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Evidence of short-range order in the disordered Cu–Ti alloys

T. ABBAS, A. B. ZIYA
Materials Research Laboratory, Department of Physics, Bahauddin Zakariya University, Multan 60800, Pakistan

Diffuse X-ray scattering measurements have been carried out on a series of Cu–Ti alloys, in order to determine the dependence of short-range order (SRO) parameters on the composition and annealing temperature. The diffuse scattering intensity (DSI) curves contain a maximum at the superstructural position 100 which provides evidence of SRO in this alloy. The degree of SRO has been estimated by calculating the Warren–Cowley parameter α_1 (WCP) and size-effect parameter β_1 from the DSI curves. The large negative values of WCP for all samples show the presence of heterogeneous SRO in these alloys. Comparison is also made between the values of experimental WCP and theoretical WCP calculated in the framework of electronic theory of short-range order and the high-temperature approximation of Clapp and Moss. A fairly good agreement between theory and experiment is observed.

1. Introduction

A metallic alloy is usually characterized by its order, i.e. the correlation in the position of neighbouring atoms. The order is complete at low temperature, whereas the arrangement of atoms becomes random at higher temperatures. Quenching of an alloy from high temperature produces a local order which is a deviation from a random distribution. The average crystal lattice looks periodic over significantly large distances, but the occupancy of atomic sites varies from one unit cell to the other and hence the physical properties of the alloy are influenced by the short-range order (SRO). Furthermore, the state of SRO directly depends upon the composition of the alloy and the history of thermal treatment. X-ray diffraction can be used for the investigation of such microscopic changes and the SRO in the alloys.

Polycrystalline alloys based on copper and 3d transition metals such as Cu–Ti have been the subject of many recent experimental investigations (neutron diffraction [1], TEM [2, 3] etc.) and theoretical studies (Monte Carlo simulation of point defects [4]). Copper and titanium form a primary solid solution (α-phase) up to 6wt %Ti above around 973 K approximately, which decomposes at lower temperatures [3]. For more details of the phase changes in the Cu–Ti system up to 973 K, see for example Tahir *et al.* [5].

Microstructural studies have established the formation of titanium-rich ordered regions on ageing between 573 and 773 K. These alloys exhibit anomalous behaviour of yield strength during ageing [6–8]. Donovan and Thomson [2] attribute this to the ordering of β' precipitates and coarsening depending on the ageing temperature T as $T^{1/3}$. On the other hand, there is hardly any significant reference in the literature in which an attempt has been made to explain this anomaly on the basis of order–disorder transformation. We are of the opinion that the above anomaly is due to the existence of SRO, and hence the direct determination of SRO using X-ray diffraction is of the utmost importance.

In this paper, we experimentally establish the existence of SRO in the Cu–Ti system. We have determined values of the Warren–Cowley parameter α_1 (WCP) by calculating the ordering energies for this alloy system by using the electronic theory of SRO and the high-temperature approximation of Clapp and Moss [9], and checked the validity of theoretical calculations by comparing the experimental and theoretical results.

2. SRO in binary alloys

The determination of SRO in binary alloys depends on the behaviour of the superstructural line after transition of the sample from an ordered to a disordered state, for which the intensity of the superstructural line is much lower than that of a fundamental line. So prior to starting the X-ray diffraction experiment, we can get a rough idea whether the line would be visible or not by the following expression:

$$\frac{I(\text{superstructural})}{I(\text{fundamental})} = \frac{|F|^2(s)}{|F|^2(f)} = \frac{(\phi_1 - \phi_2)^2}{(\phi_1 + \phi_2)^2} \quad (1)$$

where it is assumed that the integrated intensities I of the superstructural and fundamental line are given by their $[F]^2$ values; ϕ is the atomic scattering factor for $\sin\theta/\lambda = O$, for which $\phi = Z$ (the atomic number). Hence the superstructural line of a binary alloy of metals with a small difference in their atomic scattering factors is usually not observed on diffractograms taken by ordinary X-ray diffraction procedures. One method of increasing the intensity of the

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superstructure line is the use of a long wavelength. The other method for visualizing SRO is to carefully observe the diffuse maxima around the so-called 'superstructural' line in the curve of diffuse intensity of a heat-treated sample, to ascertain whether the alloy is in the disordered state or not. This, to some extent, makes the alloy suitable for X-ray diffraction work and SRO parameters may be determined for one or two coordination spheres.

