

- to T^4-T^{60} , *Z. Metallkd.*, 55(11), 704-710 (1964) in German. (Crys Structure)
- 64Sch:** Schubert, K., Raman, A., and Rossteutscher, W., "Structure Data on Intermetallic Phases (10)", *Naturwissenschaften*, 51(2), 506-507 (1964) in German. (Crys Structure)
- 65Dwi:** Dwight, A. E., Conner, R. A., and Downey, J. W., "Equiatomic Compounds of the Transition and Lanthanide Elements with Rh, Ir, Ni and Pt", *Acta Cryst.*, 18, 835-839 (1965). (Crys Structure)
- 65Pie:** Pietrokowsky, P., "Novel Ordered Phase, Pt₅Ti", *Nature*, 206(4981), 291 (1965). (Crys Structure)
- 68Kra:** Krautwasser, P., Bhan, S., and Schubert, K., "Structural Investigations in the Systems Ti-Pd and Ti-Pt", *Z. Metallkd.*, 59(9), 724-729 (1968) in German. (Equi Diagram, Crys Structure)
- 68Van:** van Reuth, E. C. and Waterstrat, R. M., "Atomic Ordering in Binary A15-Type Phases", *Acta Crystallogr.*, B24, 186-196 (1968). (Crys Structure)
- 69Sin:** Sinha, A. K., "Close-Packed Ordered AB₃ Structures in Binary Transition Metal Alloys", *Trans. AIME*, 245, 237-240 (1969). (Crys Structure)
- 70Don:** Donkersloot, H. C. and van Vucht, J. H. N., "Martensitic Transformations in Gold-Titanium, Palladium-Titanium and Platinum-Titanium Alloys near the Equiatomic Composition", *J. Less-Common Met.*, 20, 83-91 (1970). (Equi Diagram)
- 70Kau:** Kaufman, L. and Bernstein, H., *Computer Calculation of Phase Diagrams*, Academic Press, NY (1970). (Thermo; Review)
- 73Rau:** Raub, E. and Falkenburg, G., "Reactions of the Platinum Metals with the Carbides of the Group IV and V Elements of the Periodic Table", *Metall.*, 7, 669-679 (1973) in German. (Equi Diagram)
- 76Jac:** Jacob, T. and Alcock, C. B., unpublished data cited by [76Mes]. (Thermo)
- 76Jun:** Junod, A., Flukiger, R., and Muller, J., "Superconductivity and Specific Heat in Titanium-Base A15 Compounds", *J. Phys. Chem. Solids*, 37, 27-31 (1976) in French. (Equi Diagram)
- 76Mes:** Meschter, P. J. and Worrell, W. L., "An Investigation of High-Temperature Thermodynamic Properties in the Pt-Ti System", *Metall. Trans. A*, 7A, 299-305 (1976). (Thermo)
- 81Wor:** Worrell, W. L. and Ramanarayanan, T. A., "Electrochemical Cell Investigations of Platinum Binary Systems at Elevated Temperatures", in *Chemical Metallurgy - A Tribute to Carl Wagner*, Proc. Conf., TMS/AIME, 420 Commonwealth Dr., Warrendale, PA 15086, 69-81 (1981). (Thermo)

Ti-Pt evaluation contributed by **Joanne L. Murray**, Center for Materials Research, National Bureau of Standards. Thermodynamic calculations have been made using computer programs generously made available by E.-Th. Henig and H. L. Lukas, of the Max-Planck Institute, Stuttgart, Federal Republic of Germany. This work was (partially) supported by Office of Naval Research funds through the Joint Program on Critical Compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data, National Bureau of Standards. Literature searched through 1981. Dr. Murray is the ASM/NBS Data Program Category Editor for binary titanium alloys.

The Rh-Ti (Rhodium-Titanium) System

102.9055

47.88

By **J. L. Murray**
National Bureau of Standards

Equilibrium Diagram

Two phase diagrams are shown in Fig. 1 because there are irreconcilable experimental discrepancies concerning some portions of the diagram. Figure 1(a) is based on the data of [72Ere, 75Sht]; Fig. 1(b) is based on the data of [66Rau]. The three-phase equilibria and congruent transformations according to the two investigations are also separately tabulated in Table 1. Those portions of the diagram for which an evaluated phase boundary can be determined from a composite of all the data are drawn identically in the two diagrams. All investigators agree on the existence of Ti₂Rh, α TiRh, and TiRh₃. The quantitative features about which there is fair agreement are the (α Ti)/(β Ti) boundaries, the composition range of TiRh₃, part of the (Rh) solvus, and the congruent melting point of α TiRh. The most serious discrepancies concern the extent of the single-phase (β Ti) field. The problems and discrepancies concerning each phase field are separately discussed below. Critical experiments are proposed to resolve the experimental discrepancies.

