## Provisional

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## The Mo-Ti (Molybdenum-Titanium) System

95.94 amu

47.88 amu

By J. L. Murray

### **Equilibrium Diagram**

The equilibrium phases of the Ti-Mo system are (1) the liquid, (2) the body-centered cubic ( $\beta$ ) solid solution. Ti and Mo are completely miscible above the transformation temperature of pure titanium (882 °C), and (3) the close-packed hexagonal ( $\alpha$ ) solid solution with restricted solubility of Mo in Ti below 882 °C.

Two conflicting descriptions of the phase stability of the  $\beta$  phase have been presented in the literature. [51HAN], [51DUW], [70RON] and [72RON] found that the temperature of the  $\beta$  transus decreases monotonically with Mo content. The curvature of the  $\beta/(\alpha+\beta)$  boundary suggests a metastable  $\beta$ -phase miscibility gap, submerged within the equilibrium  $(\alpha + \beta)$  region. This phase diagram is corroborated by diffusion experiments.

[77TER] provide evidence of a monotectoid  $\beta$  phase separation. The critical composition and temperature of the  $\beta$  miscibility gap are 20 at.% Mo and 795 °C; the monotectic temperature of the three-phase equilibrium ( $\alpha + \beta_1 + \beta_2$ ) is 675 °C. The experimental evidence for this diagram is comprised of consistent results in resistivity, X-ray, metallographic and TEM studies.

The details of the diagram of [77TER], however, present problems for the evaluator. The miscibility gap is very narrow, strongly skewed towards the Ti-rich region of the diagram, and has a high critical temperature. The narrowness and asymmetry of the gap seem to be thermodynamically inconsistent with the known  $\alpha/\beta$ boundaries. The inconsistency seems to be modelindependent, and it is clear on simple thermodynamic grounds that a three-phase equilibrium at 675 °C cannot be reproduced. The solution arrived at by [80BRE] was to present a monotectoid diagram with a symmetric miscibility gap with a lower critical temperature than that of [77TER]. In Fig. 1, a monotectoid diagram has been drawn, together with the metastable extension of the  $\beta/(\alpha + \beta)$  boundary below the monotectoid temperature. Thus, Fig. 1 incorporates two versions of the phase diagram: (*i*) the portion of the  $\beta/(\alpha + \beta)$  boundary drawn in solid line is consistent with the miscibility gap of [77TER], and (*ii*) the dotted extension of the  $\beta/(\alpha + \beta)$  boundary represents the phase equilibrium given by [51HAN]. The details of the sources of the data are discussed fully below. Until further experimental clarification is given, neither version can be accepted over the other with certainty.

Solidus and Liquidus. The melting temperature of pure Mo is taken to be 2617 °C from the evaluation of [80BRE]. The solidus has been investigated by [51HAN] and [69RUD]. [51HAN] determined temperatures of incipient melting by metallographic examination of quenched specimens with an error estimate of  $\pm 25$  °C. The data of [51HAN] agree with that of [69RUD], except at Ti-rich compositions: [51HAN] gives 1720 °C for the melting point of pure Ti, in disagreement with the presently accepted value of 1670 °C.

The data of [51HAN] and [69RUD] can be accurately fitted by a regular solution model, and, in Fig. 1, the experimental data are compared to the calculated boundary. Details of the thermodynamic calculation are given in the section entitled "Thermodynamics". The solidus of Fig. 1 has been drawn from the thermodynamic calculation. No experimental data are pres-



# Table 1 Experimental Determinations of the $\alpha/(\alpha + \beta)$ Boundary

Reference	Solubility, at.% Mo	Temper- ature, °C	Experimental method/ comment
51HAN	0.4	600	Metallography
63CHI	<0.42	600	Resistivity, hardness, metallography
63LUZ	0.15 - 0.25	500-600	
74FLO	< 0.25	750	Optical, electron metallography

ently available on the liquidus, and the calculated liquidus has been drawn with a dotted line.

