*Russian Physics Journal, Vol. 53, No. 3, 2010*

# CONDENSED-STATE PHYSICS

## THERMOACTIVATED STRUCTURE REARRANGEMENTS IN A BINARY CuAu ALLOY UNDER DEVIATION FROM STOICHIOMETRY

**A. I. Potekaev,[1] E. A. Dudnik,[2] M. D. Starostenkov,[3]**
**V. V. Kulagina,[4] and V. S. Myasnichenko[3]**

UDC 539.2

*Thermoactivated structure rearrangements of a binary* CuAu *alloy at the micro-, meso-, and macrolevels are investigated under deviation from stoichiometry. Mechanisms of these rearrangements at the micro-, meso-, and macrolevels are identified.*

**Keywords:** phase transition, structure, ordered alloys.

### INTRODUCTION

An order–disorder phase transition is a type of phase transitions taking place in metal systems in condensed state. A distinguishing feature of this transition is its diffusion character and the relationship between the short- and long-range orders in arranging the atoms with the phase-symmetry groups, i.e., structural features of the system. Investigations of the nature and mechanisms of order–disorder (O–D) phase transitions in metallic substitutional solid solutions started as far back as the early XX century. The reason why the interest in these O–D phase transitions is still maintained lies in the fact that they are quite common in alloys and exert a significant influence on their properties.

A large number of reviews and monographs are currently available, which address the issue of atomic ordering and its effects on the properties of alloys [1–9].

Research into the ordering–disordering processes in condensed systems at the micro-, meso-, and macrolevel simultaneously was started comparatively recently [10–13]. In [14–18], special features of ordering in binary alloys (such as CuAu with $L1_2$ superstructure) were reported in the case of high-symmetry states, while our aim is to study the process of ordering in an anisotropic condensed system (such as CuAu with superstructure $L1_0$) as a function of temperature and composition. A well-known binary CuAu alloy appears to be useful for this purpose, as there is a large body of the literature data both on theoretical and experimental results of such investigations.

Based on the diffusion-induced character of the O–D transition, it is reasonable to assume a vacancy diffusion mechanism. Note, however, that when a vacancy concentration is set in the model system, which is close to the experimentally observed, the simulated ordering process is very fast. In order to study it in detail, it is useful to "retard" diffusion by setting a lower vacancy concentration in the model.

If we start from a disordered state, then, using a stochastic Monte Carlo approach, it becomes possible to obtain equilibrium configurations of the system with predetermined component concentrations within a certain temperature range.

---

[1] V. D. Kuznetsov Siberian Physical-Technical Institute at Tomsk State University, Tomsk, Russia, e-mail: potekaev@spti.tsu.ru; [2] Rubtsovsk Industrial Institute at AltSTU, Rubtsovsk, Russia, e-mail: dudnik@rubtsovsk.ru; [3] I. I. Polzunov Altai State Technical University, Barnaul, Russia, genphys@mail.ru; [4] Siberian State Medical University, Tomsk, Russia. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 3, pp. 3–13, March, 2010. Original article submitted August 3, 2009.

## THE MODEL AND EXPERIMENTAL PROCEDURE

We investigated a number of model binary alloys of the CuAu system with the following copper content: 45, 50, and 55 at.%. They have a basic fcc-lattice, with the stoichiometric alloy having a tetragonal superstructure $L1_0$ (so-called CuAu I) in a completely ordered state, a cubic $A1$ structure in a disordered state, and an orthorhombic CuAu II structure near the transition.

The alloy atoms sit in the lattice sites according to the prescribed component concentrations, with the initial state being disordered. The size of the computation grid for the crystal measures 36×36×36 unit cells of an fcc-lattice, the number of atoms $\sim 2\cdot 10^5$, with the boundary conditions at the grid margins prescribed to be periodic. The temperature was set to be constant and uniform across the grid. Since in simulating the structural rearrangement of atoms use was made of the vacancy diffusion mechanism, so a single vacancy was randomly introduced into the alloy (concentration $\sim 0.55\cdot 10^{-6}$) and the atomic hopping radius was limited by two coordination spheres as the most probable ones.

In the pair-interaction model, configurational energy of a binary alloy has the following form:

$$E = -\sum_{i=1}^{N_s}[N_{AA}^i\varphi_{AA}^i + N_{BB}^i\varphi_{BB}^i + N_{AB}^i\varphi_{AB}^i], \tag{1}$$

where $\varphi_{AA}^i, \varphi_{BB}^i, \varphi_{AB}^i$ are the interaction energies of the atomic pairs $AA$, $BB$, $AB$ (taken with the opposite sign) at a distance equal to the radius of the $i$-th coordination sphere, $N_{AA}^i, N_{BB}^i, N_{AB}^i$ is the number of the respective atomic pairs in the $i$-th coordination sphere, and $N_s$ is the number of interactions taken into account.

From the initial disordered state of the system we obtained, using a stochastic Monte Carlo method, equilibrium configurations with predetermined component concentrations within a certain temperature range. The state of the alloy was taken to be equilibrium and stable, if the parameters characterizing the system (energy, order parameter, entropy) remained constant for an arbitrary long time; note that the system was not allowed to change this state without an external action. While a conventionally used criterion of achieving equilibrium is that of achieving an extremum of one of the macroscopic characteristics, in our approach the exact dynamic behavior of the system is replaced by its discrete states, with every iteration step corresponding to one act of atomic vacancy self-diffusion. It should be noted that in every iteration step we calculate the probability of one of the atoms found in the vicinity of a vacant site to occupy it, with the probability of an atom $\boldsymbol{i}$ hopping into a vacant lattice site $\boldsymbol{j}$ being an exponential function of temperature

$$P_{ij} = A\cdot\exp\left(-(\Delta E_{\max} - \Delta E_v^{ij})/kT\right), \tag{2}$$

where $k$ is the Boltzmann constant, $T$ is the temperature, $A$ is the normalization factor ensuring that the normalization condition is fulfilled (the sum of probabilities of hopping for the atoms located in the first and second coordination spheres with respect to the site is equal to unity, i.e., $\sum_{ij}^{n} P_{ij} = 1$, where $\boldsymbol{n}$ is the number of atoms in the first and second coordination spheres with respect to the vacancy). The value of released (deposited) energy $\Delta E_v^{ij}$ is estimated for every atom $\boldsymbol{i}$ surrounding the vacancy $\boldsymbol{j}$ in the first and second coordination spheres, it is equal to the difference between the bonding energy of the atom $\boldsymbol{i}$ in the vacant site position $E_k^{ij}$ and the bonding energy of the atom $\boldsymbol{i}$ in the position prior to hopping $E_n^{ij}$: i.e., $\Delta E_v^{ij} = E_k^{ij} - E_n^{ij}$. As a result, from all the values of $\Delta E_v^{ij}$ we select the maximum value denoted as $\Delta E_{\max}$.