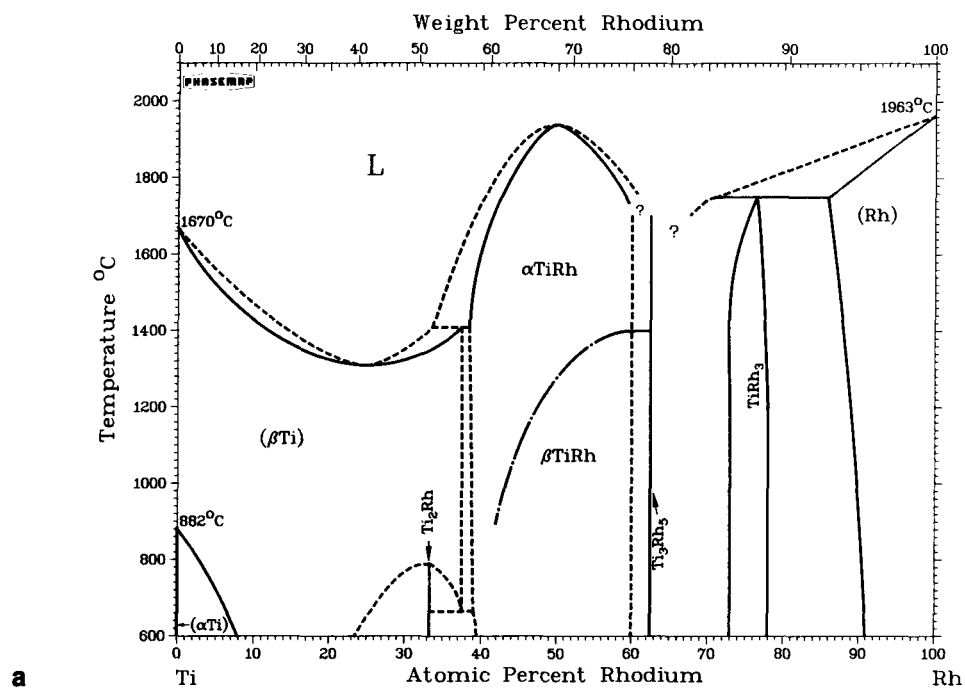
The observed phases of the Ti-Rh system are: (1)The cph (α Ti) solid solution. The cph structure is the equilibrium form of pure Ti below 882 °C. (2)The bcc (β Ti) solid solution, based on the equilibrium solid form of pure Ti above 882 °C. The maximum solubility of Rh in (β Ti) has not yet been definitively determined. (3)The fcc (Rh) solid solu-

tion. The maximum solubility of Ti in (Rh) is approximately 14 at.%. (4)The compound Ti₂Rh, with the MoSi₂ structure, stable only below 790 °C. (5)Two compounds with a wide composition range about the stoichiometry TiRh. The high-temperature form, designated α TiRh, has the CsCl structure; on cooling, it transforms to β TiRh with the tetragonal AuCuI structure. (6)The stoichiometric compound Ti₃Rh₅ with a structure isomorphous with Ge₃Rh₅. (7)The compound TiRh₃ with the Cu₃Au ordered fcc structure. TiRh₃ has a maximum composition range of 73 to approximately 78 at.% Rh. (8)A possible equilibrium compound with composition near 83 at.% Rh (TiRh₅) was identified by [66Rau].

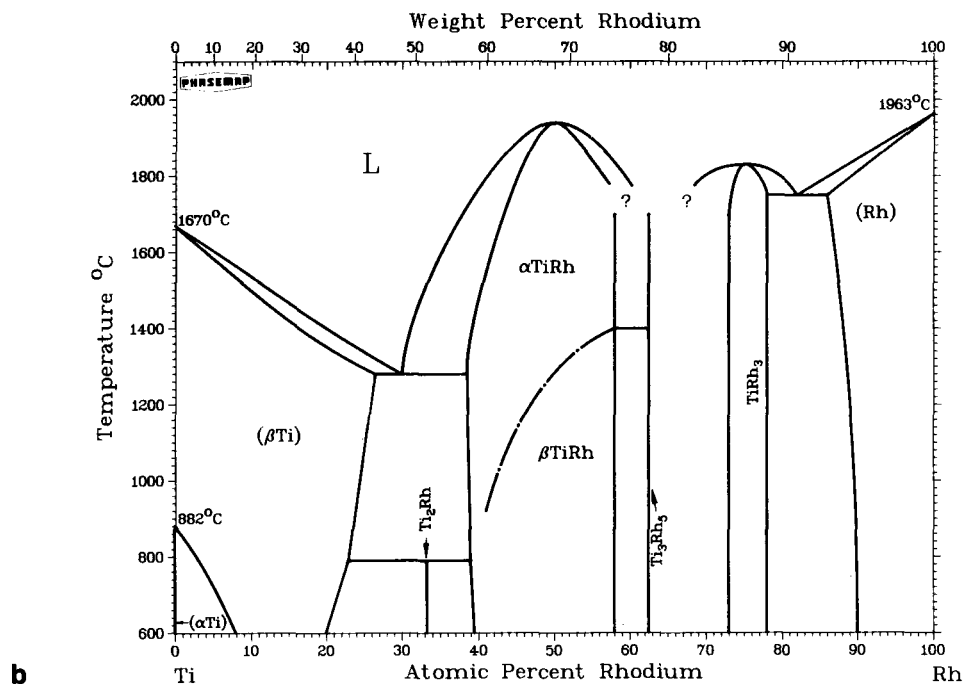
A Ti₂Ni-type phase is also often found in Ti-transition metal alloys. It is an equilibrium phase of several Ti systems (e.g., Ti-Fe), but it is more usually a ternary phase stabilized by oxygen impurities. [58Nev] and [60Nev] showed that this structure does not appear in binary Ti-Rh alloys, but that it does appear in ternary Ti-Rh-O alloys.

Ti-Rich Liquidus and Solidus and Extent of the (β Ti) Field. The addition of Rh to (β Ti) lowers its melting point. There are irreconcilable experimental discrepancies concerning the extent of the single-phase (β Ti) field and whether (β Ti) is formed from the melt by a congruent transformation or a eutectic reaction.

Fig. 1 Ti-Rh Phase Diagram



a



b

According to the two major investigations of this system: (a) [72Ere], and (b) [66Rau]. Those portions of the diagram for which an evaluated phase boundary can be determined from a composite of all the data are drawn identically in the two diagrams.