TABLE I Calculated values of SRO parameters and ordering energies

Alloy	α_1 (exptl.)	α_1 (calculated)	Ordering energy (Rydbergs)
$Cu_{98}Ti_2$	− 0.030	− 0.019	0.0064
$Cu_{95}Ti_5$	− 0.050	− 0.027	0.0062
$Cu_{90}Ti_{10}$	− 0.145	− 0.079	0.0062

3. Experimental procedure

3.1. Alloy preparation

Round-shaped master ingots (~ 5 g each) of polycrystalline $Cu_{1-x}Ti_x$ ($x = 2$, 5 and 10 at %) alloys were prepared by conventional arc-melting under an atmosphere of argon at about 400 mbar pressure, from spectroscopically pure materials and by casting on a water-cooled copper hearth. No significant weight losses were recorded and a wet chemical analysis gave nearly the starting compositions. These alloys were remelted several times and then annealed at 1073 K for 5 h in a vacuum better than 10^{-5} mbar and furnace-cooled to ensure homogeneity of the relative concentrations of the two types of atom in the alloys. These pellets were cut into two halves, surface-ground and polished to produce a mirror surface suitable for X-ray diffraction studies.

3.2. X-ray diffraction

The diffuse X-ray scattering measurements were made using a Shimadzu XD-5A diffractometer in the reflection mode, using line-focused CuK_α radiation. Two runs were always necessary for each sample, as the method of balanced filters [10, 11] was applied to extract the monochromated X-ray intensity corresponding to CuK_α wavelength. The diffracted beam was detected by a scintillation counter with a resolution better than 1 μs. The higher harmonics of the characteristic radiation were removed by the use of balanced filters and proper use of the pulse height discriminator. The intensity measurements were carried out in the angle range $10° < 2\theta < 100°$ with a step of 2° and all measurements were made in the fixed time mode with a counting time of 200 s per angle. Collimators were used to minimize the air scattering. Air scattering was measured by putting the empty specimen holder in the beam, and air scattering correction was done by multiplying the geometrical correction of Ergun [12] for the reflection mode by the experimentally measured air intensities:

$$a_r = \frac{1}{2} + \left(\frac{1}{2} - \frac{T\cos\theta}{R\gamma}\right)\exp\left(\frac{-2\mu T}{\sin\theta}\right) \quad (2)$$

where T is the thickness of the sample, γ the equatorial angle subtended at the specimen by the detector slit, R the radius of the goniometer and μ the linear absorption coefficient of air. The total intensity so obtained was standardized by calibrating with the scattering from standard 4N-grade silicon powder at high angles of scattering and subsequently converting this intensity into electron units per atom. All measurements were made at room temperature.

3.3. Data analysis

The experimental SRO diffuse intensity was obtained by subtracting the parasitic contributions from the total intensity as discussed previously [13]. Theoretically, the SRO diffuse intensity [14] for $Cu_{1-x}Ti_x$ alloy may be expressed in electron units per atom as

$$I(Q_j)_{SRO} = x_{Cu}x_{Ti}(\phi_{Cu} - \phi_{Ti})^2 C_i\alpha_i \frac{\sin(Q_j r_i)}{Q_j r_i} - C_i\beta_i\left(\frac{\sin(Q_j r_i)}{Q_j r_i} - \cos(Q_j r_i)\right) \quad (3)$$

and

$$K(Q_j) = \frac{I(Q_j)_{SRO}}{x_{Cu}x_{Ti}(\phi_{Cu} - \phi_{Ti})^2} - 1 \quad (4)$$

where $Q_j = 4\pi\sin\theta/\lambda$ and x_{Cu}, ϕ_{Cu} and x_{Ti}, ϕ_{Ti} are the atomic fractions and form factors of Cu and Ti atoms, respectively. C_i is the coordination number of the ith sphere and r_i is the distance between an atom in the ith sphere and the origin. From the measured values of $K(Q_j)$, WCP and the size-effect parameter β_1(SEP) were obtained using the method of least squares to fit the experimental points with Equation 3. This was done using our own program named SRO written in Fortran 77 described elsewhere [15]. We have chosen only the best set of experimental points which were away from the fundamental lines.

