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Title: Intermediate Phases in Binary Systems of Technetium-99
with Several Transition Elements

Authors: J. B. Darby, Jr., D. J. Lam, L. J. Norton, and
J. W. Downey

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Intermediate Phases in Binary Systems of Technetium-99 with
Several Transition Elements

by

J. B. Darby, Jr., D. J. Lam, L. J. Norton, and J. W. Downey

Abstract

An exploratory survey has been made of the intermediate phases formed when Tc-99 is alloyed with the Sc, Ti, V, Cr, Mn and Fe-group elements. A total of nineteen intermediate phases were identified and found to be isomorphous with the Cr_3O -type, CsCl-type, MgZn_2 -type, chi-phase or sigma-phase structure. The alloying characteristics of Tc are rationalized in terms of periodic table relationships.

Introduction

A large amount of information has been accumulated on the occurrence of intermediate phases in systems involving all of the transition elements except the Mn-group element Tc. This element has not been available in the quantities required for conventional experimental methods. The recent availability of gram quantities of the stable isotope Tc-99 from the Oak Ridge National Laboratory has prompted the present survey of the intermediate phases that occur in binary systems of Tc with other transition elements. The work reported in this paper is concerned with alloys containing the transition elements of the Sc, Ti, V, Cr, Mn, and Fe groups.

Ageev et al⁽¹⁾ have discussed the alloying characteristics of Mn-group elements with other transition elements in terms of periodic table relation-

ships. Their prediction that the alloying behavior of Tc should be similar to that of Re has received partial verification by the work of Compton et al.⁽²⁾ who identified the presence of the chi-phase at the compositions ZrTc_6 and NbTc_3 and which are the Tc analogs of the chi-phases occurring in the system Zr-Re⁽³⁾ and Nb-Re⁽⁴⁾. Further support was obtained by the present authors who found chi-phases in the Sc-Tc, Ti-Tc, Hf-Tc and Ta-Tc systems⁽⁵⁾. Some additional similarities in the behavior of Tc and Re have been brought to light in the present study. On the other hand, the formation by Tc of Cr_3O -type and CsCl-type phases has no parallel in the alloy chemistry of Re.

Experimental Procedure

The Tc metal, received in the form of powder, was melted under an argon-helium mixture at a pressure approaching one and one-half atmospheres. The arc melting produced a button which weighed approximately 10 pct less than the initial charge of powder. It is believed that the weight loss resulted from the presence of TcO_2 in the as-received material which vaporized in the arc and deposited on the water-cooled surfaces of the furnace during the melting process. Remelting of the button produced no further weight loss.

Typical analyses of the starting materials are given in Tables I and II. A Tc-rich alloy, usually containing 87.5 atomic pct Tc was prepared, annealed, and examined. The alloy was remelted together with an additional quantity of the second component to achieve the next composition desired. After the initial alloy was diluted twice, a new alloy was made to achieve the next desired composition in order to reduce the uncertainty of the alloy composition. Because of the limited amount of Tc metal available,

only X-ray metallography was used for phase identification.

In most cases samples for X-ray diffraction were prepared both from as-cast and annealed material. The alloys were sealed in evacuated quartz capsules, given a homogenization anneal between 1050 and 1075°C and water quenched. A few of the alloys were examined after this thermal treatment. Most of the alloys were given a subsequent anneal at 700°C for at least 48 hours and quenched. Powder specimens were prepared from the bulk material by conventional techniques and were given a strain-relief anneal. The latter procedure was omitted when the alloy was brittle.

Results and Discussion

An examination of four alloys in each of the systems, Tc-Re, Tc-Ru and Tc-Os indicated that they are characterized by a continuous series of hcp solid solutions. Figures 1, 2 and 3 show the lattice parameters as a function of composition in alloys quenched from 700°C.

The fifteen intermediate phases which have been identified in the present work, together with four intermediate phases previously reported, are given in Table III. Their lattice parameters were determined from alloys which gave single phase X-ray diffraction patterns. It should be stressed that the alloy compositions given in the table are approximate and do not define the precise composition limits of the associated phases. All phases identified belong to one of five well-known structure types: chi, Cr_3O , CsCl, MgZn_2 and sigma. In addition, three unidentified intermediate phases were observed in Sc-Tc alloys containing approximately 25, 60, and 80 at % Sc. In the following discussion, elements to the left of the Mn-group in the periodic table are designated as A-components while elements

to the right of the Cr-group are designated as B-components.

