L1$_0$ ordered phase formation at solid state reactions in Cu/Au and Fe/Pd thin films

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ABSTRACT

To understand the mechanism of mass transfer during solid state reactions and order-disorder transitions the formation processes of CuAuI and L1$_0$-FePd ordered structures at solid state reactions in Cu/Au и Fe/Pd bilayer thin films have been carried out using the method of *in situ* electron diffraction (ED). The value of the long-range order (LRO) parameter has been estimated for the L1$_0$ type ordered structures being formed; the order-disorder transition temperatures have been determined. The formation mechanism of the L1$_0$ type ordered structures formed at the initial stages of the solid state reaction in the Cu/Au and Fe/Pd thin films has been suggested. In the case of Cu/Au it has been shown that the interdiffusion of copper and gold at the initial stage of the solid state reaction results in the reduced size of the grains of the initial materials, as a result, nanocrystalites of the Cu-Au solid solution are formed, and further, grains of the CuAuI ordered solid solution appear and their growth begins.

1. Introduction

L1$_0$ type ordered structures are known to form in Fe-Pd, Fe-Pt systems [1,2], possessing large magnetocrystalline anisotropy energies, arising due to the tetrahedral distortions characteristic for the L1$_0$ structure. The L1$_0$-FePd, L1$_0$-FePt phases have unique magnetic properties: the high values of the coercive force H$_c$ ~ 10 kOe and magnetic anisotropy constant K$_u$ ~ 10^7–10^8 erg/cm^3 [3], which makes the materials based on them rather promising for the application in magnetic information storage technologies [3–6]. The L1$_0$ type ordered structure was first identified in the Cu-Au system, thus it is now referred to as the CuAuI-type structure [1,7]. At present an active search is under way aimed at finding the most optimal methods of obtaining magnetic nanomaterials based on the L1$_0$ type ordered structure with perpendicular magnetic anisotropy arising at the formation of the L1$_0$ type ordered structure with the [001] orientation to the substrate plane. Several ways of obtaining such nanomaterials were suggested: annealing of the films of disordered solid solutions with an impact outside (pressure, magnetic field) [8,9]; fast thermal annealing of the films of disordered solid solutions [10]; simultaneous deposition of two elements by the method of molecular-beam epitaxy onto a heated substrate [11].

One of the methods to form the L1$_0$ type ordered structures is a solid state reaction which allows one to obtain, at rather low tempera-

tures (0.2–0.5 T$_{melt.}$), ordered structures. In [12] it is shown that as result of fast thermal annealing of multilayer Fe/Pt films (substrate–amorphous glass) with the thickness of an individual layer of ~ 0.5 nm an L1$_0$-FePt ordered structure is formed with the predominant [001] orientation. The authors in [13] show that in Fe/Pd bilayer films, as a result of a solid state reaction initiated by thermal annealing at 400 °C the layers of palladium and iron are quickly intermixed with the simultaneous formation of an L1$_0$-FePd ordered structure. In [14] it is shown that in FePt/CuAu bilayer films the sublayer of the CuAu solid solution can contribute into the ordering temperature decrease in the FePt solid solution. It should be noted that a large part of the research of the formation processes of ordered structures at solid state reactions in the systems Fe/Pt, Fe/Pd and Cu/Au was carried out by *ex situ* methods, *i.e.* using the samples in which the ordered structure had already been formed. Thus, at present there is not enough information concerning structural phase transformations in the process of solid state reactions in nanomaterials which result in the formation of the L1$_0$ type ordered structures. Even for the well studied Cu-Au system such a type of research is scarce. The Cu-Au system can be considered to be a model in researching the formation processes of L1$_0$ type ordered structures; moreover, ordering in the Cu-Au system occurs at lower temperature than in the case with Fe-Pd, Fe-Pt, which facilitates *in situ* experimental investigations.

