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Formation of long-period ordered CuAuII phase in the non-stochiometric Cu-56 at% Au alloy

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A study of the formation of structure and properties during the disorder → order phase transformation with the formation of a long-period ordered CuAuII phase in a non-stoichiometric Cu-56 at.% Au alloy has been carried out. X-ray diffraction analysis was used in the course of this work. Annealing of deformed and quenched samples of the alloy under study was carried out in the temperature range of 275–375°C (every 25°C), the annealing duration ranged from 1 hour to 2 months. It has been established that a single-phase state ordered by the CuAuII type is formed in the Cu-56Au alloy at temperatures of 325 and 350°C. The ordered CuAuI phase is formed at a temperature of 275°C in the alloy, which somewhat diverges from the generally accepted phase diagram. A two-phase (CuAuI + CuAuII) state is formed at a temperature of 300°C. Annealing at a temperature of 375°C leads to the formation of a two-phase (disorder + order) structure (A1 + CuAuII). Using mathematical processing of X-ray peaks, an assessment of the phase relationship in two-phase states has been carried out. It has been shown that during the formation of the long-period CuAuII structure, the CuAuI superstructure is first formed.

Keywords: Cu-Au system, phase transformations, kinetics, atomic ordering, long-period CuAuII phase.

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1. Introduction

Processes of atomic ordering were for the first time observed over 100 years ago by Kurnakov, Zhemchuzhny and Zasedatelev when studying gold-copper alloys [1,2]. So temperature of phase transformation disorder-order is frequently called as „Kurnakov temperature", and ordered phases — „Kurnakov phases" [3]. Study of features of formation of atomic ordered structures in Cu-Au alloys till now attract researchers [4–7]. It was reliably identified that near equiatomic composition two atomic ordered phases (CuAuI and CuAuII) are formed [8,9]. When cooling from high-temperature range the following sequence of rearrangement of the disordered structure (A1-phase) into ordered state is observed: A1 → (A1 + CuAuII) → CuAuII → (CuAuII + CuAuI) → CuAuI [8,10]. But, in spite of rather large number of papers related to study of transformation disorder → order in gold-copper alloys answers to not all questions are obtained. For example, in known phase diagram of system Cu-Au [11] there are no experimental points, and from text it follows that part of interphase boundaries was made based on model calculations (Figure 1). But, Cu-56 at.%Au alloy is provided by the industry under grade ZlM-80 and is used in instrument engineering to manufacture the precision parts. So, it is necessary to study in detail the boundaries of existence in this alloy of long-period atomic ordered phase CuAuII, to clarify the temperature ranges of two-phase regions (A1 + CuAuII) and (CuAuII + CuAuI), determine the temperature of phase transformation disorder-order and to analyze the difference of formation kinetics of CuAuII-phase in alloy samples

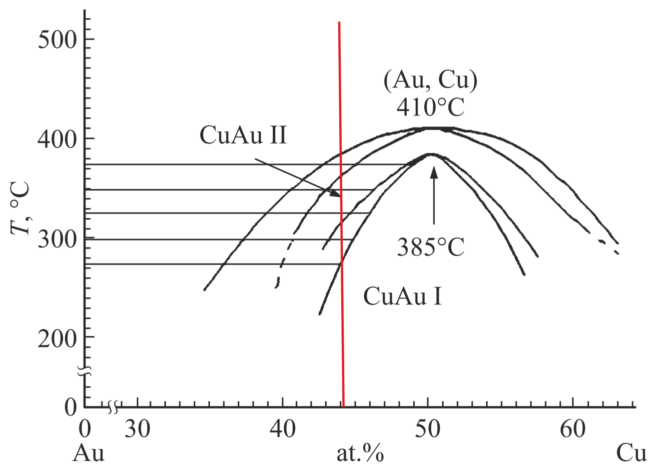

Figure 1. Section of equilibrium phase diagram of system Cu-Au from paper [11]. Vertical red line corresponds to composition of studied alloy Cu-56 at.%Au. Horizontal lines show temperatures at which experiments were performed: 275, 300, 325, 350 and 375°C.

