Structural Order and Disorder in Materials

Patrick R. LeClair
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Contents

1 Abstract

Structural order and disorder were investigated in a series of four experiments: order-disorder transition in CuPt alloys; crystallization of glass ceramics; short range order and crystallization in FeB and FeNi metallic glasses; and development of crystallographic texture in strained polystyrene-isoprene block co-polymers. X-ray techniques were used to investigate all of these processes, giving important data for determining structural order, structure-property relations, as well as providing guidelines for processing of materials to give a desired set of properties.

2   Introduction

Structural order and disorder are have important ramifications on structure-property relations and also materials processing. This work attempts to characterize various types of structural order-disorder *via* X-ray diffraction (XRD) and Small Angle X-ray Scattering (SAXS). It is demonstrated that consistent measures of various structural characteristics may be determined from these techniques along, including degree of crystallinity, long range order, phases present, grain size, and others. Finally, the importance of individual results are emphasized in the light of properties, performance, and processing.

3   Order-Disorder Transitions

3.1   Introduction

In this work, the order-disorder transformation in a $Cu_{50}Pt_{50}$ alloy was studied *via* XRD. Structural transformation upon ordering, long range order, and XRD characteristics were studied as a function of annealing time to give a profile of order-disorder characteristics vs. temperature. Methods of elucidating the order parameter and lattice distortion from XRD patterns will be discussed.

In the $Cu_{50}Pt_{50}$ alloy studied, a transformation from a high-temperature fcc (disordered) to a lower-temperature rhombohedral (ordered) structure occurs at approximately 816°C.[1] The high temperature fcc phase (Fm$\bar{3}$m) has Cu and Pt atoms placed randomly on atomic sites. At lower temperatures, ordering becomes favorable, and symmetry is lowered. The ordered structure is rhombohedral (R$\bar{3}$m) and consists of alternating (111) planes of Cu and Pt. This causes a contraction along the [111] direction and produces a lattice distortion, such that α=91° rather than 90°. (See figure 1.) Though the true structure is rhombohedral, it may be visualized as an fcc structure with alternating Cu and Pt (111) planes, and a doubled lattice parameter (thus giving the "superlattice" 32 atoms per unit cell).[1]

3.1.1 Structure Factors

The change of crystal symmetry between ordered and disordered phases may be observed via XRD; since symmetry is lowered for the ordered phase, additional XRD peaks (in addition to the fundamental fcc peaks observed) should be seen. In order to determine where these "extra" peaks will be, the structure factor for each crystal structure must be calculated. For the fcc lattice, the result is well known – peaks appear where h,k,l are all even or odd, and no peaks appear where they are mixed (defining 0 to be even)[1][2][3][4]. This gives rise the the sequence (111), (200), (220), etc. For the superlattice, the calculation is somewhat more tedious; the results are given below.

$$F = 16(f_{Pt} + f_{Cu}) \quad h, k, l \ all \ even \tag{1}$$

$$F = 16(f_{Pt} - f_{Cu}) \quad h, k, l \ all \ odd \tag{2}$$

$$F = 0 \quad h, k, l \ mixed \tag{3}$$

Where f_x is the atomic scattering factor for atom x.[1][3][4] (Figure 2 shows the expected fcc and superlattice diffractions.) From the structure factors, we can see that the extra, or "superlattice" peaks which appear will have reduced intensity, since they depend on the difference between the Cu and Pt scattering factors. The fundamental lines, those common to both structures, will have a greater intensity. (Note that the superlattice unit cell has been doubled, therefore (hkl)$_{ordered}$=2(hkl)$_{disordered}$.) Thus, the appearance of the ordered state may be elucidated by the appearance and relative intensity of the superlattice peaks. In addition, the reduced symmetry causes splitting of some fundamental lines (e.g. (311) peaks become a doublet of ($\bar{3}$11) and (311) peaks).

3.1.2 Order Parameter

In itself, the determination of phases present is useful, but limited in scope. However, the relative degree of order as well as lattice distortion may be determined from XRD. Using an order paramenter defined as $S = (f_a - F_a)/(1 - F_a)$, where F_a is the fraction of species A in the alloy, and f_a is the fraction of A ations on the correct site - S=1 for complete order, and S=0 for complete disorder. Noting that XRD intensity $I \approx m(LP)F^2$ where m is the multiplicity factor, LP the Lorentz polarization factor, and F the structure factor, we may rewrite the order parameter in terms of XRD peak intensities[1][4] :

$$S = \frac{F_f}{F_s}\sqrt{\frac{m_f(LP)_f I_s}{m_s(LP)_s I_f}} \tag{4}$$

where subscript s and f refer to superlattice and fundamental peaks, respetively. $I_{s,f}$ refers to the intensity (or area) of a given superlattice or fundamental peak. Thus, the long range order parameter may be determined from XRD alone. In addition, if we assume the Bragg-William theory is valid in this case, *i.e.* a constant interchange energy, we may deduce V_o from the plot of S vs. T. The result is $V_o = 4k_B T_c$, where T_c is the critical ordering temperature (above which order ceases).

