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VANADIUM-CHROMIUM
ALLOY SYSTEM

by

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VANADIUM-CHROMIUM ALLOY SYSTEM

O. N. Carlson and A. L. Eustice

Abstract--On the basis of data obtained from melting point determinations, microscopic examination, and x-ray investigations, a phase diagram is proposed for the V-Cr alloy system. The system forms a complete series of solid solutions with a minimum occurring in the solidus at 1750°C and approximately 70 w/o Cr. No intermediate phases were found in this system. Hardness and corrosion data are presented as a function of alloying composition.

INTRODUCTION

The investigation of the vanadium-chromium alloy system was undertaken because of interest in the corrosion resistance of the alloys and in the possible existence of intermediate phases in the system. Preliminary studies of vanadium-chromium alloys reported by other investigators^(1, 2) indicated that extensive solid solubility occurs in this system. No intermediate phases were reported.

This investigation confirms the results of the earlier studies and proposes a phase diagram for the system. Data are also reported for hardness, lattice constants, and corrosion resistance of a number of alloys.

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- (1) W. Rostoker and A. Yamamoto: A Survey of Vanadium Binary Systems. Trans. ASM (1954) 46, p. 1136.
- (2) H. Martens and P. Duwez: Phase Relationship in the Iron-Chromium-Vanadium System. Trans. ASM (1952) 44, p. 484.

EXPERIMENTAL PROCEDURE

Electrolytic chromium of 99+ percent purity was obtained from the Electro Metallurgical Company. The platelets were arc-melted into "buttons" and these were used in preparing the alloys.

The authors prepared the vanadium metal by reduction of vanadium pentoxide with calcium, as described by Long.⁽³⁾ Vanadium pentoxide (C.P. grade) was obtained from the Vanadium Corporation of America, and redistilled calcium was prepared by the authors for use as the reductant. The purity of the vanadium was estimated at approximately 99.7 percent based upon chemical and spectrographic analyses. The chief impurities were iron (.02 w/o), silicon (.02 w/o), oxygen (.02 w/o), carbon (.08 w/o), and nitrogen (.02 w/o). The as-reduced vanadium was arc-melted and cut into pieces of suitable size for preparation of the alloys.

Alloy Preparation

Weighed pieces of vanadium and chromium buttons were arc-melted together under a helium atmosphere. Each alloy was melted at least five times, inverting between each melt, to insure homogeneity. An appreciable weight loss was noted in the resulting alloys (which was attributed solely to the volatilization of chromium during the arc-melting). The compositions of these alloys, therefore, are reported on the basis of their weight after arc-melting.

(3) J. R. Long and H. A. Wilhelm: Preparation of Vanadium Metal.

USAEC Report No. ISC-244 (1951).

Heat Treatment

Filings from alloys in the intermediate composition range of the system were encapsulated in quartz tubes under a helium atmosphere, annealed at temperature for the time shown in Table I, and quenched in water.

Table I. Annealing Schedules for Intermediate					
Phase Investigations					
w/o Cr	Time (hours) at Temperature				
	800°C	900°C	1000°C	1100°C	1200°C
Vanadium-Chromium Alloys					
30	100				
40	100	500			170
50	100				
60	100	500			170

Alloy Examination

Metallographic specimens were mounted in bakelite and polished using conventional mechanical polishing techniques. A cathodic etching method⁽⁴⁾ was employed because chemical etching generally produced a film on the surface of the specimen. Bright field illumination was employed exclusively for the microscopic and photographic examination of the alloys.

(4) A. J. Carlson, J. T. Williams, B. A. Rogers, and E. J. Manthos: Etching Metals by Ionic Bombardment. USAEC Report No. ISC-480 (1954).

X-ray Powder Patterns

Debye-Scherrer powder patterns were taken using filtered copper $K\alpha$ radiation. Alloys containing greater than 60 w/o chromium were brittle enough to crush, but below this composition the powders were obtained by filing. These powders were annealed for 12 hours at 700°C in a helium atmosphere for use in the lattice constant determinations.

Filings of four alloys in the intermediate composition range were also annealed at 800°C for 100 hours as indicated in Table I. These were examined by x-ray techniques for possible evidence of an intermetallic phase in this system.

Determination of Solidus

Melting point measurements were made on bars prepared from the arc-melted alloys. A small sight hole was bored in the side of the bar by means of a Glennite ultrasonic drill with a short piece of tungsten wire serving as the drill bit. This method of drilling was necessary as most of the alloys were too hard and brittle to drill with ordinary tool steel or carbide-tipped drills. The melting bar was clamped between two copper electrodes and heated by passing a high current through the alloy specimen. The temperature was observed with an optical pyrometer focused on the sight hole, and the melting point was determined by noting the temperature at which liquid was first evident in the hole.

With high chromium alloys, filming of the sight glass was encountered even when run under an atmosphere of helium. To eliminate this, a tiny jet of helium was blown across the chamber at a point a few

millimeters above the ~~sight~~hole in the specimen, thus clearing chromium vapors from the line of sight. The change in alloy composition due to volatilization of chromium during this determination was found to be quite small, however, as indicated by the reproducibility of the melting point upon repeated runs with the same specimen.

EXPERIMENTAL RESULTS

A proposed equilibrium diagram for the vanadium-chromium system is shown in Fig. 1. The system exhibits mutual solid solubility across the entire system beneath the solidus. The melting points of the various alloys, as determined by the optical pyrometer method, are plotted in Fig. 1. The solidus curve, which is constructed from these points, exhibits a minimum at approximately 70 w/o chromium and $1750^{\circ}\text{C} \pm 10^{\circ}\text{C}$.