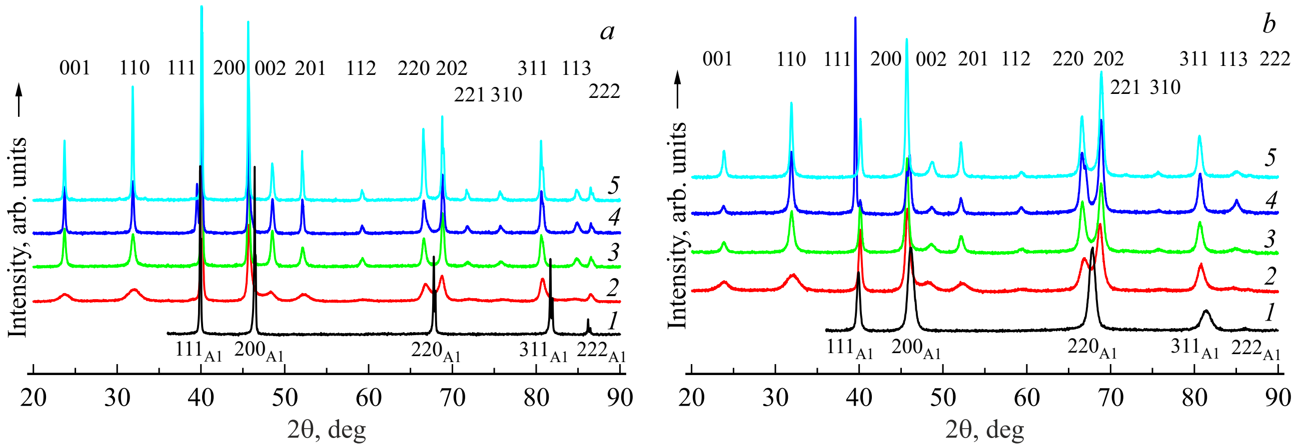

Figure 2. XRD results of samples of quenched (a) and deformed (b) alloy in initial state (1), after annealing for 1 (2), 24 (2), 168 (4) and 1440 h (3) at temperature of 275°C.

disordered by quenching from high temperature or using plastic deformation.

Besides, the issue remains unsolved whether the long-period CuAuII-phase occurs immediately from „disorder" or initially more simple ordered phase CuAuI is formed. Earlier, in paper [12] we showed that rate of atomic ordering in nonstoichiometry alloy Cu-56at.%Au is very low. Thus, to finish the transformation disorder → order (A1 → CuAuI) at temperature of 250°C this alloy annealing for at least two months is required. It is obvious that low rate of atomic ordering ensures determination of all stages of formation of long-period structure.

The study task was to determine the features of formation of long-period ordered phase CuAuII in nonstoichiometric alloy Cu-56at.%Au.

2. Material and procedure

To melt the alloy Cu-56 at.%Au (Cu-80Au, mass.%) under study the plates of copper and gold with purity 99.95% and 99.99%, respectively were taken. Melting was performed in quartz tube under vacuum 10^{-2} Pa with various pouring into graphite crucible. After homogenization at temperature of 850°C, 3 h with further quenching in water, the ingot was subjected to mechanical and thermal processing. For the phase composition certification plates 0.3 mm thick were prepared. All experiments were performed on samples, in which initial disordered state was formed in two ways: quenching from 600°C or by plastic deformation by 90%.

To determine the range of formation in the alloy under study of the ordered CuAuII phase, the annealing of quenched and deformed samples was performed with change in temperature from 275 to 375°C (with range 25°C). Selection of exactly this temperature range is due to that, for example, from phase diagram it is unclear what structural state is formed in the alloy at 275°C: single-phase CuAuI or two-phase (CuAuI + CuAuII). At higher temperatures it is also necessary to analyze the phase composition of the alloy and to determine kinetics of formation of long-period superstructure CuAuII. Annealing duration is 1, 24, 168 (1 week), 1440 (2 months) h. All heat treatments were performed in vacuum quartz or glass tubes.