J. L. Murray, 1982.

Table 1 Three-Phase Equilibria of the Ti-Rh System

Phases	Compositions, at.% Rh			Temperature, °C	Equilibrium type
Pure metal transformation points					
L \rightleftharpoons (Rh)		100		1963	Melt
L \rightleftharpoons (β Ti)		0		1940	Melt
(β Ti) \rightleftharpoons (α Ti)		0		882	Solid state
Fig. 1(a) based on [72Ere]					
(β Ti) + α TiRh \rightleftharpoons Ti ₂ Rh	22	39	33.3	790	Peritectoid
(β Ti) \rightleftharpoons Ti ₂ Rh + α TiRh	37.5	33.3	39	665	Eutectoid
L + α TiRh \rightleftharpoons (β Ti)	28.1	40.6	29.7	1325	Peritectic
L + (Rh) \rightleftharpoons TiRh ₃	71	86	75	1750	Peritectic
L \rightleftharpoons (β Ti)		25		1310	Congruent
L \rightleftharpoons TiRh		50		1940	Congruent
Fig. 1(b) based on [68Rau]					
(β Ti) + α TiRh \rightleftharpoons Ti ₂ Rh	22	39	33.3	790	Peritectoid
L \rightleftharpoons (β Ti) + α TiRh	30	26.5	38.5	1280	Eutectic
L \rightleftharpoons TiRh ₃ + (Rh)	82	75	86	1750	Eutectic
L \rightleftharpoons TiRh		50		1940	Congruent
L \rightleftharpoons TiRh ₃		75		1830	Congruent
Calculated values (this evaluation)					
(β Ti) + TiRh \rightleftharpoons Ti ₂ Rh	27.3	41.1	33.3	790	Peritectoid
L + TiRh \rightleftharpoons (β Ti)	28.1	40.6	29.7	1325	Peritectic
TiRh + L \rightleftharpoons Ti ₃ Rh ₅	60.0	66.4	62.5	1760	Peritectic
L \rightleftharpoons Ti ₃ Rh ₅ + TiRh ₃	68.9	62.5	75	1710	Eutectic
L \rightleftharpoons TiRh ₃ + (Rh)	80.4	75	85.1	1720	Eutectic
L \rightleftharpoons (β Ti)		21.5		1300	Congruent
L \rightleftharpoons TiRh		52.4		1950	Congruent
L \rightleftharpoons TiRh ₃		75		1768	Congruent

[72Ere] claimed that the maximum solubility of Rh in (β Ti) is at least 37.5 at.% Rh. They did not observe CsCl superlattice lines in X-ray diffraction patterns in alloys containing less than 37.5 at.% Rh; the X-ray evidence was supported by metallographic evidence that the same alloys were single phase after annealing at 1000 °C. [72Ere] found no well-defined two-phase ((β Ti)+TiRh) region; they interpolated a very narrow two-phase region between the observed (β Ti) and α TiRh alloys. From the solidus and metallographic data, [72Ere] concluded that the liquidus and solidus have a minimum at 1310 °C and about 25 at.% Rh.

[66Rau], on the other hand, presented metallographic evidence that a 30 at.% Rh alloy was two-phase at 1270 °C; as-cast microstructures support a eutectic reaction at about 30 at.% Rh. [66Rau] measured lattice parameters of a series of alloys annealed at 1100 °C and found the β /(β +TiRh) boundaries to be located at 26 and 37 at.% Rh, respectively.

The thermal analysis data of the two investigations were quite similar; the eutectic horizontal of [66Rau] (1280 \pm 20 °C corresponds to the congruent melting point of [72Ere] (1310 \pm 20 °C). Finally, both authors postulated peritectic reactions near 1500 °C to complete the diagram and agreed concerning the probable composition limits of α TiRh. The Ti-rich part of the solidus curve, according to both [66Rau] and [72Ere], shows a slight positive curvature. In both works, the thermal analysis data show considerable scatter and cannot be read accurately from the published graphs (see Table 2).

Figure 1(b) [66Rau] shows the composition of (β Ti) and the liquid as 26.5 and 30 at.% Rh, respectively, at a eutectic temperature of 1280 °C. The details of the (β Ti) boundaries are sketched according to [66Rau]'s approximate diagram

and do not reflect quantitative phase boundary data. Similarly, Fig. 1(a) [72Ere] shows the congruent melt at 25 at.% Rh, 1310 °C. The compositions of the liquid and (β Ti) are shown as 33.7 and 37.5 at.% Rh, respectively, at an estimated peritectic temperature of 1410 °C. The Ti-rich portion of the solidus curve has been represented as nearly linear to reflect the [72Ere] solidus data, but the liquidus and the other β boundaries have been sketched in and do not reflect further quantitative phase boundary data.

The Compound Ti₂Rh. [64Sch1] first noted the presence of a MoSi₂ structure in Ti-Rh, and they designated the phase Ti₇₀Rh₃₀. (Note that the phase designated Ti₂Rh by [64Sch1] has the CsCl structure and is not the MoSi₂ phase.) [72Ere] found single-phase alloys only at the stoichiometric composition, and these metallographic results have been preferred to the X-ray data [64Sch1].

Ti₂Rh is not stable above 790 °C [66Rau, 72Ere]. [66Rau] represented the reaction at 790 °C as of the peritectic type, [72Ere] as a congruent solid state transformation from (β Ti). This follows from the disagreement between these authors concerning the extent of the single-phase (β Ti) field.

In both Fig. 1(a) and 1(b), Ti₂Rh is shown as a stoichiometric compound. The (β Ti)/Ti₂Rh phase boundaries are drawn to illustrate the controversy concerning the reaction types, and do not reflect quantitative phase boundary data in either instance.

(α Ti)/(β Ti) Boundaries. The solubility of Rh in (α Ti) is very low (<0.07 at.%). [63Rau] originally found the compositions of (α Ti) and (β Ti) in equilibrium at 700 °C to be 2 to 3 at.% and 5 to 6 at.%, respectively, using X-ray fluorescence microprobe analysis of annealed specimens.

