The Possibility of New Ordering Reaction in Cu-50 mass% Au Alloy

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Among the large number of superlattices, there is a special group which may be classified as long period superlattices, the copper-gold system provides a classical example of such structure. Despite that historically, the copper-gold alloys containing about 25 atom percent gold were among the first investigated alloys, it still represents a subject of numerous studies. In the present work, we study all the possible phase transitions in the binary intermetallic alloy Cu₃Au using differential scanning calorimetry (DSC) and differential dilatometry. A new important anomaly due certainly to a new ordered reaction has been detected at low temperature range by these two methods. To confirm this new reaction, we have used other techniques as high resolution transmission electron microscopy (HRTEM), electrical resistivity and microhardness measurements. The kinetics parameters as activation energy E_{act} and Avrami exponent n have also been calculated respectively by Starink and John Mehl Avrami Kolmogorov (JMAK) methods. [doi:10.2320/matertrans.M2010332]

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1. Introduction

In the solid solution, the distribution of atoms is generally statistical and at random, but under certain conditions these solutions could be ordered.¹⁾ The order-disorder transition takes a very important place because of its influence on the physical and mechanical characteristics of metals. Since its observation on 1934²⁾ in Cu-Zn alloys (brass), this transition which is expressed by the existence of one state in which atoms are ordered in crystal lattice, has been widely studied.³⁻⁷⁾ On the basis of X-ray diffraction, it has been noticed that below certain transition temperature, the atoms can be ordered on two sublattices which interpenetrate, i.e. the atoms of every type have tendency to take specific places in the crystal lattice by changing their position.^{1,2)}

The ordered phase is characterized by a long-range-order parameter which vanishes in the disordered phase. Due to the symmetry breaking associated with an order-disorder transition, an ordering process leads to the coexistence of different variants (or domains) of the same ordered phase.⁸⁾

The Cu-Au system provides a classical example of such structures. Cu and Au atoms form a continuous series of solid solutions at high temperature, but several superlattices exist at low temperatures, near compositions Cu₃Au, CuAu, CuAu₃.⁹⁾ A recent study of CuAu alloy has shown an important new anomaly at lower temperature,¹⁰⁾ in addition to the known phases existing in CuAu alloy: CuAuI and CuAu II ordered phases, and A1 disordered phase.

In this work we focus on the Cu₃Au alloy which has been the subject of numerous investigations due to its relationship with materials having improved electronic properties for technological applications including catalysis, coating and high devices.¹¹⁾

The Cu₃Au ordered phase is formed in L1₂ structure from the disordered fcc solution (A1) in the temperature range below 390°C. The order-disorder transition between A1 and L1₂ is classified as first order order-disorder transition.¹²⁾

This work attempts to interpret dilatometric and calorimetric anomalies occurring during continuous heating of a

homogenized and quenched Cu-50 mass% Au alloy and to try to detect a new reaction at low temperature, by using differential scanning calorimetry (DSC) and differential dilatometric analysis; other experimental techniques as high resolution transmission electron microscopy (HRTEM), and resistivity and microhardness measurements will be used. Moreover a detailed kinetics study of this new reaction will be done.

2. Experimental Procedure

We have used in this study the Cu-50 mass% Au alloy corresponding to intermetallic Cu₃Au alloy (more exactly Cu_{0.756} Au_{0.244}), elaborated by melting of pure elements (99.999%); the composition was checked by X-ray diffraction analysis and X ray-fluorescence.

For the dilatometric analysis, a DI24 Adamel Lhomergy dilatometer connected to a computer has been used. The samples were prepared as parallelepiped pieces of 25 mm length, 5 mm width, and 5 mm thickness.

For the differential calorimetric analysis (DSC), a SETARAM DSC 131 analyzer connected to a computer has been used. The samples were in a cylindrical shape (2 mm length and 5 mm diameter) corresponding to a weight of approximately 300 mg. In the both cases tests were performed under Argon.

The dilatometric and calorimetric cycle consists of heating from room temperature to 500°C, holding of 1 min and cooling down to room temperature with the same rate.

The samples have been undergone two kinds of heat treatments; firstly they were homogenised under primary vacuum for 1 h at 500°C, quenched in water, then heated in DSC and DI24 up to 500°C with several rates ($v = 5, 7, 9, 10, 15, 20, 25$ and $30^{\circ}\text{C}.\text{min}^{-1}$); secondly, the samples were homogenised under vacuum for 1 h at different temperatures (450, 500, 700, 750, 800 and 850°C) by applying the thermal cycle in DSC and DI24 quoted above but with a constant rate $v = 5^{\circ}\text{C}.\text{min}^{-1}$.

