The Niobium (Columbium)-Platinum Constitution Diagram

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The Nb-Pt system was investigated over the entire composition range by metallography and X-ray diffraction analysis. The solubility limits of terminal and intermediate phases and solidus temperatures were determined. α-Nb dissolves ~12 at. pct Pt at 2040 °C and ~5 at. pct Pt at 1150 °C; α-Pt dissolves ~20 at. pct Nb at 2000 °C and ~18 at. pct Nb at temperatures below 1700 °C. The presence of six intermediate phases, Nb_3Pt (Cr_3O, A15 or β-W type), σ(~Nb_2Pt, β-U type), $Nb_{1-x}Pt_{1+x}$ (AuCd type), α'-Pt (undetermined structure), $NbPt_2$ ($MoPt_2$ type), α-$NbPt_3$ ($TiCu_3$ type), and β-$NbPt_3$ (β-$NbPt_3$ type) was confirmed. The phase $NbPt_3$ melts congruently at ~2040 °C, and σ forms peritectically at ~1800 °C. By analogy with related systems, the high-temperature phase α'-Pt is probably an extension of and isomorphous with α-Pt solid solution. Eight three-phase reactions are described, the mean atomic volumes are given, and crystal chemical relationships among the six homologous T_5-T_{10} systems (T_5 = V, Nb, Ta; T_6 = Pd, Pt) are discussed.

I. INTRODUCTION

In the course of an extended study of the phase diagrams of refractory and noble metals, the T_5-T_{10} systems, *i.e.*, binary systems composed of one of the T_5 transition metals, V, Nb, or Ta with one of the T_{10} metals, Pd or Pt, have been investigated in a collaborative effort. Of the six systems thus defined, studies of the V-Pt system,[1] the Nb-Pd system,[2] the Ta-Pd system,[3] and the Pt-rich portion of the Ta-Pt system[4]* have already been presented; for V-Pd a phase diagram is given in the literature.[5]* The present paper reports a phase diagram for the last remaining system, Nb-Pt, thus completing this program.

As for other T_5-T_{10} systems, a survey of intermediate phases in the Nb-Pt system was first conducted by Greenfield and Beck[6] who identified a σ phase and a phase with the Cr_3O (β-W, A15) type structure. Knapton[7] later reported that the liquidus in this system passes through a maximum near the composition $NbPt_3$. In 1961 a Nb-Pt phase diagram was presented by Kimura and Ito[8] who confirmed the presence of the σ and β-W phases and also reported an intermetallic compound having the approximate composition $NbPt_3$ (of undetermined crystal structure) and gave some evidence for a compound at the equiatomic (NbPt) composition.

Subsequently, Giessen, Grant, and Parker[9,10,11] reported in an alloy chemical study that the equiatomic compound, NbPt, possesses a AuCd(B19) type structure and that another phase occurs near this composition which is stable only at high temperatures (1670 to 1780 °C).[10] They also reported a compound, $NbPt_2$, having an orthorhombic structure isomorphous with $TaPd_2$ ($MoPt_2$ type)[11] and two compounds at the approximate composition $NbPt_3$.[9] α-$NbPt_3$ was reported as having an orthorhombic $TiCu_3$ (DO_a) type structure, and β-$NbPt_3$ was identified as a monoclinic phase with a 12-layer stacking sequence.[9] The structure of the isomorphous phase β-$TaPt_3$ has been described in detail.[4] It was suggested[9] that α-$NbPt_3$ may be stabilized with respect to β-$NbPt_3$ by very small amounts of interstitial impurities. With the exception of β-$NbPt_3$, all of the phases previously reported were independently confirmed by Maldonado and Schubert.[12] These authors also observed (without structure identification) a phase probably corresponding to β-$NbPt_3$ but assumed it to have a somewhat higher Pt content ($NbPt_3$+) than α-$NbPt_3$.

The purpose of the present study was to provide a more reliable constitution diagram by studying the solid-state phase boundaries and invariant reactions, especially those involving αPt or α'-Pt, and by resolving discrepancies between structural determinations.

II. EXPERIMENTAL METHODS

The starting materials were as follows:

(1) Niobium rondelles, 99.6 pct pure, obtained from the Electro Metallurgical Co.,* with a typical major impurity analysis (wt pct): Ta (0.15); Ti, Fe, O (0.1 each); C, H (0.05 each); niobium pellets, 99.6 pct pure, obtained from Gallard-Schlesinger Chemical Manufacturing Corp.* with typical major impurity analysis: Fe (0.1); Al, Si (0.03 each); Ca, Mg (0.01 each). Cr, Cu, and Ta could not be determined by spectrographic analysis due to niobium interferences, but Ta is known to be a principal impurity in this material. No oxygen, nitrogen, or carbon analyses were available.