4. Results and discussion

The alloy samples were annealed at 1073 K for 5 h in a vacuum better than 10^{-5} mbar and quenched in water. X-ray diffraction patterns showed that these were multiphase. Annealing at the same temperature for another 10 h did not change the condition of the samples appreciably; the complex phases showing a non-homogeneous condition still persisted. After 10 h annealing at 1173 K (Fig. 1) it was observed that the alloys attained an f.c.c. structure with lattice parameters 0.36123, 0.36101 and 0.36092 nm for the samples with 2, 5 and 10 at % Ti, respectively. The dependence of lattice parameter a on atomic concentration is shown in Fig. 2. The figure shows that these parameters do not obey Vegard's law. This may be related to around 20% difference in the sizes of copper and titanium atoms. Fig. 3 shows the increase in SEP (which is a parameter for taking into account the

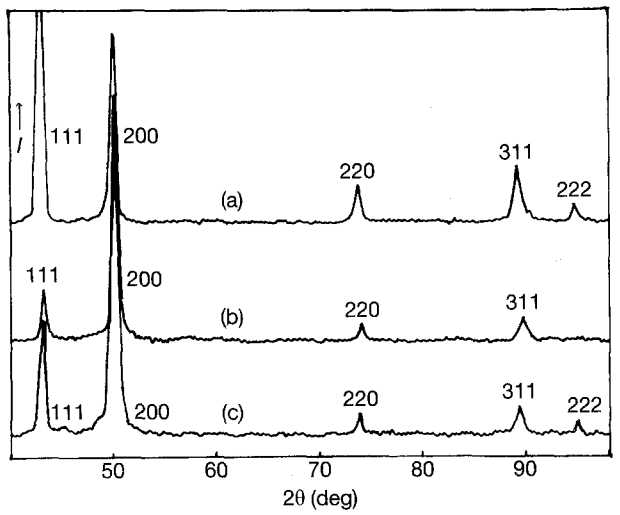

Figure 1 X-ray diffraction pattern of $Cu_{1-x}Ti_x$ alloys after annealing at 1173 K for 10 h: x = (a) 10, (b) 5 and (c) 2 at %Ti.

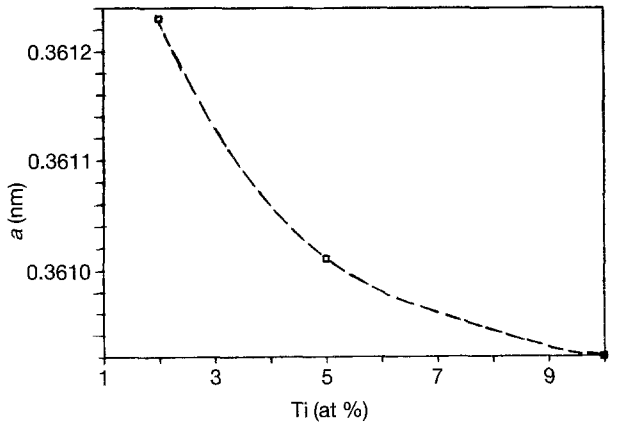

Figure 2 Dependence of lattice constant a on atomic concentration of titanium in three alloy samples.

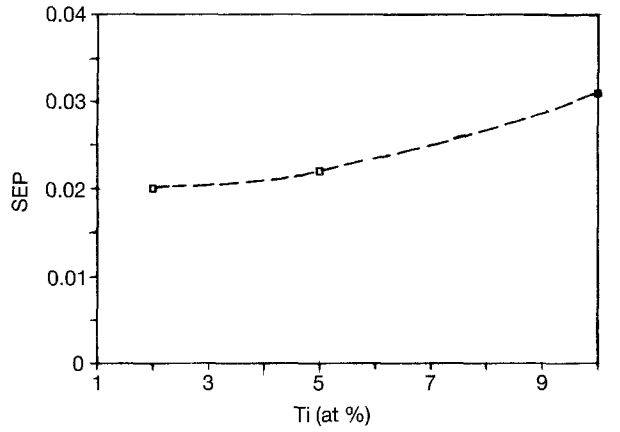

Figure 3 Variation of size-effect parameter β_1 with increase of atomic concentration of titanium in three Cu–Ti alloys.

distortion in the lattice due to the difference in the atomic sizes of the two atoms in the alloy) with the increase of atomic concentration of titanium, thus confirming the presence of a strong size-effect scattering in these alloys. The line broadening observed as a result of the increase in titanium concentration further supports this fact.