Table 2 Data Pertinent to the Ti-Rich Liquid and (β Ti) Boundaries

Reference	Composition, at.% Rh	Temperature, °C	Phase boundary or reaction	Method/Note
[64Rau]	26	1100	$\beta/\beta + \alpha\text{TiRh}$	Lattice parameters
[66Rau]	27.5-30	1100	$\beta/\beta + \alpha\text{TiRh}$	Lattice parameters
	~26	1280 \pm 20	$\beta/(\beta + L)$	Thermal analysis, estimated composition
	30	1280 \pm 20	Eutectic point	Thermal analysis, metallography
		1500	Peritectic	Postulated
			$L + \beta\text{TiRh} \rightarrow \beta$	
[72Ere]	22-28	1310	Congruent melt	Thermal analysis, metallography
	~35	1000-1200	$\beta/\beta + \alpha\text{TiRh}$	Estimated composition
		~1500	Peritectic	Postulated
			$L + \beta\text{TiRh} \rightarrow \alpha\text{TiRh}$	

[72Ere] also reported a single-phase (α Ti) alloy at about 2.5 at.% Rh and 800 °C. However, later investigation [66Rau] revealed that the solubility of Rh in (α Ti) is much lower, between 0.07 and 0.08 at.% Rh at 600 °C. They attributed the discrepancy to the grain size of the two-phase alloys, which was too small for application of microprobe analysis. The lower solubility is also more consistent with the negligible effect of Rh content on the lattice parameters of the (α Ti) phase [64Rau].

[72Ere] found the ($\alpha + \beta$)/ β boundary to lie at approximately 6 to 7 at.% Rh at 600 °C, using classical metallographic techniques. [66Rau] (metallographic and X-ray studies) reported the ($\alpha + \beta$)/ β boundary to lie between 8 and 12 at.% Rh at 700 °C.

In Fig. 1, the (α Ti)/(β Ti) boundaries have been drawn from the results of a thermodynamic calculation. The calculated composition of (β Ti) in equilibrium with (α Ti) at 600 °C is 8.0 at.% Rh, in satisfactory agreement with both experimentally determined values. The solubility being so low, the (α Ti) solvus was not modeled quantitatively, and the maximum solubility was only required to be less than 0.1 at.%.

The Composition Range 40 to 60 at.% Rh. Three structures have been observed in alloys of the composition range 35 to 60 at.% Rh: the CsCl structure in alloys containing less than 45 at.% Rh; the AuCuI structure in alloys containing more than 45 at.% Rh [66Rau, 72Ere, 64Ram]; and also, at 55 at.% Rh, an orthorhombic distortion of CsCl, the NbRu-type structure [64Ram, 66Rau].

In this evaluation, the NbRu structure has not been included in the diagrams as an equilibrium phase. A complete structure determination for several well-equilibrated high-purity alloys at and near 55 at.% Rh is needed before any reasonable conclusions can be drawn about a NbRu phase. The NbRu structure has also been observed in exactly equiatomic alloys in the Ti-Ir system (see [82Mur]). In that system also, the structure determination itself is far from definitive. (It is also interesting to note that, in the Zr-Rh system, a compound Zr_3Rh_5 was also identified by the same investigators [66Rau] as having the NbRu structure. Careful structural and phase diagram work of [69Gie] showed that this structure does not exist in the Zr-Rh system at all. Finally, the NbRu structure has not been rigorously determined, so that identification of a structure as "NbRu-type" is in itself ambiguous.)

[66Rau] and [72Ere] agreed that the microstructures of alloys containing more than 45 at.% Rh show unmis-

takable signs of transformation during quenching. In both Fig. 1(a) and 1(b), we follow the interpretation given by [72Ere]: the high-temperature form of the equiatomic compound has the CsCl structure, and only at less than 45 at.% Rh can the CsCl structure be retained during quenching. [66Rau], on the other hand, believed that the CsCl structure belongs to a separate phase near stoichiometry Ti_3Rh_5 and that the high-temperature αTiRh phase must have yet another structure. Our interpretation, however, is not contradicted by metallographic and X-ray observations of [66Rau].

The interpretation by [72Ere] has been preferred because neither investigator observed ($\text{CsCl} + L_1$) two-phase alloys and because the CsCl structure appears in all analogous systems as the high-temperature equiatomic phase with a low temperature modification (see Ti-Ir [82Mur], and Ti-Pt and Ti-Pd, p 321 in this issue). In several systems, the transformation of the CsCl structure has been observed directly by high-temperature X-ray diffraction.

A two-phase field ($\alpha\text{TiRh} + \beta\text{TiRh}$) cannot be drawn on the basis of the available information. The dot-dashed curve should be interpreted only as a representation of the observed diffusionless transformation temperatures and not as an equilibrium phase boundary. The uncertainty in its position is ± 50 °C, based on data of [66Rau] and [72Ere].

In the Rh-rich end of the single-phase field, there are discrepancies between the two studies because [72Ere] did not take into account the phase Ti_3Rh_5 . The work of [66Rau] has, therefore, been used to place this boundary at 58 ± 2 at.% Rh between 1500 and 1760 °C.

The Compound Ti_3Rh_5 . The first studies of Ti_3Rh_5 led to some confusion about this region of the phase diagram: [64Ram] identified a phase Ti_3Rh_5 as having a hexagonal structure similar to TiNi_3 ; [66Rau] also identified the structure as hexagonal, adding on the basis of thermal analysis and X-ray analysis that the compound is probably very narrow and melts congruently at an undetermined temperature near the congruent melting temperature of αTiRh . [66Ere, 72Ere] found alloys of this composition to be single phase, but did not verify the existence of Ti_3Rh_5 .