In order to identify the phases formed in the course of structural changes (here $A_3B$, $AB$, $AB_3$ and those of pure components), we used an approach based on determining the number of atomic pair bonding in the first coordination sphere corresponding to each structure formed. This implies that the $A_3B$ phase structure is found for an atom of the $A$

kind as the number of its bonds in the first sphere *A–A*, which is equal to 4, and *A–B* – 8, while for the *B* kind atom the number of bonds *A–B* is 12. For an *A* kind atom, the *AB* phase structure would control the number of bonds in the first sphere *A–A*, which is equal to 4, and *A–B* – 8, while for the *B* kind atom *B–B* is equal to 4 and *A–B* – 8. For a *B* kind atom, the $AB_3$phase structure controls the number of its bonds in the first sphere *B–B*, which is equal to 4, and *A–B* – 8, while for an *A* kind atom the number of bonds *A–B* is12. For pure component phases, the number of bonds in the first coordination sphere of similar components is equal to the number of atoms in the first coordination sphere, i.e., 12.

In order to describe the changes in the alloy state, we made use of such concepts as domain, cluster, and phase- and antiphase boundaries. Further in the text, an ordered phase will be characterized by the number, size, and shape of domain structures, with the domains denoting parts of a crystal ordered as CuAu (superstructure $L1_0$). Note that the domains can have different orientation and be shifted with respect to each other. The latter are referred to as antiphase domains. Let us take a cluster to represent a disordered structure and to contain atoms of different kind, whose number of pair bonds in the first coordination sphere would not correspond to that in the ordered CuAu phase. The disordered phase consists of cluster atoms and substitution point defects. The interface between two antiphase domains will be denoted here as an antiphase boundary, and the region separating the ordered and disordered phases will be referred to as a phase boundary. A "semi-ordered" phase would contain both antiphase and phase boundaries.

To verify the resulting model and the experimental procedure, it is useful to carry out a comparative testing of the well-established mechanisms and the respective dependences obtained within the proposed model. The parameters for this purpose were well-known lattice parameters and lattice tetragonality values, as well as short- and long-range order parameters, all taken as a function of temperature.

It is well known [16] that a measure of short-range ordering is the ratio of $N_n^{AB}$ (number of pairs of *A* and *B* atoms spaced at a distance equal to the radius of the *n*-th coordination sphere) to the number of *A* and *B* atoms that would be in these positions, given their completely chaotic distribution over the lattice sites, i.e.,

$$\sigma_n^{AB} = 1 - \frac{P_n^{AB}}{C_B}, \tag{3}$$

where $P_n^{AB}$ is the probability of finding a *B* atom in the *n*-th coordination sphere, given that an *A* atom is located in the central site.

The long-range ordering degree [17] is proportional to the deviation $P_A^{(1)}$ (probability that atom *A* is found in its sub-lattice) from $C_A$ (concentration of *A* atoms in the alloy)

$$\eta = \frac{P_A^{(1)} - C_A}{1 - \nu}, \tag{4}$$

where the probability $P_A^{(1)} = \frac{N_A^{(1)}}{N^{(1)}}$ is equal to the number of *A* atoms, sitting in their site, to the number of sites in the first sub-lattice, in this case $\nu = 1/2$.

Free energy was determined as a function of long-range ordering [17]:

$$F = E - TS(\eta), \tag{5}$$

wher *T* is the temperature and *S* is the configurational entropy.

## RESULTS AND DISCUSSION

To study thermoactivated atomic-structure rearrangement in the alloy, we performed a computer experiment using the following scheme. In the first step of simulation, we formed three types of initial crystal blocks, then

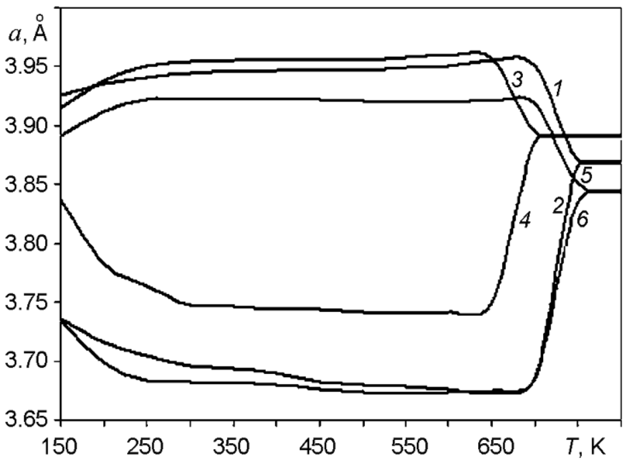

Fig. 1

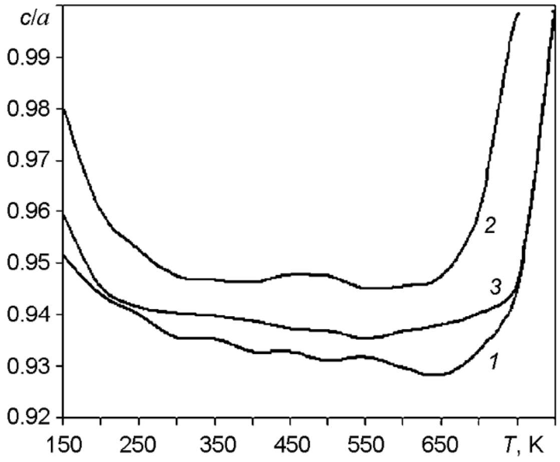

Fig. 2

Fig. 1. Lattice parameters, *a* and *c*, as a result of thermoactivated rearrangement of the alloy structure versus temperature and alloy component concentration: 50 at.% Cu (curves *1* and *2*, respectively), 45 at.% Cu (curves *3* and *4*, respectively), and 55 at.% Cu (curves *5* and *6*, respectively).

