

ELECTRICAL RESISTIVITY OF V-Cr-Ti ALLOYS — S. J. Zinkle, A. N. Gubbi, and W. S. Eatherly (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this report is to summarize electrical resistivity measurements on vanadium alloys containing 3-6% Cr and 3-6% Ti.

SUMMARY

Room temperature electrical resistivity measurements have been performed on vanadium alloys containing 3-6%Cr and 3-6%Ti in order to evaluate the microstructural stability of these alloys. A nonlinear dependence on Cr and Ti concentration was observed, which suggests that either short range ordering or solute precipitation (perhaps in concert with interstitial solute clustering) has occurred in V-6Cr-6Ti.

PROGRESS AND STATUS

Introduction

Vanadium alloys with solute contents near 4% Cr and 4% Ti are being considered for fusion energy structural applications. The microstructure of these alloys has been characterized as a solid solution bcc phase, with a moderate density of Ti-rich precipitates that are associated with O,C,N interstitial impurities [1-3]. Phase stability studies on V-Ti alloys have reported conflicting results regarding the possible existence of a miscibility gap [4-6]. If such a miscibility gap was present, then precipitation of alpha-titanium would be energetically favorable in alloys containing more than ~5-10%Ti at temperatures below ~500°C, although the kinetics of the precipitation would be very slow. Recent ultrasonic acoustic measurements suggest that there may be periodic compositional fluctuations in V-(4-10%)Cr-(4-10%)Ti alloys [7]. It would be anticipated that radiation enhanced diffusion would accelerate phase decomposition during neutron irradiation, which might cause a degradation in the ductility of the alloy. In the present study, we have employed electrical resistivity measurements to investigate the phase stability of V-(3-6%)Cr-(3-6%)Ti alloys following various thermomechanical treatments.

Experimental Procedure

The electrical resistivity measurements were performed on type SS-3 sheet tensile specimens with nominal gage dimensions of 0.76x1.52x7.6 mm and an overall length of 25.4 mm. Sheet tensile specimens of V-3%Cr-3%Ti (heat T91), V-6%Cr-3%Ti (heat T92), V-5%Cr-5%Ti (heat T87), and V-6%Cr-6%Ti (heat T90) were punched or electro-discharge machined from 0.76 mm thick sheets from several 15 kg vanadium alloy heats fabricated by Teledyne Wah Chang, Albany, Oregon (TWCA). The V-4%Cr-4%Ti tensile specimens were either punched from 0.76 mm sheet which was cold rolled at ORNL from 1.0 mm thick sheet received as part of a 500 kg heat from TWCA (heat #832665), or else electro-discharge machined from the 1.0 mm sheet. Several specimens were annealed for 2 h at temperatures ranging from 900 to 1100°C (furnace cool) in a vacuum better than 1×10^{-6} torr ($< 10^{-4}$ Pa). The chemical composition of the alloys (for solute contents >20 wt. ppm) is summarized in Table 1 [8].

Four-point probe electrical resistivity measurements were performed on the SS-3 tensile specimens following the general recommendations summarized in ASTM Standard Method of Test for Resistivity of Electrical Conductor Materials, ASTM B193-87 (reapproved 1992). The distance between the

Table 1. Chemical composition (at. ppm unless indicated otherwise) of the solutes and major impurities in the vanadium alloys examined in this study [8].

Element	V-3Cr-3Ti (T91)	V-6Cr-3Ti (T92)	V-4Cr-4Ti (832665)	V-5Cr-5Ti (T87)	V-6Cr-6Ti (T90)
Cr	2.86 at.%	5.92 at.%	3.68 at.%	4.70 at.%	5.62 at.%
Ti	3.25 at.%	3.18 at.%	4.15 at.%	5.3 at.%	6.35 at.%
C	510	440	340	470	440
N	220	340	310	320	310
O	730	890	990	1210	800
Al	380	480	300	300	440
Si	1710	1730	1420	990	1740
Fe	120	150	200	150	180
Cu	66	110	—	62	44
Mo	200	200	—	270	180