Alloys across the system were examined microscopically in the as-arc-melted condition with all of them exhibiting one-phase microstructures. Annealing of massive samples of the 40 and 60 w/o chromium alloys at 900°C for 500 hours and at 1200°C for 170 hours failed to produce any change in the microstructure. The photomicrograph of the annealed 40 w/o chromium alloy (Fig. 2) is typical of all the microstructures observed in this system. Filings from the 30, 40, 50, and 60 w/o chromium alloys were annealed for 100 hours at 800°C . A body-centered cubic solid solution phase was identified from the x-ray diffraction pattern of each of these annealed specimens.

Further confirmation of these observations was obtained from powder data taken on the series of alloys annealed at 700°C for 12 hours. The

Fig. 1 - Proposed Phase Diagram for Vanadium-Chromium System.

Fig. 2 - 40 w/o Cr Alloy Annealed at 900°C for
500 Hours. One phase, solid solution
alloy. Cathodically etched. 250X.

lattice constant of each alloy was determined by an extrapolation of the Nelson-Riley function, ⁽⁵⁾ $1/2 \frac{\cos^2 \theta}{\sin \theta} - \frac{\cos^2 \theta}{\theta}$, to $\theta = 90^\circ$. The values obtained by this method are plotted in Fig. 3 as a function of atomic percent chromium. The negative deviation from Vegard's law, which was observed, frequently occurs in systems exhibiting a minimum in the solidus. It is therefore concluded that no compounds or regions of solid immiscibility occur in this system.

It should be noted that the melting points reported for vanadium and chromium are lower than the values frequently found in the technical literature. These values were obtained on the commercial grades of metal employed in this investigation. A melting point of $1890^\circ\text{C} \pm 15^\circ\text{C}$ was obtained on some vanadium prepared by the iodide process. Likewise, a few grams of high purity chromium metal were obtained from the U.S. Bureau of Mines at Albany, Oregon. The melting point of this metal was determined to be $1845^\circ\text{C} \pm 15^\circ\text{C}$. The amounts of the common interstitial impurities in these materials are listed in Table II. From these values it is probable that the solidus and liquidus curves indicated in the proposed diagram are displaced a few degrees below their true equilibrium positions.

(5) J. B. Nelson and D. P. Riley: An Experimental Investigation of Extrapolation Methods in the Derivation of Accurate Unit-Cell Dimensions in Crystals. Proc. Phys. Soc. (London) (1944) 57, p. 160.

Fig. 3 - Lattice Constant vs Atomic Percent Chromium
for V-Cr Alloys.

Table II. Interstitial Impurity Content of High Purity V and Cr.

Impurity	w/o in Vanadium	w/o in Chromium
Oxygen	0.01	0.0080
Nitrogen	0.005	0.0050
Carbon	0.02	----
Hydrogen	0.001	0.0008

No evidence was found in this investigation for the high temperature allotropic modification reported by Stein and Grant.⁽⁶⁾ If such a crystalline modification does exist, the low temperature form could be stabilized by the addition of a few percent of vanadium by a peritectic reaction. In an attempt to establish the presence of such a two phase field, 0.5 and 1.0 w/o vanadium alloys were prepared from the high purity ingredients. These alloys were annealed at approximately 1810°C for 4 hours and quenched. Microscopic examination of the quenched specimens failed to reveal a two phase structure which would have been evidence for the phase transformation.

PROPERTIES OF ALLOYS

In addition to a study of the phase equilibrium of this system, a survey was made of the hardness and corrosion properties of vanadium-chromium binary alloys. A plot of hardness versus composition

⁴(6) C. Stein and N. J. Grant: Chromium-Rich Portion of the Cr-Ni Phase Diagram. Trans. AIME (1955) 203, p. 127; Journal of Metals (January 1955).

(see Fig. 4) gives a symmetrically shaped curve with a maximum at approximately 50 atomic percent. This behavior, which is typical of solid solution hardening, was expected for a system of this type.

The oxidation properties of tantalum-vanadium binary alloys were studied as a function of composition. Tests were carried out on alloys at ten percent composition intervals across the system and on the pure components. Data from tests made at 500°C for 600 hours are presented in Table III. At temperatures above 500°C the oxidation rate of vanadium and the alloys increases catastrophically due to the formation of a low melting, nonprotective oxide of vanadium. A curve obtained from a plot of these data (see Fig. 5) shows graphically the effect of chromium on the oxidation properties of vanadium.

Table III. - Weight Gain of V-Cr Alloys after 600 Hours in 500°C Air.

Alloy Composition	Weight Gain (mg/cm ²)
100V	32.5
90V - 10Cr	25.5
80V - 20Cr	19.5
70V - 30Cr	3.0
61V - 39Cr	4.0
50V - 50Cr	6.5
40V - 60Cr	2.0
30V - 70Cr	1.5
20V - 80Cr	2.4
10V - 90Cr	1.5
100Cr	0.5

Fig. 4 - Hardness vs Composition for V-Cr Alloys.

Fig. 5 - Oxidation Rate after 600 Hours for
V-Cr Alloys.

SUMMARY

The investigation of the vanadium-chromium alloy system revealed the following features:

1. The system consists of a complete series of solid solutions.
2. A minimum exists in the solidus at 70 w/o Cr and 1750°C.
3. No intermediate phases exist at the temperatures investigated.
4. The rate of oxidation of V-Cr alloys exhibits a pronounced increase at 30 w/o Cr at 500°C.