[69Gie] investigated the series of alloys Ti_3Rh_5 , Zr_3Rh_5 , and Hf_3Rh_5 and made complete structural determinations of Ti_3Rh_5 and Hf_3Rh_5 . Ti_3Rh_5 has a unique orthorhombic structure isomorphous with Ge_3Rh_5 . The structure is related, but not identical, to TiNi_3 .

Ti₃Rh₅ is, therefore, included as a line compound in the phase diagram. It is not known how this phase reacts with the liquid. [66Rau] hypothesized a congruent melt at about 1900 °C and eutectic reactions with α TiRh and TiRh₃. On the other hand, a peritectic reaction α TiRh + L \rightarrow Ti₃Rh₅ would better explain why this compound was overlooked in other investigations. In our thermodynamic calculations, the peritectic reaction has been found. In Fig. 1, the reaction type has been left uncertain.

Rh-Rich Alloys: (Rh), TiRh₃, and the Liquid. [59Dwi] identified the compound TiRh₃ as having the AuCu₃ structure, in common with many alloys of Ti with fcc metals. The existence of TiRh₃ has been verified by all subsequent investigations [66Rau, 72Ere, 65Ere, 66Ere, 64Ram].

Data on the composition range of TiRh₃ are consistent. [66Rau] give 73 to 78 at.% Rh determined by the lattice parametric method. [66Ere] and [72Ere] give 73 to slightly less than 80 at.% Rh, based on metallographic and X-ray examination of annealed specimens. Both indicate little dependence of the composition range on temperature. The composition range has been taken to be 73 to approximately 78 at.% Rh.

[66Rau] reported that TiRh₃ melts congruently at approximately 1760 °C and has a eutectic reaction with (Rh) at 1720 \pm 50 °C; [72Ere] claimed that it is formed by a peritectic reaction L + (Rh) \rightarrow TiRh₃ at 1750 \pm 50 °C, and found an as-cast microstructure that does not allow for a eutectic reaction. In Fig. 1, both conflicting reaction types have been shown, but in both versions the invariant temperature is taken to be 1750 °C, following [72Ere].

[66Rau] and [72Ere] reported similar data for the solidus curve; both [66Rau] and [72Ere] indicated that qualitatively the solidus lies along an approximately straight line. The thermal analysis data for the solidus are scattered and cannot be read accurately from the published graphs.

In addition to the difference in the types of the reactions, [72Ere] postulated a wide two-phase (L + (Rh)) region and [66Rau] a very narrow one. From a thermodynamic point of view, the narrow two-phase region is preferred. It is established that interaction free energies in all Ti-Pt-metal systems are very large and negative. All the calculated liquid/fcc two-phase regions appear to be constrained to be very narrow by this qualitative thermodynamic feature.

(Rh) Solvus and a Possible Compound TiRh₅. Data on the (Rh) solvus are summarized in Table 3. In the temperature range 1700 to 1200 °C, the agreement among various investigators is good. The maximum solubility of Ti in (Rh) is about 14 at.% Ti at 1750 °C.

[66Rau] identified an additional compound with a cubic structure in alloys of 81 to 90 at.% Rh that had been annealed at temperature lower than 1100 °C. The existence of such a phase was not verified by [72Ere], and further attempts to identify its structure have not been made.

Similarly, the solvus curve of the (Rh) solid solution must be considered uncertain below 1200 °C. [72Ere] found the solvus to lie at less than 88 at.% Rh at 600 °C, the only temperature below 1200 °C that was examined in that study. The high solubility at 600 °C conflicts with the solvus data above 1200 °C; indeed, at 600 °C it should be expected that the observed solubility will be larger than the equilibrium solubility. Diffusion experiments indicated that the mutual solubilities of Ti and Rh are very low at 400 °C [75DeB].

Comparison can be made to the compound TiPt₈, which appears in a solid state reaction in Pt-rich alloys. In that system, TiPt₈ appears in a composition range that had previously been thought to be single-phase fcc (Pt). A systematic study of fcc Pt-metal solid solutions may reveal a series of metastable phase transformations in a super-saturated solid solution.

Critical Experiments

- How wide is the (β Ti) field? Because [66Rau] and [72Ere] presented contradictory experimental results for the same alloy, the most likely problem is that one of them used higher purity alloys. Reexamination of as-cast and annealed microstructures in a 30 at.% Rh alloy, taking particular care to avoid contamination, will resolve the contradiction.
- If the (β Ti) field is wide, then a search for the two-phase ((β Ti) + α TiRh) region is of theoretical interest. The use of annealed diffusion couples or temperature gradient specimens could resolve this question. It is possible that the (β Ti)/ α TiRh transition is higher than first order, and that [72Ere] did not find the two-phase region because it does not exist.

Table 3 Solvus Curve (Ti in (Rh))

Reference	Composition, at.% Rh	Temperature, °C	Method/Note
[66Rau].....	84 \pm 2	1720	Intersection of solidus with eutectic
	88	1200	Lattice parameters
[72Ere].....	88-90	1200	Metallography, X-ray
	85-88	1700	...
	~86	1750	(Peritectic temperature)