Fig. 2. Dependence of the alloy tetragonality (*c*/*a*) on temperature: 50 at.% Cu (curve *1*), 45 at.% Cu (curve *2*), and 55 at.% Cu (curve *3*).

introduced a vacancy into each of them, which yielded a vacancy concentration of $0.55 \cdot 10^{-6}$. After that, we prescribed the temperature and, using a Monte Carlo method, activated the vacancy diffusion mechanism of atoms. It should be noted that the atomic interaction energy was tabulated from the distance to three coordination spheres using the Morse potential function and its parameters from [18]. Thermoactivation of the system was performed in a stepwise fashion within the temperature range from 150 to 800 K with a step of $\Delta T = 50$ K using $10^8$ iterations for every temperature value in three computation blocks. At lower temperatures, we observed the process of ordering, while at higher temperatures after a certain ordered state, depending on the alloy composition, was achieved, we observed disordering of the system.

**Investigation of the dependence of lattice parameter and tetragonality in the AuCu alloy on temperature and component concentration.** The initial configuration of every alloy was a completely disordered high-symmetry cubic phase, whose lattice parameters in three mutually perpendicular directions were equal. In the experiments the lattice parameter values were observed to vary: in two main crystallographic directions they increase, remaining to be equal, while in the third direction the lattice parameter decreases. The resulting values are in a good agreement with the experiment [19]. Shown in Fig. 1 is the lattice parameter variation under thermoactivation of the alloy within 150–800 K for different concentrations of the alloy components.

It is evident from Fig. 1 that in the alloy of equiatomic composition the lattice parameter variation was relatively small at the temperature below 650 K, further there was a sharp jump at the temperature ~700 K, eventually the values became uniform and stable. In the alloy with 45 at.% Cu, the lattice parameter variation was observed at a lower temperature compared to that of equiatomic composition: the variation started at 580 K, and the jump – at 650 K. In the alloy with 55 at.% Cu a slight variation in the lattice parameter value was observed at 640 K, and a sharp jump at 690 K. Beyond the temperature range under study the lattice parameter values were observed to vary only slightly.

Within the range of temperatures above the critical, the lattice parameter *a* increased in the course of ordering, while the value of *c* decreased. As the temperature increased above the critical temperature of the order – disorder phase transition, the values of lattice parameters *a* and *c* were observed to approach each other, the tetragonal structure

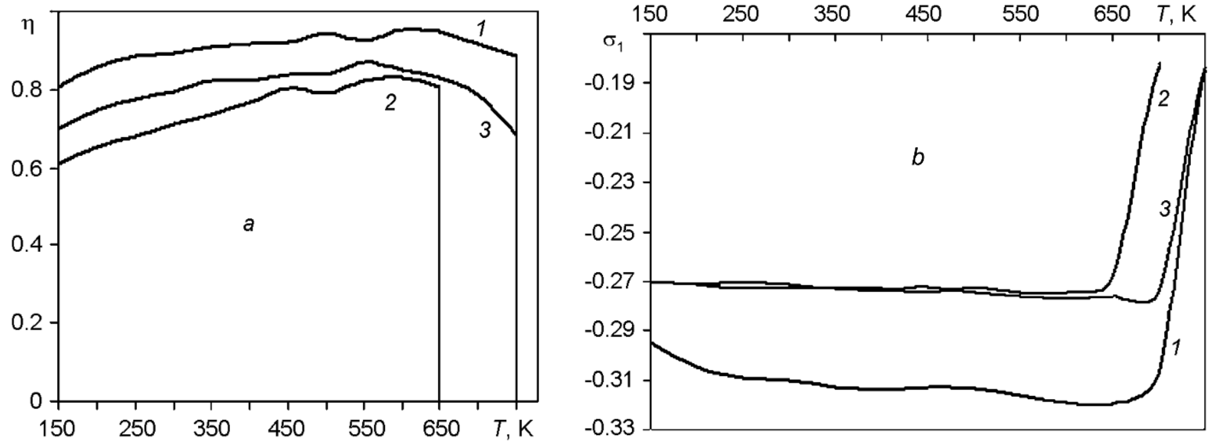

Fig. 3. Temperature dependence of the long-range (*a*) and short-range (*b*) order parameter in the alloys with: 50 at.% Cu (curve *1*), 45 at.% Cu (curve *2*), and 55 at.% Cu (curve *3*).

rearranged into cubic structure, and the average value of the lattice parameters increased. It is evident from Fig. 2, depicting a comparative analysis of variations in tetragonality (*c*/*a*) with temperature and concentration of the alloy components, that the maximum deviation of tetragonality from unity was observed in the case of an alloy of equiatomic composition and the highest degree of ordering. The alloy with the lowest copper content exhibits the lowest degree of tetragonality and the transition to a cubic structure occurs at a lower temperature than in the alloy with a higher content of copper. Note also that the lattice parameter variation in the vicinity of the order – disorder phase transition changes in a stepwise fashion, and the tetragonal structure in the course of disordering is rearranged into cubic.

At elevated temperatures, an equiatomic CuAu alloy exhibiting the lowest tetragonality is more stable. The highest stability is demonstrated by the alloy with a lower concentration of copper having the lowest tetragonality.

Thus, the highest degree of tetragonality was achieved in the alloy of an equiatomic composition, the lowest – in the CuAu alloy with 45 at.% Cu. The temperature at which lattice parameters undergo a sharp change corresponds to that of the order – disorder phase transition. The above-mentioned abrupt change in lattice parameters was observed when the rate of ordering of the model alloy was increasing.

**Behavior of long-range and short-range ordering parameters.** It was established both experimentally and theoretically that phase transitions in this system are transitions of the first type, which implies a stepwise variation in the order parameters in the region of transition with temperature [14–16, 20, 21].

