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DISPERSION-STRENGTHENED VANADIUM ALLOYS

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DISCLAIMER

DISPERSION-STRENGTHENED VANADIUM ALLOYS

ABSTRACT

Arc-melting and powder metallurgy techniques are being used to incorporate fine, refractory dispersants in vanadium-columbium base alloys in order to improve their long-time elevated-temperature strength properties. Solution annealing and aging studies of arc-melted alloys containing hafnium or zirconium in combination with carbon indicate that the hafnium carbide phase is the more stable. The hydride process was used to obtain powders of V-60w/o Cb-1w/o Ti, to which fine oxide or carbide powders were added. After blending, cold-compacting, sintering at 2800° F, and annealing at 2000 and 2400° F, specimens containing alumina and thoria exhibited a high degree of reactivity with the alloy base. Improved stability was noted in the alloys containing ceria, lanthana, yttria, hafnium carbide, and zirconium carbide.

DISPERSION-STRENGTHENED VANADIUM ALLOYS

I. INTRODUCTION

This is the second bimonthly progress report under Contract N 600(19)59567, summarizing the work performed on ARF Project B6007 during the period February 14, 1963 to April 13, 1963. Previous and current studies of vanadium-columbium alloys have demonstrated their excellent fabricability, weldability, and their very high strength to weight ratios at temperatures up to 2400° F. Oxidation-protective coatings for these alloys have exhibited a remarkable defect-tolerating ability and long-time protective capabilities to at least 2400° F. One major drawback of these alloys, however, is their lack of long-time strength properties at 2000° F or higher. Improvement of these stress-rupture and creep properties is the principal objective of this program, and the experimental work involves a study of dispersion strengthening mechanisms to accomplish this objective.

The principal method for producing dispersed phases will involve the addition of carbon or other compound-forming elements to vanadium-columbium alloys complexed with highly reactive elements such as hafnium or zirconium. These alloys will be prepared by nonconsumable-electrode arc-melting techniques, and the size and distribution of the dispersed phases as influenced by thermal treatment will be studied metallographically as well as by mechanical property data. Dispersed phases will also be produced by powder metallurgy techniques. Arc-melted alloys will be hydrogenated, crushed to pass 325 mesh, blended with various fine dispersants, vacuum treated, compacted, and sintered. The stability of the various oxides or carbides used as dispersants will be evaluated metallographically and by hardness measurements after annealing treatments at 2000° F and higher. While the powder metallurgy approach may not yield

highly ductile or weldable alloys, it should provide useful data in regard to the stability of a wide range of dispersants which may possibly be incorporated in the alloy matrix by arc melting.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Arc-Melted Alloys

1. Ingot Fabrication

A series of ten alloys are currently being investigated to determine the effects of heat treatment on the stability of the carbide phases. The following compositions* have been prepared as 150-gram arc-melted ingots:

V-60Cb-1Zr with 0.05, 0.1, and 0.2C
V-60Cb-1Hf with 0.05, 0.1, and 0.2C
V-40Cb-30Ta-1Zr with 0.05 and 0.1C
V-40Cb-30Ta-1Hf with 0.05 and 0.1C

Fabrication of these alloys involved hot rolling in evacuated stainless steel cans at 2300° F, vacuum annealing at 2400° F, then either hot working (2300° F) or warm rolling (1200° F) to a thickness of about 1/8 inch. Subsequent reduction of the more ductile alloys to 0.050 inch sheet was accomplished by cold rolling.

The results of fabrication studies to date show that only the three alloys based on V-60Cb-1Zr could be rendered to 0.050 inch sheet of good quality. Of the three V-60Cb base compositions containing 1w/o hafnium, only the alloy at the 0.1w/o carbon level could be reduced to 0.050 inch sheet stock, and this material contained edge cracks. Alloys based on V-40Cb-30Ta were more difficult to work, and only one alloy (V-40Cb-30Ta-1Zr-0.1C) could be rolled to 0.1 inch stock without excessive cracking. Neither of the two V-Cb-Ta-Hf-C alloys could be hot worked without severe cracking. While good sheet was not produced from some of the ingots, sufficient stock was available for heat-treating, metallographic, and hardness studies.

* Compositions are reported in weight per cent.

2. Hardness and Metallographic Studies

The results of Vickers (10 kg) hardness measurements of six of the as-cast alloys were presented in the previous bimonthly progress report. Recent data for the remaining alloys (V-40Cb-30Ta base) show hardness levels in the as-cast condition to be in the VPN 355 to 380 range. Six of the ten compositions were fabricated to sheet which ranged in thickness from 0.050 to 0.1 inch. Metallographic specimens were cut from these sheets and solution annealed at 2600, 2800, and 3000° F for 30 minutes and rapidly chilled by dropping the specimens onto a water cooled copper plate in the bottom of the vacuum furnace. After this treatment, the samples were annealed for varying lengths of time at 2000 and 2300° F to study the effects of heat treatment upon hardness and carbide particle morphology. While data from these investigations are not complete, some trends have been observed. Table I presents data for the as-quenched hardness of six of the alloys. It may be observed that the three V-60Cb base alloys 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 relatively unchanged at the various annealing 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 reduced carbide solubility in the alloy base with agglomeration of the carbides at higher temperatures, although this has not been confirmed by metallographic observation.

