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ALLOYS. II. DISTRIBUTIONS AND INTERACTIONS OF AU AND NI ATOMS

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ABSTRACT

Previous work (Part I) has established that the position of each Au and Ni solute atom in dilute solution in Pt can be identified in the field ion microscope (FIM) as an α -dark spot. In the present work the exact positions of large numbers of solute atoms in the lattice were first determined from measurements of α -dark spot positions on ciné films which were taken during the pulsed field evaporation of several dilute binary alloys in the FIM. From these data radial distribution functions were generated, and solute-solute interaction energies up to 9th nearest-neighbors were calculated using the Clapp-Moss model. Heats of mixing were then calculated from the interaction energies. The research was aided by specially developed computer techniques which included displaying the solute atom distributions in a rotatable coordinate system. The results indicate clustering of Au atoms and ordering (anti-clustering) of Ni atoms as expected generally from previous thermodynamic data. The calculated heats of mixing were generally consistent with measured values. It was concluded that the FIM can be used, under appropriate conditions, as an effective tool for studying solute atom distributions.

1. INTRODUCTION

In the preceding Part I⁽¹⁾ we established that both Au and Ni atoms in dilute solution in Pt appear as α -dark spots in field ion microscope (FIM) images (e.g., Figs. 4 and 5 of Part I). In the present work this result was used to determine the 3-dimensional distribution of Au and Ni solute atoms in the dilute Pt based alloys studied in Part I. The exact positions of large numbers of solute atoms in the 3-dimensional alloy lattice were first determined from measurements on the ciné films which were taken during pulsed field evaporation as described in Part I. From these data radial distribution functions were generated, and solute-solute interaction energies were calculated. Also, macroscopic heats of mixing were calculated from the interaction energies and were compared with experiment. The results show directly that Au atoms cluster and Ni atoms order (i.e., exhibit anti-clustering).

Gold and Machlin⁽²⁾ and Machlin⁽³⁾ have carried out a previous FIM study of these same alloy systems with very much the same objectives in mind. These investigators accepted the results of DuBroff and Machlin⁽⁴⁾ and assumed that all observed dark spots corresponded to the positions of solute atoms. They then proceeded to determine short range order parameters, and calculate interaction energies. Their data were generally consistent with the clustering of Au atoms and the ordering of Ni atoms. However, their results are suspect for a number of reasons. As pointed out in Part I, they were not able to establish a one-to-one relation between solute atom concentration and dark spot concentration, and no distinction was made between α - and β -dark spots. Gold and

Machlin⁽²⁾ avoided this problem by assuming local concentration variations of ~1 at. % in their nominally 2 at. % alloys and then postulating that usable FIM specimens were only obtained from high concentration regions. In addition, they obtained interaction energies using either the crude quasi-chemical model⁽⁵⁾ or a model⁽³⁾ in which it is assumed that the number of i^{th} nearest-neighbor solute atom pairs is solely dependent on the interaction energy for the i^{th} pair.

These problems were largely overcome in the present work. First of all, a satisfactory correlation was found (Part I) between the concentrations of α -dark spots and solute atoms in all specimens, and we are therefore quite confident that they represent the positions of the solute atoms. The exact lattice positions of statistically significant numbers of solute atoms were then determined from the ciné films using a relatively powerful computer-based technique which was developed especially for this purpose. Finally, the data were analyzed on the basis of the more realistic statistical model of Clapp and Moss⁽⁶⁾. The results indicate, in general, that the FIM can be used effectively under conditions such as the present to study detailed atomic arrangements in solid solutions.

2. METHOD OF DETERMINING COORDINATES OF SOLUTE ATOMS

The lattice coordinates of all the solute atoms in a stack of successive net planes which were photographed during a pulsed field evaporation sequence (see Fig. 1 of Part I) were determined in two steps. First, the relative positions of all the solute atoms (α -dark spots) in a given planar layer (e.g., Fig. 4 of Part I) were calculated with respect to a particular atomic site which

was taken as an origin. Then the relative positions of the origins on successive layers were calculated, and the coordinates of all of the solute atoms were found relative to a single common origin. In order to carry out this tedious task for the thousands of cine film frames which were analyzed, extensive use was made of computer techniques.

A ball model of a typical stack of successive planes (i.e., {315} planes) is shown in Fig. 1a. The uppermost layer, which would be imaged in the FIM, is represented by the black balls. A 'Local Planar Coordinate System' such as indicated by OX_1 and OX_2 (Fig. 1b) was used to specify the positions of any atomic site in the plane in terms of the row and column integers M , N . The origin at O was chosen arbitrarily at a convenient atomic site. In the example shown sites A and B then have the coordinates $(1,0)$ and $(0,1)$.