 $\alpha/(\alpha + \beta)$  Boundary. The maximum solubility of Mo in  $\alpha$ -Ti is approximately 0.4 at.% Mo at 600 °C from [51HAN] and [74FLO]. [63LUZ] chose heat treatments to correspond to those used in industry, and they did not necessarily produce equilibrium. Therefore, this data was not used to construct the phase boundary. The heat treatments used by [51HAN] were carefully chosen to attain equilibrium. A sample of 0.375 at.% Mo was found to be very close to the  $\alpha/(\alpha + \beta)$  boundary. In a study of transformations as a function of heat treatment and quench method, [74FLO] found a 0.25 at.% Mo specimen to be within the two-phase field at 750 °C. The data of [51HAN], [63CHI] and [74FLO] regarding the  $\alpha/(\alpha + \beta)$  boundary are consistent. (See Table 1.)

The  $\alpha$ -phase has been modeled as a regular solution; details of the thermodynamic calculations are given in the section entitled "Thermodynamics". Experimental

# Table 2 Experimental Determinations of the $\beta/(\alpha + \beta)$ Boundary

Reference	$\frac{\beta}{(\alpha + \beta)}$ t at.% Mo	oundary °C	Experimental method/comment
51HAN	4.7	800	Metallography, X-ray
51DUW	5.8	850	Thermal analysis (cooling)
61BUN	4.2	800	Electrical resis- tivity
64WIL	5.8	812	Metallography/ short anneals
70RON, 72RON	4.7	800	Diffusion, X <sup>-</sup> ray analysis
77TER	5.8	835	TEM, X-ray, resistivity, metallography

data are compared to the calculated boundary in Fig. 1. In the diagram of Fig. 1, the  $\alpha$ -solubility is represented by a calculated curve above 675 °C. The solid curve below 675 °C has been drawn in to provide a consistent monotectoid diagram and is consistent with the data.

 $(\alpha + \beta)/\beta$  Boundary (Ti-rich Alloys). Determinations of the Ti-rich portion of the  $(\alpha + \beta)/\beta$  boundary are summarized in Table 2. In these studies, the temperature of the  $\beta$  boundary was found to decrease monotonically as a function of composition, but the composition range for which this boundary could be studied was restricted.

[61BUN] and [64WIL] corroborate the phase boundary

drawn by [51HAN]. The  $\beta$  transus of [77TER] shows pronounced negative curvature and that of [51DUW] shows an even stronger curvature. The boundary of [51HAN] is very close to a straight line, but suggests a positive curvature with an inflection at a low temperature. The initial negative curvature occurs in studies of other similar systems and has been shown to be caused at least partly by insufficiently rapid quenching (see Cr-Ti).

The limit of the difference of slope between the  $\alpha/(\alpha + \beta)$  and  $\beta/(\alpha + \beta)$  boundaries,  $(dx_{\alpha}/dT - dx_{\beta}/dT)$ , is determined only by the lattice stability parameters of pure Ti. The value of  $(dx_{\alpha}/dT - dx_{\beta}/dT)$  for Ti-X systems is 0.03923 at.%/°C, based on the lattice stability parameters tabulated in the section entitled "Thermodynamic Data". The data of [51HAN] and [61BUN] agree best with this thermodynamic constraint at the Ti-rich limit. Therefore, these data have been used to fit the thermodynamic interaction parameters.

The Ti-rich  $\beta/(\alpha + \beta)$  boundary is the result of thermodynamic calculation based on the data of [51HAN] and [61BUN]. The solid portion is also consistent with the miscibility gap of [77TER]. The calculated boundary is compared to the experimental data in Fig. 1.

β Miscibility Gap. There has been controversy about whether β-phase retained during quenching exhibits a tendency towards short-range order [61DUP, 73MOR] or towards clustering [72CHA]. Short range order was found by [61DUP] in five alloys and by [73MOR] in an 8 at.% Mo alloy, using diffuse X-ray scattering. [61DUP] found the short-range order parameter to be constant with concentration, rather than to show a maximum at some stoichiometry, as might be expected. Anomalies were found in the interatomic spacings, and a large degree of charge transfer from Mo to Ti was deduced from these spacings. The results of diffuse X-ray scattering experiments conflict with more direct experiments, and, therefore, the existence of shortrange order is not proposed in this evaluation.