The X-ray diffraction analysis (hereinafter — XRD) was performed in diffractometer PANalitical Empyrean Series 2 in Cu-K_α radiation. To estimate ratio of phases in two-phase states the mathematical processing of some peaks was performed in software package „OriginPro". The experimental peaks are considered as sum of Lorentz functions, this ensures separation of contribution of from each phase and to calculate ratio of integral intensities of appropriate X-ray reflections.

3. Experimental results and discussion

Previously we reliably determined [12,13], that as a result of long-period annealing at temperature of 250°C in alloy Cu-56Au the single-phase CuAuI state is formed. So, in this paper higher temperature range of ordered phases existence is considered.

In the initial state samples of Cu-56Au alloy were in disordered FCC-state (A1-phase) with lattice parameter $a = 0.3901$ nm (after quenching from 600°C) or $a = 0.3912$ nm (after plastic deformation by 90%).

Figures 2–5 presents XRD results obtained from samples of alloy under study annealed in temperature range 275–375°C with holding from 1 to 1440 h. These diffraction patterns well indicate the evolution of phase composition of the alloy with temperature increasing. So, based on results in Figure 2 we can conclude that after annealing for 1440 h at temperature of 275°C in the alloy single-phase state is formed with superlattice of CuAuI type. Besides, it is well seen that at the first stage of transformation (after annealing for 1 h) on the X-ray patterns only diffusion peaks

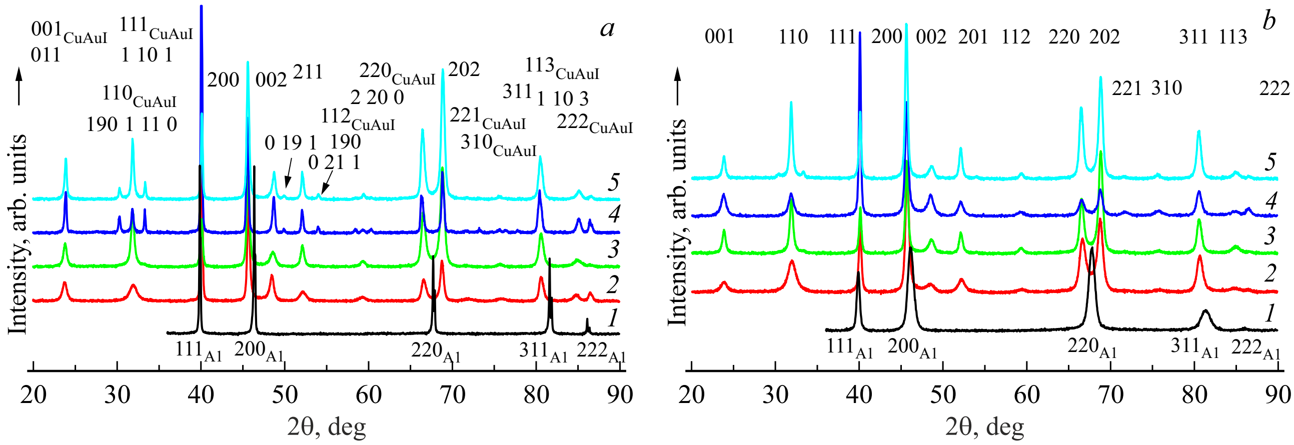

Figure 3. XRD results of samples of quenched (*a*) and deformed (*b*) alloy in initial state (*1*), after annealing for 1 (*2*), 24 (*2*), 168 (*4*) and 1440 h (*3*) at temperature of 300°C.