The coordinates of an atomic site in the plane can also be expressed in a 3-dimensional coordinate system with the same origin as that used above which is based on the standard FCC unit cell with the unit axis vectors $[100]$, $[010]$ and $[001]$. This coordinate system was called the 'Local FCC Coordinate System'. The coordinates of atoms A and B (Fig. 1b) in this coordinate system are $(1.5, 0.5, 0)$ and $(0.5, 1, 0.5)$ respectively. There is a simple transformation between coordinates in these two systems, and, in fact, the Local FCC Coordinates of a site located at (M, N) are given by

$$(1.5 M + 0.5 N, 0.5 M + N, 0.5 N).$$

Thus, by specifying the digital position (M, N) of any α -dark spot with respect to an arbitrary origin O located at a lattice site we could calculate its Local FCC Coordinates.

Finally, all of the Local FCC Coordinates were converted to a final 'Common FCC Coordinate System' by first determining the vectors connecting the local origins on successive planes in the stacking sequence and then making the appropriate transformations. This was done by using the measuring cross hairs on the Vanguard Motion Analyzer (see Section 2.3, Part I) to determine the projected positions of the origins on successive planes (e.g., points O and O' in Fig. 1b) relative to a third reference point which was recorded on each frame of the ciné film and which was fixed with respect to the specimen tip itself. The projections of the vectors connecting the origins (e.g., $\overline{OO'}$ in Fig. 1b) were then obtained, and by using computer methods, it was possible to identify quickly the correct lattice vectors in the idealized lattice (i.e., the ball model in Fig. 1a). A detailed description of the technique is given in reference (7).

3. METHOD OF CALCULATING STATISTICAL DISTRIBUTIONS AND INTERACTION ENERGIES OF SOLUTE ATOMS

The solute atom radial distribution function is defined as

$$\begin{aligned} R(r_i) &= \text{average number of solute atoms around a solute atom} \\ &\quad \text{at the distance } r_i \text{ corresponding to the } i^{\text{th}} \text{ nearest-} \\ &\quad \text{neighbor shell.} \\ &= 2N_{AAi}/N_A \end{aligned} \tag{1}$$

The quantity N_{AAi} is the number of i^{th} nearest-neighbor solute atom pairs, and N_A is the number of solute atoms in a given volume. For a random distribution,

$$N_{AAi} = \frac{1}{2} \sum_i N m_A^2 \tag{2}$$

where z_i is the coordination number for the i^{th} shell, N is the total number of atoms, and $m_A = N_A/N$ is the fraction of solute atoms. Therefore,

$$R_{\text{ran}}(r_i) = z_i m_A \quad (3)$$

Thus, we have

$$\frac{R(r_i)}{R_{\text{ran}}(r_i)} = \frac{2 N_{AAi}}{z_i m_A N_A} \quad (4)$$

If the ratio $R(r_i)/R_{\text{ran}}(r_i)$ is greater than unity, then the solid solution exhibits clustering at that particular distance. On the other hand, a value less than unity indicates ordering.

In order to calculate this ratio the distances between all pairs of solute atoms in the stack of successive $\{hkl\}$ planes were calculated using the coordinates of the solute atoms in the Common FCC Coordinate System, and values of N_{AAi} were determined. Also, the coordination number z_i in equation (4) had to be corrected for present purposes because we were not studying an infinite crystal. The volume associated with each stack of $\{hkl\}$ planes consisted of a cylinder of diameter about $10 \sim 40$ atoms, and the surface to volume ratio was therefore relatively large. The coordination numbers for those atoms near the surface of this volume were lower than in an infinite crystal, and the average effective coordination numbers of the atoms within the volume were therefore reduced. Our procedure was therefore to find the average effective coordination number, $\bar{z}_i$, for each $\{hkl\}$ volume and use it in equation (4) in place of z_i . In order to obtain $\bar{z}_i$, we chose a typical volume for each $\{hkl\}$ crystallographic plane and specified the coordinates of all the lattice sites inside that volume. Then the coordination numbers for each atom were calculated and averaged over all the

atoms to obtain the final value of $\bar{Z}_i$. The results are given in Table 1.

Having the radial distribution function $R(r_i)$, the interaction energy between two solute atoms in the lattice, U_i which are i^{th} nearest-neighbors of each other can be calculated using the statistical model of Clapp and Moss⁽⁶⁾. In this model the total energy of the alloy is represented by the sum of all the pairwise energies between both like and unlike atoms, and it then follows that

$$U_i = E_i^{AA} + E_i^{BB} - 2E_i^{AB} \quad (5)$$

where, for example, E_i^{AA} is the pairwise interaction energy between an A atom and a B atom separated by the distance r_i .