Shown in Fig. 3*a* is the calculated dependence of the long-range order parameter on temperature. It is clear that the most ordered state is observed in the alloy of an equiatomic composition (curve *1*), note that this state was maintained up to very high temperatures. The temperature of the order – disorder phase transition in the alloy of a stoichiometric composition was found to be higher than the critical temperature in the alloy with a lower content of Cu and comparable with the phase transition temperature in the alloy with an elevated copper content. Under deviation from stoichiometry, a more ordered state was observed in the alloy with 55 at.% Cu (curve *2*) compared to the state observed in the alloy with c 45 at.% Cu (curve *3*). The temperature of the order – disorder phase transition in the alloy with 45 at.% Cu is lower than that in the equiatomic alloys with an elevated content of Cu.

When analyzing the temperature dependence of the long-range order parameter (Fig. 3a), attention should be paid to the following. The shape of the curves $\eta = \eta(T)$ is similar to that found experimentally [20]. The order – disorder phase transition is a transition of the first type, as it is in the experimental investigations. Moreover, we have found out that the long-range order parameter is close to unity for the alloy of an euqiatomic composition (curve *1*) up to the phase transition temperature. This result is comparable with the experimental data, where the transition was observed at $T \sim 750$ K, and the jump in the order parameter was equal to $\Delta\eta \sim 0.95$ [20].

The behavior of the short-range order parameter in the first coordination sphere with temperature variations (Fig.3*b*) indicates that a most significant tendency of atoms to have an environment of the atoms of another kind (i.e.,

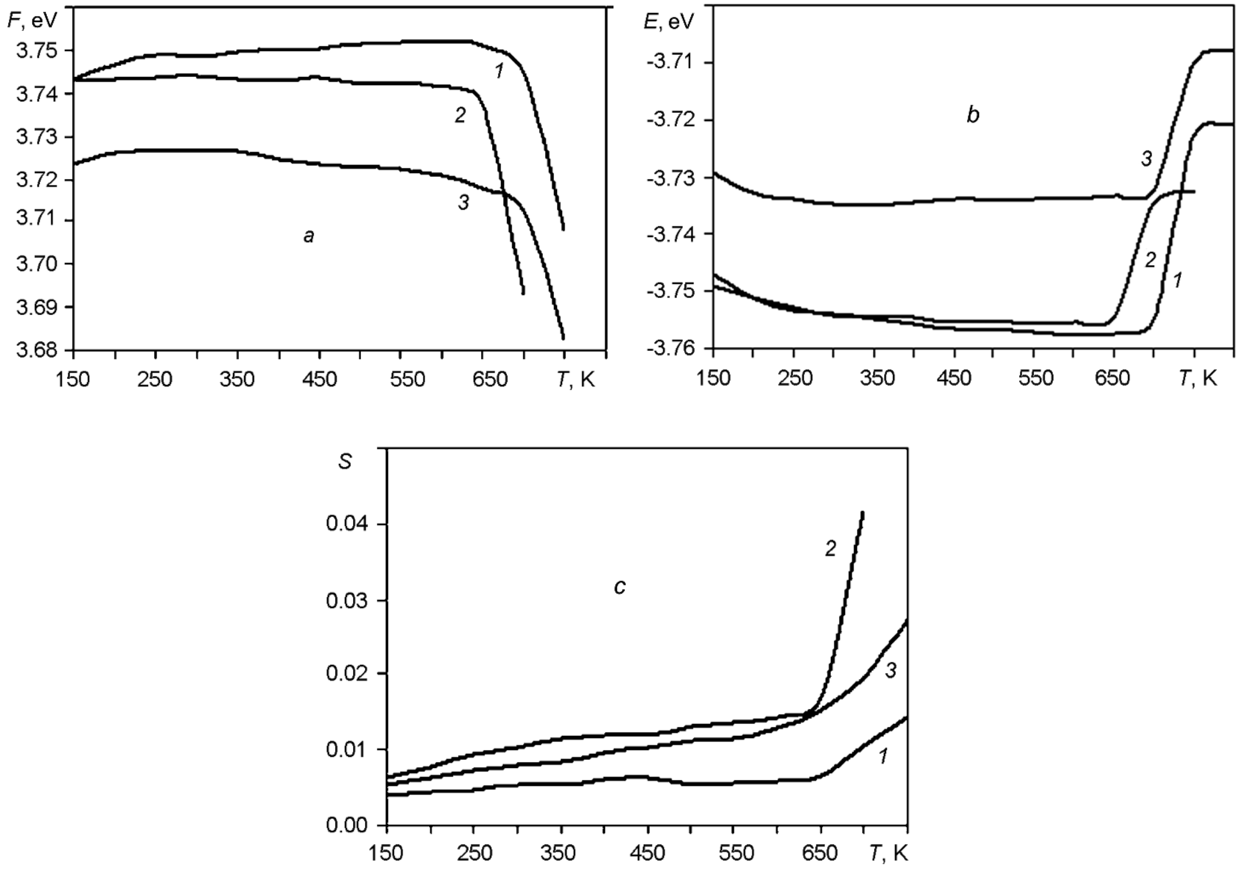

Fig. 4. Tempearature dependence of free energy (*a*), configuration energy (*b*), and entropy (*c*) on the alloy component concentration: 50 at.% Cu (curve *1*), 45 at.% Cu (curve *2*), and 55 at.% Cu (curve *3*).

a tendency to ordering) is revealed in the alloy of an equiatomic composition (curve *1*), while under deviation from stoichiometry (curves *2* and *3*) this tendency is weaker ($\sigma = -0.27, -0.28$). In the alloys where the composition deviates from equiatomic, the respective short-range order parameters are retained, which could be possibly attributed to formation of a stable “semi-ordered” phase.

The energy characteristics taken for simulating the process of structural phase transition were free energy and its components: configuration energy and entropy term. Figure 4 presents the calculated temperature dependences for free energy (Fig. 4*a*), configuration energy (Fig. 4*b*), and entropy (Fig. 4*c*).