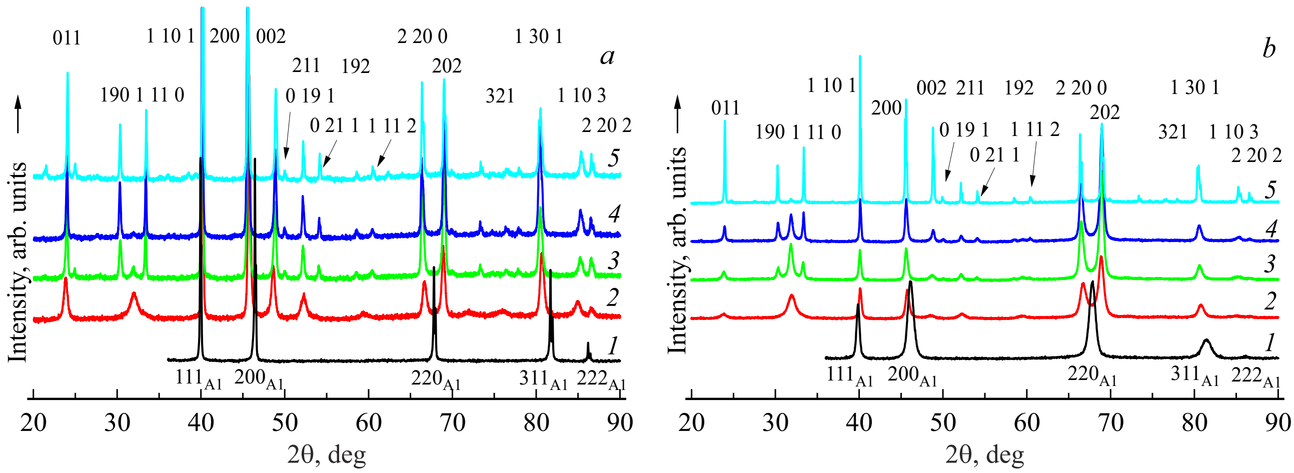

Figure 4. XRD results of samples of quenched (*a*) and deformed (*b*) alloy in initial state (*1*), after annealing for 1 (*2*), 24 (*2*), 168 (*4*) and 1440 h (*3*) at temperature of 325°C.

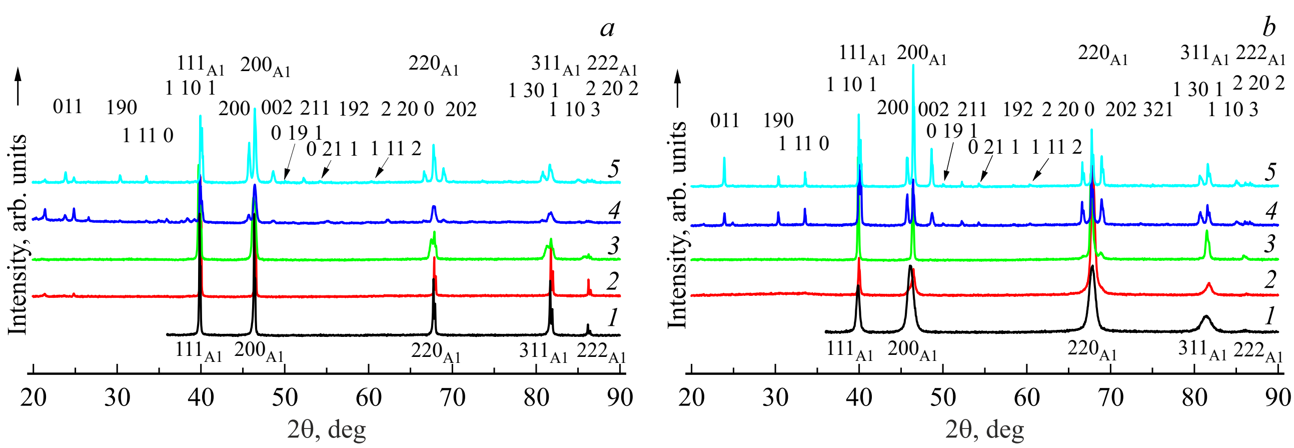

Figure 5. XRD results of samples of quenched (*a*) and deformed (*b*) alloy in initial state (*1*), after annealing for 1 (*2*), 24 (*2*), 168 (*4*) and 1440 h (*3*) at temperature of 375°C.

appear in positions of superstructural reflections. Most likely, such state corresponds to the formation in the alloy of the short-range atomic order (it can be compared with diffraction pattern of Au-51Cu alloy with short-range order formed during quenching: Figure 1, *a* in paper [14]). This once more confirms the low rate of atomic ordering in the alloy under study.