The aim of the present work is to study, using the method of *in situ*

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electron diffraction, the initial stage of solid state reactions in thin-film bilayer systems of Cu/Au, Fe/Pd as well as to research the formation process of the L1$_0$ type ordered structures in these systems in the process of a solid state reaction. The analysis of diffraction reflections in the electron diffraction patterns allows one not only to determine the changes in the phase compositions of the samples but also, to quantify the phase composition which in the case of the formation of ordered structures makes it possible to calculate the value of the long-range order (LRO) parameter – S [15]. The latter characterizes the degree of the system ordering (for the fully disordered system S = 0, for the ideal fully ordered system S = 1), and, as is shown in [16], there is a dependence between the gradual increase of K$_u$ with the increasing S.

2. Material and methods

Cu/Au and Fe/Pd bilayer thin films were obtained by the method of electron beam evaporation in high vacuum with the help of a high vacuum installation MED-020 (Bal-Tec). The base vacuum was $5 * 10^{-5}$ Pa. The bilayer films were obtained by the successive deposition of layers onto a substrate. For the evaporation the ADVENT [17] materials of a high level of purity were used: Cu (99.99%); Au (99.99%); Fe (99.5%); Pd (99.95%). A fresh cleaved single crystal of NaCl was used as a substrate. The temperature of the substrate during the deposition for the Cu/Au films was equal to room temperature and $\approx 150\,°C$ for the Fe/Pd films. The deposition rate and layer thickness during the deposition process were controlled with the help of a quartz crystal thickness monitor. The deposition rate was 0.1–0.3 nm/s. The total thickness of the bilayer films under study was 30–50 nm. The thickness of the individual layers was chosen in such a way so that to provide the atomic ratio necessary for the formation of the L1$_0$ type ordered structures [7]. The real element ratio in the samples under study amounted to: Cu:Au $\approx 48:52$ at%, Fe:Pd $\approx 46:54$ at%. The structure and the local element composition of the obtained samples were studied with a transmission electron microscope JEOL JEM-2100, equipped with an energy-dispersive spectrometer Oxford Inca x-sight, at the accelerating voltage of 200 kV.

The Cu/Au and Fe/Pd films were separated from the substrate in bidistilled water at room temperature, and then, the films were put on a molybdenum TEM grid (SPI) and heated. The heating of the film samples was carried out directly in the column of the transmission electron microscope with the help of a special sample holder (Gatan Model 652 Double Tilt Heating Holder), which allows controlled sample heating from room temperature up to as high as 1000 °C. This method had successfully been used by the authors earlier in researching the processes of solid state reactions in various thin film

systems [18–23]. In the frames of this work the authors carried out *in situ* electron diffraction investigations of the processes of solid state reactions and ordering initiated by thermal heating in Cu/Au и Fe/Pd bilayer films. Simultaneously with the heating, electron diffraction patterns were registered and synchronous sample temperature measurements were carried out. The intensity analysis of the electron diffraction reflections and interpretation of the electron diffraction patterns were made using the Gatan DigitalMicrograph software and ICDD PDF 4+ crystallographic database [24].

3. Results and discussion

3.1. Initial state

At the initial state the Cu/Au and Fe/Pd bilayer films consisted of crystallites with the size of $\approx 10-20$ nm. The diffraction reflections in the electron diffraction pattern (Fig. 1a), obtained from an Cu/Au film by the method of selected area electron diffraction (SAED) from the area with the diameter of $\approx 1\,\mu m$, have polycrystalline features. The interpretation of the diffraction reflections (Fig. 1a) showed the presence of 2 phases with face-centered cubic (FCC) lattices: Cu (the space group *Fm-3m* (225), lattice constant a = 3.62 Å, PDF 4+ card #00-004-0836), and, Au (the space group *Fm-3m* (225), lattice constant a = 4.08 Å, PDF 4+ card #00-004-0784). The analysis of the electron diffraction pattern obtained from a Fe/Pd film at the initial state (Fig. 1b), also showed the presence of two phases in the sample: α-Fe (body-centered cubic lattice, the space group *Im-3m* (229), lattice constant a = 2.87 Å, PDF 4+ card #00-006-0696) and Pd (FCC lattice, the space group *Fm-3m* (225), lattice constant a = 3.89 Å, PDF 4+ card #04-001-0111). Here, the iron and palladium crystallites had mainly, coherent orientation, the orientation ratio being α-Fe (001)[110] || Pd (001)[100]. The orientation of the crystallites of α-Fe и Pd is accounted for by the influence of the NaCl single crystal substrate (001) in the process of obtaining the films. The presence of textured reflections of Pd and Fe in the electron diffraction pattern (see Fig. 1b) is due to a small amount of the disordered crystal phase of Pd and Fe on the crystallite boundaries.