Chi-phases, which are isostructural with α -Mn, have been found in alloys of Tc with Sc, Ti, Zr, Hf, Nb, and Ta. The compositions of the chi-phases exhibit systematic shifts which depend upon the periodic table positions of the components. Although uncertainties exist as to the exact composition limits, it is clear from Table III that the minimum concentration of the A-component required to stabilize the chi-phase decreases as the periodic table positions of the stabilizing elements shift progressively farther to the left of Tc.

The absence of a chi-phase in the V-Tc system suggests that it is stabilized in Tc alloys only by alloying with A-partners whose radii are larger than that of Tc. The present results are consistent with the point of view expressed by Nevitt⁽⁶⁾ that both electronic structure and atomic size govern the occurrence of chi-phases.

A Cr_3O -type phase was found in the Mo-Tc binary system. This structure has not previously been observed in systems having a Mn-group element as the B-component. A diffraction pattern of an as-cast alloy with 40 atomic pct Mo contained only the lines of this phase. However, when the alloy was annealed at 1050°C and subsequently at 700°C, the X-ray results showed the presence of both a sigma and a Cr_3O -type phase. A more detailed investigation of annealed alloys indicated that the latter phase occurs in the vicinity of 46 atomic pct Mo and thus its composition exhibits a unique deviation from the usual A_3B stoichiometry. Should Mo and Tc atoms randomly occupy the lattice sites in the structure, a more appropriate designation for the structure would be βW -type rather than Cr_3O -type⁽⁶⁾. The atomic scattering factors of Mo and Tc are unfavorable for a study of atomic

ordering by X-ray intensity measurements.

The occurrence of CsCl-type phases in the systems Ti-Tc, V-Tc, Hf-Tc and Ta-Tc in the present study together with that reported in the alloy VMn⁽⁷⁾ demonstrate that the selection of the B-component is less restricted as regards its periodic table group than previous data had suggested⁽⁸⁾.

It is noteworthy, however, that no corresponding CsCl-type phases are known to occur in Re binary systems and thus a similarity in the alloying behavior of Tc and Re is not evident in this instance.

The present results on the occurrence of Laves phases supports Dwight's prediction⁽⁹⁾ that the MgZn₂-type structure should be favored when Tc is paired with the transition elements Sc, Zr, and Hf.

In the formation of sigma phases two features appear significant in comparing the behavior of Tc with that of Mn and Re. First, Mn and Re form the sigma phase with elements of the V and Cr-groups, whereas Tc forms sigma phases only with Cr-group elements. In this respect Tc resembles Ru more closely than it does Mn and Re. Because of the restricted scope of the present study it is, of course, possible that sigma phases involving V, Nb and Ta do exist but have escaped detection. The second feature concerns the parallel behavior of Tc and Re in forming sigma phases with Mn and Fe. The phase (Tc,Mn) σ has been studied only in one as-cast alloy, and its composition range is uncertain.

Figure 4 shows the average concentration of Tc and Re⁽⁴⁾ in the sigma phases which they form with first long period partners, plotted as a function of group number of the second component. The similarity in the shift in average composition with group number is clearly demonstrated.

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Table I. Typical spectrographic analysis of impurities
in Tc-99 metal

<u>Element</u>	<u>Impurity content less than (ppm by weight)</u>
Ag	200
Al	300
B	500
Ba	100
Be	1
Bi	500
Ca	200
Cd	500
Co	200
Cr	50
Cs	5000
Cu	2000
Eu	100
Fe	500
Ga	100
Hf	200
K	200
La	100
Li	1
Mg	50
Mn	20
Mo	100
Na	1000
Ni	200
Pb	200
Rh	200
Ru	200
Sb	5000
Sc	100
Sn	1000
Sr	1
Th	1000
Ti	200
U	1000
V	200
W	1000
Y	100
Zn	1000
Zr	200

Table II. Typical analysis of impurities in transition
metals in weight percent

	Th	Zr	Hf	V	Nb	Ta	Mo	W
Al	0.005		0.01					
Co	0.003							
Cr	0.002	0.003						
Cu	0.003	0.0007	0.05					0.005
Fe	0.002	0.04	0.05		0.010	0.015	0.005	0.005
Hf		0.05						
Mg	0.003							
Mn	0.003							
Nb		0.01				0.02		
Ni	0.0001							
Si	0.005	0.015			0.015			0.02
Ta		0.05			0.16			
Th		0.002			0.025	0.05		
V		0.002						
W		0.01						
Zr	0.05		4.0					
C	0.001			0.028	0.2	0.01	0.003	
O ₂	0.002		0.1	0.05			0.003	0.04
N ₂	0.002		0.007	0.027				

Table III. Crystal structures and lattice parameters for intermediate phases found in this investigation