spring-loaded voltage contacts was 7.10 mm. The temperature was recorded for each measurement and the resistivity data were corrected to a reference temperature of 20°C using the V-Cr-Ti temperature coefficient for resistivity of $dp/dT = 0.75 \text{ n}\Omega\text{-m/K}$ [9-13]. A Keithley 237 Source Measure Unit was used to supply a constant current of 100 mA, and the voltage drop was measured with a Keithley 182 Sensitive Digital Voltmeter equipped with a low thermal connector cable. Thermal emf offset potentials were subtracted using the "relative reading" offset function on the Keithley 182. The specimen thickness and width were measured to a nominal accuracy of $\pm 1 \mu\text{m}$ in two different gage locations with a Mitotoyo precision digital micrometer in order to convert the resistance measurements to resistivity values. Nonuniformities in the width and thickness in the specimen gage region caused the typical experimental uncertainty of individual resistivity measurements to be $\pm 0.5\%$. A minimum of two different unirradiated specimens were tested for each thermomechanical condition.

Results and Discussion

Table 2 summarizes the results of the electrical resistivity measurements. A moderate scatter in the resistivity data ($\pm 5 \text{ n}\Omega\text{-m}$) was obtained from different lots of specimens machined from a given heat that were given nominally identical heat treatments, which suggests that there may be some slight inhomogeneities in the chemical composition at different positions within each alloy heat. The resistivity data did not exhibit any systematic dependence on heat treatment (900-1100°C) or cold-work level (0-24%), partly because of the aforementioned variability of resistivity data obtained from different specimen lots in the same alloy heat. A previous study reported that a cold work level of 16% produced a resistivity increase of $\sim 3.5 \text{ n}\Omega\text{-m}$ in vanadium [14]. Therefore, a significantly higher resistivity would have been expected for the 24% cold-worked specimens compared to the annealed specimens in this study.

Table 2. Summary of electrical resistivity measurements, including standard error of the mean.

V-3Cr-3Ti	V-4Cr-4Ti	V-6Cr-3Ti	V-5Cr-5Ti	V-6Cr-6Ti
$276.8 \pm 1.5 \text{ n}\Omega\text{-m}$ (11 specimens)	$285.4 \pm 0.5 \text{ n}\Omega\text{-m}$ (66 specimens)	$281.1 \pm 1.3 \text{ n}\Omega\text{-m}$ (8 specimens)	$304.4 \pm 0.8 \text{ n}\Omega\text{-m}$ (10 specimens)	$302.0 \pm 1.1 \text{ n}\Omega\text{-m}$ (11 specimens)

Table 3. Summary of vanadium electrical resistivity literature.

	Resistivity	Reference
Pure Vanadium		
base resistivity	$\rho_V=196 \text{ n}\Omega\text{-m}$	[9-12]
temperature coefficient	$d\rho_V/dT=0.75 \text{ n}\Omega\text{-m/K}$	[9-12]
dislocation resistivity	$\Delta\rho_d=3.5 \text{ n}\Omega\text{-m for 16\%CW}$	[14]
Solute		
Ti	$\rho_{Ti} \geq 15.5 \text{ n}\Omega\text{-m/at.}\%Ti$	[10]
Cr	$\rho_{Cr}=4.0 \text{ n}\Omega\text{-m/at.}\%Cr$	[13]
H	$\rho_H \sim 10 \text{ n}\Omega\text{-m/at.}\%H$	[15,16]
O	$\rho_O=52 \text{ n}\Omega\text{-m/at.}\%O$	[17,18]
N	$\rho_N=50 \text{ n}\Omega\text{-m/at.}\%N$	[17]
C	$\rho_C \sim 90 \text{ n}\Omega\text{-m/at.}\%C$	[19]
Mo	$\rho_{Mo} \sim 5 \text{ n}\Omega\text{-m/at.}\%Mo$	[20]
W	$\rho_W \sim 3 \text{ n}\Omega\text{-m/at.}\%W$	[20,21]
Ta	$\rho_{Ta}=13 \text{ n}\Omega\text{-m/at.}\%Ta$	[22]
Re	$\rho_{Re} \geq 10 \text{ n}\Omega\text{-m/at.}\%Re$	[23]
Nb	$\rho_{Nb} \sim 8 \text{ n}\Omega\text{-m/at.}\%Nb$	[21]

Table 4. Calculated resistivity contributions (nΩ-m) from solute atoms in the vanadium alloys.