(2) Platinum sheet, 1/32-inch thick, with a nominal purity of 99.9 pct. Spectrographic analysis revealed (wt pct): Pd (0.1); Ru, Cu, Mg (0.01 each); and all other impurities (<0.01 each).

Sample preparation, vacuum heat treatment, metallography, and X-ray diffraction studies followed closely the methods used in earlier, related studies by the authors and

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*See also Reference 18.

*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

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their collaborators for which details are given in References 1 through 4 and 13 (see especially References 1 and 13). Procedures will therefore be described only where they differ from those described in the recently published study of the Nb-Pd system.[2]

The alloy samples typically weighed 10 to 20 g. They were prepared by arc melting, and weight losses after melting were always <1 pct and generally <0.2 pct. Nominal starting compositions were used in lieu of chemical analyses. Such a procedure had proven to be acceptable in a previous study of the Nb-Ir system[14] and many subsequent studies,[1-4,13] which utilized similar methods of melting and annealing. Reported alloy compositions (Figure 1), including the microprobe data, are estimated to have an accuracy of ± 1 at. pct.

Temperature measurements, including solidus temperatures, are accurate to ± 10 °C unless otherwise noted. Metallographic, electron microprobe, and X-ray diffraction techniques (Cu-K_α radiation) and the determination of invariant reaction temperatures followed exactly the techniques described in References 1 and 13. In critical regions of the phase diagram, where it is important to establish whether one sample melts at the same temperature as the other or at slightly different temperatures, it was possible for us to measure the solidus temperatures of two adjacent samples simultaneously. This is done by substituting the second sample for the standard wire (see Figure 1 in Reference 1). This method was particularly helpful, for example, in establishing that the αPt solid solution forms by a peritectic reaction at 2000 °C rather than forming a congruent maximum as reported by Kimura and Ito.[8] In this case we observed that two samples containing 77.5 and 80.0 at. pct Pt, respectively, melted at the same temperature with a sensitivity of ± 5 °C even though the absolute accuracy of the temperature measurement was ± 10 °C. The location of liquidus lines was determined, approximately, by microscopic examinations of our melting point samples which included visual estimates of the relative percentages of solid and liquid phases present.

Heat treatment included homogenization annealing at 1900 °C for 3 hours for Nb-rich alloys containing up to 20 pct Pt and homogenization at 1600 to 1700 °C for 6 to 12 hours for all other alloys. Annealing treatments above 1100 °C and solidus temperature determinations were conducted in a high-temperature vacuum furnace using methods which have been described in previous publications.[1,2,3] Annealing treatments at or below 1150 °C were done in evacuated quartz tubes. The equilibration treatments following the homogenization anneals were carried out following the typical schedule given in Table I.

Table I. Typical Equilibration Treatments for Niobium-Platinum Alloys

Temperature (°C)	Time, Hours
1900	3
1700	6
1600	12
1500	24 (1 day)
1300	168 (1 week)
1150	504 (3 weeks)
1000	744 (1 month)

Quenching at rates of 30 to 100 °C per second, as generally obtained in this work, was fast enough to retain the high-temperature phases encountered in this study with the exception of the α'-Pt phase. The presence of this phase was established by metallographic and DTA studies.

III. RESULTS AND DISCUSSION

A. *The Constitution Diagram*

The proposed constitution diagram for the niobium-platinum system is shown in Figure 1. Crystallographic data, composition limits, and melting temperatures of the intermediate phases are summarized in Tables II and III. The phase diagram differs significantly from the only one previously published. There are nine invariant reactions:

a peritectic reaction, $L + \alpha$-Nb solid solution = Nb_3Pt at 2040 °C;
a peritectic reaction, $L + Nb_3Pt = \sigma$ at 1800 °C;
a eutectic reaction, $L = Nb_{1-x}Pt_{1+x} + \sigma$ at 1700 °C;
a peritectic reaction, $L + \alpha'$-Pt = $Nb_{1-x}Pt_{1+x}$ at 1750 °C;
a peritectic reaction, $L + NbPt_2 = \alpha'$-Pt at 1780 °C;
a eutectoid reaction, α'-Pt = $Nb_{1-x}Pt_{1+x} + NbPt_2$ at 1670 °C;
a peritectic reaction, $L + NbPt_3 = NbPt_2$ at 1990 °C;
congruent solidification of $NbPt_3$ at 2040 °C;
a peritectic reaction, $L + NbPt_3 = \alpha$-Pt solid solution at 2000 °C.

