Investigation of the order -disorder phase transition series in AuCu by in-situ temperature XRD and mechanical spectroscopy

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Abstract

In-situ temperature XRD and mechanical spectroscopy were applied to study phase transitions in AuCu alloy from the disordered FCC state (A1). The phase transition temperature intervals were investigated upon heating and cooling using a rate of 1K/min in order to be thoroughly determined. The following sequences of phase transitions were recorded upon continuous heating: A1->AuCuI ->AuCuII->A1 and on subsequent cooling: A1 ->A1+AuCuI+AuCuII ->AuCuI+AuCuII ->AuCuI. This transition sequences determine also temperature dependency of elastic and anelastic properties. Mechanical spectroscopy using a forced torsion pendulum shows a peak due to antiphase boundaries motion characterizing the orthorhombic phase AuCuII and a transient peak with the that appears in the tetragonal phase AuCuI together with the classical Zener peak in the A1 phase.

1. Introduction

It is well known that order-disorder transitions produce significant effects on the properties of alloys [1, 2]. AuCu alloys appear to be a testing ground for different approaches and models that are aimed at describing phase changes in stoichiometric alloys [1, 3]. A pioneering in-situ work on Au-Cu alloy is that of Pasheley et *al.* on thin evaporated films [4, 5]. Phase transitions in AuCu system have been investigated using several techniques: micro hardness [6], acoustic emission and optical cinematography [7, 8]. The study of phase transitions in quenched Au-Cu alloys under different annealing conditions have been reported in several studies [2, 9-12]. Sometimes, results and interpretations related to temperature intervals and kinetics

of phase transitions are quite divergent [10,13,14] but, in any case, binary AuCu system presents two successive solid-solid transformations (between a disordered A1 fcc phase and a long period orthorhombic AuCuII phase together with a tetragonal AuCuI phase [3,15].

The work of Beaunnaux *et al.* [10] represents the last and most general investigation of phase transitions in AuCu alloy, using in-situ temperature controlled TEM. They have shown that different contradictions appear in previous studies and concluded that the in-situ TEM study presents some experimental difficulties. Therefore, these authors concluded that an in-situ XRD study would be necessary. Furthermore, mechanical spectroscopy has recently shown as a new approach to understanding the order-disorder phase transition [13, 16-19]. Important works have been devoted to the mechanical behavior [25] of gold alloys related to their industrial uses [18-24, 26, 27]. In fact, the re-arrangement of Au and Cu atoms can be monitored by Cu diffusion and in particular by the re-orientation of Cu pairs or clusters in the cell, which produces a characteristic peak called the Zener peak [18, 19]. In 1947, Zener first described this anelastic phenomenon, which gives rise to a thermally activated mechanical loss peak [25]. Under the application of an external stress, atoms locally rearrange, thereby minimizing the strain energy. Stress induced directional ordering causes energy dissipation, which is manifested by a damping peak.

In this paper, we used in-situ X ray diffraction to monitor the temperature intervals and kinetics of phase transitions in annealed and quenched AuCu (binary 18-carat) system, during the complete thermal cycle upon heating and cooling. To the best of our knowledge this is the first such study on this alloy. The paper mainly focuses on phase transformation in bulk sample from the disordered state A1. Direct observation of the phase transformations starting from the metastable phase A1 is also a peculiarity of this study. The purpose of this research is to show how these transitions may affect the mechanical properties by measuring both the internal friction and mechanical shear modulus in temperature scanning tests performed at the same conditions as the x-ray diffraction.

2. Materials and methods

The Au-Cu sample was fabricated by induction melting under vacuum. High purity raw materials (Au: 99.999%, Cu: 99.999 %) have been used for its production. The Electron Probe Microanalysis shows that the chemical composition of the ingots was Au-25.14.wt %Cu (Au-51Cu hereafter), with an accuracy of 0.2%. A disc of 10mm of diameter and 0.5mm of thickness was prepared from the ingots for the in-situ XRD study. The sample was homogenized at 973K for 2 hours, under primary vacuum (~1x10^{-3}mbar), followed with water quenching in order to obtain the disordered state A1 at room temperature (RT). The samples were polished with diamond paste to remove impurities or deposition on the sample surface before the analysis.