After solution annealing and "quenching" the specimens were aged at 2000 and 2300° F. Although these data are incomplete, it has been observed that annealing for 50 hours at 2000° F produced hardness decreases for most of the V-60Cb base alloys, regardless of solution annealing temperature. An exception was the V-60Cb-1Hf-0.1C alloy which exhibited a rise in hardness, as did the V-Cb-Ta-Zr-C alloy. Results of aging at 2300° F are limited to 8-hour data, and little hardness or microstructural change has been observed on specimens solution annealed at 2800 and 3000° F. However, samples solution annealed at 2600° F and aged 8 hours at 2300° F exhibit a marked hardness rise for all compositions based on V-60Cb.

TABLE I

ROOM TEMPERATURE HARDNESS (VPN)
OF VANADIUM-COLUMBIUM ALLOYS

Composition, w/o	Solution Annealing Temperature		
	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

The hardness data currently being obtained on these compositions show values which indicate reduced room-temperature ductility, especially in alloys containing 0.1 or 0.2w/o carbon. These compositions are included in the studies for the purpose of obtaining data trends and also to provide greater quantities of carbides for metallographic observation. Alloys selected for mechanical property evaluation will be limited to those which exhibit better than marginal fabricability.

3. Stress-Rupture and Creep Tests

In order to screen a wide range of compositions for resistance to creep and for stress-rupture properties, it has been decided to restrict initial tests to the relatively short time intervals of 4 to 16 hours. It has previously been observed that exceptionally high purity atmospheres must be used for elevated-temperature testing of these materials, even for short-time tensile tests. Thus creep or stress-rupture tests should be conducted in oxygen- or nitrogen-free atmospheres to obtain meaningful data. Recent studies of oxidation-protective coatings for these alloys indicate that the silicide coatings protect the base metal, even after considerable plastic deformation, in 2000 and 2200°F air. It has therefore been decided to conduct the initial screening tests in air utilizing silicide coated samples. This method avoids the use of atmosphere capsules which require a considerable amount of set-up time. Specimen contamination, in the event of a coating defect or failure, would be indicated by surface appearance and by a hardness survey of the base metal after elevated-temperature air exposure.

Stress-rupture specimens have been prepared from five alloys to investigate the feasibility of utilizing coated specimens. The following compositions, including two alloys for which inert-atmosphere stress-rupture data are available for comparison, are currently being siliconized by pack cementation:

V-20Cb-5Ti
V-60Cb-1Ti
V-60Cb-1Zr-0.05C
V-60Cb-1Zr-0.1C
V-60Cb-1Zr-0.2C

Initial data will be obtained at 2000° F, with applied stresses approximately 25 to 30 per cent of the yield strength.

B. Powder Metallurgy Alloys

1. Alloy Preparation

While the feasibility of producing vanadium or columbium alloys by powder metallurgy techniques has not been adequately demonstrated, the process has been utilized for other reactive metals and will be used under this program primarily for studying the stability of dispersants in a vanadium-columbium alloy matrix. These investigations involve 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 is compacted, sintered, and annealed for varying lengths of time at temperatures in the 2000 to 2400° F range. The stability of the dispersed phase is evaluated metallographically and by hardness tests which indicate solubility in the matrix.

Initial studies utilized the alloy V-60Cb-1Ti which was hydrided 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:

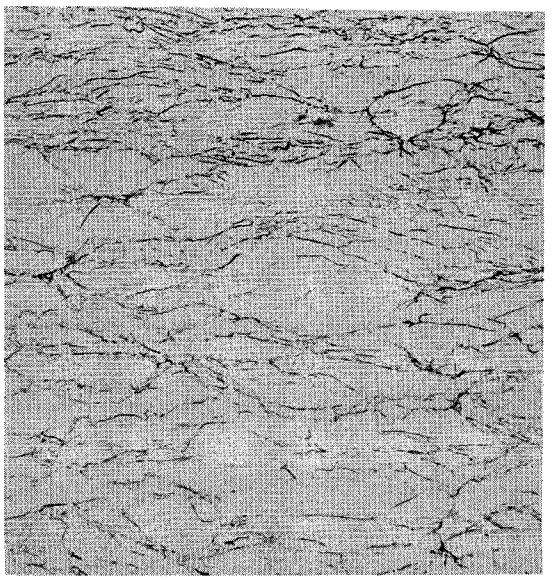
Oxides	Carbides
Al_2O_3	HfC
CeO_2	ZrC
La_2O_3	
ThO_2	
Y_2O_3	

The blended powders were compacted at 50 tsi, then sintered under vacuum for 15 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 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. Annealing Studies