In the following, the proposed phase diagram, Figure 1, and some metallographic, X-ray diffraction, electron microprobe, and DTA evidence for it will be discussed.

Platinum is soluble in the bcc α-Nb solid solution up to ~12 at. pct Pt at 2040 °C, but there is a significant decrease in solubility at lower temperatures, and the solid solution range extends only to 5 at. pct Pt at 1150 °C. The solvus boundary was established by metallographic and electron microprobe analyses of equilibrated alloys with 10 to 18 at. pct Pt quenched from various temperatures. The α-Nb solid solution produced by quenching from the homogenization temperature (1900 °C) and then re-annealing at 1150 °C contains fine, plate-like precipitates of Nb_3Pt (Figure 2). The identification of these precipitates as Nb_3Pt is based on the X-ray diffraction patterns which contain only the lines of the α-Nb solid solution and Nb_3Pt.

The microstructure of an alloy equilibrated in the narrow composition range between Nb_3Pt and σ is shown in Figure 3. It consists of Nb_3Pt particles in a matrix of σ. The σ phase equilibrates with $Nb_{1-x}Pt_{1+x}$ at higher Pt contents, as shown in Figure 4.

The existence of the eutectic reaction at 1700 °C is confirmed by the "as-cast" microstructure for the alloy containing 45 at. pct Pt shown in Figure 5.

The existence of the high-temperature phase α'-Pt was originally deduced from the observation of structures showing evidence of decomposition on cooling (Figure 6).[10] The existence of this phase was subsequently confirmed by DTA measurements conducted at the University of Geneva by R. Flukiger.[15] The thermal arrests observed by Flukiger (using two alloys containing 57 and 62 at. pct Pt) are in complete agreement with the temperatures of the peritectic and eutectoid transformations of α'-Pt shown in Figure 1, within