3.2. Solid state reaction in the Cu/Au films

To study the processes of the solid state reaction initiated by thermal heating in the Cu/Au bilayer thin films the samples were heated from room temperature to 500 °C at a rate of 4 °C/min. The beginning of the solid state reaction on the interface between copper and gold in the Cu/Au films was identified at 180 °C, which was
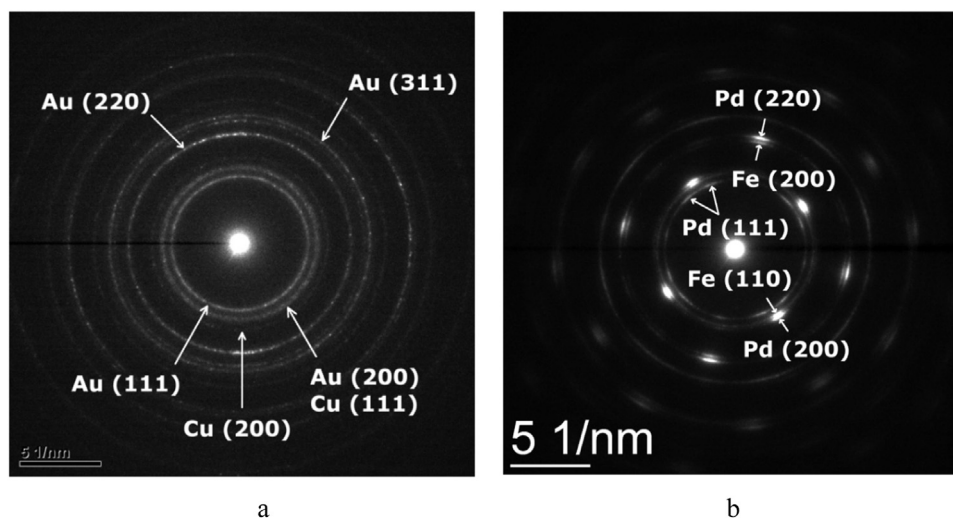

Fig. 1. SAED patterns of Cu/Au (a) and Fe/Pd (b) bilayer films at the initial state.
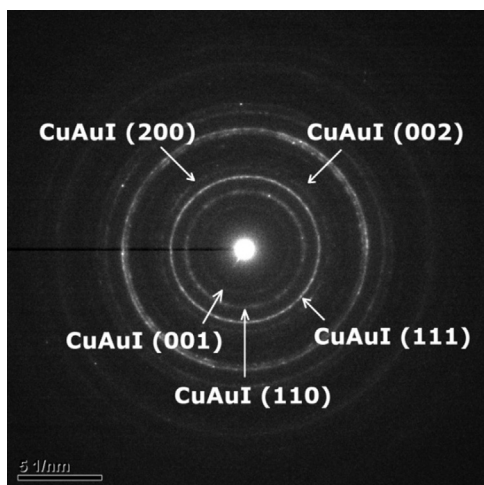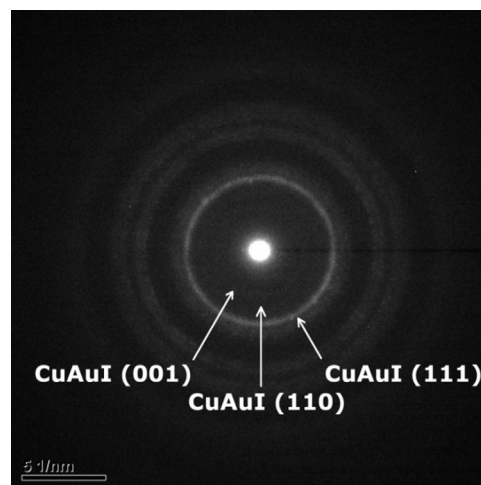
Fig. 2. SAED pattern of Cu/Au film at 350 °C.

