appeared to be the most stable at 2400°F.

TABLE OF CONTENTS

DISPERSION-STRENGTHENED VANADIUM ALLOYS

I. INTRODUCTION

This report summarizes the work performed during the period December 14, 1962, to December 13, 1963, under Contract N600(19)-59567, entitled "Dispersion-Strengthened Vanadium Alloys" (IITRI Project No. B6007). Vanadium alloy development studies to date have centered on compositions containing 20 to 60 w/o columbium which are highly workable and weldable and have excellent strength-to-density ratios to at least 2400°F. Silicide-base coatings for these alloys exhibit excellent protective qualities to well over 2400°F under static and dynamic conditions. To further increase the usefulness of these alloys, an improvement in the long-time elevated-temperature properties must be made. Experimental work under this program is aimed at utilizing dispersion-strengthening mechanisms to accomplish this objective.

Previous vanadium alloy studies have shown that compositions in the vanadium-columbium system exhibit greatly improved elevated-temperature tensile properties when complexed with a reactive metal (titanium, zirconium, or hafnium) plus a compound-forming element such as carbon, oxygen, or nitrogen. Dispersions of these compounds were produced in the alloy matrix during solidification and cooling of the arc-melted ingots. Early work on age-hardening alloys also included studies of vanadium-columbium base materials containing boron, beryllium, and silicon. The results to date indicate that carbon, in combination with zirconium or hafnium, is the most effective strengthener of the vanadium-columbium base for short-time exposure; other combinations were also effective in raising the elevated-temperature strength properties but generally produced severe room-temperature embrittlement, especially after prolonged elevated-temperature exposure.

A number of techniques may be used to produce dispersions of ultrafine refractory hard phases in metallic matrices. These methods include solid-state precipitation from a supersaturated solid solution, internal oxidation of a solute metal which is more reactive than the primary alloy constituent, or a wide variety of techniques which are applicable to metals or alloys that can be produced by powder metallurgy. Although it would be possible to produce vanadium-columbium materials by powder metallurgy methods, the very high reactivity of the powders requires ultra-high purity processing atmospheres, and it would be difficult to maintain the high degree of ductility found in the conventionally arc-melted counterparts. Thus the formation of dispersed phases by solid-state reactions in melted alloys was selected as the primary method to be investigated under this program. Powder metallurgy techniques were also used, however, to evaluate the compatibility of various dispersants in the alloy matrix.

The primary considerations for the development of dispersion-strengthened alloys are the particle size, volume fraction, interparticle spacing, and thermal stability of the dispersant. Solution or agglomeration of the dispersed phase during elevated-temperature service must be avoided. Compounds such as oxides are generally more stable than the carbides, nitrides, borides, silicides, etc., but the temperature range of interest for the vanadium alloys (1800° to about 2500° F) is sufficiently below the melting point (about 3400° F) so that stability of compounds such as carbides may be satisfactory. The typical dispersion-strengthened alloy contains particles which range in size from about 0.1 to 0.01 micron, and the interparticle spacing may be near 0.1 micron; such fine particles may be examined by electron microscopy. Their effect on tensile strength, creep, and stress-rupture properties may readily be evaluated.

This program was primarily concerned with the development of arc-melted vanadium-columbium alloys containing reactive metal additions in combination with carbon or other compound-forming elements. The principal alloy base was V-60Cb* although compositions based on V-40Cb-30Ta were also investigated. The effects of composition and thermal treatments on microstructure, fabricability, hardness, tensile, creep, and other properties were evaluated. While substantial improvements in long-time elevated-

---

*Compositions are reported in weight per cent.

temperature strength properties were sought, it was also desired to maintain the excellent fabricability which characterizes alloys of the vanadium-columbium system.

II. EXPERIMENTAL PROCEDURES

A. Materials

The mechanical properties of vanadium, columbium, and other reactive metal alloys are markedly affected by the presence of impurities such as oxygen, nitrogen, and carbon. It has been found that a total of 0.12 w/o of combined oxygen and nitrogen causes greatly reduced fabricability in vanadium-columbium alloys. At least 0.2 w/o carbon may be added to the more ductile alloy bases before fabricability is seriously impaired. Table I presents the analyses of the melting stock used under this program. While the vanadium was somewhat more impure than the columbium and tantalum, the impurity levels in the alloys under investigation were within the range for good fabricability since the vanadium was a minor constituent on a weight per cent basis. Most of the alloys studied under this program were prepared with Lot No. 1 vanadium; compositions prepared with Lot No. 2 are so indicated in tabular data.

B. Preparation of Alloys

Nonconsumable-electrode arc-melting was used to prepare the majority of compositions investigated. These ingots weighed 150 or 200 grams, and were melted at least five times to insure homogeneity. One of the alloys studied was V-60Cb-1Ti; this material was prepared both as a nonconsumably melted 150-gram ingot and also as a 100-pound ingot prepared by consumable-electrode arc-melting followed by extrusion and warm rolling. The latter material contained 0.027 w/o oxygen, 0.013 w/o nitrogen, and 0.026 w/o carbon after melting (prepared under Contract NOw 62-0101-C).

Powder metallurgy techniques were used to prepare a series of alloys for an investigation of compatibility between refractory compound powders (oxides and carbides) and the V-60Cb-1Ti matrix. The hydride process was used to prepare the vanadium-columbium alloy powders. This process is described in detail under Section III-H.

TABLE I

MELTING STOCK IMPURITY ANALYSES

Element	Impurity Content, w/o			
	Carbon	Oxygen	Nitrogen	Other
Vanadium, Lot 1(a)	0.05	0.04	0.027	H_2 0.004
Vanadium, Lot 2(b)	0.03	0.04	0.046	
Columbium	0.003	0.005	0.005	H_2 0.0004
Tantalum	0.003	0.005	0.002	

(a) VPN (10 kg) 170 after arc melting.

(b) VPN (10 kg) 155 after arc melting.

C. Sheet Fabrication

The addition of carbon in combination with the reactive metals zirconium, hafnium, etc., caused considerably reduced workability in some of the V-60Cb and other alloy bases. This reduced workability was particularly pronounced at the higher carbon levels, and a number of hot and warm working treatments were given to these compositions in order to accomplish ingot breakdown without severe cracking.

After melting, all ingots were machined on the top and bottom surfaces in order to provide parallel faces; a thickness of about 0.35 inch was typical. Alloys which were to be hot worked (2350°F) were canned in evacuated stainless steel sheaths. Most of the difficult-to-work compositions were first hot-rolled at 2350°F to a reduction in thickness of about 15 to 20 per cent. The materials which passed this critical ingot breakdown operation were then removed from the cans and warm rolled (1200°F) to a total reduction of about 50 to 60 per cent, after which they could be cold-rolled to 0.050 inch sheet. Those materials which exhibited some degree of edge cracking during warm rolling were given at least two intermediate 2400°F anneals during the warm and cold rolling operations.