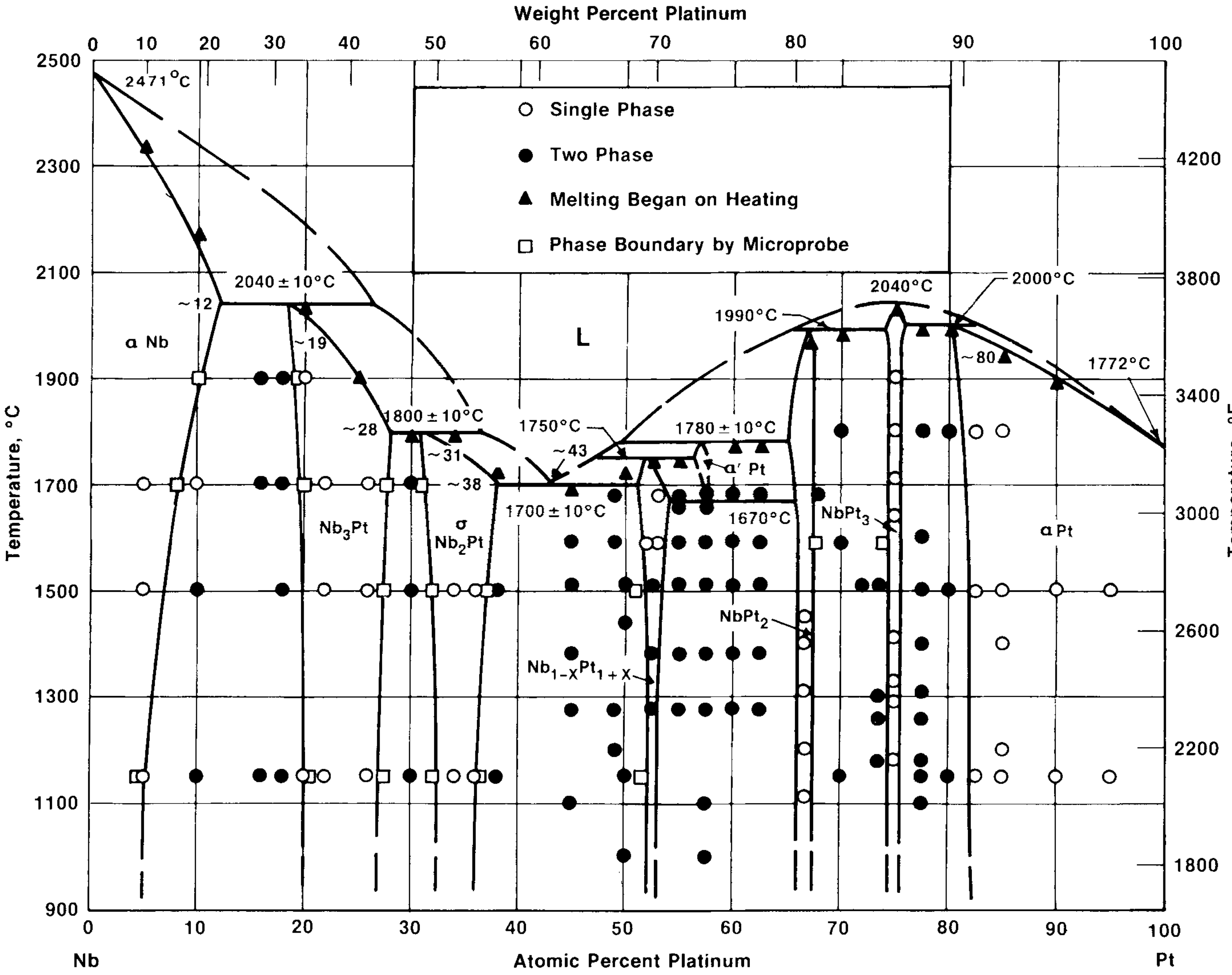

Fig. 1 — The Nb-Pt constitution diagram.

Table II. Crystallographic Data for Niobium-Platinum Intermediate Phases

Intermediate Phase	Crystal System	Space Group	Structure Type	No. Atoms Per Unit Cell	Ref.	Composition Limits, At. Pct Pt	Melting Point, °C
Nb_3Pt	cubic	Pm3n	A15, Cr_3O, β-W	8	6, 16	19 to 28 1800 °C	2040*
σ(~Nb_2Pt)	tetragonal	P4/mnm	β-U, $D8_b$	30	6	31 to 38 1700 °C	1800*
$Nb_{1-x}Pt_{1+x}$	orthorhombic	Pmma	AuCd, B19	4	9, 12	51 to 53 1700 °C	1750*
α'-Pt	undetermined		undetermined	—	10	~57 1750 °C	1780*
$NbPt_2$	orthorhombic	Immm	$MoPt_2$	6	9, 11, 12	~67 1600 °C	1990*
α-$NbPt_3$	orthorhombic	Pmnm	β-$TiCu_3$, DO_a	8	9, 12	~75 1600 °C	
β-$NbPt_3$	monoclinic	$P2_1/m$	β-$NbPt_3$	48	4, 9	~76 1600 °C	2040

*peritectic decomposition temperature

Table III. Lattice Parameters of Intermediate Phases and Terminal Solid Solutions in the Niobium-Platinum System

At. Pct Pt	Phase	Lattice Parameter(s), Å†			c/a	Ref.
		a	*b*	*c*		
5	α-Nb	3.277				*
10	α-Nb	3.260				*
20	Nb_3Pt	5.182				*
28	Nb_3Pt	5.139				*
32	σ	9.940		5.145	0.518	*
38	σ	9.902		5.132	0.518	*
50	$Nb_{1-x}Pt_{1+x}$	2.780	4.983	4.611		9
67	$NbPt_2$	2.801	8.459	3.951		9
75	α-$NbPt_3$	5.534	4.873	4.564		9
75	β-$NbPt_3$	5.537	4.870	22.33	$\alpha = 90°32'$	9
82	α-Pt	3.940				*
85	α-Pt	3.935				*
90	α-Pt	3.927				*
95	α-Pt	3.924				*

†The X-ray data were measured at room temperature and are generally accurate to 0.1 pct.
*this study

the experimental error of the measurements (±10 °C). The thermal arrests were reproducible on three separate heating and cooling cycles.[15] In the present study, the eutectoid transformation temperature was bracketed by metallographic studies on samples quenched from above and below 1670 °C. Samples annealed below this temperature always contained a fine spheroidized structure (Figure 7), in contrast to samples annealed above 1670 °C which have the unresolved eutectoid microstructure (Figure 6). The quenching rates used in this study (30 to 100 °C per second) were too slow to prevent the eutectoid decomposition completely, but some undecomposed α'-Pt may have been retained. Similar microstructures have been observed in the Nb-Pd,[2] Ta-Pd,[3] and Ta-Pt[4] systems for analogous high-temperature phases (α-NbPd, β-TaPd, and TaPt(HT), respectively).