HRTEM specimens were prepared by Ion Slicer (Em-09100) and were examined in JEM-2100 Lab 6 High

Fig. 1 DSC curve of Cu_3Au alloy homogenised 1 h at 500°C and water quenched.

Resolution Transmission Electron microscope operating at 200 KV.

The resistivity measurements were made using direct current potentiometric method with two probes.

The microhardness tests were made using a Zwick Vickers hardness indenter with a 300 mg load.

3. Results and Discussion

3.1 DSC results

The DSC scan obtained during heating ($V = 3^\circ\text{C}.\text{min}^{-1}$) of the sample homogenised under vacuum and water quenched (Fig. 1), reveals two exothermic peaks P1 and P2 in the temperature range $[61\text{--}160^\circ\text{C}]$ and $[288\text{--}373^\circ\text{C}]$ respectively and an endothermic one P3 between 373°C and 405°C .

- the appearance of P1 is probably linked to one phase transformation though the Cu-Au phase diagram, does not show any phases at this range of temperature. This first reaction is probably identical to that found recently in the equiatomic CuAu alloy.¹⁰⁾

- P2 is certainly due to the formation of Cu_3Au ordered phase,

- P3 is attributed to the order-disorder transformation from Cu_3Au ordered phase to the disorder solid solution.

3.2 Dilatometry study

The derivative curve of the heating segment of homogenised and water-quenched alloy with the same heating rate ($3^\circ\text{C}.\text{min}^{-1}$), is shown in Fig. 2. One can observe the presence of the first reaction detected already by DSC analysis, and characterised here by a contraction at lower temperature with a minimum P1 situated at 123°C , before the contraction peak P2 corresponding to the Cu_3Au ordered phase formation and situated between 274°C and 368°C , followed by an important expansion P3 linked to the decrease of the ordering of Cu_3Au phase and its transformation to the A1 disordered phase.

3.3 Heating rate effect

The variation of the heating and cooling rate during DSC and dilatometric tests (for DSC: $v = 5, 7, 9, 10, 15, 20, 25$

Fig. 2 Dilatometric curve of Cu_3Au alloy homogenised 1 h at 500°C and water quenched.

Fig. 3 DSC heating curves during of samples homogenised 1 h at 500°C and water quenched then heated with different rates.

Fig. 4 Differential dilatometric heating curves of samples homogenised 1 h at 500°C and water quenched then heated with different rates.

and $30^\circ\text{C}.\text{min}^{-1}$ and for dilatometer: $v = 1, 2, 3, 5, 7$, and $9^\circ\text{C}.\text{min}^{-1}$) leads practically to the same effects and anomalies (Figs. 3 and 4); in addition to the effects corresponding to the formation of Cu_3Au ordered (P2) and A1 disordered (P3) phases, the presence of P1 at lower temperature (exothermic peak and contraction in DSC and dilatometric curves respectively), shows always the occurring of one phase transition at this temperature range.

Fig. 5 DSC heating curves of Cu_3Au alloy homogenised 1 h at different temperatures: 450°C (a), 500°C (b), 700°C (c), 750°C (d) and 800°C (e) and quenched.

Fig. 6 Differential dilatometric heating curves of Cu_3Au alloy homogenised 1 h at different temperatures: 450°C (a), 500°C (b), 700°C (c), 750°C (d), 800°C (e) and 850°C (f) and quenched.

All these effects shift toward the higher temperature with the increase of heating rate. Such behaviour is easy to understand by referring to the transformation mechanism. The total number of vacancy jumps taking place during heating up to a fixed temperature is higher when the heating rate is lower.¹³⁾

3.4 Homogenisation temperature effect

The variation of the homogenisation temperature from 450°C to 800°C gives the same anomalies in DSC and dilatometric curves (Figs. 5 and 6): the three peaks P1, P2 and P3 (two exothermic and one endothermic peaks in DSC curves and two contractions and an important expansion in dilatometric curves); the first unknown one at lower temperature and two others corresponding to the Cu_3Au ordered and A1 disordered phases formation, exist for the samples homogenised at temperatures below 700°C. However, starting from this latter temperature, one can see the rearrangement of P1 and P2 and the obtaining of only one peak, which can be explained by the disappearance of one of them or their overlapping.

Fig. 7 DSC heating curves of Cu_3Au alloy for different states.

However, the obtained effects shift towards lower values of temperature when the homogenisation temperature increases because of the increase of non-equilibrium (quenched-in vacancies) concentration which improves the diffusion process.

So, one can note that the two analyses show always the presence of effect or anomaly P1 with various heating rate and homogenisation temperature.