Some of the ingots cracked severely during the initial hot rolling operation. The cracks were intergranular, and often occurred after an initial 0.005 inch pass. Additional ingots of these compositions were prepared, and alternate working methods were attempted. One technique which was successful in some cases involved warm rolling (1200°F) to a reduction of about 10 per cent, using very light passes, followed by a 2400°F recrystallization anneal. Subsequent working was done at 2400°F without severe cracking, after which the materials were warm, then cold rolled with intermediate anneals. A variation of this method involved a very light reduction (5 to 10 per cent) at a somewhat higher temperature (1800°-1900°F), but below the recrystallization range. After this light reduction, a 2400°F anneal was given; then the ingots were further warm or hot worked.

D. Mechanical Property Evaluations

Vickers 2 1/2 or 10 kg hardness measurements were taken on polished metallographic specimens of the as-cast and the wrought alloys. Micro-hardness values (25- to 100-gram loads) were also measured on the polished samples to indicate the extent of surface contamination, segregation, etc.

Elevated-temperature creep tests were conducted on siliconized specimens heated in air. This procedure was used for several reasons. Firstly, the relative simplicity of the testing operation represented a considerable saving in time which would ordinarily be required for the loading, pump-down, or purging of vacuum or inert atmosphere capsules. Secondly, the data obtained would be more representative of the materials in the conditions under which they would ultimately be used. Thirdly, it was found that the pack-cementation silicide coatings were capable of providing excellent protection from atmospheric contaminants, at least when total creep was less than 2 per cent. This was indicated by the fact that in room-temperature tensile tests of specimens which had been subjected to 2000°F creep tests, a considerable portion of the original strength and ductility of the alloys was retained. While creep values in excess of 2 per cent generally caused a decrease in strength and ductility of the alloy, the creep data obtained were consistent and reproducible. The following procedure was employed in the preparation of specimens and in obtaining short-time creep data:

1. Specimens 0.050 inch thick were machined to a 0.150 inch wide by 1.0 inch long gage length.
2. The specimens were tumbled in an alumina grit-water slurry for 100 hours to round off sharp edges and corners.
3. Pack-cementation silicide coatings, about 0.0025 inch thick, were produced by heating in a mixed pack of silicon and NaF activator for 8 hours at 2200°F.
4. The coated specimens were exposed to static air for 20 hours at 2200°F to insure adequate protective quality of the coating.
5. Using Udimet-700 grips, the specimens were direct-loaded at various stress levels in 2000°F air for 2 1/2 hours. Creep was measured by a dial gage, and total plastic deformation was obtained by taking micrometer

measurements of the specimens before and after stressing.

6. Room-temperature, 300°, or 600°F tensile data were obtained for each specimen after creep testing; a strain rate of 0.06 in/in/min was used.
7. Metallographic and hardness surveys were conducted on the materials after testing.

E. Miscellaneous Evaluation

The effects of various solution annealing and aging treatments on the hardness and structure of a number of alloys was investigated. Recrystallization temperatures were determined by metallographic examination and also by hardness tests. All of these elevated-temperature treatments were conducted under a high vacuum (at least 1 x 10^{-6} mm Hg). Other evaluations conducted under this program included room-temperature bend tests which involved a relatively slow strain rate bending of sheet stock 180 degrees around mandrels of various sizes; bend tests were also performed on coated specimens to determine the ductile-to-brittle transition temperature.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Alloy Systems Investigated

A major portion of the experimental work under this program was centered on alloys based on V-60Cb. Earlier studies had shown that the composition V-60Cb-1Ti possessed excellent fabricability and weldability, and also had very high density-corrected strengths to at least 2200°F. Replacing titanium with zirconium plus small carbon additions (up to 0.1 w/o) resulted in considerably increased tensile strength at elevated temperatures. Similar additives to V-60Cb were studied under this program to determine whether or not the 2000°F creep properties could be improved. Previous alloy development studies had also shown that alloys based on V-Cb-Ta were among the strongest, on a short-time basis, of the experimental materials at 2400°F. The system V-40Cb-30Ta was also selected for investigation of creep properties. Titanium, zirconium, or hafnium plus carbon was added to each of these alloy bases as follows:

V-60Cb-1Ti plus 0.025, 0.05, and 0.075 w/o carbon
V-60Cb-1Zr plus 0.05, 0.1, and 0.2 w/o carbon
V-60Cb-1Hf plus 0.05, 0.1, and 0.2 w/o carbon
V-40Cb-30Ta-1Zr plus 0.05 and 0.1 w/o carbon
V-40Cb-30Ta-1Hf plus 0.05 and 0.1 w/o carbon

In addition to the above alloys, the basic compositions without carbon additions were also studied. Minor compositional variations of these systems were also included in these investigations, as was the alloy V-60Cb-1Ti, prepared by different melting methods and containing different levels of interstitial impurities.

B. Fabricability

Most of the compositions studied under this program were considerably more difficult to fabricate than the V-20Cb-5Ti and V-60Cb-1Ti materials investigated under previous alloy development programs. These earlier alloys contained only about 0.04 to 0.08w/o combined carbon, oxygen, and nitrogen, most of which were contained as impurities in the vanadium melting stock. At these impurity levels, the alloys could be cold-rolled from the arc-melted ingots directly to 0.050 inch thick sheet--in some cases without intermediate annealing. The alloys studied under this program, on the other hand, contained up to 0.2w/o carbon additions as well as the oxygen, nitrogen, carbon, etc., which were present in the melting stock. As a consequence, the latter compositions could be fabricated to sheet only by hot or warm rolling techniques, and some of these alloys could not be rolled to acceptable sheet.

A list of the compositions studied, together with the fabrication techniques and comments on the fabricability and sheet quality, is presented in Table II. Sheet of good quality was produced from most of the alloys based on V-60Cb-1Ti and V-60Cb-1Zr, whereas most of the compositions based on V-60Cb-1Hf could not be rolled to sheet. Increasing carbon levels generally produced decreased workability in all of the alloys studied. The compositions based on V-40Cb-30Ta were much more difficult to fabricate than the V-60Cb base materials; the workability of these high-tantalum alloys decreased with increasing carbon additions, especially when complexed with hafnium.