Comparison of XRD data in Figure 2, *a* and Figure 2, *b* shows that in the initial quenched state the formation of atomic order occurs quicker. Especial it is easy understandable during analysis of peak evolution (200) of disordered phase. Due to tetragonality of ordered lattice, this peak during phase transformation disorder → order is split into 2 peaks: (200) and (002) [12,15].

After annealing for 24 h of the initial quenched alloy at temperature of 275°C the X-ray pattern clearly shows both peaks (diffraction pattern 3 in Figure 2, *a*). In turn, during annealing of preliminary deformed alloy clear peak (002) is not observed even after holding for 168 h (diffraction pattern 4 in Figure 2, *b*). Higher rate of atomic ordering in initially quenched gold-copper alloys was several time observed earlier [12,13].

After annealing at temperature of 300°C composition of alloy under study abruptly changes (Figure 3): it becomes two-phase and contains mixture of ordered phases (CuAuI + CuAuII). CuAuI phase has following parameters of crystal lattice: $a = 0.3963$, $c = 0.3671$ nm. This permits evaluation of degree of tetragonality of lattice of CuAuI phase as $c/a = 0.92$, this corresponds to high degree of long-range atomic order ($S \approx 1$) [10]. Parameters of crystal lattice of CuAuII phase are: $a = 0.4067$ nm, $b = 4.3382$ nm, $c = 0.3790$ nm. Therefore, degree of tetragonaly of orthorhombic lattice of CuAuII phase is $c/a = 0.93$, modulation period is $M = b/a = 10.67$. It is known [16] that half-period of modulation ($M/2$, i.e. number of CuAuI cells between periodic antiphase boundaries of offset type in long-period CuAuII-phase) in equiatomic alloy is estimated as $M/2 \approx 5.1$. It was also determined that upon deviation from stoichiometry the value of $M/2$ slightly increase [16]. As in the alloy under study the half-period of modulation is $M/2 \approx 5.3$, our obtained results are within known perceptions and amend them.

The formation of the orthorhombic superstructure CuAuII is clearly revealed in X-ray diffraction patterns by the appearance of additional, satellite reflexes near the superstructure reflections from CuAuI phase [17]. For example, after long-time annealing from both sides of superstructural peak $(110)_{\mathrm{CuAuI}}$ satellite peaks $(090)_{\mathrm{CuAuII}}$ and $(1\,11\,0)_{\mathrm{CuAuII}}$ appear (Figure 3, *a*).

When comparing the diffraction patterns in Figures 3, *a* and 3, *b* we clearly see the difference in rates of formation of alloy structure in dependences on initial state of samples. At the same time, both in initially quenched alloy the reflections from to ordered phases are clearly separated after annealing for 168 h, after preliminary deformation weak satellite peaks occur only after annealing for 1440 h.

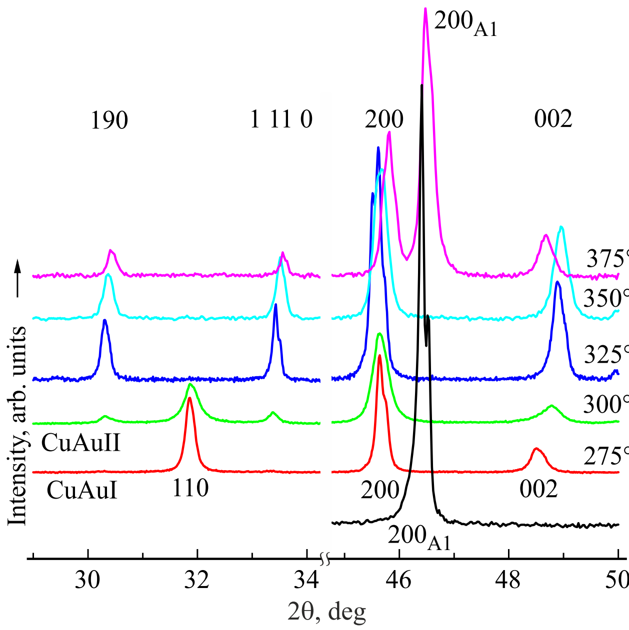

Figure 6. Sections of X-ray diffraction patterns in range of angles 2θ from 29° to 50°, obtained from preliminary quenched samples of Cu-56Au alloy annealed in temperature range from 275 to 375°C for 1440 h. In bottom for comparison the diffraction pattern of disordered alloy is shown.