It is evident from Fig. 4*a* that for the alloy of an equiatomic composition an ordered state (curve *1*) is thermodynamically more favorable than a mixture of phases with 55 at.% Cu (curve *2*) and 45 at.% Cu (curve *3*), which is natural for the Cu–Au system.

Thus, the comparative analysis of the integral characteristics demonstrates a fairly good performance of the proposed model and experimental procedure.

**Peculiarities of the ordering–disordering process in alloys of the Cu–Au system in the vicinity of a CuAu composition.** The model and investigation procedure proposed here allow examining the macroscopic pattern of the ordering–disordering process at every selected temperature and predetermined alloy composition. Variation in the component concentration significantly affects the creation of order in the distribution of atoms in the crystals, the conditions for different mechanisms of the order–disorder phase transition to be realized, and the formation of transient alloy structures and states.

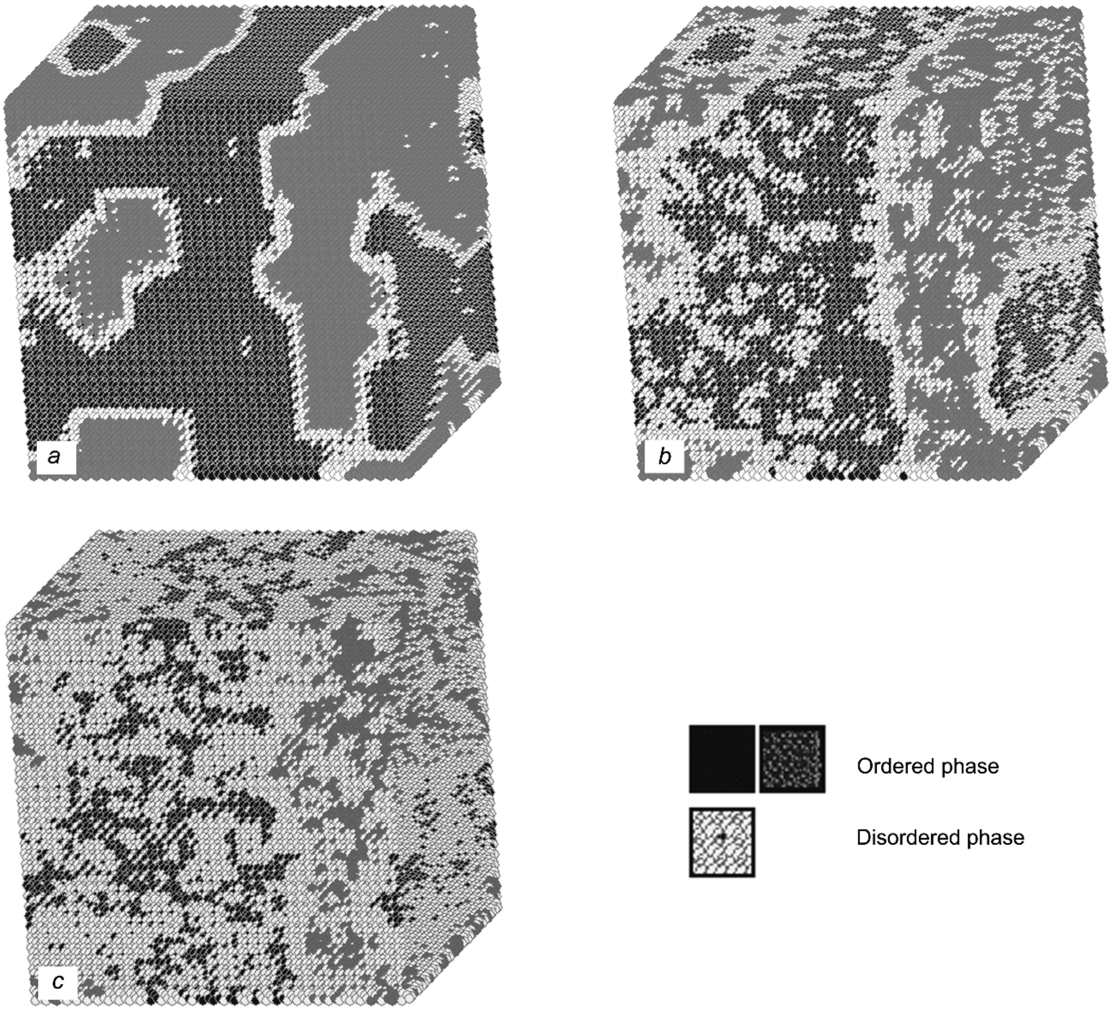

Fig. 5. Distribution of structural elements in the ordered and disordered phases in an equiatomic CuAu alloy at the temperature $T = 450$ (*a*), 650 (*b*) and 750 K (*c*).

In the case of an equiatomic composition, where the concentration of copper is 50 at.%, within the temperature interval 300–550 K large anti-phase domains are observed (note that they occur in pairs), surrounded by a thin disordered interlayer (Fig. 5*a*). As the temperature increases, the antiphase boundaries are nearly nonmobile but become flatter. The fluctuations in the domain structure were observed to be only due to faceting of the antiphase boundaries.

Shown in Fig. 5 are the structural elements of the ordered, disordered, and "semi-ordered" phases, with the latter phase made up of the atoms at the boundaries, which go beyond the 3-D calculation grid onto its surface. The ordered phase (antiphase domains) is shown in different shades and gray color marks the disordered phase with a partially ordered phase (clusters, substitutional point defects and their complexes, antiphase and phase boundaries). Note that the antiphase domains are surrounded by an interlayer of faceting antiphase boundaries. Fluctuation of domains occurs due to segregation at the boundary of microstructural features, which introduces a significant contribution in the process of atomic ordering. Within the temperature range 600–800 K (phase transition temperature) it is disordering which predominates; the "thickness" of antiphase boundaries increases, substitutional point defects and their complexes are formed, and the disordered phase fraction increases (Fig.5*b*). Peculiarities of the alloy disordering are due to the formation of a flow of point defects and their complexes. At the temperature above $T = 750$ K, the alloy is nearly completely disordered (Fig.5c), and microdomains, nuclei of a new phase, are observed to start forming.