The evidence for clustering comes from thermodynamic measurements (see "Thermodynamic Data") and phase diagram investigations. [72CHA] used X-ray and metallographic studies to examine an 11 at.% Mo sample heat treated above the temperature of  $\omega$  phase formation (~550 °C, see "Metastable Phases"), and they found two  $\beta$  phases. They proposed that the phase separation was the effect of a metastable miscibility gap and short-range clustering.

[70KOU] looked for separation into two  $\beta$  phases in a 15 at.% Mo alloy. This composition would lie within a  $\beta$  phase miscibility gap at the temperatures studied. They did not find any phase separation after prolonged aging at 350 °C.

[77TER] have deduced the existence of an equilibrium  $\beta$ -phase miscibility gap from X-ray detection of two  $\beta$ -phase lattice parameters, and TEM and optical metallographic evidence of a bcc second phase. They detected arrests in the electrical resistivity at temperatures on the proposed miscibility gap and at 675 °C. The resistivity data extends from 0 to 20 at.% Mo, and metallographic data from 0 to 33 at.% Mo. The data on the Ti-rich alloys may be considered more accurate, because the sluggishness of the reactions makes the attainment of equilibrium more difficult at higher Mo concentrations.

The miscibility gap in Fig. 1 is the result of a thermodynamic calculation; the thermodynamic parameters are not the same as those used to calculate any other boundaries of the diagram. The conditions used to determine the parameters were (1) the gap passes through the proposed monotectoid at 12 at. % Mo, 675 °C; this composition simultaneously agrees with the data of [77TER] and [51HAN] for the  $\beta/(\alpha + \beta)$  boundary and, therefore, produces a consistent diagram; (2) the critical point is located at 795 °C with composition near 20 at.% Mo. The calculated miscibility gap fits these requirements, but the isotherm extends further toward the Mo-side of the diagram. Because the phase boundaries have not been experimentally determined at Mo-rich compositions, and the calculated boundary is more plausible, the isotherm in Fig. 1 extends further to the right than it does in the diagram originally proposed by [77TER].

### **Metastable Phases**

Metastable phases are formed from the nonequilibrium  $\beta$  phase retained during quenching. In Ti-rich alloys, the cph phase ( $\alpha'$ ) can form martensitically during quenching; in alloys of slightly higher Mo content, an orthorhombic distortion of cph ( $\alpha''$ ) is formed. The  $\omega$  phase is formed as an intermediate phase in the decomposition of metastable  $\beta$  to the equilibrium  $\alpha$ . At successively higher Mo concentrations,  $\alpha', \alpha'', \alpha'' + \beta + \omega$ ,  $\beta + \omega$  and  $\beta$  are found after quenching from the  $\beta$  region. A summary of experimental determinations of the composition ranges of the various metastable phases is given in Table 3. Discrepancies are not large

### Table 3 Composition Range of Metastable Phases (As-quenched from $\beta$ Region)

Reference	α΄	Metastable phases, at.% Μ α"	lo ω
58BAG	0 to 2	2 to 4	4
70COL		$\sim 6.5$	~14
72FED	0 to 2.5	2.5 to 4.5	4.5
73MOR		4.7 to 6.9	6.4 to 11
74GUS	0 to 2	2 to 6	5 to 10
59AGE, 75AGE	0 to 2	3.1 to 6	6 to 10
75KOL	0 to 2	2 to 4.5	4.3 to 6
79DAV	0 to 2	2 to 5.3	
80LEIb	0 to 3	2 to 5	5 to $\sim 14$

Table 4Martensitic TransformationTemperatures

Composition, at.% Mo	Temperature, °C	Composition, at.% Mo	Temperature, °C
70HUA		52DEL	
1.0	780	0.5	675
2.0	700	4.7	<b>46</b> 0'
3.1	610		
4.2	515		

and can be attribu'  $\iota$  to differences in oxygen levels, different sensitiv' of the experimental probes to the presence of fine precipitates, and differences because of the necessarily small number of alloys studied by each investigator. The effect of oxygen impurities is to widen slightly the stability range of the  $\alpha'$  and  $\alpha''$ phases [75AGE].