The occurrence of the congruently melting phase $NbPt_3$ is straightforward and is not documented here further. It coexists with $NbPt_2$, as shown in Figure 8. The peritectic formation of $NbPt_2$ is indicated by the solidus measurements, particularly in the case of the alloy containing 70 at. pct Pt, which would have to possess a solidus temperature <1990 °C if a eutectic existed in this region. The available evidence, therefore, suggests that $NbPt_2$ forms by a peritectic reaction. Similar arguments support the peritectic formation of the α-Pt solid solution at 2000 °C. The coexistence of α-Pt and $NbPt_3$ is demonstrated by the coherent structure shown in Figure 9. Such structures may be metastable and are often associated with extensions of the terminal solid solutions. Our metallographic and X-ray studies indicate that the α-Pt solid solution dissolves up to ~20 at. pct Nb at 2000 °C and about 18 at. pct Nb at lower temperatures, which leads us to construct the solvus boundary as shown in Figure 1. However, it is important to remember that this solvus boundary may, in fact, be a metastable "coherent" boundary. The true equilibrium boundary may perhaps be located at lower solute concentrations.

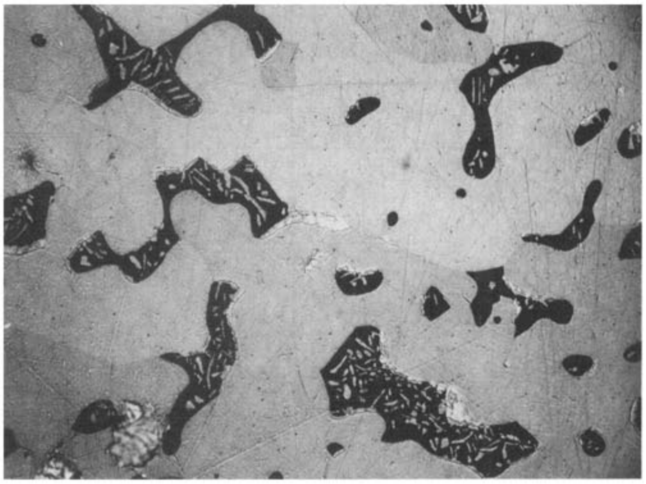

Fig. 2—18 at. pct Pt annealed at 1150 °C for three weeks. Nb_3Pt (light) matrix containing α-Nb (dark) globules in which precipitation of Nb_3Pt has occurred during annealing. Magnification 296 times.

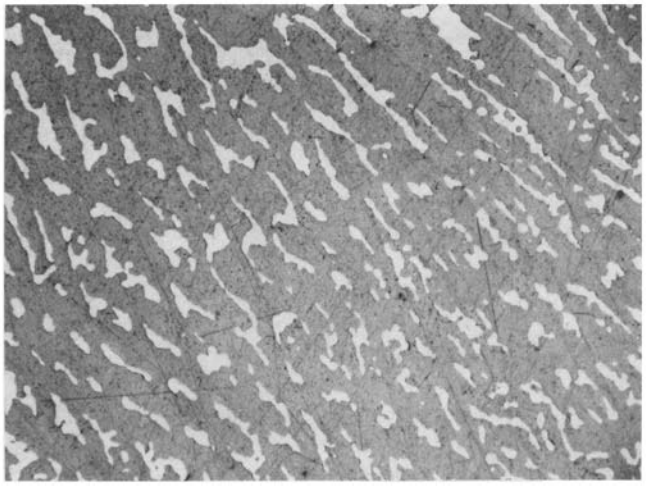

Fig. 3—30 at. pct Pt annealed at 1500 °C for one day. Nb_3Pt (light) particles in a matrix of σ (dark). Magnification 117 times.

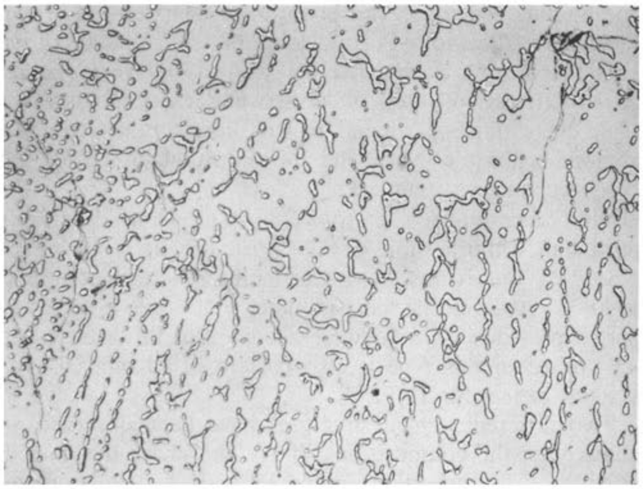

Fig. 4 — 38 at. pct Pt annealed at 1500 °C for one day. $Nb_{1-x}Pt_{1+x}$ (gray) globules in a matrix of σ (light). Magnification 118 times.