Element	V-3Cr-3Ti	V-6Cr-3Ti	V-4Cr-4Ti	V-5Cr-5Ti	V-6Cr-6Ti
V	196	196	196	196	196
Cr	11.4	23.7	14.7	18.8	22.5
Ti	52.0	50.9	66.4	84.8	101.6
O,C,N	9.5	10.3	9.8	12.1	9.7
Al,Si,Fe,Cu,Mo	2.4	2.6	2.4	1.6	2.5
Total	271.3	283.5	289.3	313.3	332.3

The resistivity increased with increasing Cr and Ti solute content, with Ti exerting a stronger influence than Cr on an atom percent basis. The measured resistivity values were compared with the resistivities calculated from Matthiessen's rule

$$\rho = \rho_V + \rho_{Cr} \cdot X_{Cr} + \rho_{Ti} \cdot X_{Ti} + \rho_C \cdot X_C + \rho_N \cdot X_N + \dots \quad (1)$$

where ρ_V is the resistivity of pure vanadium (196 nΩ-m) [9-12] and ρ_i and X_i are the specific resistivity (nΩ-m/at.%) and atomic concentration of the *i*th solute species. The calculations used experimental specific resistivities that have been measured for various solute atoms in vanadium, as summarized in Table 3. The resistivities of the Al, Si, Fe, Cu, and Mo solutes were assumed to be ~10 nΩ-m/at.%, based on data for W, Ta, Re and Nb solutes in vanadium [20-23]. The results of the calculation are shown in Table 4. In all of the alloys, Ti had the largest solute contribution to the calculated resistivity.

Figure 1 compares the measured and calculated electrical resistivities of the five alloys. The experimental and calculated values are in good agreement (<2% difference) for V-3%Cr-3%Ti, V-6%Cr-3%Ti and V-4%Cr-4%Ti. On the other hand, the measured resistivities for the V-5%Cr-5%Ti and V-6%Cr-6%Ti alloys were significantly lower than the calculated values. The data for all of the alloys except for V-6%Cr-6%Ti could be equally well fitted by a Matthiessen equation consisting of an effective base vanadium resistivity of 215 nΩ-m and lower specific resistivities for Cr and Ti solutes compared to the literature values. This

suggests that a resistivity component associated with a moderate amount of chemical ordering or precipitation (e.g., Ti(O,C,N) precipitates) may be present in all of the alloys. The large discrepancy for the V-6%Cr-6%Ti alloy, where the measured resistivity was 10% less than the calculated value, suggests that a more pronounced chemical ordering or precipitation process may be occurring for the alloys containing 5-6% Ti. It should be noted that the measured resistivity in the V-6%Cr-6%Ti alloy was less than that for the V-5%Cr-5%Ti alloy.

As noted in the introduction, a previous study has reported the existence of a miscibility gap in binary V-Ti alloys [5]. Conversely, another study refuted the existence of the miscibility gap [6]. The nonlinear dependence of the resistivity in the present study (particularly for V-5-6%Cr-5-6%Ti alloys) is evidence for some type of phase instability, but further microstructural work is needed to investigate this issue. X-ray diffraction studies on these alloys are currently in progress, and the results will be summarized in the next reporting period.