Table 4 Ti-Rh Crystal Structure Data

Phase	Maximum observed composition range, at.% Rh	Pearson symbol	Strukturbericht designation	Space group	Prototype
(α Ti).....	0-0.075	<i>hP2</i>	A3	<i>P6₃/mmc</i>	Mg
(β Ti).....	0-30	<i>cI2</i>	A2	<i>Im3m</i>	W
Ti ₂ Rh.....	33.3	<i>tI6</i>	C11 _b	<i>I4/mmm</i>	MoSi ₂
α TiRh.....	39-58	<i>cP2</i>	B2	<i>Pm3m</i>	CsCl
β TiRh.....	45-58	<i>tP2</i>	L1 ₀	<i>Pm3m</i>	AuCuI
Ti ₃ Rh ₅	62.5	<i>oP16</i>	...	<i>Pbam</i>	Ge ₃ Rh ₅
TiRh ₃	73-78	<i>cP4</i>	L1 ₂	<i>P4/mmm</i>	AuCu ₃
(Rh).....	85-100	<i>cF4</i>	A1	<i>Fm3m</i>	Cu

- Examination of as-cast structures on either side of 62.5 at.% Rh will elucidate the reactions between Ti_3Rh_5 and the liquid.
- Examination of as-cast structures near 80 at.% Rh will resolve the discrepancy between the proposed peritectic vs eutectic formation of (Rh). If the reaction type turns out to be peritectic, then a few careful solidus and liquidus points between 88 and 100 at.% Rh would be of interest for the purpose of thermodynamic calculations.
- Structure determinations of $TiRh_5$ (83 at.% Rh) and $TiRh$ are needed.
- TEM observations are needed to verify the extent of the single-phase (Rh) solid solution. The appearance of $TiRh_5$ suggests that apparently single-phase alloys may reveal more complex precipitation processes.

Metastable Phases

In Ti-transition metal systems, metastable phases are formed from (β Ti) during quenching: in Ti-rich alloys, the cph phase (α' Ti) can form martensitically, and at slightly higher transition metal content, ω phase forms as an intermediate phase in the decomposition of retained β into α at low temperatures. In the Ti-Rh system, the formation of supersaturated (α Ti) has been verified, but not that of ω phase [66Rau].

Crystal Structures and Lattice Parameters

The structures of the equilibrium and metastable phases of the Ti-Rh system are summarized in Table 4. Lattice parameter measurements are presented in Tables 5 and 6. For a discussion of the structures of the equiatomic phases see "Equilibrium Diagram".

Thermodynamics

The only experimental thermodynamic work on the Ti-Rh system has been on formation of molecules in the gaseous state [74Coc].

Thermodynamic Models. The free energies of the solution phases are represented as:

$$G^i = F_{Ti}^i(1-x) + F_{Rh}^i x + RT(x \ln x + (1-x) \ln(1-x)) + B^i x(1-x) + C^i x(1-x)(1-2x)$$

where i designates the phase; x , the atom fraction of Rh; F^i , the lattice stability parameters of the pure metals; and B^i and C^i , the interaction parameters. The lattice stability parameters used here have been taken from [70Kau] and not varied during the calculations.

Table 5 Lattice Parameters of Ti-Rh Phases

Phase	Reference	Composition, at.% Rh	Lattice parameters, nm		Annealing temperature, °C
			a	c	
(βTi)	[62Buc]	5	0.3264
		10	0.3242
		12.5	0.3240
		15	0.3228
	[64Rau]	4	0.3245
		12	0.3223
	[66Rau]	12	0.3217	...	700
		15	0.3214	...	600-1000
		20	0.3178	...	600-650
		25	0.3164	...	800-1100
Ti_2Rh	[66Ere]	27.5	0.3157	...	1100
		33.3	0.3078	0.9882	...
Ti_3Rh_5	[64Rau]	30	0.306	0.981	...
		62.5	0.536	1.042	...
$TiRh_3$	[59Dwi]	75	0.3845	...	900, 600
					(a)
(Rh)	[66Ere]	73-80	0.3823	...	1500
		75	0.3821
		77.5-80	0.3815	...	1630-600
	[66Rau]	95	0.3807	...	1200-1600

(a) Crushed powders.

Table 6 Lattice Parameters of Structures near 50 at.% Rh

Reference	Composition, at.% Rh	Structure	Lattice parameters, nm			Annealing temperature, °C
			a	b	c	
[62Dwi]	50	Tetragonal	0.2735	...	0.3679	Distorted CsCl
[66Ere]	50	Monoclinic	0.296	0.286	0.341	$\alpha = 90^\circ 37'$
[64Ram,	35	CsCl	0.311
64Sch1,	50	CuAuI	0.4173	...	0.354	...
64Sch2]	55	NbRu	0.415	0.4111	0.340	...
	57	CuAuI	0.411
[66Rau]	45	CuAuI	0.427	...	0.333	1190-1300
	55	CuAuI	0.3120	640-1630
	37.5	CsCl	0.3120	1200
	40	CsCl	0.3121	800-1200
	42.5	CsCl	0.3100	1200

α TiRh and β TiRh have been represented as a single Wagner-Schottky phase, TiRh, with free energy:

$$G^i = F_{\text{TiRh}} + RT(x_{\text{Ti}} \ln x_{\text{Ti}} + x_{\text{Rh}} \ln x_{\text{Rh}} + v \ln v + s \ln s - (1 + v) \ln (1 + v)) + C^i s + D^i v$$

Table 7 Thermodynamic Parameters

Lattice stability parameters of Ti and Rh [70Kau], J/mol, J/mol · K

$$\begin{aligned} F_L(\text{Ti}) &= 0 \\ F_{\text{bcc}}(\text{Ti}) &= -16234 + 8.368 T \\ F_{\text{cph}}(\text{Ti}) &= -20585 + 12.134 T \\ F_{\text{fcc}}(\text{Ti}) &= -17238 + 12.134 T \end{aligned}$$

$$\begin{aligned} F_L(\text{Rh}) &= 0 \\ F_{\text{bcc}}(\text{Rh}) &= -11841 + 12.761 T \\ F_{\text{cph}}(\text{Rh}) &= -18117 + 8.996 T \\ F_{\text{fcc}}(\text{Rh}) &= -18711 + 8.368 T \end{aligned}$$