3.5 Annealing state

The previous results give idea to study some annealing states and to follow the temperature peaks of the effects found by DSC. Thus samples are annealed at 100°C and 300°C during 2 h; obtained DSC results are shown in Fig. 7. As P1 appears at low temperature, the study has been restricted to the temperature interval [20–400°C].

Compared to the quenched state, the annealing of 2 h at 300°C leads to the disappearance of the two peaks P1 and P2. The absence of P2 is certainly due to the complete transformation of the disordered phase to the antiphase domain of Cu_3Au ordered phase during this annealing. The main question is about the absence of P1 which is probably attributed to the same phase transformation having a relation with Cu_3Au ordered phase formation because P1 would appear during heating in DSC, if these phases (Cu_3Au ordered phase and that corresponding to P1) were independent.

3.6 X-ray diffraction XRD study

Although DSC and dilatometry results reveal the existence of the new peak around 100°C, the XRD study of the alloy homogenised 1 h at 500°C and heated up to 100°C shows no new peaks (Fig. 8(b)) in comparison with the obtained spectrum of quenched state (Fig. 8(a)) which corresponds to the A1 disordered state. The peaks which are marked by an asterisk indicate the presence of copper oxide.

This behaviour can be explained by the kind of transition kinetic in this alloy which is slow. It is the case of the Cu_3Au ordered phase; the obtained XRD spectrum of the Cu-50 mass% Au alloy homogenised and heated up to 300°C (Fig. 9(a)) shows no peaks corresponding to the Cu_3Au ordered phase. The spectrum corresponding to the Cu-50 mass% Au alloy homogenised and annealed 1 h at 300°C

Fig. 8 X-ray diffraction patterns of the Cu_3Au homogenised 1 h at 500°C and quenched (disordered state) (a), then heated up to 100°C (new reaction) (b).

(Fig. 9(b)) also shows no peaks of Cu_3Au ordered state, nevertheless the DSC and dilatometry studies of this alloy reveal the complete formation of Cu_3Au phase after 1 h at 300°C . The appearance of the different peaks of Cu_3Au ordered state is obtained only for a long annealing time when the order degree of this phase becomes higher, as it is shown in Fig. 9(c) for the Cu-50 mass% Au alloy annealed for 40 h at 300°C .

3.7 High resolution transmission electron microscope (HRTEM) study

Figure 10 shows a $(110)^*$ electron diffraction pattern of Cu-50 mass% Au alloy homogenised 1 h at 500°C and water quenched then heated up to 100°C . On this diffraction pattern the strong spots $((000), (\bar{2}20), (2\bar{2}0), (002), (00\bar{2}), (1\bar{1}1), (\bar{1}11), (1\bar{1}\bar{1}), (\bar{1}\bar{1}\bar{1}))$ are attributed to the disordered phase of FCC structure and the weak spots $((001), (00\bar{1}), (\bar{1}10), (1\bar{1}0))$ are attributed to the superlattice reflections where atoms are arranged in the form of a structure having periodicity, but there is some weak spots which are not indexed (marked with (?)). These spots can be attributed to this new reaction detected before by DSC and DI_{24} .

A HRTEM image of Cu-50 mass% Au alloy homogenised for 1 h at 500°C , then heated up to 100°C is represented in Fig. 11. This latter shows the cross of two different directions corresponding to the directions observed in SAED in Fig. 10.

3.8 Electrical resistivity measurements

It is well known that any form of disorder in metallic structure, e.g. impurities, dislocations or point defects will make a large contribution to the electrical resistance.^{14,15)} Accordingly, superlattices below T_c (the critical temperature

Fig. 9 X-ray diffraction patterns of the Cu_3Au homogenised for 1 h at 500°C and quenched then heated up to 300°C (a), annealed 1 h (b) and 40 h (c) at 300°C .

Fig. 10 $[100]$ electron diffraction pattern of the Cu_3Au alloy homogenised 1 h at 500°C and heated up to 100°C .

of order-disorder transition) have a low electrical resistance, but a temperature rising increases the resistivity.¹⁵⁾ The obtained results are shown in Table 1.

Fig. 11 HRTEM image of the CuAu alloy homogenised 1 h at 500°C, heated up to 100°C and quenched.

Table 1 Electrical resistivity measurements of Cu₃Au alloy for different states.

treatment	*10 ⁻³ ρ (Ω .cm)
heated up to 100°C	0.07 $\pm$ 0.014
heated up to 300°C	0.07 $\pm$ 0.017
homogenised 1 h at 500°C	0.0021 $\pm$ 0.0056

It is evident to have the resistivity value of the quenched (disordered) alloy higher than that in Cu₃Au ordered phase. But one can note that the resistivity of a sample heated up to 100°C has the same value as in quenched (disordered) alloy, so this new reaction can be attributed to the formation of a periodic antiphased (PAP) structure with stacking faults.

