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Atomic Displacements in Palladium/Platinum Solid Solutions

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X-ray measurements reveal that Pd/Pt solid-solution alloys have higher Debye temperatures and lower root-mean-square dynamic displacements than the average for the pure metals. The root-mean-square static displacements are quantitatively interpreted in terms of a shortening of the Pd/Pt interatomic distance and the asymmetry of unlike neighbours about an average atom.

1. Introduction

Because of thermal vibrations, most of the atoms of a crystal are, at any instant, displaced from their ideal positions. The mean square magnitude of these "dynamic displacements", which are directly related to the Debye temperature, can be deduced from the measurement at two different temperatures of the intensities of Bragg peaks in the X-ray diffraction patterns. This applies both to elements and to compounds or solid solutions. However, atoms in solid solutions are subject to another, quite distinct form of disturbance. These are the "static displacements" arising from the size difference between solute and solvent atoms [1]. Thus, in a close-packed, cubic solid solution few of the atoms sit exactly on the lattice nodes. The magnitude of the static displacements is a measure of the structural distortion caused by the disparity of atomic sizes, and is also related to the variation of lattice parameter with composition. The thermal (dynamic) vibrations of the atoms take place about mean positions which are "statically" displaced from the lattice nodes.

If there is a measure of local order in the spatial arrangement of solute and solvent atoms, this should modify the local distortions and thus change the average magnitude of the static displacements. Studies of local order and of static displacements in solid solutions are thus complementary.

From measurements of the intensities of each of a series of Bragg peaks of a cubic (i.e. isotropic) solid solution at two temperatures, the static displacements (assumed invariant with temperature) can be determined separately from the dynamic displacements.

The system Pd/Pt was chosen for study primarily to provide a basis for comparison with short-range order studies using the field ion microscope (not yet conducted). The results obtained have intrinsic value, however, for comparison with similar studies on other solid solutions. In particular, the Pd/Pt system exhibits similarities with respect to the Ag/Au system, in that both systems exhibit negative deviations from Vegard's law [2, 3] and complete mutual solubility. Measurements have been made of Debye temperatures and of mean, dynamic and static displacements.

2. Experimental Procedures

The alloys were supplied in button form by Engelhard Industries*. Their compositions, checked by chemical analysis, were 7.4, 24.0, 32.2, 49.0, 64.5, 74.0, and 89.1 at. % Pd in the solution. Filings from the buttons were sieved through 325 mesh screens, then pressed into 2.5 × 1.3 cm briquettes under a pressure of

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*Engelhard Industries, Newark, New Jersey, USA.

5×10^3 lb/in.^{2} (1 lb/in.^{2} = 7×10^{-2} kg/cm^2). In this way, specimens of about 1 mm thickness were obtained.

The briquettes were sintered in a graphite crucible under a stream of helium for 1 h at 900° C. Each one was then polished and put back in a graphite crucible, which was in turn enclosed in a Pyrex capsule and sealed under a low pressure of helium. The capsules were heated for 18 h at 600° C and then furnace-cooled to room temperature. Back-reflection X-ray patterns, taken from the specimens after this treatment, revealed that they were fine-grained and had no preferred orientation. Each specimen was reannealed at 600° C for a few hours and then quenched to room temperature. The Bragg lines from these specimens were sharp and well defined.

A low-temperature specimen holder was constructed for use with the Norelco X-ray diffractometer. With this device, diffraction data were obtained both at room temperature and at boiling liquid-nitrogen temperature. Filtered molybdenum radiation was used. A proportional counter with suitable pulse-height discrimination gave nearly monochromatic radiation and eliminated the harmonics corresponding to one-half and one-third wavelengths.

The procedure of Chipman and Paskin [4] was used to correct the Bragg reflections for the contribution to the peak intensities due to temperature diffuse scattering, with the following modification. Because no value of Debye temperature was available from elastic constant data, a procedure of iteration was used as follows. The uncorrected intensities were used to calculate a Debye-Waller factor in the standard manner. This value was then substituted into the Chipman-Paskin correction formula to obtain corrected intensities, and the cycle was repeated until no change was obtained in the Debye-Waller factor. The resulting pseudo-Debye-Waller factors* for two different temperatures for each alloy were treated as described by Houska and Averbach [5]. They were also corrected for change with temperature, as given by Paskin [6].