In situ X-ray thermo-diffraction was performed inside an Anton Pear HTK 1200N chamber between 298 and 973 K using a rate of 1 K/min under secondary vacuum (~1x10^{-5}mbar). This platform is mounted on the goniometer of a Panalytical XPERT-PRO diffractometer, which uses copper K$_\alpha$ radiation (1.5418 Å) and a PIXcel detector to record diffraction patterns measured in sweep mode. The disk is fixed on the top of an alumina rod with a diameter of 15 mm. Suitably fixed slits and masks are selected to illuminate only the surface of the sample. NIST standard reference material SRM 660a was used to determine precisely angle and/or height errors on the equipment and sample position. Besides, two equivalent experiments have been carried out over a large diffraction angle range (from 20 to 90⁰ on 2Theta) and a short diffraction angle range (from 29 to 42⁰ on 2Theta) in order to establish the type and temperatures of each phase transformations respectively. The heating and cooling rate was 1K/min and one pattern was acquired every 10min for the large diffraction angle scans and repeated every 1.1min (1 min 6 sec) for the short diffraction angle scans. Finally, X-ray diffraction patterns have been analyzed by the Le-Bail method [28] implemented in the Fullprof Suite package [29], allowing us to settle the parameters of every peak.

Measurements of internal friction and of dynamic shear modulus were performed in an inverted torsion pendulum as a function of temperature. Temperature scanning spectra were obtained in forced mode at a frequency of 1 Hz and 0.5 Hz during heating/cooling at the rate of 1 K/min under vacuum.

The strain amplitude was 5×10^{-5}. The samples had dimensions of 20x4x0.3 mm^3. The phase lag δ between stress and strain is directly measured and can be related to the mechanical loss, tan(δ). The dynamic shear modulus, M, at the frequency, *f,* is obtained from the ratio of stress and strain amplitude [24].

3. Results

Upon continuous heating, an optimum heating rate was chosen in order to evidence ordering from the quenched state [13]. A heating rate of 1K/min has been chosen. Long diffraction scans, with rate of one pattern taken every 10K (1pattern/10min), have been performed to well distinguish the characteristic peaks of every phase since the highest peak of the disordered cubic A1 overlaps with the related peaks of the tetragonal AuCuI and the orthorhombic AuCuII. On the other hand, scans performed in the short diffraction angle range, with a rate of one pattern taken per 1 K (precisely 1 pattern /1.1 min), have been used to determine the precise temperatures of the phase transitions.

Fig.1. shows the RTX-Ray patterns measured in the initial state (annealed and water quenched) (a) and in the final state after a heating-cooling cycle (b). All Bragg peaks observed in the initial state belong to reflections of the disordered cubic A1 structure although small tetragonal AuCuI ordered phase peaks are present. They appear as humps in Fig. 1a at low diffraction angles, which suggests that the AuCuI phase grain size is very small. At the end of the heating/cooling cycle, a single microcrystalline ordered tetragonal AuCuI is obtained.

Fig. 2a and Fig. S.1 present the 3D plots of the XRD measurements upon heating and cooling for the large diffraction angle scans and for the short diffraction scans, respectively. Three phase transitions can be discerned upon heating as follow: A1 - AuCuI-AuCuII-A1, and two upon cooling: A1-AuCuI+AuCuII–AuCuI. Moreover, in every transition there is an interval of temperatures where two phases coexist. The exact temperatures of every phase transition are presented in Table 1 mainly obtained by analyzing the short diffraction scan data. However, the phase transition temperature upon heating that correspond to the onset of the tetragonal AuCuI and the total disappearance of the cubic A1 (i.e. the presence of the pure tetragonal

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AuCuI) were extracted not only from short diffraction angles spectra, but also from the long diffraction angles spectra shown in Fig. 3.