Equation (5) can be obtained by considering an infinitely large lattice containing only two A atoms with all the rest being B atoms. If the two A atoms, which initially are very far apart, are brought together so that they are i^{th} nearest-neighbors of each other, the energy change of the system is given by the differences in the pairwise energies given in equation (5). The quantity U_i in this model is therefore the interaction energy between two A atoms in a matrix of B atoms. A positive value of U_i corresponds to an increase in energy of the system and therefore a repulsive interaction.

According to the Clapp-Moss model the interaction energies are related to the Warren short-range order parameters through

$$\ln(1 + \frac{\alpha_{0j}}{(1-\alpha_{0j})^2 m_A m_B}) = - \frac{1}{kT} \sum_f U_{Of} \alpha_{fj} \quad (6)$$

Here we take site 0 to be the origin and let j be any other site. The sum on the right is over all values of the dummy index f which runs over all sites except the origin. The quantity α_{0j} is the short-range order parameter which is related to the correlation between the types of atoms occupying sites 0 and j (see reference 6), and U_{0f} is the interaction energy between solute atoms in sites 0 and f as described by equation (5). All of the values of α_{0j} are equal when the j sites are in the same nearest-neighbor shell, and the same is true for the values of U_{0f} when the f sites are in the same shell. In the present work we assumed that all interactions were negligible beyond 9th nearest-neighbors. Therefore, the summation in equation (6) was cut off for all sites beyond the 9th nearest-neighbor shell. Under these conditions, equation (6) reduces to a set of 9 linear equations containing 9 different short-range order parameters, α_i ($i = 1, 2, \dots, 9$) and 9 interaction energies U_i ($i = 1, 2, \dots, 9$) where we have replaced all the α_{0j} values for the i^{th} shell by α_i and all the U_{0f} values for the i^{th} shell by U_i .

Furthermore, it can also be shown that α_i is related to the radial distribution function through

$$\alpha_i = \left(\frac{R(r_i)}{R_{\text{ran}}(r_i)} - 1 \right) \frac{m_A}{m_B} \quad (7)$$

Therefore, the α_i may be calculated from a knowledge of the experimentally determined radial distribution functions, and the U_i may then be calculated by means of equation (6).

Having the interaction energies, the heat of mixing can be calculated by means of the relation

$$\Delta H_M = \frac{N}{2} m_A m_B \sum_i z_i (\alpha_i - 1) U_i \quad (8)$$

Equation (8) may be obtained from equation (7) of Lin and Spruiell⁽⁸⁾ by taking the reference state for the enthalpy to be the unmixed components rather than the random alloy.

4. RESULTS

The numbers of sites which were examined for solute atom distributions in the 4.0 at. % Au-Pt, 0.62 at. % Au-Pt and 0.65 at. % Ni-Pt alloys were 29,309, 75,504 and 48,741 respectively. The radial distribution functions for the first 9 nearest-neighbor shells for these alloys are shown in Figs. 2, 3 and 4.

In order to obtain a more direct impression of the solute atom distributions the positions of all the solute atoms in each volume associated with a given stack of {hkl} planes were displayed visually using the computer technique described in Section 3.3 of Part I. Examples for the two Au-Pt alloys are shown in Figs. 5 and 6.

Using the radial distribution function results, the solute atom interaction energies were calculated by means of equations (6) and (7). The temperature, T , in equation (6) should, of course, be the equilibrium temperature of the alloy. Actually, each specimen was equilibrated at an elevated temperature and then cooled at a relatively rapid rate to room temperature. Under these conditions the solute atoms redistributed somewhat during the initial part of the cooling but then became frozen-in at a characteristic

"freeze-in" temperature. The freeze-in temperature, estimated to be 1200°K for the Au-Pt alloys and 1100°K for the Ni-Pt alloy, was then used in equation (6). The details of the method which was used in arriving at these results are given in Appendix A of reference 7. The resulting interaction energies out to 9th nearest-neighbors are given in Figs. 7 and 8. The error bars represent the uncertainties (standard deviations) arising from uncertainties in the measurements of $R(r_i)/R_{\text{ran}}(r_i)$.

Finally, the heats of mixing were calculated using equation (8), and the results are listed in Table 2 along with corresponding values estimated from thermodynamic data in the literature^(9,10). The latter values were obtained by extrapolating data taken at higher solute atom concentrations^(9,10) to the relatively low concentrations of the present alloys. These values are therefore approximate and may contain uncertainties as large as ±50%.