3.1.3   Lattice Distortion

In addition to the order parameter, the lattice distortion may also be calculated from XRD data. For a lattice angle $\alpha = \frac{\pi}{2} + \delta$, where δ is the distortion, unit cell parameter a, Bragg angle θ, and wavelength λ the distortion is given by[1] :

$$sin^2\theta = \frac{\lambda^2}{4a^2}\left[\frac{(h^2 + k^2 + l^2)(1 - \delta^2) + 2\delta(hk + kl + hl)}{1 - \delta - 2\delta^2}\right] \tag{5}$$

In order to obtain δ, we make use of the splitting of fundamental lines. For a doublet with peaks at angles θ_1 and θ_2,

$$\frac{4a^2}{\lambda^2}(hk + kl + hl)^{-1}(sin^2\theta_1 - sin^2\theta_2) = \frac{2\delta}{1 - \delta - 2\delta^2} \tag{6}$$

Since the lattice distortion is expected to be small (verified by the small degree of doublet splitting), $\delta \ll 1$ (in radians) we may simplify the previous expression to :

$$\frac{4a^2}{\lambda^2}(hk + kl + hl)^{-1}(sin^2\theta_1 - sin^2\theta_2) \approx 2\delta \tag{7}$$

Using the known a,λ, and miller indicies for each of the double peaks, one may use the difference between the squared sines of the doublet angles. This procedure gives little error for the small angles considered, and has the advantage of simplifying analysis a great deal.

3.2 Procedure

The CuPt samples used were made by casting and then cold rolling pure Cu and Pt to a thickness of ~ 0.1mm. Heat treatment was then performed at several different temperatures (RT, 700, 750, 775, 800, and 915°C) in an argon atmosphere (to prevent oxidation) and then rapidly quenched in water to retain the structure at each particular annealing temperature. This procedure allows high temperature structures to be studied without the added difficulty of performing *in situ* measurements at elevated temperatures.

After heat treatment, XRD was performed on the samples, using Cu K_α radiation at 1.54Å, scanning from 2θ=15-95° at 60kV, 300mA.

3.3 Results

A superimposed plot of XRD peaks at three different annealing temperatures is shown in figure 3 (F denotes fundamental peaks, S denotes superlattice peaks). Comparing the XRD data with the calculated fcc and superlattice patterns indicates that superlattice peaks are present, as well as doublet splitting of some peaks, in all but the 915°C sample. Using equation 4 along with the known Lorentz polarization and multiplicity factors and calculated structure factors, S may be calculated by taking the intensity ratio of the first superlattice peak and the fcc (111) peak; this result is shown in figure 4. The samples show nearly complete order up to 775°C, and past 800°C the order parameter decreases. We may estimate from this data that $T_c \approx$ 820°C and $V_o \approx 0.28$eV.

In order to calculate lattice distortion, δ, we use the (311) peak, which is split into (311) and $(\bar{3}11)$ peaks. Using the measured angles for each of the doublet peaks, the calculated lattice parameter of a$\approx 7.5\text{Å}$, and the miller indicies, we have

$$\delta_{degrees} = (\frac{180}{\pi})(0.0632)(sin^2\theta_1 - sin^2\theta_2) \tag{8}$$

Figure 4 also shows the lattice distortion (in degrees) as a function of annealing temperature. As expected, the lattice distortion in the completely ordered regime is approximately 1-1.2°. The critical temperature estimated from the lattice distortion is also $T_c \approx 820$°C.

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3.4 Discussion

The XRD plots clearly show the absence of superlattice peaks at 915°C, but superlattice peaks are present at all lower temperatures. The 915°C sample matches the expected fcc structure quite well, while the lower temperatures display the expected superlattice pattern. Using the order parameter and lattice distortion data, and examining the slope of S vs. T near the transition temperature, we may extrapolate the data to estimate T_c and then V_o. This procedure is somewhat inaccurate in this case, since the transistion occurs somewhere in the 115°C interval between 800 and 915°C. However, by 800°C there is a downward trend of the data; considering the phase diagram of the CuPt system[1], the data is consistent with the quoted transistion temperature.

The lattice distortion, $\approx 1°$, is near the expected value for the [111] contraction and resulting rhombohedral transformation and loss of symmetry. This is supported by the fact that the XRD pattern is nearly identical to the simulated fcc pattern. The use of the doublet splitting to estimate lattice distortion is approximate, but for the small distortion angles in this case, the error is $\sim$1-2% at most. The use of split doublet peaks also has uses only peaks affected by the loss of symmetry and the lattice distortion, giving a simpler and more direct measurement of the distortion.

As seen from figure 3, the order parameter and lattice distortion have nearly identical functional dependence. This is expected, since during the order-disorder transformation, the lattice distortion should relax roughly as the proportion of ordered atoms in the lattice; one expects both δ and S to have the same T_c and roughly the same form for T$\ll$T$_c$. In the region T$\sim$T$_c$, the lattice distortion seems to have a more sharp transition than the order parameter; this would seem to indicate a rather sudden and discontinuous loss of symmetry, as expected for this system. Probing the temperature range closer to T_c would verify this, as well as determining T_c and functional form of S and δ more accurately.

3.5 Conclusion

The order-disorder transformation in a $Cu_{50}Pt_{50}$ alloy was studied as a function of annealing temperature. Transformation temperature, as well as interchange energy, long range order parameter, and lattice distortion were

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also determined at each of the temperatures used. Superlattice XRD peaks appearing with the ordered structure were used to determine long range order; splitting of fundamental XRD peaks into lower symmetry doublets was used to determine lattice distortion. It was found that $T_c \approx 820°$, consistent with published phase diagrams, and $V_o \approx 0.28eV$. A lattice distortion of approximately $1.2°$ was observed for the ordered samples; the lattice distortion and order parameter followed nearly the same temperature dependence, with the former having a slightly more narrow transition region.

References

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