Fig. 6 — 55 at. pct Pt annealed at 1690 °C for six hours. Metastable primary $Nb_{1-x}Pt_{1+x}$ dendrites and an unresolved fine structure of $Nb_{1-x}Pt_{1+x}$ + $NbPt_2$ produced by decomposition of prior α'-Pt. Magnification 296 times.

The Nb-Pt phase diagram presented here resembles that given by Kimura and Ito[8] in some features, including the observation of the phases Nb_3Pt, $\sigma(\sim Nb_2Pt)$, α-NbPt (here $Nb_{1-x}Pt_{1+x}$), and $NbPt_3$, but differs primarily in that Kimura and Ito indicated the phase $NbPt_2$ to be an extension of the α-Pt solid solution. This is in contrast to subsequent crystallographic work,[11,12] which has identified $NbPt_2$ as having a distinctly different crystal structure, in agreement with the present study. The two investigations (Reference 8 and the present one) are in agreement in regard to the existence of the eutectic reaction at 1700 °C but disagree significantly concerning the solidus and liquidus temperatures. However, it should be noted that Kimura and Ito[8] placed their samples on an electrically-heated Mo sheet during their melting point determinations. This may have produced significant contamination of their samples.

B. *Intermediate Alloy Phases*

The observed alloy phases are of interest, particularly when making comparisons with related T_5-T_{10} alloy systems. A comparative review summarizing the crystallographic and melting mode data for all six T_5-T_{10} systems with Pd and Pt has been published;[17] therefore, the Nb-Pt phases will be described here only briefly as to their structure, composition, literature history, and alloy chemistry. They will be reviewed in order of increasing Pt content.

Nb_3Pt was first discovered by Geller, *et al.*[16] who also reported on the degree of atomic ordering. Its presence was confirmed by Greenfield and Beck[6] and later by other workers.[8,10,11] Its structure is of the cubic Cr_3O(A15, β-W) type. Of the six T_5-T_{10} systems, Nb-Pt resembles the systems

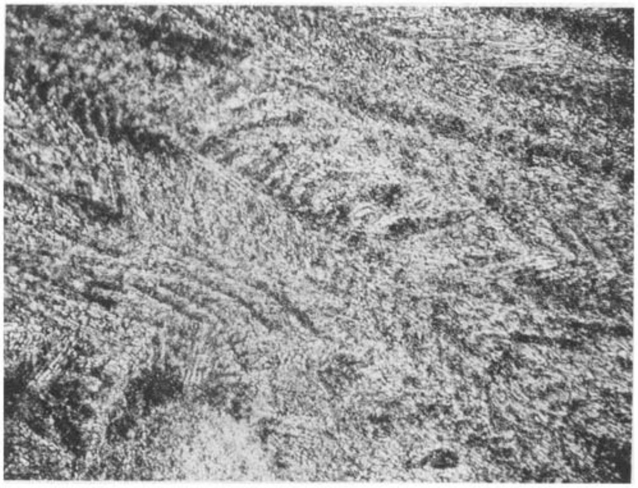

Fig. 5 — 45 at. pct Pt "as-cast" fine eutectic of σ + $Nb_{1-x}Pt_{1+x}$. Magnification 296 times.

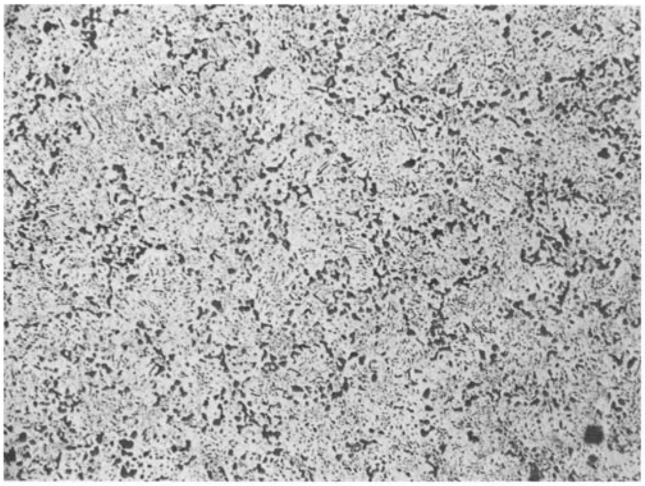

Fig. 7 — 57.5 at. pct Pt annealed at 1000 °C for one month. Globules of $NbPt_2$ in a matrix of $Nb_{1-x}Pt_{1+x}$. Magnification 296 times.