The wide range of stability of the various dispersants was immediately evident upon metallographic examination after the annealing treatments at both 2000° and 2400° F. Specimens of the V-60Cb-1Ti alloy containing alumina and thoria were extremely porous, and oxides were not visible in the microstructures. Alloys containing ceria and lanthana exhibited coarse oxide agglomerates, but melting or spheroidizing of the oxides were not detected. This agglomeration may have occurred during blending of the powders prior to compacting and sintering. The specimens containing yttria were characterized by the presence of irregular oxide masses at the grain boundaries, but melting was not observed. Photomicrographs of the powder metallurgy V-60Cb-1Ti alloy and of a similar alloy base containing Y_2O_3 are presented in Figures 1 and 2. The undispersed alloy was cold-compressed to a 70 per cent reduction in height after sintering, demonstrating the room temperature ductility. The composition containing yttria (Figure 2) was annealed for 8 hours at 2400° F.

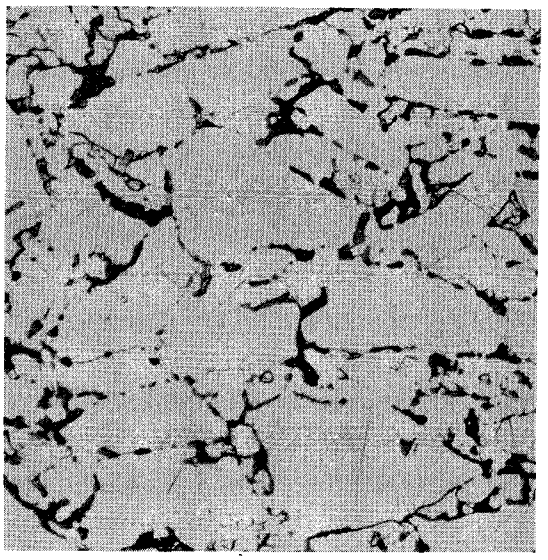
Two of the alloys contained carbide additions (HfC and ZrC). Microstructures of these materials contained mostly fine, angular carbide particles, although some rounding and agglomeration of the carbides was noted in each alloy. Metallographic specimens were not obtained after the sintering treatment, so as yet it is not known whether particle agglomeration or rounding occurred during sintering or during the subsequent annealing treatments. A limited number of hardness measurements were taken; some of the specimens contained porosity which produced erroneous hardness values. These initial experiments were conducted mainly to demonstrate the feasibility of utilizing powder metallurgy techniques to study the stability of dispersed phases in vanadium-columbium alloys. Another series of alloys containing refractory dispersants will be prepared using finer oxide or carbide powders, improved milling and blending techniques, and more detailed metallographic and hardness studies.



Neg. No. 24704 X500

Fig. 1

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. 2

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

III. SUMMARY

Refractory dispersed phases in vanadium-columbium alloys are being investigated as a means of improving the long-time elevated-temperature strength properties of the alloy base. Alloys were prepared by arc-melting and by powder metallurgy techniques. Arc-melted alloys included the V-60Cb and a V-40Cb-30Ta base with 1w/o hafnium or zirconium to which 0.05 to 0.2w/o carbon was added. Three V-60Cb-1Zr base alloys were readily fabricated to 0.050 inch sheet, while the V-60Cb-1Hf base alloys were more difficult to work. Only one of the compositions containing tantalum (V-40Cb-30Ta-1Zr-0.1C) could be fabricated to 0.1 inch thick sheet. Solution annealing of these alloys at 2600 to 3000°F, followed by aging at 2000 to 2300°F, indicate greater stability for the materials containing hafnium, although current data are too cursory to show pronounced trends. Specimens of the more fabricable alloys are being siliconized in preparation for stress-rupture tests to be conducted in 2000°F air.

Powder metallurgy alloys based on V-60Cb-1Ti were prepared by the hydride process. Refractory dispersants, oxides and carbides, were added at the 7v/o level, and the blended powders were cold-compacted, sintered at 2800°F, then annealed at 2000 and 2400°F. Specimens containing alumina and thoria exhibited severe reactions as evidenced by a large volume of porosity after the annealing treatments. Dispersed phases of ceria, lanthana, yttria, hafnium carbide and zirconium carbide appeared to be more stable.

IV. FUTURE WORK

The experimental work described in the preceding sections will be continued. Stress-rupture or creep testing of silicide-coated samples will be initiated, and some short-time (4 to 16 hour) data should become available during the subsequent reporting interval. Aging curves for the arc-melted alloys containing hafnium or zirconium in combination with carbon will be obtained. Another series of powder metallurgy alloys will be prepared with refractory oxide or carbide dispersants. Metallographic and hardness studies will be made after sintering and also after annealing for various time intervals at 2000 and 2400°F.

V. LOGBOOKS AND CONTRIBUTING PERSONNEL

Data for this report are recorded in Foundation Logbooks No. C-13170 and C-13171.

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A. L. Hess	-	Technician, Powder Metallurgy Alloys
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Respectfully submitted,

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