Martensitic transformations in titanium alloys have been reviewed by [73WIL] and [76WIL]. The start temperature  $M_s$  for the  $\beta/(\alpha' \text{ or } \alpha'')$  martensitic transformation has been studied as a function of Mo concentration by [51DUW], [52DEL], [60SAT] (see also [70HUA]) and [73FED]. [51DUW] and [70HUA] used thermal analysis, [52DEL] used a metallographic technique and [73FED] used Young's modulus and other elastic property measurements. The M<sub>s</sub> values of [51DUW] and [70HUA] agree and are considerably higher than the M<sub>s</sub> temperatures detected by [52DEL] and [73FED]. In a study of martensite structures in dilute alloys, [74FLO] concluded that Ms is greater than 750 °C in 0.5 at.% Mo, in agreement with the results of [51DUW] and [70HUA]. Some data of [70HUA] and [52DEL] are given in Table 4. The data of [52DEL] lie close to a straight line between the two points given in the table. At compositions greater than 5 to 6 at.% Mo, the  $\beta$  (or  $\beta + \omega$ ) phase is retained completely during quenching [52DEL, 51DUW], that is, the  $M_{\rm s}$  temperature falls below room temperature.

The  $\alpha'$  martensite forms between 0 and 2 at.% Mo (see Table 4). The morphology of the observed product in the most dilute alloys is referred to as "packet", "lath" or "colony". The transition from the colony microstructure to an acicular microstructure takes place over the composition range 0.25 to 2.0 at.% Mo [58BAG, 79DAV].

At 2 at.% Mo, the structure becomes orthorhombic. The orthorhombic martensite  $\alpha''$  of symmetry CmCm exists between 2 and 4 at.% Mo (see Table 4). If the closepacked hexagonal structure is described as an orthorhombic lattice, using three parameters, a, b, c; then  $a = \sqrt{3} b$ . The orthorhombic distortion of the hexagonal structure consists of a deviation of the b/a ratio from the "ideal" value of  $\sqrt{3}$  to smaller values [72HAM]. The structure is intermediate between the cph and bcc structures, the number of nearest neighbors passing from 12 to 8 with increasing distortion [79DAV]. [79DAV] suggest that the transition from  $\alpha'$  to  $\alpha''$  is second order in character, because of the continuous change of the lattice parameters (see "Crystal Structures and Lattice Parameters") and because the orthorhombic martensite shows a fine modulated structure indicative of spinodal decomposition. Theoretically, the martensite is expected to exhibit the orthorhombic structure over its whole composition range [77CAH].

The  $\alpha''$  martensite can be produced by deformation of metastable  $\beta$  or  $(\beta + \omega)$  alloys in the alloys containing 5 to 8 at.% Mo [63WOO, 68BLA, 76WHI]. The crystallography of the martensitic  $\beta$  to  $\alpha$  transformation has been studied by [54WEI], [58GAU] and [70HAM]. Additional studies of  $\beta$  phase decomposition have been made by [71NOV], [76FED] and [75IVA].

**ω Phase.** The ω structure was incompletely described by [57AUS] and [58SPAa], and identified correctly by [58SIL] in various alloys as a hexagonal phase of symmetry P6/mmm. Under certain conditions, the ω phase can become distorted to a trigonal structure of symmetry  $D_{3h}^3P3m1$  [55BAG, 58SIL, 72SAS, 77LYA]. The ω phase also is an equilibrium phase of pure Ti at high pressure [74DON]. The ω phase can be regarded as a transition structure between the high temperature β(Ti) and the low temperature α.

The  $\omega$  structure can be generated from the  $\beta(Ti)$  structure as follows: The  $\beta(Ti)$  structure can be viewed as a sequence of (111) planes along the  $[111]_{\beta}$  direction, each with hexagonal symmetry. The stacking can be regarded as *ABC* type, and the  $\omega$  modification consists of the collapse of any pair of these planes into a common plane. If the collapse is incomplete, the symmetry of the  $\omega$  structure is trigonal rather than hexagonal.