Fig.4 and Fig.S.2 show the intensity behaviors of the selected peaks of every phase during the heating/cooling cycle, where data have been extracted from the fitting of the short and large diffraction angle range scans respectively. The intensity of (111) A1 peak upon heating increases abruptly (up to 50%) in two scans i.e. two degrees before decreasing continuously from 408K with the onset of (101) AuCuI peak and the increase of (100) AuCuI peak. The (101) AuCuI peak decreases before stabilization with the net presence of AuCuI phase. In Fig.S.2, the data have been extracted from the large diffraction angle range scans. The intensity of (220) A1 (Fig.S.2 (a)) decreases remarkably upon heating at around 368K followed by a second decrease with the onset of (200) AuCuI peak. Fig.4 and Fig.S.2 emphasize the sequences of the phase transitions and the transition temperatures upon heating and cooling. The phase transition temperatures are referred with dotted lines. After that, the temperature dependence of peak intensities are correlated with different phase transitions.

On the other hand, the phase transitions in Au-51Cu system show a noticeable difference in thermal expansion coefficients of different phases in terms of normalized volume of the unit cell of the corresponding phases per atom (Fig.S.3) and in terms of total normalized volume (Fig.5). The normalized unit cell volumes have been calculated from fitting XRD patterns of the large diffraction angles scans, where, the obtained unit cell of every phase has been divided by the corresponding number of atoms per cell then used to obtain the normalized volume. To obtain the total normalized volume, V_T, we have used the relation (1).

$$V_T = V_\alpha . fr_\alpha + V_\beta . fr_\beta + ... \qquad (1)$$

being $V_{(\alpha, \beta, ...)}$ and $fr_{(\alpha, \beta, ...)}$ the normalized volume and fraction for the phases α, β, ...

In both figures, a noticeable decrease of the normalized unit cell volume of A1 phase is manifested in two steps, firstly at the onset of the AuCuI phase and then continuously until the total disappearance of A1. Above 550 K, the normalized unit

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cell volume corresponding to AuCuI increases homogenously with respect to the temperature, until the temperature of the second transition (AuCuI - AuCuII) whereas a noticeable expansion is observed when the AuCuII phase appears. A second expansion occurs upon the third transition (AuCuII - A1). Upon cooling, a noticeable contraction accompanies the ordering transition at the passage from A1 to AuCuI+AuCuII; followed by an expansion when only the AuCuI phase remains. Fig. S.4 exhibits the evolution of phase fractions upon heating and cooling.

This dilatometric behavior of the phase transitions at the atomic level obtained for the analysis of XRD patterns is in a good agreement with the macroscopic expansion obtained by means of a dilatometer (Fig.S.5)

Fig.6 shows the temperature dependence of the internal friction (TDIF) and the elastic modulus (TDEM) of the AuCu alloy obtained with the disordered phase A1 as a starting point. Two frequencies have been used: 1Hz (top) and 0.5 Hz (bottom). Three peaks are visible on both heating curves (red lines), denoted by P_1, P_z and P_{APB} as temperature increases. First, the P_1 peak appears at the same temperature as the first phase transition shown in the structural study (A1 - AuCuI). Then, the P_z peak arises as a broad bump, which spreads over the range where AuCuI is observed and has a maximum at the temperature of the AuCuI->AuCuII phase transition. Finally, the P_{APB} appears as a sharp spike that is cut off by the transformation into the disordered phase A1. The shear modulus presents dip and shoulders that are synchronized with each internal friction peak. Concerning the frequency, the thermally activated peak P_z widens toward low temperatures when the frequency decreases but P_{APB} remains at the same temperature. On the other hand, the two cooling curves (blue lines) for each frequency have a similar shape and both contain two peaks, the peak P_z and the peak P_{GB} that is probably due to a grain boundary sliding. The position of P_z is almost the same and it becomes sharper at low frequency (0.5Hz) where its maximum gets closer to the temperature of the phase transition. The shear modulus upon cooling shows the obvious increase corresponding to the relaxation peak P_z. However, superimposed to this appear some fluctuations that coincide with the region of co-existence of the AuCuI and AuCuII phases. Coming from the high temperatures, the rapid increase of the Zener