The diffuse scattering intensity (DSI) for the three alloys is plotted against the diffraction angle 2θ in Fig. 4. In all three alloys, a diffuse maximum at the position of the first superstructural line 100 is observed, which is evidence for the presence of SRO. The WCPs were calculated from the DSI curves and the results are shown graphically in Fig. 5. The negative values of WCP show that the first nearest neighbours are unlike and there is a tendency for short-range ordering between copper and titanium atoms. In magnitude, the values of WCP are observed to be larger than the limiting values, i.e. $\alpha_{1(max)} = |-x_{Ti}/x_{Cu}|$. It may be said that there are heterogeneous domains having SRO in these alloys. The behaviour of WCP as a function of atomic concentration is similar to the results reported by Sakata *et al.* [16], although in that work the alloys were in a non-crystalline form and the atomic concentration of titanium was not the same as we have studied in our paper. However, this similarity may have been due to the presence of submicroregions of crystallites having SRO in the non-crystalline and relatively concentrated Cu–Ti alloys.

Although the homogenization of the samples was made for quite a long time (nearly 30 h), there may be some local heterogeneity still present in these samples. This heterogeneity could not be observed by X-ray diffraction. We can say that type II SRO [17] is present in all the samples under the conditions mentioned above.

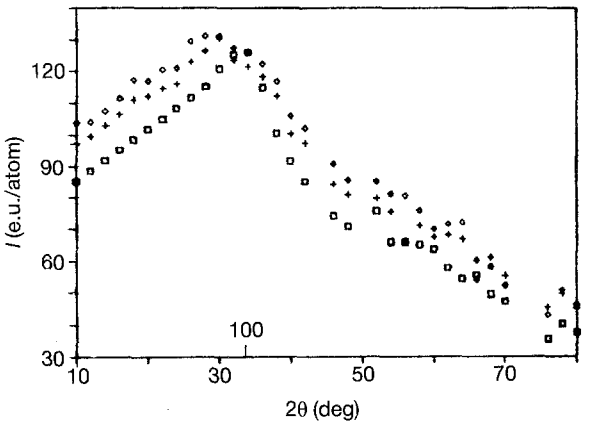

Figure 4 Plot of diffuse scattering intensity for the three alloy samples after annealing at 1173 K for 10 h: (□) 2, (+) 5, (◇) 10 at % Ti.

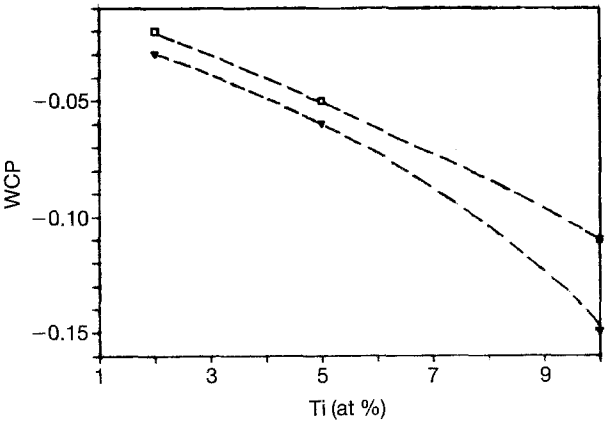

Figure 5 Variation of Warren–Cowley parameter α_1 with increase of atomic concentration of titanium in three Cu–Ti alloys: (□) limiting, (▽) experimental.

The electronic theory of short-range ordering based on a pseudopotential approximation is a good theoretical model for the evaluation of experimental observations. We have utilized this model for calculating the WCPs for these samples. The methods proposed by Khawaja *et al.* [18] and Clapp and Moss [9] were used for these calculations. One can observe a relatively good agreement between the experimental and calculated value of WCP. Thus this theoretical model is appropriate for the Cu–Ti system.

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