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ORDERING IN TERNARY β PHASE Cu Zn Al ALLOYS

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1. Introduction

A large number of β phase noble metal alloys show long range order below a critical ordering temperature. The contribution of order to the stability of the phases has been analyzed by the Bragg-Williams-Gorski (BWG) model. In this model it is assumed that the internal energy can be described in terms of chemical interchange energies

$$W_{ij}^{(k)} = -2\, V_{ij}^{(k)} + V_{ii}^{(k)} + V_{jj}^{(k)}$$

where $V_{ij}^{(k)}$ and $V_{ii}^{(k)}$, $V_{jj}^{(k)}$ are the k-th neighbor interaction energies between unlike and like atoms, respectively, generally taking into account only next and next nearest neighbor ("nn" and "nnn") interactions. The entropy contribution in the BWG model is the configurational entropy, thus neglecting vibrational and electronic contributions. More elaborate models have been used in order to obtain better approximations. The various models have been discussed in detail by Inden (1). He has shown that the simple BWG model with nn and nnn interactions can describe experimental results quite well in bcc structures, if a correction factor χ is introduced which takes account of short range order effects which have been neglected in the BWG theory (1,2). The chemical interchange $W_{ij}^{(k)}$(BWG) of the BWG model are only fictitious parameters, whereas

$$W_{ij}^{(k)} = \frac{1}{\chi}\, W_{ij}^{(k)}(\mathrm{BWG})$$

are the physically relevant real interchange energies. The numerical value of χ is a function of the ratio of nn and nnn interchange energies, and ranges between 0.57 and 0.84(1). For the bcc phase binary Cu Zn alloys Inden derived χ=0.67,

$$W_{\mathrm{Cu\ Zn}}^{(1)} = 955k,\quad W_{\mathrm{Cu\ Zn}}^{(2)} = 535k\quad (k = 13.8.\ 10^{-24}\mathrm{J})$$

The theory was extended also to ternary alloys, and the relevant equations are found in reference 2.

Many noble metal alloys transform martensitically to close packed structures. Thus a study of order in these alloys is of interest not only to obtain information on the contribution of order to the stability of the β phase, but also to better understand the martensitic transformation. With the latter aspect in mind, ternary β phase Cu Zn Al alloys were studied (3). In this letter the results concerning order in the β phase Cu Zn Al are reported. Its effect on the martensitic transformation will be published separately (3).

2. Experimental procedures and results

Single crystals of Cu Zn Al ternary alloys of various compositions, all having an electron concentration of 1.48 were prepared in the usual way by first melting together the high purity elements (99.999%) in sealed quartz capsules, and then growing the single crystals in sealed quartz tubes by the

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Bridgman method. The single crystals were then spark machined and electropolished to a diameter of 2.8 mm. In order to measure the resistivity, leads were spot welded to the samples (distance between the leads 20 mm). The resistivity was measured while the samples were heated in a furnace and then cooled again. The heating (cooling) velocity was approximately 10°C/min. In order to make sure that the heating (cooling) velocity had no influence on the resistivity curve, some samples were heated (cooled) at a higher velocity of 100°C/min approximately. Alloys having an electron concentration of 1.48 lie near the eutectoid compositions in the ternary system (4) and thus are stable to quite low temperatures. Therefore a decomposition during cooling at the described rates is not expected, and indeed no indications for it were found by transmission electron microscopy studies. For transmission electron microscopy (TEM) observations, slices were cut from the samples and thin foils were prepared in the usual way (5). In order to ascertain to what extent the composition of the samples had changed during the preparation of the single crystals, some samples were analyzed chemically. For those alloys which transformed martensitically, the transformation temperature Ms served as a further sensitive check of the deviation from the nominal composition. The measured M_S temperature deviated no more than 20°C from that corresponding to the nominal composition. Although the heating during the resistivity measurements was done in air, no loss by evaporation was noticed and M_S did not change, as was evidenced by measuring M_S before and after the heating. Apparently the Al helps to form a quite stable oxide surface layer.