Interaction parameters of the Ti-Rh solution phases, J/mol

This evaluation	[70Kau] (calculated)
$B_L = -161000$	$B_L = -150783$
$C_L = 0$	
$B_{\text{bcc}} = -180000$	$B_{\text{bcc}} = -148038$
$C_{\text{bcc}} = 40000$	
$B_{\text{fcc}} = -131000$	$B_{\text{fcc}} = -146658$
$C_{\text{fcc}} = 40000$	
$B_{\text{cph}} = -95000$	$B_{\text{cph}} = -109420$
$C_{\text{cph}} = 40000$	

Compound free energy functions, J/mol, J/mol · K

$$\begin{aligned} F_{\text{Ti}_2\text{Rh}} &= -56037 + 8.0 T & C_{\text{TiRh}} &= 102500 \\ F_{\text{TiRh}} &= -70000 + 8.0 T & D_{\text{TiRh}} &= 47000 \\ F_{\text{Ti}_3\text{Rh}_5} &= -59363 + 5.0 T & & \\ F_{\text{TiRh}_3} &= -56660 + 8.3 T & & \end{aligned}$$

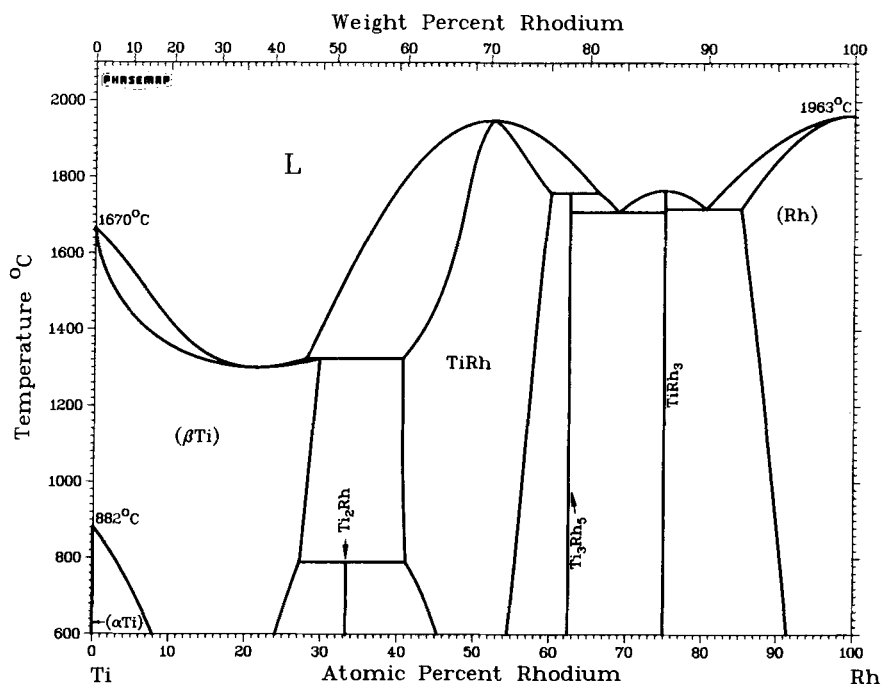
The Wagner-Schottky compound is conceptually resolved into Ti and Rh sublattices; v is the concentration of vacancies on the Ti sublattice; s is the concentration of substitutional Ti atoms on the Rh sublattice; X_{Ti} and x_{Rh} are the concentrations of Ti and Rh on their respective sublattices; and x is the overall composition. All concentrations are referred to the total number of atoms. The concentrations of vacancies and substitutions are determined by minimizing the Wagner-Schottky free energy with respect to the variables s and v .

Ti₂Rh, Ti₃Rh₅, and TiRh₃ have been represented as stoichiometric line compound with compositions 33.333, 62.5, and 75 at.% Rh, respectively.

Thermodynamic Calculations. Because many details of this phase diagram are not known, they could not be modeled by thermodynamic calculations. The purpose of the present calculations has been rather to explore the types of equilibria that seem to be possible thermodynamically. For the purpose of the calculations, some tentative choices had to be made between the two versions of the diagram, and it must be emphasized that the present choices do not constitute an evaluation of the experimental data. On the (Rh)-rich side, the eutectic transformation was chosen because it is the most simply reconciled with large negative interaction free energies. On the Ti-rich side, however, the congruent melt was chosen because it falls naturally in a series of congruent points (Ti-Ru, Ti-Rh, Ti-Pd).

The solution phases were modeled using asymmetric interactions, but no excess entropies. The minimum in the (β Ti) liquidus and solidus requires a large difference between the asymmetries of the liquid and bcc interactions. The liquid was modeled as a regular solution, and all asymmetry was attributed to the solid phases. The liq-

Fig. 2 Calculated Phase Diagram



Using thermodynamic parameters listed in Table 7.

J. L. Murray, 1982.

uidus and solidus curves determine differences between the interaction free energies. The overall magnitude of the interactions is determined by the $(\beta\text{Ti})/((\alpha\text{Ti}) + (\beta\text{Ti}))$ boundary. These calculations give free energies that agree in magnitude with those calculated by [70Kau] and good representations of the solution phase boundaries.

The parameters of TiRh_3 were determined by the (Rh) solvus and by placing a (Rh) eutectic at about 1720 °C. The parameters of TiRh were determined by the congruent melt and the extent of the single-phase region. Finally, the free energies of the compounds Ti_3Rh_5 and Ti_2Rh were determined by their three-phase equilibria (in the instance of Ti_3Rh_5 , by a rough guess at a peritectic temperature). None of the enthalpies or entropies thus determined is unreasonable and the model of the system appears to be a reasonable and self-consistent, if very approximate, representation of the thermodynamics.