TABLE II

FABRICATION DATA FOR VANADIUM ALLOYS

Composition, w/o[a]	Fabrication Method[b]	Results
V-60Cb-1Ti	CR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Ti[c]	Extrude-WR-Ann.-WR	Good 0.050 in. sheet
V-60Cb-1Ti-0.025C	HR-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Ti-0.05C	HR-WR-Ann.-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Ti-0.075C	HR-WR-Ann.-WR-Ann.-WR	Good 0.050 in. sheet
V-60Cb-1Zr[d]	WR-Ann.-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Zr-0.05C	HR-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Zr-0.1C	HR-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Zr-0.2C	HR-WR-Ann.-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Hf[d]	WR-Ann.-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-1Hf-0.05C	HR	Severe edge cracking on initial breakdown
V-60Cb-1Hf-0.1C	HR-WR-Ann.-WR-Ann.-CR	Fair quality sheet, some edge cracking
V-60Cb-1Hf-0.2C	HR	Severe edge cracking on initial breakdown
V-60Cb-10Ta-1Zr-0.075C[d]	HR-WR-Ann.-WR-Ann.-CR	Good 0.050 in. sheet
V-60Cb-10Ta-1Hf[d]	HR-WR-Ann.-WR-Ann.-CR	Good 0.050 in. sheet
V-40Cb-30Ta	HR	Severe edge cracking on initial breakdown
V-40Cb-30Ta-1Zr	HR-WR-Ann.-WR	Poor quality sheet, numerous edge cracks
V-40Cb-30Ta-1Zr-0.05C	HR-WR-Ann.-WR	Poor quality sheet, numerous edge cracks
V-40Cb-30Ta-1Zr-0.1C	HR-WR-Ann.-WR	Fair quality sheet, moderate edge cracking
V-40Cb-30Ta-1Hf[d]	HR-WR-Ann.-WR-Ann.-CR	Fair quality sheet, some edge cracking
V-40Cb-30Ta-1Hf-0.05C	HR	Severe edge cracking on initial breakdown

TABLE II (Cont.)

Composition, w/o(a)	Fabrication Method(b)	Results
V-40Cb-30Ta-1Hf-0.1C	HR	Severe edge cracking on initial breakdown
V-30Cb-35Ta-1Hf(d)	HR-WR-Ann.-WR-Ann.-Cr	Good 0.050 in. sheet
V-35Cb-25Ta	HR	Severe edge cracking on initial breakdown
V-35Cb-25Ta-1Zr	HR	Severe edge cracking on initial breakdown

(a) Prepared with Lot No. 1 vanadium (see Table I), unless otherwise noted.

(b) HR = hot roll, ∼2350°F.

WR = warm roll, ∼ 1200°F.

CR = cold roll, room temperature.

Ann. = anneal 30 minutes at 2300° or 2400°F.

(c) From 100-pound extruded and warm rolled ingot (refer to text, Section II-B).

(d) Prepared with Lot No. 2 vanadium (see Table I).

Much of the cracking which was observed in the difficult-to-fabricate alloys occurred during the initial 5 to 15 per cent reduction in thickness. This was attributed to the comparatively coarse and columnar grain structure typical of the arc-melted product. Refinement of the as-cast structure by thermal homogenization did not improve the workability, but in some cases a light (10 per cent) reduction at 1200°F followed by a 2400°F anneal produced improved fabricability because of the finer recrystallized grain size. It was found that if little cracking occurred during the first 25 to 35 per cent reduction by hot or warm working methods, most of the ingots could then be warm or cold rolled to 0.050 inch thick sheet with very little additional cracking. At least one intermediate 2400°F anneal was required for the harder compositions during the warm or cold rolling procedures.

Ten compositions near the center (on a weight per cent basis) of the V-Cb-Ta system were investigated. Only one of these materials, V-30Cb-35Ta-1Hf, could be fabricated into sheet of good quality. The remainder either broke up during initial ingot breakdown or contained numerous edge cracks after rolling to 0.050 inch thick sheet. Some of this cracking may be attributed to the large carbon additions in combination with hafnium which produced very high hardnesses and probably very high elevated-temperature strength values. However, one of these compositions, V-40Cb-30Ta-1Hf, was a duplicate of an alloy which had been readily fabricated to sheet under a previous alloy development program. The current less-fabricable material differed from the more workable stock only in that the vanadium contained slightly more total oxygen and nitrogen (0.09 vs. 0.07w/o); carbon levels in the melting stock were similar. These results may indicate that lower levels of oxygen and nitrogen are required for good fabricability in the V-Cb-Ta system compared to the 0.1w/o level which can be tolerated by V-Cb.

It was also noted that the V-Cb-Ta ingots were not as homogeneous as those of the V-60Cb base. Considerably more coring and a coarser grain size were noted in the ingots containing 30 or 35 w/o tantalum. Thermal homogenization at 2400°F did not significantly improve the fabricability of these materials, and no definite correlation between as-cast grain size and workability could be made. In general, alloys with higher carbon contents had the finer grain size but were less fabricable.

C. Hardness Evaluations

The effect of composition on hardness of a series of vanadium alloys is shown in Table III. These alloys are based on V-60Cb and V-40Cb-30Ta and contain varying amounts of carbon in combination with hafnium or zirconium, and the hardness values were obtained on fully recrystallized specimens. Most of the alloys had been hot or warm rolled to sheet, followed by a 2400°F anneal; a few of the alloys were hot-worked only a few per cent before cracking prevented further reduction.

Data in Table III show that hardness is primarily a function of carbon content, regardless of the alloy base to which the carbon was added. It may be noted that all of the compositions containing 0.1w/o carbon were in the VPN 383 to 390 range, while the materials containing 0.05w/o carbon had hardnesses in the VPN 352 to 365 range. Alloys of the V-60Cb base containing 0.2w/o carbon were considerably harder--VPN 412 to 423. These high hardness values indicate a marked reduction of room-temperature ductility compared to the base alloys which are in the VPN 330 to 335 range. From the standpoint of fabricability and ductility, it is likely that carbon additions above 0.1 w/o will result in relatively brittle materials.

D. Heat-Treating Studies

The comparatively high carbon levels in the alloys under investigation suggest the possibility of heat treating to produce improved elevated temperature mechanical properties. A study of the effects of various solution annealing and aging treatments on hardness and structure was conducted on a series of alloys which exhibited sufficient workability to permit fabrication into sheet. Metallographic specimens were cut from these sheets and solution-annealed at 2600°, 2800°, and 3000°F for 30 minutes and were rapidly chilled by dropping the specimens onto a water-cooled copper plate in the bottom of the vacuum furnace.