In figure 1 is shown a resistivity curve obtained during cooling of a Cu-13,3 at % Al-21.4 at % Zn alloy. The curves show two well marked points where the slope starts to change on cooling. The corresponding temperatures are denoted by T_{B2} and T_{D03}, the first being the higher one. In figure 2 are plotted T_{B2} and T_{D03} versus Zn concentration (e/a = 1.48). The binary Cu-Al and Cu-Zn compositions are given by $C_{Zn} = 0$ and $C_{Zn} = 0.48$ respectively.

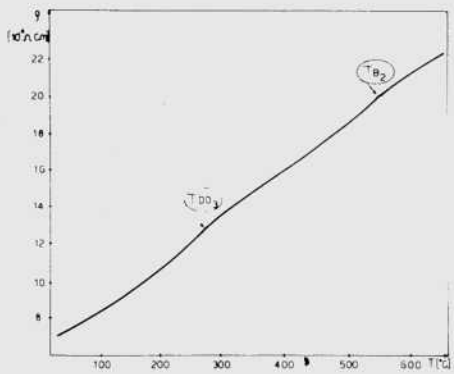

FIG. 1

Electrical resistivity as a function of temperature during cooling. Changes in slope occur at temperatures denoted T_{B2} and T_{D03}.

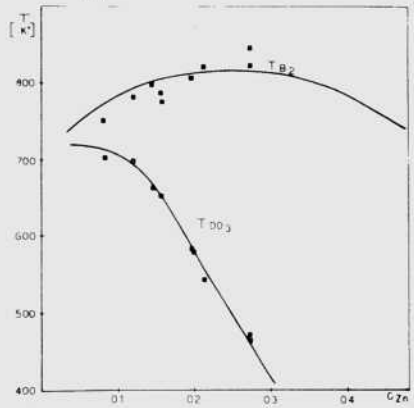

FIG. 2

T_{B2} and T_{D03} versus Zn concentration for constant electron concentration 1.48.

The average uncertainty in composition lies within the lateral extension of the squares. The continuous lines are the calculated curves discussed below. T_{B2} is the critical ordering temperature for nn ordering which leads to a B_2 structure. It varies relatively little with Zn concentration and extrapolates

to the B_2 ordering temperature T_{B2} = 740 °K for binary Cu-48% Zn(6). At T_{DO_3} order in nnn occurs, leading to a DO_3 structure. It depends strongly on composition, the T_{B2} and T_{DO_3} approach at the Al-rich side, leading to a two phase A_2 and DO_3 mixture for Cu-Al (7). That T_{B2} and T_{DO_3} are indeed the critical ordering temperatures has been proved by TEM. Samples that were cooled to below the T_{DO_3} temperature have a selected area diffraction pattern that is shown in figure 3 a. In addition to the spots from the bcc structure superlattice reflections from B_2 and DO_3 order are seen, as is drawn schematically in figure 3b.

FIG 3a

β phase (110).diffraction pattern.

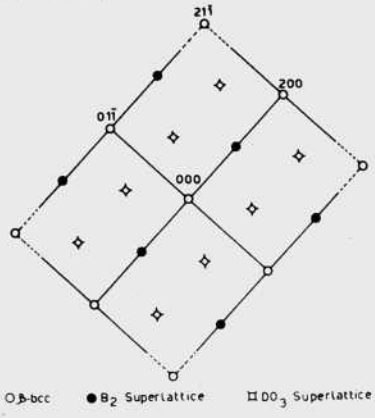

FIG 3b

Key diagram of the pattern of fig. 3a, showing the matrix and superlattice spots.

When samples are compared which were quenched either from above or from below T_{B2}, it is found that in the latter case large order domains have formed, with only few or no domain boundaries visible in a dark field micrograph using the B_2 superlattice reflections, whereas after quenching from above T_{B2}, the domains are smaller since they have formed during quenching, as discussed by Cupschalk and Brown (8) for binary Cu-Zn. The influence of quenching temperature above or below DO_3 ordering on DO_3-order domains was studied in alloys of Cu-27.3 at % Zn-10.4 at % Al and Cu-18.9 at % Zn-14.6 at % Al. In figure 4 and 5 are shown some TEM results.