3. Results

The results for the Debye temperature, θ, the root-mean-square dynamic displacement, $<\overline{U_{300}{}^2}>^{\frac{1}{2}}$, and the root-mean-square static displacement, $<\overline{U_s{}^2}>^{\frac{1}{2}}$, are given in table I and are shown plotted in figs. 1 to 3. From the scatter of the data in Debye temperature, an uncertainty of at least ±10° K may be estimated. A more thorough error analysis was not considered worthwhile. The values of θ for pure Pd and Pt were taken from specific heat and elastic constant data [7]. For Pt this value (>225° K) is in agreement with a recent X-ray measurement [8].

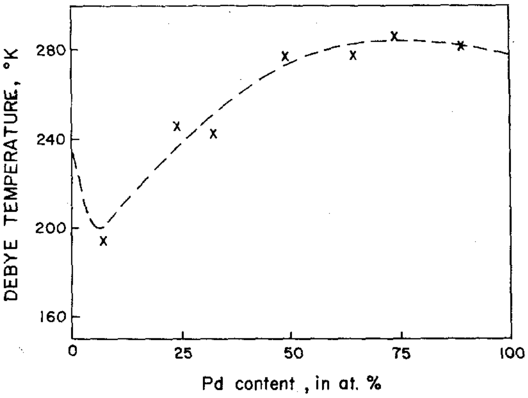

Figure 1 Debye temperatures of Pd/Pt alloys.

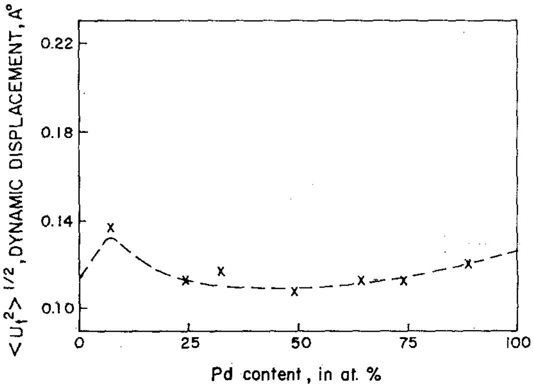

Figure 2 Dynamic displacements in Pd/Pt alloys.

4. Discussion

Fig. 1 shows that the alloys have a higher Debye temperature than the average calculated from

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*i.e. Debye-Waller factors incorporating the intensity reductions due to the static and dynamic displacements combined. The subsequent computations allow a true Debye temperature to be deduced.

TABLE I Debye temperature, dynamic and static displacements.

Pd (at. %)	θ_1 (300° K)	θ_2 (79° K)	$<\overline{U_t^2}>^{\frac{1}{2}}$ (300° K)	$<\overline{U_t^2}>^{\frac{1}{2}}$ (79° K)	$<\overline{U_s^2}>^{\frac{1}{2}}$
7.4	192.5	195.6	0.138	0.075	0.070
24.0	245.8	249.7	0.113	0.064	0.112
32.2	242.8	246.6	0.117	0.066	0.063
49.0	276.3	280.7	0.108	0.063	0.041
64.5	277.2	281.6	0.113	0.066	0.040
74.0	286.0	290.6	0.113	0.066	0.079
89.1	282.0	286.5	0.121	0.070	0.081

the values for the metals, except for the 7.4% Pd alloy.

The mean thermal displacements mirror the trend exhibited by the Debye temperatures, and both suggest that the binding in the alloy is stronger than in the pure metals.

The mean static displacements shown in fig. 3 reveal a behaviour believed not to have been observed by others. The interpretation of static displacements normally requires the assumption of some model for the solid solution. Although our results cannot yield a conclusion that the Pd/Pd and Pt/Pt interatomic distances are unchanged in solution, we can predict the behaviour observed in fig. 3 on the basis of a model in which the main local displacement is due to the Pd/Pt pair, and in which the observed mean static displacement results from an asymmetry in the arrangement of unlike atoms about any given atom.

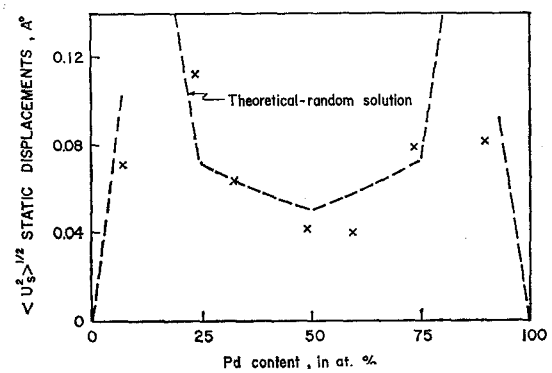

Figure 3 Static displacements in Pd/Pt alloys. The dotted line is a theoretical line based on an asymmetry model.