3.9 Microhardness measurements

The ordering often produces a change of crystal structure and leads to hardening. The Cu₃Au crystals have a lower yield stress when it is well ordered than when it is only partially ordered. Experiments show that such effects can be accounted for if the maximum strength, as a result of ordering, is associated with a critical domain size,¹⁴⁾ i.e. the hardness increases with antiphase domain growth until a critical size then decreases with the process of coalescence of the antiphase domain boundaries (APDB). In our case, the microhardness of quenched (disordered) alloy equals to 102 $\pm$ 2 N.mm⁻² and the ordering of Cu₃Au phase leads to its increase until 122 $\pm$ 5 N.mm⁻² (Table 2).

For the sample heated up to 100°C, the microhardness equals to 86 $\pm$ 5 N.mm⁻²; this result indicates that the first peak is attributed to a low ordered phase, which may be a transitory phase with some periodic antiphased structure.

3.10 Kinetics analysis based on non isothermal DSC tests

It is well known that the isoconversion methods are the most reliable methods for the calculation of activation energies of thermally activated reactions. A large number of these methods have been proposed in the literature. For this study, we have chosen the Starink method¹⁶⁾ because it has the best accuracy, combined with a simple application; it has the following form:

Table 2 Microhardness of the different phases in Cu₃Au alloy.

type of phase	new phase	Cu ₃ Au phase	disordered phase
H _v (N.mm ⁻²)	86 $\pm$ 5	122 $\pm$ 5	102 $\pm$ 2

Table 3 Activation energy E_{act} and Avrami exponent n values of the different phases formation in Cu₃Au alloy.

type of phase	new phase (P1)	Cu ₃ Au phase (P2)	disordered phase (P3)
E_{act} (KJ.mol ⁻¹)	94 $\pm$ 7	296 $\pm$ 16	1659 $\pm$ 46
n	1.23 $\pm$ 0.09	1.04 $\pm$ 0.09	0.81 $\pm$ 0.16

$$\ln T_p^{1.92}/V = (1.0008E_{act}/RT_p) + \text{const}$$

where V is the heating rate, T_p is the peak temperature observed in DSC curves and R is the perfect gas constant.

For isothermal treatments where the temperature is constant (the chosen temperature is 130°C), it will be easy to obtain the Avrami exponent n from the following equation:¹⁷⁾

$$\ln[\ln(1 - \alpha)^{-1}] = -n \ln V + \text{const}$$

where α represents the transformation fraction.

The calculated activation energies E_{act} and Avrami exponent n are summarised in Table 3. The obtained activation energy values show that the formation of disordered phase requires a higher energy which means that the order-disorder transition in this alloy is the first order. For the first reaction, the value of E_{act} is lower than that of Cu₃Au ordered phase. These results are reasonable if we take in consideration that this first reaction corresponds to a modulated structure with long periodicity i.e. the first reaction is less ordered than Cu₃Au because of the presence of defects as stacking faults. But concerning the n values, one can observe that n is lower in disordered state because of the type of order-disorder transformation in this alloy, which is very weak due to the existence of four kinds of antiphase domains in this lattice, and that n corresponding to the transition from disordered phase to this new phase is higher, which means that this transformation is rapid.

4. Conclusion

In the present study, we have followed the all possible phase transition in the binary intermetallic Cu₃Au alloy. We first detected a new reaction at low temperature range before the Cu₃Au ordered phase formation by differential scanning calorimetry (DSC) and dilatometry. Then we confirmed the existence of this new reaction at different heating rates during the non isotherm tests by the two methods.

We have found the same anomalies for sample homogenised at various temperatures and starting from 700°C, the first effect and that of Cu₃Au ordered phase are rearranged and give only one; thus the annealing of 2 h at 300°C leads to conclude that these two effects are probably dependents.

The XRD study reveals that the kinetic of the different transitions in this alloy are slow.

The electron diffraction pattern and a HRTEM image for alloy homogenised 1 h at 500°C then heated up to 100°C are indicative of the presence of ordered phase having a periodic structure.

A detailed analysis of this new reaction by calculation of different parameters: the resistivity $\rho = 0.0021 \cdot 10^{-3} \Omega \cdot \text{cm}$, the microhardness $Hv = 86 \text{ N} \cdot \text{mm}^2$, the activation energy $E_{\text{act}} = 94 \text{ KJ} \cdot \text{mol}^{-1}$ and the Avrami exponent $n = 1.23$, confirms the presence of this new reaction.

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