Fig. 3. SAED pattern of Cu/Au film after annealing at 240 °C during 1 h (film thickness ≈ 48 nm).

accompanied by the reflection broadening in the electron diffraction patterns. The maximum reflection broadening was observed at 240 °C. At 245 °C the beginning of the formation of a solid solution, i.e a disordered phase of CuAu was revealed (FCC, the space group *Fm-3m* (225), lattice constant: a = 3.87 Å, PDF 4+ card #04-007-4433). Besides, simultaneously with the formation of the CuAu disordered phase, an CuAuI ordered structure began to form (the $L1_0$ type ordered structure, space group *P4/mmm* (123), lattice constants: a = b = 3.96 Å, c = 3.67 Å, PDF 4+ card #00-025-1220), which was accompanied by the appearance of superstucture reflections in the electron diffraction patterns having the low intensity of the CuAuI phase d(110) = 2.80 Å and d(001) = 3.67 Å. In the course of further heating up to 350 °C the growth of the CuAuI ordered phase was observed (Fig. 2). Upon reaching 390 °C the intensity of the superstructure reflections of the CuAuI phase was observed to decrease which evidenced the transition of the order-disorder type. At 410 °C the CuAuI ordered phase was completely transferred into a CuAu disordered solid solution. In the process of heating in the temperature range of 385–410 °C in the present research, the formation of the phase CuAuII was not observed. This was likely to have occurred due to the lack of time for the formation of the CuAuII phase. At a heating rate of 4 °C/min, the sample heating from 385 to 410 °C occurred during only 6 min. The direct transition CuAuI→CuAu was observed in [25], where the authors also explained it by the lack of time for the formation of the CuAuII long-period ordered structure. According to [26], for the formation of the CuAuII phase, annealing, at least, during 30–45 min at 390 °C is necessary.

For a more detailed research of the initial stage of the solid state reaction in the Cu/Au thin film system, phase formation in the process of thermal annealing of the Cu/Au films at 240 °C during 1 h was investigated. As soon as the temperature of 240 °C was reached the beginning of the diffraction reflection broadening was observed, corresponding to the Au and Cu phases. After 8 min of annealing the electron diffraction patterns showed the appearance of diffraction reflections corresponding to the solid solution of Cu-Au – CuAu disordered phase (FCC, the space group *Fm-3m* (225), lattice constant: a = 3.87 Å, PDF 4+ card #04-007-4433). Moreover, diffraction reflections with very low intensity, corresponding to the ordered structure CuAuI were found to appear (Fig. 3), with the intensity of these reflection increasing in the process of further annealing.

To carry out investigations by the method of high resolution transmission electron microscopy (HRTEM) the sample after annealing at 240 °C for 1 h was thinned to the thickness of ≈ 10 nm using argon ion bombardment. The thinning regime was chosen so that to minimize thermal influence on the sample. The elemental analysis of the sample after thinning showed the sample to contain ≈ 60 at% of copper and ≈

40 at% of gold (in contrast to the sample before thinning, with the ratio Cu:Au ≈ 48:52 at%). The mechanism of the gold concentration decrease due to the sample thinning is to be discussed at the end of Section 3.2. The HRTEM analysis of the sample (Fig. 4a) showed the sample to consist of crystallites with the size of 4–6 nm, with the crystallites being surrounded by some kind of matrix. In the nanobeam electron diffraction (NBD) pattern (Fig. 4b), obtained by the method of nanodiffraction both the spot reflections and the broad ring ones were present. The electron diffraction pattern analysis (Fig. 4b) showed the spot reflections to correspond to CuAuI with the orientation [111]. The size of the area from which the nanobeam electron diffraction pattern was obtained amounted to ≈ 5 nm, which was comparable with the size of one crystallite (see Fig. 4a). In all the SAED patterns obtained from the Cu/Au films after annealing at 240 °C, the intensity of the CuAuI type reflections (110) was considerably lower than the intensity of the (220) type reflections, it provided evidence for the partial ordering in the CuAu crystallites. Thus, one could argue that the crystallites with the size of 4–6 nm, observed in the HRTEM image (see Fig. 4a), were a partially ordered solid solution of CuAu. The lattice constants obtained based on the analysis of the spot reflections corresponded to the CuAuI and CuAu phases having stoichiometric composition. Based on this it was possible to make a conclusion that the crystallites with the size of 4–6 nm contained ≈ 50 at% of copper and ≈ 50 at% of gold.