Table IV presents data for the as-quenched hardness of six of the alloys. It may be observed that the three V-60Cb base alloys

TABLE III

ROOM-TEMPERATURE HARDNESS OF VANADIUM ALLOYS

Composition, w/o	Hardness, VPN (10 kg)[a]
V-60Cb-1Zr	334
V-60Cb-1Zr-0.05C	352
V-60Cb-1Zr-0.1C	383
V-60Cb-1Zr-0.2C	412
V-60Cb-1Hf	335
V-60Cb-1Hf-0.05C	352
V-60Cb-1Hf-0.1C	385
V-60Cb-1Hf-02C	423
V-40Cb-30Ta-1Zr-0.05C	355
V-40Cb-30Ta-1Zr-0.1C	385
V-40Cb-30Ta-1Hf-0.05C	365
V-40Cb-30Ta-1Hf-0.1C	390

(a) After recrystallization anneal for 30 minutes at 2400°F.

TABLE IV

ROOM-TEMPERATURE HARDNESS OF RAPIDLY COOLED VANADIUM-COLUMBIUM ALLOYS

Composition, w/o	Hardness on Quenching from Solution-Annealing Temperature, VPN 2600°F	2800°F	3000°F
V-60Cb-1Zr-0.05C	344	353	381
V-60Cb-1Zr-0.1C	407	433	442
V-60Cb-1Zr-0.2C	408	462	475
V-60Cb-1Hf-0.1C	370	367	376
V-60Cb-1Hf-0.2C	451	437	450
V-40Cb-30Ta-1Zr-0.1C	415	405	375

containing zirconium and carbon exhibited a progressive increase in hardness as the solution-annealing temperature was raised from 2600° to 3000°F. Hardness levels of the two V-60Cb-Hf-C alloys remained essentially unchanged at the various solution-treating temperatures, while the single V-Cb-Ta-Zr-C alloy exhibited decreasing hardness as the solution-annealing temperature was increased. The latter behavior could indicate a low carbon solubility at these temperatures with agglomeration of the carbides at the higher temperatures; this was not confirmed by metallographic examination.

Metallographic studies of the solution-treated alloys revealed a significant increase in grain size with annealing temperature for all of the alloys listed in Table IV with the exception of the V-40Cb-30Ta-1Zr-0.1C composition. This alloy was by far the finest grained at 3000°F, although even this material showed a significant grain size increase as the annealing temperature was raised from 2600° to 3000°F.

The solution-treated alloys were subsequently aged at 2000° and 2300°F. The initial aging studies were carried out for periods of time up to 100 hours on specimens which were encapsulated in Vycor or quartz bulbs which had been evacuated and back-filled with argon prior to sealing. A progressive increase in hardness with annealing time was noted for all of the V-60Cb base materials, and in some cases the hardness values were well above VPN 500. It was subsequently found that this hardness increase was primarily due to the absorption of oxygen and/or nitrogen existing as impurities in the bulbs. Additional aging treatments were carried out under vacuum or in bulbs which contained zirconium turnings as a getter. These latter treatments showed that very slight (less than 10 VPN) hardness increases occurred after 48 hours at 2000°F or 24 hours at 2300°F. These data indicate that for relatively short times, no gross loss of ductility may be expected upon exposure at 2000° to 2300°F.

E. Recrystallization Behavior

Cold-rolled sheet specimens of six alloys were annealed for 30 minutes at 2000°, 2200°, and 2400°F under a high vacuum. The results of metallographic observations on recrystallization are presented in Table V.

TABLE V

METALLOGRAPHICALLY OBSERVED RECRYSTALLIZATION OF COLD-ROLLED VANADIUM-COLUMBIUM-BASE ALLOYS

	Recrystallization, per cent		
Composition, w/o	2000°F, 1/2 hr	2200°F 1/2 hr	2400°F, 1/2 hr
V-60Cb-1Zr-0.1C(a)	90	100	100
V-60Cb-1Zr-0.2C(a)	85	100	100
V-60Cb-1Zr-0.05C(a)	80	100	100
V-60Cb-1Hf-0.1C(b)	5	50	100
V-40Cb-30Ta-1Zr-0.1C(b)	0	10	90
V-60Cb-1Hf-0.2C(b)	0	5	60

(a) Cold worked 80-90 per cent.

(b) Cold worked 50-75 per cent.

These data show that the V-60Cb base alloys containing hafnium and carbon have higher recrystallization temperatures than their zirconium-carbon counterparts. A comparatively high recrystallization temperature is also noted for the V-40Cb-30Ta-1Zr-0.1C alloy. The three alloys with the highest recrystallization temperatures had received the smallest amounts of cold work prior to annealing. However, it is believed that the difference in cold reduction was not sufficient to produce the 200° to 400°F difference in recrystallization temperatures between these alloys and the three V-60Cb-1Zr base materials. The latter group were 80 to 90 per cent recrystallized after 30 minutes at 2000°F.

F. Creep Tests

Elevated-temperature (2000° and 2100°F) creep tests were conducted on pack-siliconized sheet specimens as described under Section II-D. Stress levels ranged from 5,000 to 15,000 psi, calculated on the basis of total siliconized cross section, or 5,600 to 16,700 psi calculated on the basis of area of the vanadium alloy base metal beneath the coating. After the creep tests, which produced elongations of 0.3 to 4.75 per cent, the specimens were tensile tested at room temperature or at temperatures of 300° and 600°F. The latter temperatures were used when it was found that the ductile-to-brittle transition temperature of the coated composites was raised to above room temperature by the coating process and/or elevated temperature exposure in air under stress.

Results of the creep tests and the subsequent lower temperature tensile tests are presented in Table VI. A few compositions based on V-60Cb-1Ti had been prepared under Contract NOw 62-0101-c, and were included in these evaluations to show the effects of carbon and oxygen additions on creep properties of the alloy containing titanium. Some two dozen specimens were evaluated at elevated temperature under stress, and only one obvious coating failure occurred in the gage portion of a sample. However, a number of the alloys were embrittled after creep testing, as will be discussed subsequently. Three of the specimens exhibited incipient coating failures at the shoulders which were in contact with the Udimet grips. Otherwise, the creep-tested samples had adherent coatings which appeared to be intact after plastic deformations of as much as 4.75 per cent.

TABLE VI

CREEP AND TENSILE DATA FOR SILICONIZED VANADIUM ALLOYS

	Creep Test Data(a)			Tensile Properties after Creep Test		
Composition, w/o(b)	Stress, psi(c)	Time, hr	Creep, % in 1 in.	Temp., °F	UTS psi(c)	Elong., %
V-60Cb-1Ti(d)	5,700	2.5	0.4	70	113,000	6
	6,800	2.5	0.45	70	73,500	<1
	8,750	2.5	0.5	70	129,000	20
	11,200	2.5	2.0	300	88,500	<1
	16,700	1.67	4.75	300	75,790	<1
	8,300(e)	2.0	4.1	600	70,000	<1
V-60Cb-1Ti(f)	5,700	7.5	1.1	300	124,600	14
	11,200	2.5	2.1	300	100,200	2
V-60Cb-1Ti-0.025C	11,200	2.5	2.5	600	99,200	<1
	16,700	1.2	4.4	600	54,400	<1
V-60Cb-1Ti-0.05C	11,200	2.5	2.5			
V-60Cb-1Ti-0.075C	11,200	2.5	2.6	600	81,400	<1
V-60Cb-1Ti-0.05O	8,300	2.5	1.05	600	109,000	2
	11,200	2.5	2.5	300	117,400	5
V-60Cb-10Ta-1Hf	11,200	2.5	2.5	600	110,000	5
V-60Cb-10Ta-1Zr-0.075C	11,200	2.5	1.25	600	129,000	7
V-60Cb-1Zr(f)	5,600	2.5	0.3	300	130,500	18
	11,200	2.5	2.0	300	90,400	<1

TABLE VI (Cont.)