Alloy System	Phases Identified	Composition Atomic %	Heat Treatment	Lattice Parameters
Sc-Tc	chi	12.5 Sc	As-Cast	$a_0 = 9.509 \pm 0.001$
	MgZn ₂	33.3 Sc	700°C	$a_0 = 5.223 \pm 0.001$ $c_0 = 8.571 \pm 0.001$ $c/a = 1.641$
Ti-Tc	chi	12.5 Ti	As-Cast	$a_0 = 9.579 \pm 0.001$
	chi	14.3 Ti	As-Cast	
	CsCl	33.3 Ti	700°C	
	CsCl	50 Ti	700°C	$a_0 = 3.110 \pm 0.005$
Zr-Tc	chi	14.3 Zr	700°C	$a_0 = 9.637 \pm 0.001$
	MgZn ₂	33.3 Zr	700°C	$a_0 = 5.219 \pm 0.001$ $c_0 = 8.655 \pm 0.001$ $c/a = 1.658$
Hf-Tc	chi	12.5 Hf	As-Cast	$a_0 = 9.603 \pm 0.001$
	chi	14.3 Hf	700°C	
	MgZn ₂	33.3 Hf	700°C	$a_0 = 5.200 \pm 0.001$ $c_0 = 8.616 \pm 0.001$ $c/a = 1.657$
	CsCl	50 Hf	700°C	$a_0 = 3.270 \pm 0.004$
V-Tc	CsCl	50 V	700°C	$a_0 = 3.025 \pm 0.005$
Nb-Tc	chi	14.3 Nb	700°C	$a_0 = 9.547 \pm 0.001$
	chi	25 Nb	700°C	
Ta-Tc	chi	16.6 Ta	As-Cast	$a_0 = 9.565 \pm 0.001$
	chi	20 Ta	As-Cast	
	CsCl	50 Ta	700°C	$a_0 = 3.172 \pm 0.003$
Cr-Tc	sigma	25 Cr	700°C	$a_0 = 9.290 \pm 0.003$ $c_0 = 4.846 \pm 0.001$ $c/a = 0.521$

Table III (cont'd.)

Alloy System	Phases Identified	Composition Atomic %	Heat Treatment	Lattice Parameters
Cr-Tc (cont'd)	sigma	40 Cr	700°C	$a_o = 9.217 \pm 0.001$ $c_o = 4.803 \pm 0.001$ $c/a = 0.521$
Mo-Tc	sigma	30 Mo	1050°C	$a_o = 9.509 \pm 0.001$ $c_o = 4.945 \pm 0.001$ $c/a = 0.520$
	Cr ₃ O	40 Mo	As-Cast	$a_o = 4.934 \pm 0.001$
	Cr ₃ O* + trace of sigma	44 Mo	1050°C	$a_o = 4.941 \pm 0.001$
	Cr ₃ O* + trace of α-Mo	47 Mo	1050°C	$a_o = 4.942 \pm 0.001$
W-Tc	sigma	25 W	1050°C	$a_o = 9.479 \pm 0.005$ $c_o = 5.166 \pm 0.005$ $c/a = 0.545$
Tc-Mn	sigma	40 Mn	As-Cast	$a_o = 9.15 \pm 0.01$ $c_o = 4.80 \pm 0.01$ $c/a = 0.525$
Tc-Fe	sigma	40 Fe	1075°C	$a_o = 9.130 \pm 0.005$ $c_o = 4.788 \pm 0.005$ $c/a = 0.524$
	sigma	50 Fe	700°C	$a_o = 9.077 \pm 0.003$ $c_o = 4.756 \pm 0.003$ $c/a = 0.524$
	sigma	60 Fe	700°C	$a_o = 9.010 \pm 0.001$ $c_o = 4.713 \pm 0.001$ $c/a = 0.523$

*The single phase region occurs somewhere between these two compositions.

Figure Captions

- Figure 1. Lattice Parameters as a Function of Re Content in Tc-Re Binary System
- Figure 2. Lattice Parameters as a Function of Ru Content in Tc-Ru Binary System
- Figure 3. Lattice Parameters as a Function of Os Content in Tc-Os Binary System
- Figure 4. Average Tc or Re Content in Sigma Phases as a Function of Group Number of the Second Component

Figure 1. Lattice Parameters as a Function of Re Content in Tc-Re Binary System. Micro No. 34297

Figure 2. Lattice Parameters as a Function of Ru Content in Tc-Ru Binary System. Micro No. 34296

Figure 3. Lattice Parameters as a Function of Os Content in Tc-Os Binary System. Micro No. 34295

Figure 4. Average Tc or Re Content in Sigma Phases as a Function of Group Number of the Second Component. Micro No. 34299