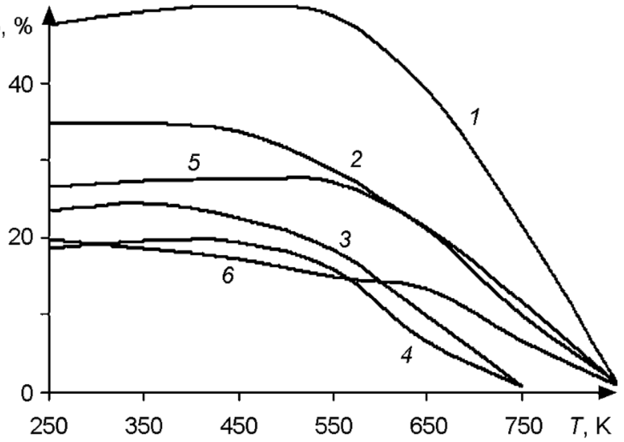

Fig. 6. Atomic distribution in the ordered phase of superstructure $L1_0$ along <001> (curves *1*, *3*, *5*) and <100> (curves *2*, *4*, *6*) versus the alloy temperature for the following component concentrations: 50 at.% Cu (curves *1* and *2*), 45 at.% Cu and 55 at.% Au (curves *3* и *4*), 55 at.% Cu and 45 at.% Au (curves *5* and *6*).

The results obtained show a qualitative agreement with the experimental data and calculations by other authors [16, 19, 21, 22], that the equiatomic alloy maintains its ordered state well up to the critical temperature followed by an order–disorder phase transition occurring in a jump.

An analysis of domain structure variation in the alloys with 55 at.% Cu and 45 at.% Cu reveals that the process of the disorder–order–disorder phase transition tends to be similar to that in the alloy of an equiatomic composition, but with a larger fraction of a partially ordered phase. Two types of domains with decreased intradomain ordering appear, and fluctuations between the domains occur due to lesser ordering within the domains and broadening of the phase boundary. It should be noted that the alloy with a higher content of copper is more resistant to temperature that that with a higher content of Au, in which the ordered phase decays at a lower temperature.

**Phase structure analysis.** Thermal activation helps reveal certain kinetic features of the alloy domain structure and, as a result, one can perform a structure analysis of the ordered, disordered, and "semi-ordered" phases, the latter containing both antiphase and phase boundaries.

An example of the results of such an analysis of antiphase boundaries forming in the CuAu alloy, which corresponds to the component distribution along <001> and <100>, a pattern quite common for the superstructure $L1_0$, is given in Fig. 6. This allows one to reveal peculiar features of the domain shape development in the ordering alloys exhibiting deviation from stoichiometry.

A kinetic analysis of the domain structure has shown that in the course of ordering two types of antipahse domains of the same orientation predominate, which are of different size and elongated shape along <001> in the case of an equiatomic composition and elevated concentration of Cu. In the equiatomic alloy, the maximum fraction of each of these antiphase domains was as high as 35–50% (curves *1* and *2*). At the temperature higher than 650 K, the fraction of atoms belonging to the domains decreases. In the equiatomic alloy, the difference between the number of atoms in the antiphase domains forming the domain region along all direction is equal to 10%, in the alloy with a higher Cu content it is around 6%, in the alloy with lower Cu content the domains are of approximately equal dimensions. In particular, the maximum size of each of two domains in a highly ordered state in the alloy with 45 at.% Cu (curves *3* and *4*) is as low as 20–25 at.%, while in the alloy with 55 at.% Cu (curves *5* and *6*) – 25–30 at.%. In all cases at the temperature increasing above critical the domains are observed to destroy. It is clear that these results correlate quite well with the data on short- and long-range ordering presented in Fig. 3. For instance, the increase in the short-range order degree is associated with an increase in the size of two antiphase domain regions. The temperature at which the long-range order parameter attains its maximum value corresponds to the temperature at which the domain structure volume is the largest.

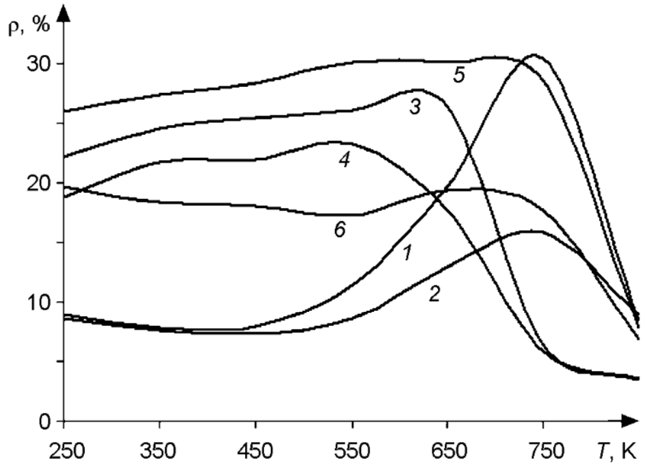

Fig. 7. Atomic distribution in the disordered phase along <001> (curves *1*, *3*, *5*) and <100> (curves *2*, *4*, *6*) versus the alloy temperature for the following component concentrations: 50 at.% Cu (curves *1* and *2*), 45 at.% Cu and 55 at.% Au (curves *3* and *4*), 55 at.% Cu and 45 at.% Au (curves *5* and *6*).

It is clear from Fig. 7, which shows atomic distribution over the disordered and "semi-ordered" phases, where the latter phase contains both phase and antiphase boundaries, that the semi-ordered phase in the equiatomic composition occupies as low as 30%, while in the course of transition from an ordered to disordered state there is a sharp increase in the volume of the semi-ordered phase. In the alloys where the composition deviates from equiatomic, the total fraction of the semi-ordered phase is 50%, while the fraction of the disordered phase sharply increases at the temperatures above the critical temperature and that of the semi-ordered sharply decreases.