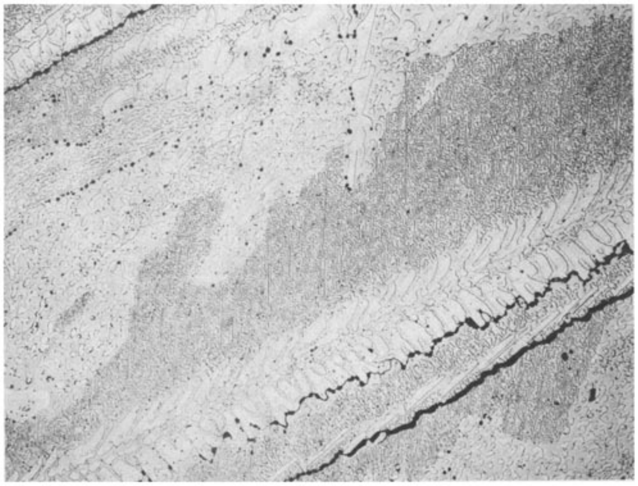

Fig. 8—70 at. pct Pt annealed at 1800 °C for four hours. $NbPt_3$ dendrites and globules in a matrix of $NbPt_2$. Magnification 118 times.

with T_5 = vanadium in having a Cr_3O-type intermediate phase; the other three systems do not show this phase.

The σ phase ($\sim Nb_2Pt$) was first reported by Greenfield and Beck[6] who identified its tetragonal crystal structure. Its presence in the Nb-Pt system has been confirmed by various investigators.[8,10,12] In the occurrence of a σ phase, Nb-Pt resembles the T_5-T_{10} systems with T_5 = Ta; the other three systems do not show this phase. Nb-Pt is unique in containing both a Cr_3O-type and a σ-type phase.

$Nb_{1-x}Pt_{1+x}$ was independently identified[9,12] as having the orthorhombic AuCd-B19 type structure. It coexists with σ and $NbPt_2$. An analogous phase having the same crystal structure occurs in the V-Pt system,[1] where it is observed at the equiatomic composition, in contrast to its marked off-stoichiometry in the present system which is expressed by its designation as $Nb_{1-x}Pt_{1+x}$.

As discussed above, the existence of α'-Pt was deduced from solidus measurements, DTA, and metallographic studies. By analogy to all other T_5-T_{10} systems, especially V-Pt[1] and Nb-Pd,[2] we expect this phase to be an extension of the face-centered cubic α-Pt solid solution. Confirmation of its crystal structure, however, must await a high-temperature X-ray diffraction study or, somewhat less conclusively, rapid quenching experiments such as those conducted on the analogous phase α-NbPd and β-TaPd in which the fcc Cu type structure was retained.[2,3]

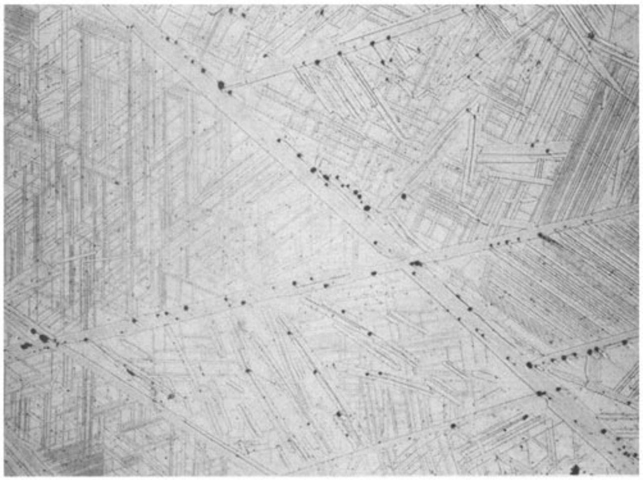

Fig. 9—80 at. pct Pt annealed at 1500 °C for one day. Coherent precipitate of $NbPt_3$. Magnification 118 times.