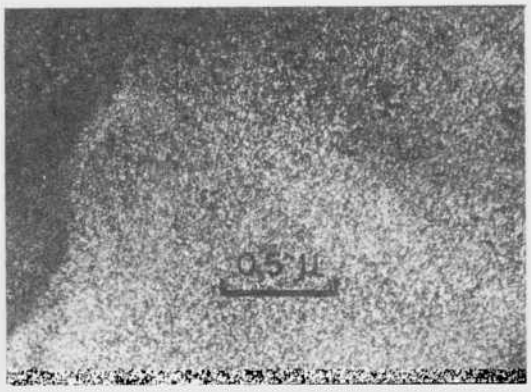

FIG. 4

Dark field micrograph using a DO_3 superlattice spot. Sample quenched from above T_{DO_3}.

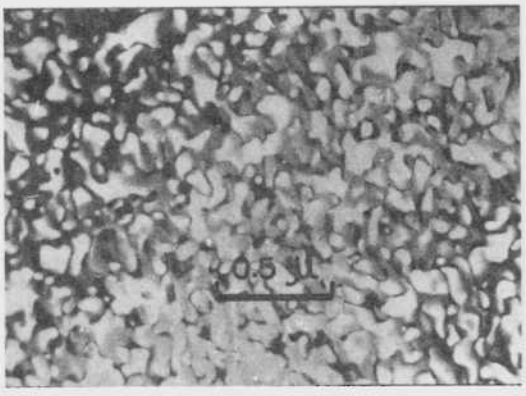

FIG. 5

Same as fig. 4, but for a sample quenched from below T_{DO_3}.

When quenched from below T_{DO_3} order domains of average diameter 0.1µm are visible, whereas after quenching from slightly above T_{DO_3} the domains are so small that they are difficult to discern, although DO_3 superlattice spots in the diffraction pattern are easily recognized. Heating such a foil in the electron microscope leads to a growth of the domains. Thus T_{B_2} and T_{DO_3} are indeed the temperatures of B_2 and DO_3 ordering respectively.

From the experimentally determined T_{B_2} and T_{DO_3}, chemical interaction energies can now be deduced in the way described in detail by Inden (1,2). Using the known interchange energies for Cu and Zn and a χ parameter of 0.67 as in the binary Cu Zn system, the four parameters $W^{(1)}_{Cu\ Al}$, $W^{(2)}_{Cu\ Al}$, $W^{(1)}_{Zn\ Al}$, and $W^{(2)}_{Zn\ Al}$ have been calculated for nn and nnn interactions between Cu-Al and Al-Zn. The best adjustment is achieved using the following values:

$$W^{(1)}_{Cu\ Al} = 1345k \pm 25k$$
$$W^{(2)}_{Cu\ Al} = 825k \pm 15k$$
$$W^{(1)}_{Al\ Zn} = -50k \pm 100k$$
$$W^{(2)}_{Al\ Zn} = 200k \pm 100k$$

The continuous curves in figure 2 were calculated with these parameters. The ratio $W^{(1)}_{Cu\ Al} : W^{(2)}_{Cu\ Al}$ is thus 1.63. According to the phase diagram calculated by Inden for this ratio (9), the binary Cu Al system around 25 at % Al shows DO_3 order at low temperatures, separated by a two phase A_2 and DO_3 region from the disordered A_2 phase at higher temperatures. This is in agreement with the experimental results (7). The χ-value corresponding to this $W^{(1)}_{Cu\ Al} : W^{(2)}_{Cu\ Al}$ ratio is 0.63 (1). Thus the χ-value varies little between the binary Cu-Zn and Cu-Al system, which justifies the present analysis with a constant $\chi = 0.67$ for the ternary system. The interaction energies between Al and Zn are small, which is consistent with the phase diagram of Zn-Al, where ordering tendencies are absent.

In conclusion, the ordering in ternary Cu Zn Al alloys can be accounted for quite well by the modified Bragg- Williams-Gorski model, and real physical interchange energies have been derived.

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