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Metallurgy and Ceramics

38392

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THE VANADIUM-URANIUM CONSTITUTIONAL DIAGRAM

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For The Atomic Energy Commission
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Chief, Declassification Branch

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ABSTRACT

Vanadium-uranium equilibrium studies were made on alloys prepared from high-purity vanadium and good biscuit uranium. No intermetallic phases occur in the system. Additions of vanadium lower the uranium melting point and transformations producing a eutectic at 1240 ± 5 C and eutectoid reactions at 727 ± 5 and 652 ± 5 C. The maximum solubility of uranium in vanadium is about 4 atomic per cent (15 weight per cent).

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INTRODUCTION

A study of the constitutional diagram of vanadium-uranium was started at Battelle Memorial Institute in 1949 and tentative data were presented at the February, 1950, Metallurgical Conference which was held at the Knolls Atomic Power Laboratory. More recently, the diagram was reviewed at the April, 1951, Metallurgical Conference at Oak Ridge National Laboratory. The diagram and details of the investigation leading to the diagram are summarized in this report. The diagram is believed to be adequate for general use, and no further work on these alloys is planned.

EXPERIMENTAL PROCEDURE

Materials

In order to prepare suitable alloys for equilibrium-phase studies, it is desirable to have the purest possible starting materials. For this investigation, calcium-reduced vanadium, de Boer process crystal-bar vanadium, and good Mallinkrodt Chemical Company biscuit uranium were used. The first work was done using the best vanadium then available, that being calcium-reduced vanadium produced at Knolls Atomic Power Laboratory. Subsequently, the important features of the diagram were checked using alloys made with good crystal-bar vanadium produced at Battelle. These checks were in agreement with the earlier work.

Analyses of the starting materials are contained in Table 1. Only minor amounts of any impurities were present in either the vanadium crystal bar or biscuit uranium. Nevertheless, care was exercised in selecting the uranium for the alloys. The biscuit was sectioned into suitable pieces for melting and then were macroetched. Only the cleanest pieces were used for alloying.

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TABLE 1. ANALYSES OF MATERIALS

Element Detected	Uranium Biscuit,	Iodide Vanadium, ppm
Fe	< 0.01%	150-250
Ni	"	50
Al	"	20-100
Mo	"	50
Cr	"	Trace
W	-	200
Cu	< 0.01%	50
V	"	-
Si	"	50-150
P	"	-
Mg	"	50
O ₂	-	280-370
H ₂	-	6-17
N ₂	-	40-60

Melting

Alloys with 0 to 50 atomic per cent vanadium were induction melted in beryllia crucibles. A number of remelts were frequently required to insure uniformity of the individual ingots. No visible reaction between the alloy and crucible occurred in any of these operations. This was checked by spectroscopic analysis which showed only trace amounts of beryllium in the resulting alloys.

High-vanadium alloys, 50 to 100 per cent vanadium, were arc melted in a water-cooled copper crucible under an atmosphere of helium. Ingots of 10 to 15 grams were produced readily by turning and remelting a few times. Ingots thus produced were sectioned, examined metallographically for segregation, and consolidated by remelting before fabrication was attempted. Spectroscopic analyses showed that no appreciable contamination occurred during the arc-melting process.

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Fabrication

High-uranium alloys up to 20 atomic per cent vanadium were worked readily by rolling in air at 600 C with five minutes between passes. After each pass, alloys were returned to a furnace with an atmosphere of argon. High-vanadium alloys containing up to 10 atomic per cent uranium were fabricated by jacketing in stainless steel and rolling at 1000 C with five minutes between passes.

Working of intermediate alloys was not attempted since preliminary work showed two-phase regions extending across the system with no intervening compounds. It is expected that these intermediate compositions would also be readily workable using picture-frame or jacketing techniques.

Sampling for Chemical Analysis

Samples for chemical analyses were cut from the top and bottom of small ingots of high-uranium alloys. Sampling of small arc buttons with high-vanadium content varied. Sometimes whole metallographic samples of these alloys were submitted for analysis after thorough examination.

Heat Treating

Before heat treating for metallographic examination, sections of the rolled alloys were homogenized by soaking for 40 hours at 1000 C unless other treatment was indicated. All heat treatments were made under vacuum of 10^{-3} mm of mercury or better.