A structural analysis of the *AB*, $A_3B$, $AB_3$, *A*, and *B* phases formed in the course of thermal activation of the alloy allowed us to construct the dependences for distribution of their fractions (see Figs. 8 and 9). It should be noted that the total fraction of the superstructure phase *AB* is predominating. In the equiatomic alloy, the maximum percentage of this fraction is 97%, while there are no *A* or *B* (pure metals) phases and the fractions of the $A_3B$ and $AB_3$ phase nuclei are insignificant and are found to be less than 0.5%. In the alloy with 45 at.% Cu, the maximum fraction of the *AB* phase ~82%, while that of the $AB_3$ phase is as low as 2.5%. in the alloy with 55 at.% Cu, the maximum fraction of the *AB* phase is ~88%, while that of the $A_3B$ phase is as low as 3% of the total number of atoms.

According to the experimental data and calculations of other authors [1, 3, 7, 10, 15–17, 19–24], ordering in the CuAu alloy is a first-kind phase transition, which implies that the process of setting an equilibrium state with long-range ordering in the course of annealing of preliminary recrystallized material to the temperature below the critical ordering temperature ($T_K = 680$ K) starts from formation of nuclei of a new phase in individual points of the system, whose ordering degree is nearly equilibrium [19, 20]. A transition into an ordered state is associated with diffusion-induced redistribution of atoms. At low temperatures (on the order of 470 K for the CuAu alloy) these processes are slow. At the annealing temperature close to that of the order – disorder phase transition, the locomotive force of ordering is considerably decreased, since the difference between free energies of the ordered and disordered phases decreases. If we compare these experimentally obtained results with the analysis of the above dependences, we can readily notice their agreement.

## SUMMARY

The investigations carried out in this study have demonstrated the efficiency of the proposed vacancy-diffusion model for structural rearrangement of ordering condensed-state systems having a tetragonal or orthorhombic lattice in the ordered state.

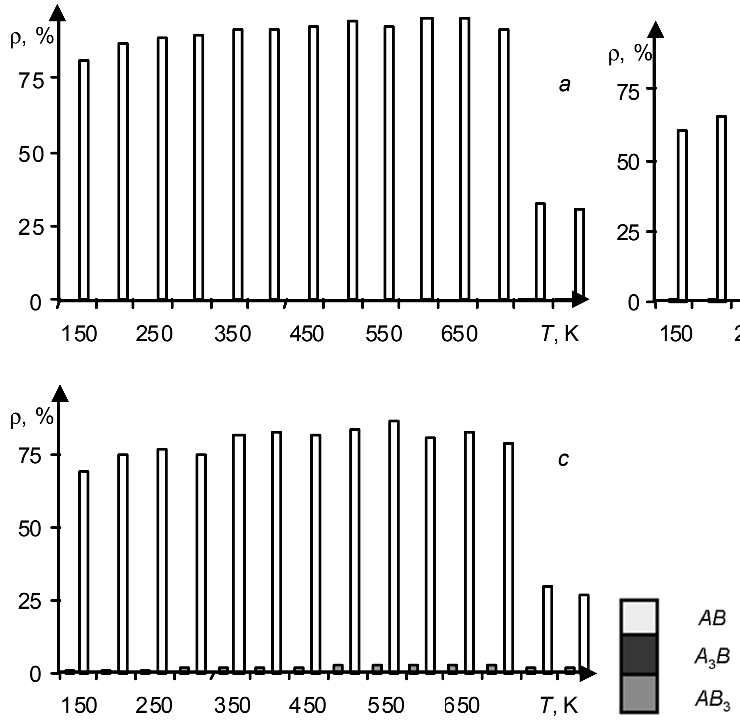

Fig. 8. Distribution of the *AB*, $AB_3$ and $A_3B$ phase fractions as a function of temperature in the alloys with the copper concentration: 50 at.% (a), 45 at.% (b), and 55 at.% Cu.

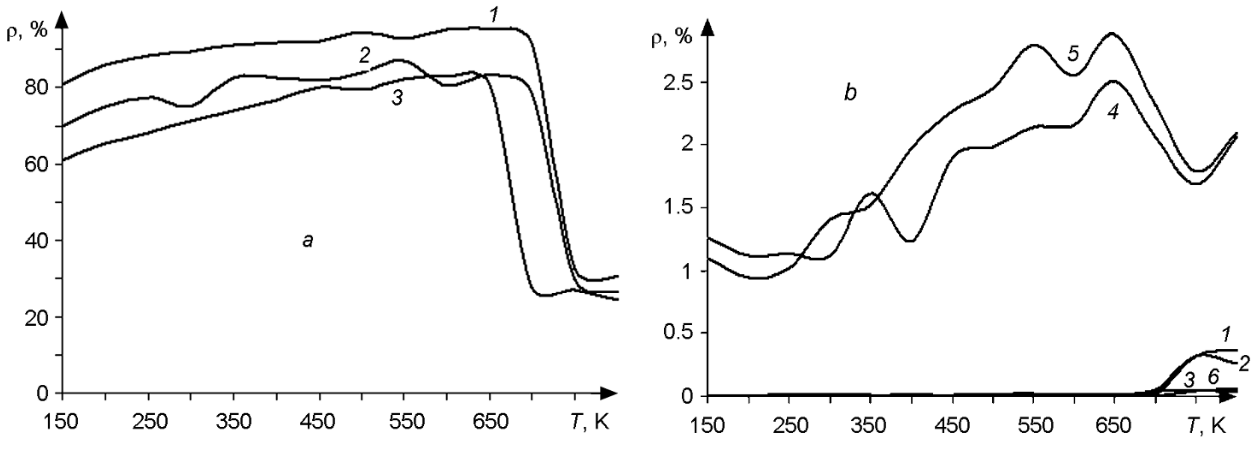

Fig. 9. Distribution of the phase fractions *AB* (*a*), $AB_3$ (*b*, curves *1*, *3*, *5*) and $A_3B$ (*b*, curves *2*, *4*, *6*) as a function of temperature with the copper concentration: 50 at.% Cu (curve *1* (*a*), curves *1* and *2* (*b*); 45 at.% Cu (curve *2* (*a*), curves *3* and *4* (*b*)); 55 at.% Cu (curve.*3* (*a*), curves *5* and *6* (*b*)).