	Creep Test Data(a)			Tensile Properties after Creep Test		
Composition, w/o(b)	Stress, psi(c)	Time, hr	Creep, % in 1 in.	Temp., °F	UTS psi(c)	Elong., %
V-60Cb-1Zr-0.1C	8,450	2.5	1.1	70	138,200	4.5
	11,200	2.5	3.3	600	66,300	< 1
V-60Cb-1Zr-0.2C	8,300	2.5	1.2	70	167,000	7
V-60Cb-1Hf(f)	11,200	2.5	2.5	300	101,500	1
V-30Cb-35Ta-1Hf(f)	11,200	2.5	3.2	600	105,000	1

(a) Tests conducted in air at 2000°F unless otherwise specified
(b) Alloys prepared with Lot No. 1 vanadium unless otherwise specified
(c) Calculated on vanadium alloy base cross section underneath coating
(d) From 100-pound ingot, impurity analysis given in Section II-B of text
(e) Tested at 2100°F
(f) Prepared with Lot No. 2 vanadium

A number of observations may be made from the creep and tensile data presented in Table VI:

1. Increasing amounts of carbon added to V-60Cb-1Ti or V-60Cb-1Zr resulted in increased creep.
2. The addition of 0.05 w/o O also produced a larger amount of creep in the V-60Cb-1Ti base.
3. Creep rates in V-60Cb-1Ti, prepared by two different methods and containing varying amounts of carbon, oxygen, and nitrogen impurities, were similar.
4. Alloys based on V-60Cb-1Zr-C had creep rates similar to those of V-60Cb-1Ti-C alloys at 2000°F, whereas all compositions containing hafnium had considerably higher creep rates.
5. The lowest amount of creep was found in the alloy V-60Cb-10Ta-1Zr-0.075C.
6. Most specimens which had creep values in excess of 2 per cent were found to be brittle when tensile tested at 70° to 600°F.
7. Most of the samples which had less than 2 per cent creep were ductile in tensile tests at 70° to 600°F.

These results show an over-all range of 1.25 to 3.3 per cent creep among the alloys tested at 2000°F under a stress of 11,200 psi. The most creep-resistant composition, V-60Cb-10Ta-1Zr-0.075C, was the only carbon-containing alloy which had a lower creep rate than the V-60Cb-1Ti or V-60Cb-1Zr compositions without carbon additions. This tantalum-containing material was found to be strong and reasonably ductile at 600°F after creep testing. However, a V-60Cb-10Ta-1Hf alloy had a creep rate exactly twice that of the V-Cb-Ta-Zr-C material. The reason for this behavior is not known, as all other carbon-containing alloys had greatly increased creep rates. It must be noted that all compositions containing hafnium exhibited relatively high creep rates at 2000°F.

Many of the creep-tested specimens were found to have greatly reduced strength and ductility when subsequently tensile tested at temperatures up to 600°F. Hardness measurements (VPN, 50 grams to 10 kg load) were taken on gage sections of the brittle samples, and only very slight hardness increases were noted. The possibility of oxygen and/or nitrogen embrittlement should not be discounted, however, because it was found that in general the specimens which had the higher amounts of creep were weaker and more brittle than materials which exhibited less than 2 per cent creep. Excessive deformation may have caused the silicide coatings to become permeable to the air atmosphere.

A second factor was involved in the room-temperature brittleness of some of the alloys. It was found that contamination during the pack-cementation siliconizing process produced an increase in ductile-to-brittle transition temperature of the vanadium alloys. This embrittlement occurred during some, but not all, of the pack runs. Since the specimens listed in Table VI were coated in four separate coating runs, the embrittlement produced during the coating process was variable, and in most cases the as-coated V-60Cb-1Ti specimens were ductile at 200°F. Since many of the creep-tested samples were brittle at 600°F, it must be assumed that additional contamination occurred during the elevated-temperature stressing.

The effect of stress level upon creep for the V-60Cb-1Ti alloy may be noted from the data in Table VI. Relatively low creep rates (0.5 per cent in 2.5 hours) were obtained at stresses up to 8750 psi, whereas 4.75 per cent creep was measured for the specimen stressed at 16,700 psi in 1.7 hours at the same temperature (2000°F). A pronounced increase in creep rate with increasing temperature was also noted for the V-60Cb-1Ti material: at 2100°F, a stress of 8300 psi produced 4.1 per cent creep in 2 hours, compared to the 0.5 per cent in 2.5 hours under 8750 psi at 2000°F.

G. Electron Microscopy

Three of the creep-tested specimens were selected for electron microscope studies of the dispersed phases. One of the alloys was V-60Cb-10Ta-1Zr-0.075C which exhibited the lowest creep value (1.25 per cent) in 2.5 hours under 11,200 psi at 2000°F. The high-carbon V-60Cb-1Zr 0.1C alloy was selected for study since it had the highest amount of creep--3.3 per cent--under the same conditions. A third alloy, V-60Cb-1Ti prepared by double consumable-electrode arc melting and extrusion, was included in these investigations because it combined fair creep resistance (2 per cent under 11,200 psi in 2.5 hrs at 2000°F) with a very low carbon content (0.026 w/o). All three materials had a similar grain size of about 250 grains per mm^2. Because of the complex nature of the precipitates, no attempts were made to identify the dispersed phases under these preliminary microscopic studies.

The V-60Cb-1Ti material exhibited particularly clean grain boundaries and contained a fine spheroidal dispersion within the grains. Most of the particles were less than 0.2μ in diameter, as illustrated in Figure 1 and 2 which are representative of the range of particle sizes and concentration of the dispersed phase found in this alloy. The absence of a grain boundary precipitate may be due to the low carbon content and to the large amount of mechanical work and subsequent recrystallization anneals involved in fabricating this 100-pound ingot into 0.050 inch sheet.