The orientation relationship of the  $\omega$  precipitate to the  $\beta$  matrix is  $<111>_{\beta}//[0001]_{\omega}$  and  $(110)_{\beta}//(1120)_{\omega}$  [68BLA, 68MIY, 61CRO]. The  $\omega$  phase can form either during quenching from the  $\beta$  region (athermally) or after quenching from the  $\beta$  region and aging.

Data on the composition range in which athermal  $\omega$  can be found are summarized in Table 3.  $\omega$  phase formation starts at approximately 4 at.% Mo, but there is no good agreement about the maximum composition for  $\omega$ formation. [69HIC] found no  $\omega$  phase in as-quenched alloys between 8 and 14 at.% Mo. [72FLO] found no evidence of  $\omega$  phase in the diffraction patterns of an as-quenched 11 at.% Mo alloy, but only diffuse streaking indicative of  $\omega$ -like defects. The precipitates take the form of ellipsoidal particles aligned with the long axis in the <111><sub> $\beta$ </sub> direction [61CRO, 68 MIY]. In an 8.1 at.% Mo sample, particles were 4 nm in diameter and 20 nm long [61CRO]. [78GUS] and [68BLA] report particle sizes of 5 to 6 nm.

The aged form of  $\omega$  occurs in alloys of composition between approximately 4 and 15 at.% Mo [69HIC, 73COL, 75BAG]. In alloys of higher Mo content,  $\omega$  is discernible as diffuse streaking in the diffraction patterns. The optimal aging temperature is approximately 350 °C. At an aging temperature of 500 °C, equilibrium  $\alpha$  is formed directly from the  $\beta$  [69HIC]. During aging, the compositions of the  $\omega$  and  $\beta$  tend toward saturation values, and then equilibrium  $\alpha$  begins to precipitate. The saturation composition of  $\omega$  has been reported as: [69HIC], 4 to 4.5 at.% Mo; [73COL], ~4 at.% Mo; and [74GYS], 3.4 at.% Mo. The  $\beta$  tends toward compositions of 14 to 16 at.% Mo [69HIC].

Particles of aged  $\omega$ , like those of athermal  $\omega$ , are ellipsoidal in shape. Particle sizes are between 10 and 60 nm; the maximum particle size that has been observed in Ti-Mo alloys is approximately 300 nm.

The  $\omega$  phase is an equilibrium phase of pure Ti at high

#### Table 5Crystal Structures

Phase	Structure H	Prototype	Space group	Composition range, at.% Mo
α	hP2	Mg	$P6_3/mmc$	0 to 0.4
β	cI 2	w	Im3m	0 to 100
α΄	hP2	Mg	$P6_3/mmc$	0 to 2
α″	Orthorhombi	c	Cmcm	2 to 4
ω	Hexagonal	•••	P6/mmm	4 to 15

Table 6 Lattice Parameters of the  $\beta$  Phase

Alloy, at.% N	Лo	Lattice parameters, nm <i>a</i>	Alloy at.% M	, pa Io	Lattice trameters, nm a
51 <b>H</b> A	N		69RU	D	
11.7		0.3257	10		0.3256
18.1		0.3243	20		0.3238
33.5		0.3206	30		0.3216
42.4		0.3190	40		0.3196
53.4		0.3171	50		0.3174
66.6		0.3155	60		0.3163
82.5		0.3148	70		0.3155
80LE	Tb (hig	h pressure)	80		0.3149
5 11.5		0.3280 0.3251	90 100	· · · · · · · · · · · ·	$\begin{array}{c} 0.3148\\ 0.3147\end{array}$
15		0.3247	78TE.	ĸ	
18	• • • • • • •	0.3243	8.2		0.3266
25		0.3229	11.1		0.3260
61HA	АK		14.2		0.3252
7.1 9.0		0.3264 0.3260	$17.6 \\ 21.2 \\ 25.0$	• • • • • • • • • • • •	$\begin{array}{c} 0.3245 \\ 0.3238 \\ 0.3226 \end{array}$
9.0	• • • • • • •	0.3203	29.0		0.3218
12.2 15.6 15.6		0.3253 0.3247 0.3248	33.3 37.9		$0.3205 \\ 0.3200$
16.3		0.3248	42.8	• • • • • • • • • •	0.3190
23.3		0.3223	$\begin{array}{c} 60.0 \\ 73.9 \end{array}$		$0.3172 \\ 0.3162$

pressure, and it can also be found in dilute Ti-Mo (3 at.% Mo) alloys after quenching from the  $\beta$  region and high-pressure soaking at room temperature [79LEI, 80LEIb]. *TTT* diagrams for  $\omega$  formation are given by [58LOE], [68MIY], [70YUK] and [72IKA].