Annealing at temperature of 325°C again changes the phase composition of the alloy under study (Figure 4). The X-ray diffraction patterns obtained after the alloy annealing at temperature of 350°C practically do not differ from those in Figure 4, and therefore are not shown here: at these temperatures in alloy CuAuII phase gradually forms. At that, the rate of phase transformation disorder → order during annealing of the deformed alloy again is significantly lower, this ensures tracking of sequence of superstructure formation. Figure 4, *b* clearly shows that at the first stage of ordering the ordered CuAuI phase is formed: after annealing for 24 h large intensity of peak (110)CuAuI is observed on background of rather weak satellite peaks to the right and left from it, they indicate the presence of CuAuII phase. During further increase in annealing time the intensity of peak $(110)_{\mathrm{CuAuI}}$ decreases. In turn, in quenched alloy this peak practically disappears after annealing for 168 h, see diffraction pattern 4 in Figure 4, *a*). So, at temperatures 325 and 350°C the alloy becomes single-phase, ordered as per CuAuII type.

Annealing at temperature of 375°C again changes the phase composition of the alloy under study: except reflexes from ordered CuAuII phase in all diffraction pattern the reflections from disordered A1 phase are observed (Figure 5). We can conclude that annealing at temperature of 375°C transits Cu-56Au alloy into two-phase state disorder + order (A1 + CuAuII).

For better visualization of the phase composition of Cu-56Au alloy at different temperatures Figure 6 shows

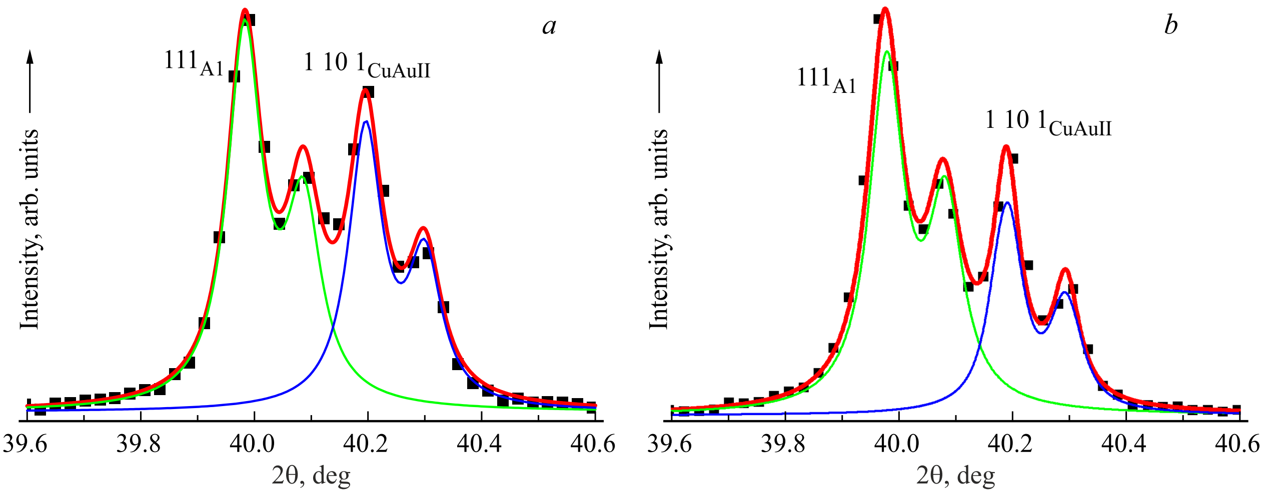

Figure 7. Sections of X-ray diffraction patterns with peaks $(111)_{A1}$ and $(1\,10\,1)_{CuAuII}$ obtained from preliminary quenched (*a*) and deformed (*b*) samples of Cu-56Au alloy after annealing at temperature of 375°C for 1440 h. The experimental data are presented by dots, calculated data — by solid lines.