5. DISCUSSION

The results clearly indicate solute clustering in the Au-Pt alloys and ordering (anti-clustering) in the Ni-Pt alloy. This is the result expected on the basis of previous thermodynamic measurements^(9,10). This behavior is also in agreement with that deduced previously by Gold and Machlin⁽²⁾ on the basis of their FIM data. However, as we have pointed out previously, their data are probably unreliable in many respects.

In the case of Au atoms the Clapp-Moss model yields an attractive interaction which is significant at distances up to ~5-6Å (Fig. 7) while for Ni atoms there is a repulsive interaction

which is somewhat shorter-ranged (Fig. 8). This result for Au atoms seems consistent with the actual Au atom distribution displayed in Fig. 5. Here it can be seen that the Au atoms show a tendency to group themselves into clustered regions having radii $\sim 5\text{\AA}$.

The reason for the apparently larger interaction energy and larger value of the radial distribution function in the 0.62 at. % Au-Pt alloy than in the 4.0 at. % Au-Pt alloy at short distances is not entirely clear at present. At least some of this effect may be due to the fact that the pair-wise interaction energies are sensitive to the chemical environment. Actually, we would expect the effective pairwise interaction energy between two atoms in the relatively simple Clapp-Moss model to be a complex many-bodied parameter.

The values of the heat of mixing derived from the present FIM data are in general agreement with values estimated from data in the literature as seen in Table 2. Unfortunately, the comparatively large uncertainties in the different values make a detailed comparison impossible.

Finally, we note that the values in Figs. 7 and 8 are not sufficiently accurate to establish whether oscillatory type potentials (Friedel oscillations) exist at the larger distances of separation such as claimed by Machlin⁽³⁾. Clearly, the positive and negative values at the tails of the interaction energy curves, particularly for the Ni-Pt alloy in Fig. 8, fall within the expected range of the experimental uncertainty. We note in this

respect that there is no a priori reason to expect the total interaction energy to be strongly oscillatory, since other factors besides the distribution of free electron charge around the solute atoms may play an important role in determining the interaction energies.

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Table 1. Average Effective Coordination Numbers $\bar{z}_j$
for Volumes Associated with Different
Crystallographic Planes.

	{315}	{203}	{517}	{214}	{213}	Infinite Crystal
$\bar{z}_1$	11.0	10.2	8.8	11.3	10.3	12
$\bar{z}_2$	5.3	4.8	4.0	5.3	4.1	6
$\bar{z}_3$	18.2	17.2	14.5	18.0	18.6	24
$\bar{z}_4$	9.3	8.2	5.8	8.2	9.8	12
$\bar{z}_5$	18.4	15.8	11.0	15.3	16.6	24
$\bar{z}_6$	5.7	4.7	3.0	5.6	5.6	8
$\bar{z}_7$	32.6	27.8	18.5	29.1	32.6	48
$\bar{z}_8$	4.1	3.2	1.8	3.1	3.4	6
$\bar{z}_9$	23.5	20.2	10.5	20.2	22.7	36

Table 2. Heats of Mixing, ΔH_M

Alloy	Calculated from Present FIM Data (cal/mole)	Estimated from Thermodynamic Data (cal/mole)
4.0 at.% Au-Pt	440±150.	~400 (ref. 9)
0.62 at.% Au-Pt	140±50	~100 (ref. 9)
0.65 at.% Ni-Pt	-75±60	~-40 (ref. 10)

FIGURE CAPTIONS

- Fig. 1. (a) Ball model of stack of successive {315} planes. Origins of 'Local Planar Coordinate Systems' are located at O and O' on two successive planes.
- (b) Schematic diagram of two uppermost planes in (a). Local Planar Coordinate axes OX_1 and OX_2 shown in upper plane.
- Fig. 2. Radial distribution function of Au atoms in 4.0 at. % Au-Pt alloy.
- Fig. 3. Radial distribution function of Au atoms in 0.62 at. % Au-Pt alloy.
- Fig. 4. Radial distribution function of Ni atoms in 0.65 at. % Ni-Pt alloy.
- Fig. 5. Computer generated display of solute atom distribution in volume associated with 156 consecutive {315} planes in 4.0 at. % Au-Pt alloy. Each bend represents position of a Au atom. $L = 33a_0$.
- Fig. 6. Computer generated display of solute atom distribution in volume associated with 195 consecutive {203} planes in 0.62 at. % Au-Pt alloy. Each bend represents position of a Au atom. $L = 26a_0$.
- Fig. 7. Interaction energies between pairs of Au atoms in Pt matrix from Clapp-Moss model.
- Fig. 8. Interaction energies between pairs of Ni atoms in Pt matrix from Clapp-Moss model.

(a)

(b)