Metallography

Specimens were cut using Allison, Number 46A3, cutoff wheels 0.020 inch thick. The samples were then ground wet through the usual rough papers and were finished wet on 240-, 400-, and 600-grit abrasives.

Alloys with 0 to 30 atomic per cent vanadium were polished and etched in a solution of chromic and acetic acids (Table 2). Polishing was usually complete after 30 seconds to one minute at 50 volts with a current density of approximately 20 amperes per square inch. Etching was obtained by dropping the voltage to six to ten volts in the same solution.

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Relief, sometimes troublesome in two-phase alloys, was readily avoided by polishing mechanically with stannic oxide on a billiard-cloth-covered wheel. This was followed by etching at six to ten volts in the chromic and acetic acid electrolyte. The same etch also served as a macroetch.

TABLE 2. POLISHING AND ETCHING SOLUTIONS

-
-
1. Electrolyte for high-uranium alloys.
1 part base solution - 100 grams CrO_3 and 118 ml H_2O
3 parts glacial acetic acid
 2. Electrolyte for high-vanadium alloys.
20 volume per cent conc H_2SO_4
80 volume per cent methyl alcohol
Few drops H_2O
 3. Acid etching solution for high-vanadium alloys.
1 part conc HNO_3
1 part conc HF
1 part H_2O
-
-

High-vanadium alloys, 30 to 100 atomic per cent vanadium, were prepared for examination by grinding through the same abrasive papers, finishing on a billiard cloth with stannic oxide abrasive and electropolishing for a few seconds at 10 to 20 volts. The solution for this operation consisted of sulfuric acid and methyl alcohol. The exact composition is shown in Table 2. This polish served to remove scratches and worked metal and also to etch two-phase alloys. Solid-solution-type high-vanadium alloys were further etched by swabbing with a solution of hydrofluoric and nitric acids in water, Table 2. This etch brought out grain boundaries which were not visible after the electropolishing operation.

X-Ray Examination

A general survey of the alloy system was not made by X-ray examination. However, a number of confirming checks were made on the results of other studies by making X-ray diffraction patterns from metallographic sample surfaces.

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Thermal Analysis

Thermal analyses were performed on alloys across the constitutional diagram to determine solid-phase transformations. Runs were also made for liquidus-solidus data on high-uranium alloys. Standard techniques of analysis were employed using the differential-thermocouple arrangement shown in Figure 1⁽¹⁾. The temperature differential between the neutral and active samples was plotted against the temperature of the active sample under test. Solid-phase transformations were then readily detectable in alloys containing appreciable amounts of a high-uranium phase. Best results were obtained by cycling through transformation temperatures one or more times. The data obtained by heating appeared to be most reliable and were little affected by variations of heating rates between one and five degrees C per minute. Cooling data are not considered to be reliable, since difficulty was encountered with supercooling.

Note: Thermocouple wires protected with refractory insulators
Bead is open to radiation from specimen hole

FIGURE 1. DIFFERENTIAL THERMOCOUPLE FOR THERMAL ANALYSIS

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In all this solid-phase work, the thermocouple head was protected from the uranium by refractory insulators. A piece of refractory in the specimen hole prevented contact between the thermocouple head and specimen, but allowed radiation directly between them, as shown in Figure 1. By using a fine-wire, 30-gage thermocouple, this arrangement was found to give good sensitivity at the temperatures of testing.

(1) National Bureau of Standards, Technical Paper 170, 1921.

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The best data on the liquidus-solidus determinations were obtained by heating once through the melting range. After the first melting, alloys were usually segregated and unuseable. During melting runs the thermocouples were protected by using a small BeO protection tube.

RESULTS

The Constitutional Diagram

As a result of this study, the vanadium-uranium constitutional diagram has been established and is shown in Figure 2. No intermetallic phases are formed between vanadium and uranium. The diagram is characterized, generally, by a high temperature eutectic and lowering of the uranium allotropic transitions by additions of vanadium.

The eutectic temperature and composition are 1040 ± 5 C and 18 atomic per cent vanadium. The maximum gamma-uranium solubility is 12 atomic per cent vanadium at the eutectic, decreasing to nine per cent at the eutectoid temperature of 727 ± 5 C, Figure 2. The beta-uranium solubility is less than the gamma, being about 2.0 per cent at 700 C. A second eutectoid occurs at 652 ± 5 C where the beta-uranium transforms. The alpha-solubility is less than the beta, being less than 1.5 atomic per cent at 600 C.