Consider the nearest-neighbour sites about any given site. For a given concentration, all the possible arrangements of unlike atoms among the nearest-neighbour sites may be determined. Under the assumption that the atoms in the nearest-neighbour sites are not displaced, the displacement of the given central site for each of these possible arrangements may be calculated. As an example, the following calculation is performed for a fcc lattice at a solute concentration of 1/6 atom fraction. There are then two solute atoms to be mixed on twelve sites. Choose one such site and place one solute atom in that site. If the line through the central atom and this solute atom is vertical, the nearest-neighbour atoms appear as shown in fig. 4a. There are five horizontal planes containing the nearest-neighbour atoms, and these planes are shown viewed from the side in fig. 4b. The numbers of nearest-neighbour atoms in these planes are as follows: I – 1, II – 4, III – 2, IV – 4, V – 1.

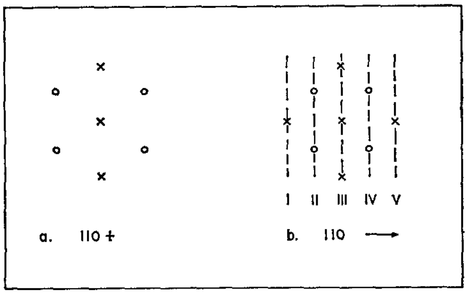

Figure 4 Nearest-neighbour positions in fcc lattice.

With one solute atom in I, there are eleven different arrangements for the other solute atom. These arrangements and associated displacements are listed below.

Arrangement	*Number*	*Displacement*
I-II	4	$(\sqrt{3}/2)\ \lvert y \rvert$
I-III	2	$(1/\sqrt{2})\ \lvert y \rvert$
I-IV	4	$(1/2)\ \lvert y \rvert$
I-V	1	0

Hence, the average displacement equals $\lvert y \rvert/11\ (4.\sqrt{3}/2 + 2/\sqrt{2} + 4/2 + 0) = 0.624\ \lvert y \rvert$, where y is the increment in distance (absolute value) between an A and B atom in solution. This average is the same for all the other arrangements corresponding to different initial positions of the first solute atom.

In a similar way, calculations can be made for different solute concentrations. An approximation procedure was adopted for large concentrations to make the calculations less tedious. In these calculations, a rule was followed: that, if two or more displacements are inconsistent with the initial requirement that the nearest-neighbour sites are not displaced, then the maximum displacement is accepted and the others are considered to adjust to yield consistency. The results for the approximate method are as follows.

Solute concentration	*Mean displacement*
0	0
1/12	1 $|y|$
1/6	0.73 $|y|$ (Compare with the exact value of 0.624 $|y|$ above.)
1/4	0.29 $|y|$
1/3	0.26 $|y|$
1/2	0.2 $|y|$

(These results are symmetrical about the concentration 1/2.)

For dilute concentrations less than a few at. %, the mean displacements may be roughly estimated as equal to $12x|y|/2$, where x is the solute concentration, to the same degree of approximation as used in the previous calculation. Here, we neglect other than nearest-neighbour interactions and overestimate the mean displacement. We consider the solute atoms to be isolated and calculate the displacement of the surrounding solvent atoms. The function yielded by these calculations is shown (dotted line) in fig. 3, for the value $|y| = 0.25$.

In view of the approximations made, the deviation between the calculated curve and the observations is not believed to be significant. However, the fact that the deviation is not large leads us to conclude that the asymmetry effect can explain the concentration-dependence of the mean static displacement.

We have investigated the concentration dependence of the root-mean-square static displacement as reported in the literature. Unfortunately, these data are not sufficiently numerous or accurate to conclude whether or not other systems with negative, Vegard's-law deviations exhibit the same behaviour. Certainly, a careful experimental evaluation of our suggestion is indicated. Incidentally, it should be noted that there may well be a concentration-dependence of $|y|$ to yield a non-symmetrical plot of the mean static displacement as a function of composition.

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