Examination of the V-60Cb-1Zr-0.1C material with the high creep rate revealed the presence of large quantities of carbides, not only in the matrix but also in the grain boundaries as illustrated in Figure 3. A structure of this type not only would reduce fabricability but might also cause increased creep rates. It is very likely that a high temperature (2600° to 3000°F) solution anneal followed by rapid cooling would eliminate a major portion of this grain boundary phase, and improved workability and creep resistance might be obtained.

Structures in the V-60Cb-10Ta-1Zr-0.075C alloy were in general similar to those shown in Figures 1 and 2. However, the carbides were not as fine and a few grain boundaries contained precipitates as illustrated in Figure 4. The structures do not clearly indicate the reason for the improved creep resistance of this material. It is possible that some solid solution strengthening was achieved by the tantalum addition.

Neg. No. EM156E X10,000

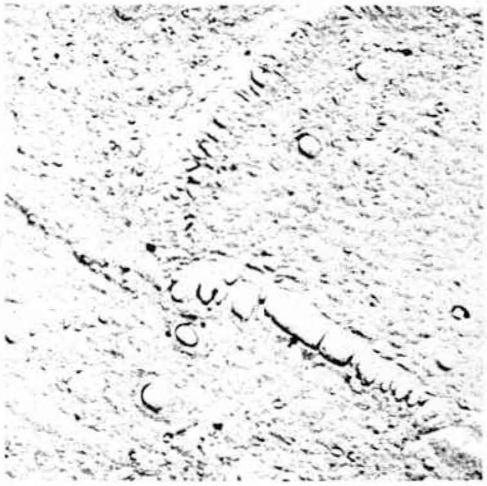
Fig. 1

V-60Cb-1Ti alloy showing grain boundary and precipitate in the matrix.

Neg. No. EM156D X10,000

Fig. 2

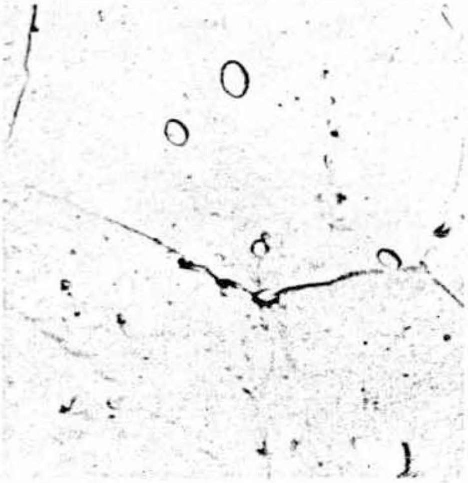
V-60Cb-1Ti alloy showing fine matrix precipitate.



Neg. No. EM158C X14,000

Fig. 3

V-60Cb-1Zr-0.1C alloy showing precipitated phases in the matrix and also in the grain boundaries.



Neg. No. 160C X10,000

Fig. 4

V-60Cb-10Ta-1Zr-0.075C alloy showing that the dispersed phase occurred primarily in the matrix

Figs. 1 - 4 Electron microscope photographs of vanadium-columbium alloys. Formvar replicas shadowed with palladium at 45°; carbon backed.

H. Powder Metallurgy Alloys

1. Alloy Preparation

While the feasibility of producing vanadium-columbium alloys by powder metallurgy techniques has not been adequately demonstrated, the process has been utilized for other reactive metals and was used under this program primarily for studying the stability of dispersants in a vanadium-columbium alloy matrix. These investigations involved the preparation of the vanadium-columbium alloys in the form of finely divided powders to which various oxide or carbide powders are added; after blending, the powder mixture was compacted, sintered, and annealed for varying lengths of time at temperatures in the 2000° to 2400°F range. The stability of the dispersed phase was evaluated metallographically and by hardness tests which indicated solubility in the matrix.

Initial studies utilized the alloy V-60Cb-1Ti which was hydrided in the form of lathe turnings at 1400°F, then crushed to pass a 325 mesh screen. After vacuum dehydrogenation, 7 per cent by volume of the following dispersants were blended with the alloy powders:

Oxides: Al_2O_3, CeO_2, La_2O_3, ThO_2, Y_2O_3, HfO_2
Carbides: HfC, ZrC

The blended powders were compacted at 50 tsi, then sintered under vacuum for 10 minutes at 2800°F. Portions of each sample were then annealed in quartz bulbs under argon for 50 hours at 2000°F and for 8 and 16 hours at 2400°F. A specimen of the alloy powder without a dispersant was also used for the purpose of comparing metallographic and hardness data.

2. Metallographic Observations

Metallographic examination of the as-sintered specimens revealed that relatively high densities were obtained, and there was very little reaction between the dispersant and the vanadium-columbium alloy grains after the brief 2800°F treatment. The wide range of stability of the various dispersants was immediately evident upon metallographic examination after the 16-hour annealing treatment at 2400°F. Specimens of the V-60Cb-1Ti alloy containing alumina and thoria were extremely porous, and oxides were not visible in the microstructures. Some rounded pores were also observed in the material to which hafnia had been added. Some reaction was also observed in the alloys containing lanthana and ceria, while the specimen containing yttria appeared to have undergone little change during the 2400°F treatment. The two carbide dispersants appeared to have reacted slightly with the alloy base. The specimen containing HfC had a fine precipitate within the vanadium alloy grains, indicating solution and precipitation of the carbide during annealing. A somewhat different reaction was noted in the sample containing ZrC: some of the carbide had dissolved, as indicated by a precipitate within the grains, and a gray-colored reaction zone was noted around each carbide particle.

Photomicrographs of the powder metallurgy V-60Cb-1Ti alloy and of a similar alloy base containing Y_2O_3 are presented in Figures 5 and 6. The undispersed alloy was cold-compressed to a 70 per cent reduction in height after sintering, demonstrating the room-temperature ductility as illustrated in Figure 5. The composition containing yttria (Figure 6) was annealed for 8 hours at 2400°F, and shows the oxide phase present in the grain boundaries.

The lower-temperature (2000°F) annealing treatment did not produce as significant structural changes in 50 hours as did the 2400°F, 16-hour treatment. None of the specimens exhibited melting or large pores, although fine porosity was present in nearly all of the specimens. The grain size of the vanadium-columbium alloy matrix was finer than observed after the 2400°F anneals, indicating that grain growth took place during the latter treatment.

3. Hardness Surveys

Microhardness measurements of the individual V-Cb-Ti alloy grains were obtained after sintering and also after the 16-hour 2400°F annealing treatment; these data are presented in table VII. Some solution of the dispersant was expected during the brief 2800°F sintering treatment, and this appears to have occurred in all compositions to a varying extent. The base hardness of V-60Cb-1Ti, fully annealed wrought stock is, VPN(10 kg) 340. Taking into consideration the extremely light load (50-gram) used to obtain the data in Table VII, the alloys containing yttria and zirconium carbide

Neg. No. 24704 X500

Fig. 5

V-60Cb-1Ti alloy prepared by powder metallurgy. After sintering at 2800°F, this material was compressed 70 per cent in height at room temperature.