peak intensity coincides with an increase of the shear modulus curve. When the Zener peak falls down, a steady increase in the shear modulus is observed. Finally, it is worth to notice that the position of the P_Z relaxation peak, is not the same upon heating and cooling.

4. Discussion

4.1. Heating

In-situ XRD temperature sweeps produce the most accurate picture of the phase transitions in the studied material. However, we can notice that in many cases different phases coexist in a metastable state. The very first transition from the disordered A1 phase to the ordered AuCuI needs to be carefully analyzed since, from the beginning of the experiment, AuCuI nanograins are present as a result of quenching. Thus, while the intensity of (100) AuCuI peak shows a constant value from RT to 408K, corresponding to the constant quantity of the tetragonal AuCuI nanograins, we cannot determine the intensity of the (101) AuCuI peak because of the overlapping with the main peak (111) of the cubic phase A1. So, assuming a constant quantity of the tetragonal AuCuI nanograins, its intensity is presented as a dotted red line (Fig.4(a)) from RT to 408K. Close to this point (exactly two degrees before), the intensity of the peak (111) of the A1 phase shows a sudden increase in the intensity, which may be due to the coalescence of the disordered crystalline cubic domains. Therefore, the thermally induced decrease of vacancy concentration, generated in the supersaturated phase A1 after quenching, may lead to some dislocation relaxation that sharpens the diffraction peaks and produces the corresponding raise of intensities too. After that, the interval from 408 to 538 K shows a gradual decrease in the intensity of the (111) A1 peak, which is associated with the corresponding intensity increase observed for the (100) and (101) peaks of AuCuI phase (Fig.4(a)). Nevertheless, the assessment of the transition temperature from A1 to AuCuI upon heating is visualized at high diffraction angles in the large range scans, while the overlap between (220) A1 and (200) or (212) broad reflections is better resolved in the short range scan (Fig.3). In contrast, the onset of the orthorhombic phase AuCuII upon heating, which starts at 637K and ends with pure AuCuII at 657K, and the nucleation of the cubic A1 from AuCuII (beginning at 677K

and finishing at 685K) are accurately determined from the data of short angle scans (Fig.3). In the region where AuCuI is growing to the detriment of A1, a volume contraction proceeds in two steps (Fig.5(a), Fig.S.3(a) and Fig.S.4(a)) and an inflection point around 458K is observed. The same effect is noticeable in the macroscopic dilatometer measurements (Fig.S.5).

On the other hand, the internal friction and shear modulus spectra give a better understanding of the defect diffusion or rearrangement processes that occur in the material. In Fig.6, the first phase transition A1-AuCuI is visible through the P_1 peak that reveals a split shape, which can be explained by the ordering reaction that precedes the A1-AuCuI transition as reported previously [30]. What is more important, however, is the modulus variation. Despite the "jumpy" shape of the curve that demonstrates that the transformation probably occurs by successive bursts in different parts of the sample, we have noticed that the transformation always shows a decrease of the modulus followed by an increase. Therefore, one may suppose that the transformation needs some softening of the elastic constants to be triggered. At about 630 K, a maximum is always observed but it is clearly more visible at 0.5 Hz. According to the earlier studies [23], this maximum should be attributed to a Zener relaxation that appears in the ordered phase AuCuII and disappears abruptly when such phase transform to the disordered phase A1 takes place. As demonstrated by Henning [19], the Zener relaxation can only occur if the Au and Cu have the possibility to exchange. The presence of the Zener peak in the AuCuII ordered phase indicates that the state of atomic order is not perfect. Indeed, due to the non-perfect stoichiometric composition of the alloy, some substitutional disorder must exist i.e. Au atoms occupy sites on the Cu sublattice [19]. The temperature range, which corresponds to the presence of the pure ordered phase AuCuII, is characterized by the P_{APB} peak that may be the antiphase boundaries relaxation peak. Such peak disappears with the onset of the cubic A1. According to refs.[10, 31], the AuCuI and AuCuII phases are characterized by the presences of twins, which create P_{APB}. However, Tkalcec *et al.* [27] suggested a better explanation. They showed that two different peaks can appear: a twin boundaries peak that appears in AuCuI and a peak in AuCuII that they attribute to the movement of antiphase boundaries. In the present study, the peak P_{APB} appears in the AuCuII region and it is more likely due to