sections of all obtained X-ray diffraction patterns in the range of angles 2θ from 29° to 35°, and from 45° to 50°. Since, as it was shown above, preliminary deformation somewhat reduces the transformation rate, all XRD results in Figure 6 correspond to initially quenched samples after annealing during the maximum period.

In the range of angles from 29° to 35° reflection (110) from CuAuI phase and satellite peaks (1 9 0) and (1 11 0), corresponding to CuAuII phase were observed. So, comparison of diffraction patterns at these angles ensures tracking of change in ordered state of the alloy in studied temperature range: from one CuAuI phase at temperature of 275°C, via two-phase state (CuAuI + CuAuII) at 300°C, to single-phase CuAuII state in range 325–350°C. At temperature of 375°C except peaks typical for CuAuII phase, in range of angles 45–50° there is additional reflection from disordered phase.

During transformation disorder–order the initial peak (200)A1 rather quickly disappears (Figures 2, 3). But, after annealing during maximum time period at temperature of 375°C in range of angles 2θ from 45° to 50° in Figure 6 all three peaks are observed: $(200)_{A1}$, (200) and (002). At that the peaks intensity of disordered A1 phase stays high. Note here that reflections (200) and (002) from ordered phase are much closer to the initial peak $(200)_{A1}$ as compared to diffraction patterns obtained after annealing at lower temperatures. This phenomenon was observed earlier in the initial stages of atomic ordering in gold-copper alloy [15]. We can conclude that at temperature of 375°C parameters *a* and *c* of ordered lattice are still far from equilibrium values, and ordered phase in the alloy has low degree of atomic order. It is known that degree of long-range order depends on temperature and significantly decrease upon approaching to the temperature of phase transformation, this is associated with „temperature disordering“ [3].

It is interesting to evaluate relationship of ordered and disordered phases in alloy at temperature of 375°C. Sections of experimentally obtained diffraction patterns for initially quenched and preliminary deformed samples in range of angles 2θ from 39.4° to 40.6° with peaks from disordered $(111)_{A1}$ and ordered phases $(1\,10\,1)_{CuAuII}$ are shown by dots in Figure 7. The calculated curve obtained as a result of mathematical processing describes well the experimental data, while the peaks from different phases are clearly separated. According to the obtained data after annealing during maximum time period of initially quenched alloy the relationship of integral intensities of reflections from two phases $I(1\,10\,1)_{CuAuII}/I(111)_{A1}$ is ~ 0.713 (Figure 7, *a*). The obtained result indicates that at 375°C in two-phase (A1 + CuAuII) alloy the content of disordered A1 phase is somewhat higher then of the ordered one. It was stated earlier, the transformation disorder → order in deformed alloy goes with lower rate. Actually, annealing for 1440 h of the preliminary deformed alloy results in formation of significantly lower volume of CuAuII phase: relationship $I(1\,10\,1)_{CuAuII}/I(111)_{A1}$ decreases to ~ 0.468 (Figure 7, *b*).

Above approach can be also applied to evaluate relationship of ordered phases CuAuI and CuAuII formed in the alloy under study as result of long-time annealing at temperature of 300°C (Figure 3 and Figure 6). For analysis we again use peak (111) in diffraction patterns obtained from the initially quenched and preliminary deformed samples (Figure 8). Certainly, for the accurate evaluation of phases relationship we need processing of maximum possible number of peaks in the X-ray pattern. At that consider that presence of texture can change the intensity of peaks. But in this paper we have no need to perform detail phase analysis. Assuming that studied phases have one type of texture, the evaluation of phases relationship by one peak will lead to rather acceptable result.