$NbPt_2$ forms over a narrow composition range. It possesses an orthorhombic crystal structure of the $MoPt_2$-type[9,11,12] and forms by a peritectic reaction at about 1990 °C. Accurate lattice parameter values have been reported previously[9,11] and were accepted in this study. An AB_2 phase of this type is also present in all other T_5-T_{10} systems except for Ta-Pt.[4,11]

Two different crystal structures have been observed in alloys with the composition $NbPt_3$. The phase designated α-$NbPt_3$[9,12] has an orthorhombic $TiCu_3$-DO_a-type structure with a two-layer stacking sequence. The phase designated β-$NbPt_3$[4,9] has a monoclinic structure with a 12-layer stacking sequence and the same layer type as α-$NbPt_3$; β-$TaPt_3$[4] is the only other T_5-T_{10} phase isomorphous with β-$NbPt_3$. We did not determine the relative location of the stability ranges of α-$NbPt_3$ and β-$NbPt_3$ in this study. Maldonado and Schubert[12] have stated that the $TiCu_3$-type structure (here α-$NbPt_3$) is stable below 1000 °C, and they designate β-$NbPt_3$ as having a Pt content somewhat higher than the stoichiometric composition. Additional X-ray studies including high-temperature X-ray diffractometry would be needed to clarify the stability ranges of these phases. Accurate lattice parameters for $NbPt_3$ phases have been reported previously and were accepted in this study.[9] $NbPt_3$ coexists with $NbPt_2$ and α-Pt.

The mean atomic volumes $\overline{V}$ of all phases listed in Tables II and III that are observable at room temperature are plotted in Figure 10. Almost all $\overline{V}$ values show a negative deviation from a linear "Zen's Law" interpolation

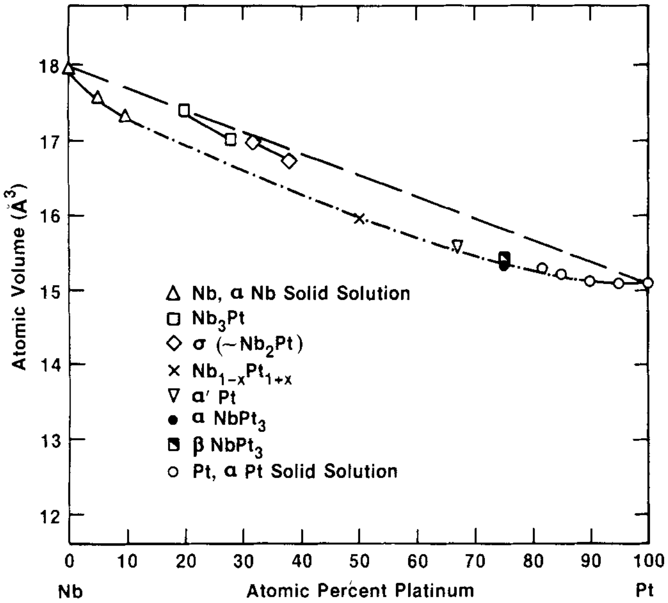

Fig. 10—Mean atomic volumes, $\overline{V}$, of Nb-Pt alloys. The dashed line represents a linear interpolation between pure Nb and pure Pt; the dashed-dotted line connects terminal solid solutions and 12-coordinated close-packed phases.

line (dashed). $\overline{V}$ for both terminal solid solutions and the three 12-coordinated, ordered close packed phases lies on a common, roughly parabolic $\overline{V}$ curve (dash-dotted), with the maximum negative deviation of $\overline{V}$ from the linear interpolation line occurring for $Nb_{1-x}Pt_{1+x}$. By contrast, the two Frank-Kasper phases Nb_3Pt and σ have much smaller or vanishing contractions, lying almost on the linear interpolation curve. The $\overline{V}$ data discussed are similar to those for other T_5-T_{10} systems[1-4] in their general behavior. It is of particular interest to compare the relatively large contraction of the ordered phase $Nb_{1-x}Pt_{1+x}$ to the small contraction found for a disordered equiatomic phase such as α-NbPd.[2]

IV. CONCLUDING REMARKS

The overall similarities and the subtle differences in the alloy chemistries of the six T_5-T_{10} systems containing Pd and Pt have been experimentally established by a series of studies concluded with the present paper. While some further comparative descriptive correlations can be made by a detailed comparison of the phase diagrams, a deeper understanding must now await the calculation of the structural energies of the alloy phases involved.

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