the presence of the antiphase boundaries. The spectra recorded at a frequency of 0.5Hz allow a better discrimination of the phenomena. The Zener peak, which is thermally activated, appears at a lower temperature.

4.2. Cooling

The phase transition sequences from high temperature to RT shown by XRD are as follows: A1->A1+AuCuII+AuCuI->AuCuII+AuCuI->AuCuI. From short range diffraction angle scans, there is a small temperature range (649 – 645 K) where the three phases A1+AuCuI+AuCuII coexist (Table1, Fig.3 and Fig.4). From 644 to 604K,the concomitant presence of only two phases, AuCuI and AuCuII, can be deduced from the intensities of the (019) and (0111) reflections of AuCuII (see Fig.4(b)). By cooling strictly below 604K, only the pure tetragonal AuCuI is present. The appearance of order upon cooling down is associated with a noticeable contraction (Fig. 5(b) and Fig.S.3(b))

Upon the cooling the peak P_Z clearly starts only when the phase A1 is present. Therefore, the right flank of the peak should be attributed to the disordered phase A1. This is the classical Zener peak already investigated in the past [25]. The maximum of the peak is close to the temperature where the A1 phase disappears. While Its amplitude dropped down going toward lower temperatures with the increase of the order. This drop is less abrupt at 0.5Hz, where the peak appears at lower temperatures. This observation shows that the Zener relaxation effectively falls down with the ordering when A1 disappears. Still, the AuCuI and the AuCuII phases allow the presence of a lower but visible peak P_Z, which is manifested as a low temperature shoulder. The Zener relaxation peak maximum is accompanied with an increase of the shear modulus and the total disappearance of A1. In the area where there are two phases, the shear modulus presents fluctuations that accompany the disappearance of the small quantities of the orthorhombic phase AuCuII before its stabilization when only phase AuCuI is present. P_{GB} represents the grain boundaries relaxation peak that appears adjacent to Zener peak at high temperature [26,27] in A1.

5. Conclusion

We assess the temperature-dependent phase transition sequence in a Au-25wt%Cu alloy upon heating and cooling from RT to 973 K when combining in-situ thermodiffraction experiments and mechanical spectroscopy at a sweep rate of 1 K/min. The initial state after the quenching is mainly a metastable cubic A1 disordered phase but unavoidable nanograins of AuCuI are present. The onset of the AuCuI phase upon heating generates a transient peak together with a volume contraction. The AuCuI phase shows a Zener peak, which suggests that a certain degree of disorder is present or at least appearance of the non thermal vacancies. The AuCuII phase is characterized by a relaxation peak that should be attributed to the movement of antiphase boundaries. The transformation from AuCuI to AuCuII also leads to an expansion of the lattice. Upon cooling, the presence of all three possible phases is detected at the same time from 650 to 644K. Then, only AuCuI and AuCuII are present between 644 and 604 K, before the stabilization of the tetragonal AuCuI as the final state. This time the Zener peak seems to appear before the transition A1 ->AuCuI+AuCuII and partially disappears when only the AuCuI phase is present. Therefore, a consistent part of the peak should be attributed to the copper relaxation in the disordered phase A1.

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