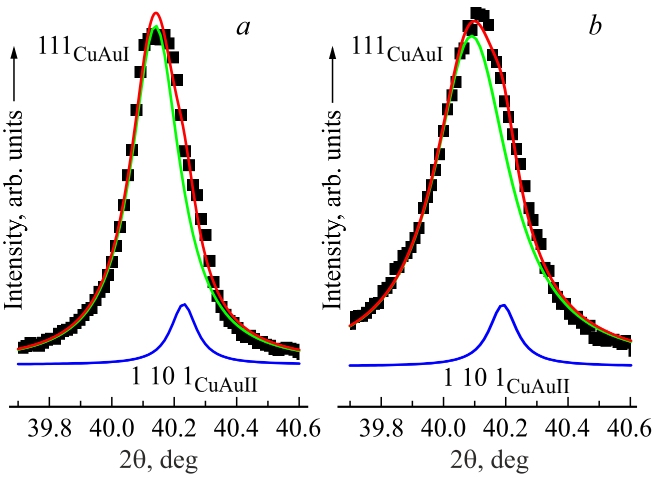

Figure 8. Sections of X-ray diffraction patterns near peaks $(111)_{\text{CuAuI}}$ and $(1\,10\,1)_{\text{CuAuII}}$, obtained from preliminary quenched (*a*) and deformed (*b*) samples of Cu-56Au alloy after annealing at temperature of 300°C for 1440 h. The experimental data are presented by dots, calculated data — by solid lines.

Due to vicinity of parameters of lattices of ordered phase and low amount of phase CuAuII, peak (111) visually looks like reflection from single phase. But, during mathematical processing the peak (111) in these X-ray patterns is most well described by sum of Lorentz functions from two reflections: $(111)_{\text{CuAuI}}$ and $(1\,10\,1)_{\text{CuAuII}}$. According to the made evaluations for the initially quenched alloy after annealing for maximum time period at 300°C the relationship of integral intensities $I(1\,10\,1)_{\text{CuAuII}}/I(111)_{\text{CuAuI}}$ is ~ 0.094. For the preliminary deformed alloy after same annealing this relationship decreases to ~ 0.069.

Conclusion

The performed work is the first step in study of poorly investigated long-period phase CuAuII in Cu-56at.%Au. alloy. Further we planned detail study of structure and properties of this phase using different methods (transmission electron microscopy — to identify where excess gold atoms present; measurement of mechanical properties — to identify contribution of large number of periodic antiphase boundaries into the strength properties etc.).

This study makes it possible for the first time to clarify the temperature ranges for the formation of various phases in the nonstoichiometric Cu-56at.%Au alloy. The following basic results are obtained:

1. As result of long-time annealing at temperature of 275°C in alloy under study ordered CuAuI phase is formed. Annealing at 300°C leads to formation of two-phase (CuAuI + CuAuII) ordered state. After annealing at temperatures of 325 and 350°C we record single-phase, ordered state by CuAuII type. Annealing at temperature of 375°C results in two-phase structure disorder + order (A1 + CuAuII) formation.

2. As at temperature of 300°C the alloy contains below 10% of CuAuII phase, we can assume, that interface between ordered CuAuI phase and two-phase (CuAuI + CuAuII) state appears at $\sim (290{-}295)$°C.

As at temperature of 325°C the alloy is single-phase CuAuII state, hence, width of two-phase (CuAuI + CuAuII) region in the alloy under study does not exceed 30°. Thus, the temperature range of two-phase ordered state is somewhat narrower than shown in phase diagram.

4. The obtained in paper relationship of disordered (A1) and ordered (CuAuII) phases at temperature of 375°C generally corresponds to the phase diagram. From this result it follows that temperature boundary of transformation A1-(A1 + CuAuII) in the studied alloy corresponds to phase diagram and is ~ 390°C.

5. It is shown that long-period orthorhombic superstructure CuAuII is formed via more simple ordered phase CuAuI.

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Conflict of interest

The authors declare that they have no conflict of interest.

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