# Crystal Structures and Lattice Parameters

The crystal structures of the equilibrium and metastable phases of the Ti-Mo system are summarized in Table 5. Lattice parameter data are separately given in Tables 6 and 7. The lattice parameters of the  $\alpha'$  martensite do not vary with composition, as do the lattice parameters of the  $\alpha''$  martensite.

The data of [80LEIb] were obtained after quenching from the  $\beta$  region and high-pressure soaking. Error estimates are  $\pm 0.0006$  nm. [80LEIa] have represented atomic volumes as a function of atomic fraction Mo (x) in the following relations:

 $V_{\omega}(x) = 10.47 (1 - 0.152 x) \text{ cm}^3/\text{ g-at}$  $V_{\beta}(x) = 10.60 (1 - 0.180 x) \text{ cm}^3/\text{ g-at}$  $V_{\alpha}(x) = 10.66 (1 - 0.302 x) \text{ cm}^3/\text{ g-at}$ 

# Table 7Lattice Parameters ofMetastable Phases

		Composition,	Lattic	e paramete	rs, nm
Struct	ure	at.% Mo	а	b/ <del>√3</del>	c
79DA	V				
α'.		. 1.0	0.2945		0.4681
α'.		. 2.0	0.2943		0.4676
α''.		. 3.1	0.2965	0.2913	0.4662
α".		. 4.2	0.2994	0.2881	0.4644
70WI	L				
α''.		. 4.0	0.3001	0.2886	0.4657
80LE	Ib (high pr	essure)			
α'.		. 3	0.2954		0.4650
α''.		. 3	0.3007	0.2899	0.4650
ω.		. 3	0.4612		0.2821
ω.		. 5	0.4602		0.2820
ω.		11.5	0.4591		0.2815
ω.		. 15	0.4587	•••	0.2808
75AG	E				
α''.		. 3.1	0.2980	0.2880	0.4649

## **Thermodynamic Data**

Vapor pressure measurements were made by [62KUZ] using the Langmuir method. [71HOC] determined the activity of Ti in the  $\beta$  phase using the Knudsen cell technique. The Knudsen cell experiment is preferred over the Langmuir cell experiment for deriving regular solution parameters because it is an equilibrium method, but it must be noted that the errors on the partial free energy of titanium become very large at high Mo concentrations. Fitting the data to regular solution theory, [71HOC] found the  $\beta$  Ti-Mo interaction parameter to be 12134 ± 2900 J/g·at. This value implies a metastable miscibility gap with a critical temperature of 459 °C.

A positive interaction parameter thus supports observations of metastable  $\beta$ -phase immiscibility, but it does not necessarily imply the existence of the monotectoid version of the phase diagram. The value of 12134 J/g at for the regular solution parameter is an average between a much higher value for Ti-rich alloys and a much lower value for Mo-rich compositions. This is qualitatively in agreement with the asymmetry of the  $\beta$ -phase miscibility gap found by [77TER].

**Thermodynamic Modeling.** The free energies of the three equilibrium phases have been represented as:

$$G^{i} = F^{i}{}_{\text{Ti}} (1 - x) + F^{i}{}_{\text{Mo}} x + RT(x \ln x + (1 - x) \ln(1 - x)) + B^{i} x(1 - x) + C^{i} x(1 - x)(1 - 2x)$$

where *i* designates the phase; *x*, the atom fraction of  $Mo; F^i$ , the lattice stability parameters of the pure metals; and  $B^i$  and  $C^i$ , the interaction parameters. Values of the lattice stability parameters were taken from [70KAU] and kept fixed throughout the calculations.