Four atomic per cent uranium (15 weight per cent) is soluble in vanadium at temperatures near the eutectic, 1000 C (1832 F). This decreases slightly with decreasing temperature.

Microstructures of Cast Alloys

Many of the general features just described are readily observed in the as-cast series of micrographs shown in Figures 3 to 13. A typical micrograph of arc-melted uranium is shown in Figure 3. Seven per cent vanadium produces a nonequilibrium structure having small amounts of vanadium-uranium eutectic surrounding primary uranium, Figure 4. At 15 per cent, a micrograph shows large primary-uranium islands surrounded by transformed eutectic, Figure 5. Precipitation has occurred in the primary-uranium islands due both to decreasing solubility with cooling in the gamma-phase region and to gamma- and beta-eutectoid transformations. Also, the eutectic is modified by the eutectoid transformations causing breaking up of the fine plates of the original eutectic structure.

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Weight Per Cent Vanadium

FIGURE 2. VANADIUM-URANIUM CONSTITUTIONAL DIAGRAM

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A 20 atomic per cent sample appears to be on the vanadium-rich side of the eutectic, Figure 6. Additional alloys on the vanadium side of the eutectic are shown in Figures 7, 8, and 9. The structures contain high-vanadium particles surrounded by high-uranium alloy. The eutectic in this case is not evident as a two-phase structure. This is apparently due to precipitation of vanadium on the primary-vanadium particles during the eutectic reaction.

High-vanadium alloys are shown in Figures 10, 11, and 12. A decreasing or disappearing uranium phase is observed as the vanadium content increases from 80 to 95 atomic per cent, Figures 9 and 10. At 96.2 per cent, Figure 11, only scattered particles of uranium are present while the as-cast 97.5 per cent vanadium is single phase, Figure 12. The structure of arc-melted crystal-bar vanadium is shown in Figure 13. Although the preceding microstructures do not give quantitative data on solid solubilities at equilibrium, the general nature of the diagram is readily determined.

Thermal Data

Some of the general features of the diagram have been illustrated by metallographic studies; however, as much, or perhaps more, data are also observable from a survey of thermal studies. The eutectic, gamma-eutectoid, beta-eutectoid, and even approximate solubilities might be determined from these data alone, Figure 2, although the diagram is the result of combined studies.

Metallographic Studies of Solid Solubilities

The results of metallographic studies are summarized and plotted in Figure 2. Data are shown for high-uranium alloys quenched from temperatures of 1000, 750, 700, 600, and 450 C, and for high-vanadium alloys from 1100, 1000, and 700 C.

Alloys for this work were homogenized by holding for 40 hours at 1000 C and quenching. Samples thus treated were held for appropriate times and quenched from the temperatures of interest. In determining the solubilities of vanadium in alpha uranium and of uranium in vanadium, the alloys were cold worked before heat treatment to accelerate the approach to equilibrium.

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100X

66411

FIGURE 3. 100 PER CENT URANIUM, AS CAST

250X

68352

FIGURE 4. 7 ATOMIC PER CENT VANADIUM, AS CAST

250X

68353

FIGURE 5. 15 ATOMIC PER CENT VANADIUM, AS CAST

250X

66347

FIGURE 6. 20 ATOMIC PER CENT VANADIUM, AS CAST

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250X

76006

FIGURE 7. 27 ATOMIC PER CENT VANADIUM,
AS CAST

250X

68350

FIGURE 8. 47 ATOMIC PER CENT VANADIUM,
AS CAST

250X

65402

FIGURE 9. 80 ATOMIC PER CENT VANADIUM,
AS CAST

250X

69747

FIGURE 10. 95 ATOMIC PER CENT VANADIUM,
AS CAST

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250X

69748

250X

69749

FIGURE 11. 93.2 ATOMIC PER CENT VANADIUM, AS CAST

FIGURE 12. 97.5 ATOMIC PER CENT VANADIUM, AS CAST

250X

66358

FIGURE 13. 100 PER CENT VANADIUM, AS CAST

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END