Neg. No. 24914 X500

Fig. 6

V-60Cb-1Ti alloy containing 7v/o yttria. After sintering at 2800°F, the specimen was annealed for 8 hours at 2400°F; the dark grain-boundary phase is yttria

Etchant: 1 part HNO_3, 1 part HF, 3 parts glycerin.

TABLE VII

MICROHARDNESS OF V-60Cb-1Ti ALLOYS CONTAINING DISPERSED PHASES

	Microhardness in V-60Cb-1Ti Grains, VPN(50 g)		
Dispersant (7 v/o)	As Sintered(a)	As Annealed(b)	Hardness Increase
HfC	423	423	0
ZrC	396	487	91
Y_2O_3	386	655	269
La_2O_3	524	766	242
HfO_2	453	825	372

(a) 10 minutes at 2800°F under vacuum

(b) Sintered as above, then annealed 16 hours at 2500°F under argon.

were hardened only slightly during sintering (VPN 386 and 396, respectively). Slightly greater hardnesses were measured in the alloy containing hafnium carbide (VPN 423) and hafnia (VPN 453), and the alloy containing lanthana was the hardest (VPN 524) in the as-sintered condition.

A much wider spread of hardness in the V-Cb-Ti alloy grains was found after annealing for 16 hours at 2400°F. The composition containing hafnium carbide remained unchanged in hardness, and the zirconium carbide dispersant produced a rise of 91 points to VPN 487. Hardness rises near 250 points occurred after annealing the alloys containing yttria and lanthana, and the greatest hardness increase (372 points) was found in the alloy containing hafnia.

Hardness measurements were not taken on the specimens annealed at 2000°F because the fine porosity and smaller grain size did not permit accurate impressions. Efforts to cold work these samples were not successful because accumulation of the rather coarse dispersants and porosity at the grain boundaries drastically reduced the strength of the composites. The use of finer dispersants plus a wrought structure may have yielded results at 2000°F more in line with observations made on the creep-tested wrought alloys-- i.e., that zirconium carbide was more stable than hafnium carbide at 2000°F. Since creep tests were not conducted on wrought stock at 2400°F, the superiority of hafnium carbide as a dispersant at higher temperatures has not been verified. However, tensile data obtained under earlier alloy development studies showed that hafnium additions to V-Cb-Ta produced the highest 2400°F strength on a short-time basis.

IV. SUMMARY AND CONCLUSIONS

Finely dispersed carbide phases in vanadium-columbium alloys were investigated for the purpose of improving the long-time elevated-temperature strength properties of these materials. The majority of alloys were based on V-60Cb, although a few compositions based on V-40Cb -30Ta were also investigated. These alloy bases were further complexed with titanium, zirconium, or hafnium in combination with up to 0.2 w/o carbon. Nonconsumable-electrode arc-melting techniques were used to prepare 150- to 200-gram ingots which were fabricated to 0.050 inch thick sheet by hot, warm, and/or cold rolling. A series of powder-metallurgy alloys, based on V-60Cb-1Ti and containing 7 volume per cent of various oxides or carbides, were also prepared for studying compatibility between dispersants and the alloy matrix.

The fabricability of the arc-melted alloys varied considerably. Alloys based on V-60Cb-1Zr containing up to 0.2 w/o carbon could be rendered to sheet, whereas the V-60Cb-1Hf alloys containing carbon were very difficult to work. Satisfactory sheet could not be obtained from any of the V-40Cb-30Ta base alloys containing hafnium or zirconium in combination with 0.05 or 0.1 w/o carbon.

Hardness levels of the annealed alloys were primarily dependent on carbon content: the 0.05 w/o carbon materials, VPN 352-365; the 0.1 w/o carbon alloys, VPN 383-390; and the 0.2 w/o carbon compositions, VPN 412-423. The hafnium-containing materials had higher recrystallization temperatures than did the alloys containing zirconium, and in general, higher carbon levels produced higher recrystallization temperature.

Short-time creep tests were conducted in air at 2000° or 2100°F on sheet samples which were siliconized by pack-cementation. The stress levels ranged from 5,600 to 16,700 psi for up to 7.5 hours, and the creep-tested specimens were then tensile tested at room temperature, 300° or 600°F. It was found that samples which exhibited less than 2 per cent creep retained most of their strength and ductility when tensile tested at or near room temperature. If higher creep values were obtained, the specimens were usually brittle when subsequently tensile tested. Some of the increase in ductile-to-brittle transition temperature of the samples was attributed to oxygen and/or nitrogen pickup during the siliconizing process. In spite of the room-temperature embrittlement of some of the specimens, the 2000°F creep data were reproducible and consistent.

Creep rates among the different alloys tested under a single set of conditions varied by a factor of 2.6 to 1. Most of the specimens were stressed for 2.5 hours under 11,200 psi at 2000°F, and the most creep-resistant alloy was V-60Cb-10Ta-1Zr-0.075C which had 1.25 per cent elongation. Under the same stress conditions, V-60Cb-1Ti and V-60Cb-1Zr alloys containing up to 0.1 w/o carbon had up to 3.3 per cent creep, and similar high creep rates were found in the alloys containing hafnium. The latter behavior cannot be explained, as studies of powder metallurgy alloys containing ZrC or HfC dispersants indicated that hafnium carbide was the more stable dispersant at 2400°F. It was found that creep rates were greatly accelerated by increasing the stress level to 16,700 psi, or by increasing the temperature to 2100°F.

Electron microscope studies showed that the more creep-resistant alloys had relatively clean grain boundaries, and the grains contained a spheroidal precipitate having a maximum diameter of 0.2 microns. Higher creep rates in high-carbon alloys were associated with larger volumes of precipitates, both within the grains and in the grain boundaries.

These investigations have shown that alloys based on V-Cb-Ta with zirconium and carbon offer the best combination of fabricability and 2000°F creep resistance. Suitable heat treatments may be devised for V-Cb-Ta-Hf-C alloys so that grain boundary carbides which inhibit workability may be avoided. Such alloys may exhibit improved creep resistance at temperatures near 2400°F. A large area of the V-Cb-Ta system has not been investigated, and it is possible that useful compositions may be found at tantalum levels of 15 to 25 w/o, with 40 to 50 w/o columbium and 30 to 45 w/o vanadium.

V. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data accumulated on this program are recorded in IITRI Logbooks C-13170 and C-14231.