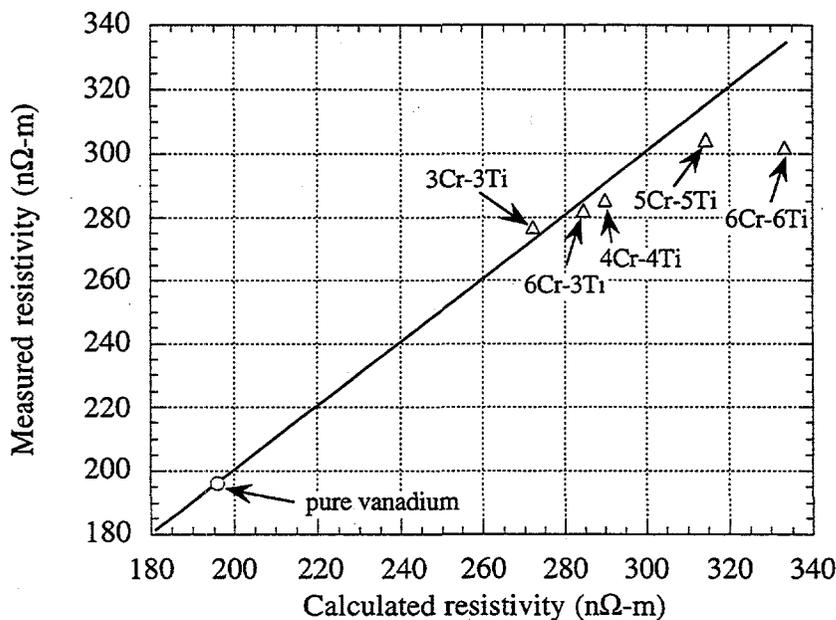


Fig. 1. Comparison of measured and calculated electrical resistivity for the 5 vanadium alloys.

References

- [1] T. Schober and D.N. Braski, *Metall. Trans. A* 20 (1989) 1927.
- [2] H.M. Chung, L.J. Nowicki, and D.L. Smith, in *Fusion Reactor Materials Semiannual Progress Report for Period ending September 30, 1991*, DOE/ER-0313/11 (Oak Ridge National Lab, 1991) p. 215.
- [3] M. Satou and H.M. Chung, in *Fusion Reactor Materials Semiannual Progress Report for Period ending September 30, 1992*, DOE/ER-0313/13 (Oak Ridge National Lab, 1992) p. 227.
- [4] M. Enomoto, *Journal of Phase Equilibria* 13 (1992) 195.
- [5] O. Nakano, H. Sasano, T. Suzuki and H. Kimura, in *Titanium '80 (Proc. 4th Int. Conf. on Titanium)* vol. 2, eds. H. Kimura and O. Izumi, 1980) p. 2889.
- [6] F. Wei and H.M. Flower, *Mater. Sci. Technol.* 5 (1989) 1172.

- [7] V.M. Chernov, personal communication.
- [8] A.N. Gubbi, A.F. Rowcliffe, and W.S. Eatherly, in Fusion Materials Semiannual Progress Report for Period ending March 31, 1995, DOE/ER-0313/18 (Oak Ridge National Lab, 1995) p. 187.
- [9] G.T. Meadon, Electrical resistance of metals (Plenum, New York, 1965).
- [10] E.W. Collings, Phys. Rev. B 9 (1970) 3989.
- [11] B.N. Aleksandrov et al., Sov. J. Low Temperature Phys. 1 (1975) 1904.
- [12] V.E. Peletskii, High Temperature 16 (1978) 57.
- [13] A. Giannuzzi, H. Tomaschke, and K. Schroeder, Philos. Mag. 21 (1970) 479.
- [14] M. Eto and M. Narutani, J. Mater. Sci. Lett. 9 (1974) 1902.
- [15] E. Lang and J. Bressers, Z. Metallkde. 67 (1976) 66.
- [16] H.P. Bleichert, Kernforschungsanlage Jülich, Jülich, Germany Report Jül-2005 (1985).
- [17] G. Hörz, Z. Metallkde. 61 (1970) 371.
- [18] E. Lang and J. Bressers, Z. Metallkde. 66 (1975) 619.
- [19] J.T. Stanley, J.M. Williams, W.E. Brundage, and M.S. Wechsler, Acta Metall. 20 (1972) 191.
- [20] I.P. Druzhinina, A.A. Fraktovnikova, and T.M. Vladimirskaia, High Temperature 14 (1976) 200.
- [21] M.V. Vedernikov, V.G. Dvunitkin, and A. Zhmagulov, Sov. Phys. Solid State 20 (1978) 1904.
- [22] N.A. Chernoplekov et al., Phys. Met. Metallogr. 36 (1973) 72.
- [23] I.P. Druzhinina, A.A. Fraktovnikova, and T.M. Vladimirskaia, High Temperature 14 (1976) 579.