The parameters used in the present calculation are compared to the regular solution parameters calculated by [70Kau] in Table 7. The phase diagram calculated using the thermodynamic parameters listed in Table 7 is shown in Fig. 2.

Cited References

- 58Nev: Nevitt, M. V., "Atomic Size Effects in Cr30-Type Structure", *Trans. AIME*, 212, 350-355 (1958).
- 59Dwi: Dwight, A. E. and Beck, P. A., "Close-Packed Ordered Structures in Binary AB_3 Alloys of Transition Elements", *Trans. AIME*, 215, 976-979 (1959).
- 60Nev: Nevitt, M. V., Downey, J. W., and Morris, R. A., "A Further Study of Ti_2Ni -Type Phases Containing Titanium, Zirconium or Hafnium", *Trans. AIME*, 218, 1019-1023 (1960).
- 62Buc: Buckel, W., Dummer, G., and Gey, W., "Superconductivity and Lattice Structure of Titanium-Rhodium Alloys", *Z. Angew. Phys.*, 14, 703-706 (1962) in German.
- 62Dwi: Dwight, A. E., "Equiatomic Phases", USAEC Report ANL-6677, 258-259 (1962).
- 63Rau: Raub, Ch. J. and Andersen, C. A., "On the Superconductivity of Ti- and Zr-Rh Alloys", *Z. Phys.*, 175, 105-114 (1963) in German.
- 64Ram: Raman, A. and Schubert, K., "Structural Investigations on some Alloy Systems Homologous and Quasi-Homologous to T^4-T^{99} ", *Z. Metallkd.*, 55(11), 704-710 (1964) in German.
- 64Sch1: Schubert, K., Meissner, H. G., Raman, A., and Rossteutscher, W., "Structure Data for Intermetallic Phases (10)", *Naturwissenschaften*, 51(2), 506-507 (1964).
- 64Sch2: Schubert, K., Meissner, H. G., Raman, A., and Rossteutscher, W., "Structure Data for Intermetallic Phases (9)", *Naturwissenschaften*, 51(12), 287-288 (1964).
- 65Ere: Eremenko, V. N., Shtepa, T. D., and Gritsenko, E. E., "Intermediate Phases in Titanium Alloys with Iridium and Rhodium", paper from Novye Issled Titan Splavov, Nauka, Moscow, 25-29 (1965).
- 66Ere: Eremenko, V. N., Shtepa, T. D., and Sirotenko, V. G., "Intermediate Phases in Alloys of Titanium with Iridium, Rhodium, and Osmium", *Poroshk. Metall.*, 42(6), 68-72 (1966) in Russian; TR: *Sov. Powder Metall.*, 42(6), 487-490 (1966).
- 66Rau: Raub, E. and Roschel, E., "The Titanium-Rhodium Alloys", *Z. Metallkd.*, 57(7), 546-551 (1966) in German.
- 69Gie: Giessen, B. C., Wang, R., and Grant, N. J., "New A_3B_5 Phases of the Titanium Group Metals with Rhodium", *Trans. AIME*, 245(6), 1207-1210 (1969).
- 70Kau: Kaufman, L. and Bernstein, H., *Computer Calculation of Phase Diagrams*, Academic Press, NY (1970).
- 72Ere: Eremenko, V. N. and Shtepa, R. D., "Phase Equilibria in the Binary Systems of Titanium with Ruthenium, Osmium, Rhodium, Iridium, and Palladium", *Colloq. Int. CNRS*, (205), 403-413 (1972) in German.
- 74Coc: Cocke, D. L. and Gingerich, K. A., "Thermodynamic Investigation of the Gaseous Molecules TiRh , Rh_2 and Ti_2Rh by Mass Spectrometry", *J. Chem. Phys.*, 60(5), 1958-1965 (1974).
- 75DeB: DeBonte, W. J., Poate, J. M., Melliar-Smith, C. M., and Levesque, R. A., "Thin-Film Interdiffusion. Pt. 2. Ti-Rh, Ti-Pt, Ti-Rh-Au and Ti-Au-Rh", *J. Appl. Phys.*, 46(10), 4284-4290 (1975).
- 75Sht: Shtepa, T. D., "Interaction of Titanium with Platinum-Group Metals", *Fiz. Khim. Kondens. Faz. Sverkhverd. Mater.*, 175-191 (1975) in Russian.
- 82Mur: Murray, J. L., "The Ir-Ti (Iridium-Titanium) System", *Bull. Alloy Phase Diagrams*, 3(2), 205-211 (1982).

Ti-Rh evaluation contributed by Joanne L. Murray, Center for Materials Research, National Bureau of Standards. Thermodynamic calculations have been made using computer programs generously made available by E.-Th. Henig and H. L. Lukas, of the Max-Planck Institute, Stuttgart, Federal Republic of Germany. This work was (partially) supported by Office of Naval Research funds through the Joint Program on Critical Compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data, National Bureau of Standards. Literature searched through 1981. Dr. Murray is the ASM/NBS Data Program Category Editor for binary titanium alloys.

The Ni-V (Nickel-Vanadium) System

58.69

50.9415

By J. F. Smith and O. N. Carlson
Iowa State University

and

P. G. Nash
Illinois Institute of Technology

Phase Relationships

General Features. Of historical interest is the initial investigation of the Ni-V system by Giebelhausen [15Gie] in 1915. With V of only 94% purity, he was able to show solubility on the Ni-rich side as extending to at least 39 at.% V, and his reported depression of melting

temperatures on both the Ni-rich and V-rich sides is qualitatively compatible with subsequent investigations, which have found a eutectic near the center of the system.

These subsequent investigations have added appreciably to the understanding of the system and, as shown in