The following personnel contributed to the work reported herein:

F. C. Holtz	-	Project Leader
L. B. Richard	-	Technician

Respectfully submitted,

IIT RESEARCH INSTITUTE

F. C. Holtz, Senior Metallurgist
Metals and Ceramics Research

Approved by:

R. J. Van Thyne

R. J. Van Thyne
Assistant Director
Metals and Ceramics Research

FCH:ae

DISTRIBUTION LIST

Contract No. N600(19)59567

Commander
Aeronautical Systems Division
Wright-Patterson Air Force Base
Ohio
Attn: ASRCM-3. Mr. I. Perlmutter

Nuclear Metals Incorporated
Concord, Massachusetts
Attn: Dr. A. Kaufmann

Battelle Memorial Institute
505 King Avenue
Defense Metals Information Center
Columbus 1, Ohio

University of California
Lawrence Radiation Laboratory
Post Office Box 808
Livermore, California
Attn: Mr. Clovis G. Craig
Technical Information Div.

Lockheed Aircraft Corporation
Lockheet Missile Systems Division
Hanover Street
Palo Alto, California
Attn: WDTLA

Commander
Watertown Arsenal
Watertown 72, Massachusetts
Attn: Mr. S. Arnold

Commander
Ordnance Corps
Frankford Arsenal
Pitman Dunn Laboratory
Philadelphia 37, Pennsylvania
Attn: Mr. D. Kleppinger

Chief of Naval Research (ONR:423)
Department of the Navy
Washington 25, D. C.

Director
U. S. Naval Research Laboratory
Metallurgy Division
Washington 25, D. C.
Attn: Mr. W. Pellini

U. S. Atomic Energy Commission
Division of Reactor Development
Engineering Development Branch
Washington 25, D. C.
Attn: Mr. J. M. Simmons
Chief, Metallurgy

Department of the Navy
Bureau of Ships
Washington 25, D. C.
Attn: Code 343

Boeing Company
Seattle, Washington
Attn: Mr. Cyrus Noritake

Republic Aviation Corporation
Farmingdale, Long Island, N. Y.
Attn: Dr. S. Karman, Chief
Materials Development
Division

U. S. Atomic Energy Commission
Technical Information Service
Post Office Box 62
Oak Ridge, Tennessee

Commanding Officer
Naval Air Material Center
Aeronautical Materials Laboratory
Philadelphia Naval Base
Philadelphis 12, Pennsylvania

National Aeronautics and Space
Administration
1520 H. Street, N. W.
Washington 25, D. C. (3 copies)

National Academy of Sciences
Materials Advisory Board
2101 Constitution Avenue, N. W.
Washington 25, D. C.
Attn: Dr. Joseph Lane

Oregon Metallurgical Corporation
Post Office Box 484
Albany, Oregon
Attn: Mr. Russell G. Hardy

General Electric Company
Aircraft Nuclear Propulsion Dept.
Cincinnati 15, Ohio
Attn: Mr. James McGurty

National Aeronautics and Space Administration
Lewis Research Center
21000 Brookpark Road
Cleveland 35, Ohio
Attn: Mr. Charles A. Barrett

Aerojet-General Nucleonics
San Ramon, California
Attn: Mr. Irwin Rhen

E. I. du Pont de Nemours and Company, Inc.
Wilmington 98, Delaware
Attn: Mr. J. Symonds
Pigments Department

Crucible Steel Company of America
Mellon Square
Pittsburgh 22, Pennsylvania
Attn: Mr. Walter L. Finlay

Union Carbide Metals Company
4625 Royal Avenue
Post Office Box 580
Niagara Falls, New York

Battelle Memorial Institute
Columbus 1, Ohio
Attn: Mr. H. R. Ogden

General Electric Company
Flight Propulsion Laboratory
Cincinnati 15, Ohio
Attn: Mr. R. G. Frank, Manager
Space Metallurgy Projects

Chromalloy Corporation
169 Western Highway
West Nyack, New York
Attn: Mr. Richard L. Wachtell

Harvey Aluminum
Research and Development Division
19200 South Western Avenue
Torrance, California

Haynes Stellite Company
Division of Union Carbide Corp.
Kokomo, Indiana
Attn: Mr. H. F. Kuhns

U.S. Bureau of Mines
Boulder City Metallurgy Research Laboratory
Boulder City, Nevada
Attn: Dr. D. H. Baker, Jr.

Armed Services Technical Information Agency
Arlington Hall Station
Arlington 12, Virginia (5 copies)

Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.
Attn: Mr. Richard Schmidt
Code RRMA-222'

Office of Naval Research
86 East Randolph Street
Chicago 1, Illinois
Attn: Mr. R. Hedlund (3 copies + repro)

SYLCOR Division
Sylvania Electric Products Inc.
208-20 Willets Point Blvd.
Bayside, Long Island, New York
Attn: Mr. L. Sama
Section Head
Metallurgy Department

National Aeronautics and Space
Administration
Langley Research Center
Langley Station
Hampton, Virginia
Attn: Mr. Charles Manning

McDonnell Aircraft Corporation
Lambert-Saint Louis Municipal
Airport
Post Office Box 516
St. Louis 66, Missouri
Attn: Mr. Howard Siegel
Dept. 272

Bell Aerosystems Company
Division Bell Aerospace Corp.
Buffalo 5, New York
Attn: Mr. E. A. Dalega

North American Aviation, Inc.
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, California
Attn: Mr. R. J. Thompson, Jr.
Director Research

North American Aviation, Inc.
Los Angeles Division
International Airport
Los Angeles 9, California
Attn: Mr. H. H. Crotaley
Manager, Applied Science

Chance-Vought Corporation
Astronautics Division
Post Office Box 6267
Dallas 22, Texas
Attn: Mr. M. J. Rudick
Mgr., Space Technology

Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base
Ohio
Attn: Mr. James J. Mattice
Acting Chief, Coatings Section
Nonmetallic Materials Laboratory
Directorate of Materials and
processes

U.S. Department of the Interior
Bureau of Mines
Washington 25, D.C.
Attn: Richard F. Stevens, Jr.

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois
Attn: Mr. Ross Mayfield

Pratt and Whitney Aircraft
East Hartford 8, Connecticut
Attn: E. Dalder
Materials Development
Laboratory

Scientific and Technical Information Facility
Post Office Box 5700
Bethesda, Maryland
Attn: NASA Representative
(SAK/DL-440)

Commanding General
U.S. Army Weapons Command
Attn: AMSWE-RDR
Rock Island, Illinois

Commanding Officer
Watervliet Arsenal
Attn; SWEWV-RDR
Watervliet, New York

Dr. A. F. Weinberg
General Atomics Division
General Dynamics Corporation
San Diego, California

Martom-Marietta Corporation
P.O. 5837 (MP-275)
Orlando, Florida
Attn: B. R. Rajala