The model thus constructed and the use of the Monte Carlo method have yielded a number of acceptable results, which agree with the results obtained earlier [1, 3, 7, 10, 15–17, 19–24].

Primarily we have managed to follow the pattern of ordering of a binary alloy with a tetragonal and orthorhombic latticeas a function of temperature and composition. Furthermore, the process was investigated at the micro-, meso, and macroscale levels.

As a result, we have found out that the main mechanism in the early alloy-ordering stage is the process of antiphase domain formation, the main feature of the domain formation in a tetragonal alloy being the formation of a pair of antiphase domains. Note that the larger domain did not absorb the smaller one until complete disordering of the alloy, where the disordered phase predominated.

The mechanism of structural transformations essentially depends on mesostructural features (domain structure, domain shape and size, length and thickness of antiphase and phase boundaries, etc.). In an alloy of equiatomic composition, the fraction of clusters is small, and the main role is played by the mechanism of faceting of antiphase boundaries and formation of microstructure segregations, which is accompanied by the lowering of the intradomain order. The mechanism of structural transformations is primarily associated with smearing of domain structures by the disordered phase.

We have revealed peculiar features of migration of antiphase and phase boundaries in the tetragonal structure: the boundaries are slow and flat. Disordering occurs both due to an increase in the thickness of antiphase boundaries and a lower intradomain long-range order.

In an equiatomic alloy, the fraction of semi-ordered phase sharply increases in the course of alloy transition into a disordered state, and is then absorbed by the disordered phase.

In the alloys whose composition deviates from equiatomic, the fraction of a partially ordered phase is comparable with that made up by a pair of antiphase domains; there is no any homogenized phase in these alloys and ordering inside domains is very low. It is likely that lower tetragonality and symmetry and a smaller difference in the volumes of the ordered phase formed along <100> and <001> in the alloy with a smaller content of copper are some of the reasons for the lower temperature of the order – disorder phase transition.

In the alloy with 45 at.% Cu, the maximum fraction of the $Cu_3Au$ phase is as low as 3% of the total number of atoms. No phases corresponding to agglomerations of pure Cu or Au components were observed in the alloy in the course of the order – disorder phase transition.

## REFERENCES

1. A. I. Potekaev, I. I. Naumov, V. V. Kulagina, *et al.*, Natural Long-Period Nanostructures [in Russian] (Ed. A. I. Potekaev), NTL Publishers (2002).
2. L. E. Popov and E. V. Kozlov, Mechanical Properties of Ordered Solid Solutions [in Russian], Moscow, Metallutgiya (1970).
3. S. V. Starenchenko, E. V. Kozlov, and V. A. Starenchenko, The Mechanisms of Thermal Order – Disorder Phase Transition in Alloys with Superstructures $L1_2$, $L1_2$ (M), $L1_2$ (MM), $D1_a$ [in Russian], Tomsk, NTL Publishers (2007).
4. B. A. Grinberg and V. I. Syutkina, New Methods for Hardening Ordered Alloys [in Russian], Moscow, Metallurgiya (1985).
5. A. A. Bondar, *et al.*, Stability and Phase Equilibria in Transition Metal Alloys (Ed. V. N. Eremenko) [in Russian], Kiev, Naukova Dumka (1991).
6. Z. A. Matysina and S. Yu. Zaginaichenko, Crystal Structure Defects [in Russian], Dnepropetrovsk, Nauka i Obrazovaniye (2003).
7. A. I. Potekaev, Rus. Phys. J., No. 6, 549–562 (1995).
8. A. I. Potekaev, *Ibid*., No. 6, 521–533 (1996).
9. M. D. Starostenkov, E. A. Dudnik, and V. G. Dudnik, Izvestiya RAN, Physics, **68**, No. 5, 639–641 (2004).
10. A. I. Potekaev, E. A. Dudnik, M. D. Starostenkov, and L. A. Popova, Rus. Phys. J., No. 10, 1053–1063 (2008).
11. S. V. Dmitriev, Yu. V. Medvedev, A. I. Potekaev, *et al.*, Rus. Phys. J., No. 8, 858–867 (2008).
12. S. V. Dmitriev, A. I. Potekaev, A. A. Nazarov, *et al.*, *Ibid*., No. 2, 132–137 (2009).
13. A. I. Potekaev and V. V. Kulagina, Izv. Vyssh. Uchebn. Zaved. Fiz., No. 11/3, 148–150 (2008).
14. M. D. Starostenkov and E. A. Dudnik, Bulletin of the Russian Academy of Sciences: Physics, **71**, No. 5, 638–641 (2007).
15. A. I. Potekaev, Phys. Stat. Sol. (a), **134**, 317–334 (1992).

16. V. I. Iveronova and A. A. Kanzelson, Short-Range Order in Solid Solutions [in Russian], Moscow, Nauka (1977).
17. M. A. Krivoglaz and A. A. Smirnov, The Theory of Ordering Alloys [in Russian], Moscow, Fizmatgiz (1958).
18. N. V. Gorlov, Computer Modeling of Planar Defects in Ordered Alloys of the $A_3B$ and $A_3B(C)$ Type, Thesis of Cand. Phys.-Math. Sci., Tomsk (1987).
19. A. E. Vol and I. K. Kagan, Structure and Properties of Binary Metal Systems, Vol. III [in Russian], Moscow, Nauka (1976).
20. E. V. Kozlov, Izv. Vyssh. Uchebn. Zaved. Fiz., No. 8, 82–92 (1976).
21. A. A. Smirnov, Molecular Kinetic Theory of Metals [in Russian], Moscow, Nauka (1966).
22. J. W. Christian, The Theory Of Transformations In Metals And Alloys, Oxford, Pergamon Press (1975).
23. E. A. Dudnik, G. M. Poletaev, O. V. Andrukhova, and M. D. Starostenkov, Izv. Vyssh. Uchebn. Zaved. Fiz., No. 8 (Appendix), 37–46 (2002).
24. E. A. Dudnik, V. S. Myasnichenko, L. A. Popova, and M. D. Starostenkov, Fundamental Problems of Modern Materials Science [in Russian], Barnaul, AltSTU, **5**, No. 3, 84–89 (2008).