Two calculations have been performed for this evaluation; first, the miscibility gap of  $\{77TER\}$  was fitted. The  $\beta$ -phase parameters thus determined are given in Table 8. They are not inconsistent with the thermo-

Table 8	Thermodynamic	Parameters,	J/g·at, T	ˈ in K
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Lattice stability parameters of Ti and Mo [70KAU]

Reference	BL	Interaction parameters $oldsymbol{B}_eta$
Ti-Mo interaction parameters	L' ex	(110) = 0.508
$F_{\rm L}$ (Ti) = 16234 ~ 8.368 T $F_{\rm L}$ (Ti) = -4.351 + 3.77 T	$F_{L}$	$(M_0) = 24267 + -8.368 T$ $(M_0) = -8.368$
$F_{\beta}$ (Ti) = 0	$F_{\scriptscriptstyleeta}$	$(M_0) = 0$

Reference	BL	$B_{\beta}$	$oldsymbol{B}_{lpha}$
80BRE	18125-13.6T	36500-18.7T	42 404
70KAU	6537	5192	15359
This evaluation	10136	10 000	24 386
This evaluation (miscibility gap)	• • • • • • • • • • • • • • • • • • • •	10000 + 9000(1 - 2x)	

dynamic measurements of [71HOC]. With these values of the  $\beta$  parameters, it was not possible to make a satisfactory fit to the  $\alpha/(\alpha + \beta)$  boundary or the monotectoid composition and temperature. The miscibility gap in Fig. 1 is the result of this calculation.

Next, a calculation was made to fit the  $\alpha(\alpha + \beta)$  boundary; the  $\beta/(\alpha + \beta)$  boundary, according to [51HAN], without the miscibility gap; and the solidus. The starting parameters were taken from [70KAU]. The procedure was to keep the  $\beta$  parameters fixed and determine the  $\alpha$  and liquid parameters by the leastsquares optimization procedure. It was found that the  $\beta$ -phase parameter also had to be increased in order to fit the  $\alpha/(\alpha + \beta)$  boundary, and this was done by trial and error. When a satisfactory fit could be obtained, the  $\beta$  parameter was fixed and the  $\alpha$  and liquid parameters independently varied. The metastable miscibility gap obtained has a critical temperature of 450 °C. The calculated boundaries were used to plot Fig. 1, and the dotted curves are continuations of these same curves.

The solidus can be reproduced by either set of  $\beta$  parameters. Using the first set (with the miscibility gap), the separation between the liquidus and solidus varies with composition; in the second, the separation is essentially uniform, as shown in Fig. 1. Unfortunately, there are no liquidus data for this system to distinguish between the two possibilities.

[80BRE] calculated a phase diagram using regular solution theory and produced a miscibility symmetric in composition. Regular solution theory was used because  $\beta$ -phase interaction parameters are nearly symmetric unless the strain energies in the  $\beta$  phase are very large and asymmetric. Additional thermodynamic studies have been made by [75CHE] and [78LES]. [80LEIa] performed thermodynamic analysis of high-pressure soaking experiments to formulate a thermodynamic representation of the *P*-*x* diagram for the  $\omega$  phase.

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# The Ti-W (Titanium-Tungsten) System

47.88 amu

183.85 amu

### By J. L. Murray

## **Equilibrium Diagram**

The equilibrium phases of the Ti-W system are (1) the liquid. The liquidus and solidus curves join the melting points of the pure metals without minimum or maximum. (2) The Ti-rich close-packed hexagonal solid solution ( $\alpha$ ), below the temperature of the bcc-cph transition in pure Ti. (3) The body-centered cubic solid solution ( $\beta$ ). Ti and W exhibit complete mutual solid solubility in the  $\beta$  phase at temperatures between the solidus and the critical temperature of the miscibility gap.

The diagram of Fig. 1 is significantly different from that of the compilations [Hansen, Elliott, Shunk] in that the critical temperature of the  $\beta$ -phase miscibility gap has been lowered to 1250 °C from approximately 1700 °C.

**Liquidus and Solidus.** The melting point of pure W is taken to be 3380 °C, from the [Hultgren, Elements] evaluation. Experimental studies of the liquidus and solidus have been made in the composition ranges summarized in Table 1.

The phase diagram drawn by [53MAY] represents the