The ring diffraction reflections observed in the NBD pattern (Fig. 4b) had low intensity and corresponded to the following interplanar spacings: 2.12 ± 0.02 Å, 1.83 ± 0.02 Å, 1.32 ± 0.04 Å, 1.12 ± 0.02 Å. The given interplanar spacings were ≈ 2% greater than the ones characteristic for the four most intensive FCC Cu reflections: d(111) = 2.09 Å, d(200) = 1.81 Å, d(220) = 1.28 Å, d(311) = 1.09 Å, which was due to the increase of the lattice constant of copper in the formation of the solid solution of gold and copper. As is known [27], the lattice constant of the Cu-Au solid solution has the dependence, close to the liner one, on the atomic ratio of gold and copper. The lattice constant of the Cu-Au solid solution a = 3.67 ± 0.02 Å allowed one to estimate the content of copper and gold in the nanocrystallites: ≈ 90 ± 5 at% of copper, ≈ 10 ± 5 at% of gold. The ring reflections were obtained from the matrix filling the space between the crystallites, the width of the reflections and the intensity distribution were characteristic for polycrystalline materials. Taking into account the size of the diffraction area (≈ 5 nm) and the thickness of the film under study (≈ 10 nm), the size of the crystallites which could form such ring reflections was to be ≈ 1 nm. Thus, one could make a conclusion that the Cu/Au film under study after annealing at 240 °C during 1 h and thinning to ≈ 10 nm consisted of partially ordered CuAu crystallites with the size of 4–6 nm (Fig. 4a), surrounded by other smaller nanocrystallites of the solid
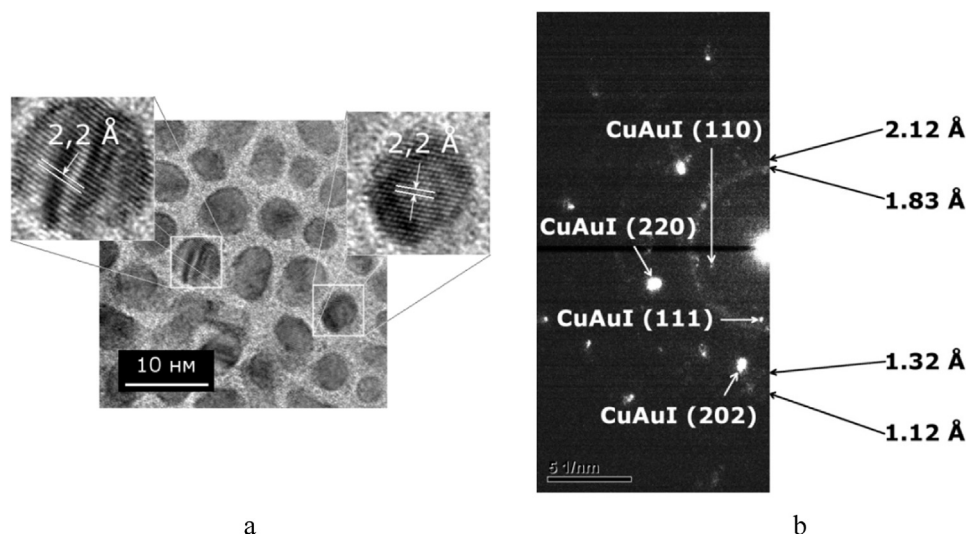
a   b

Fig. 4. HRTEM image (a) and NBD pattern (b) of a Cu-Au film after annealing at 240 °C during 1 h and thinning up to 10 nm.

solution of gold in copper with the coherent scattering region ≈ 1 nm.

In the selected area electron diffraction (SAED) pattern (Fig. 3), obtained from the studied Cu/Au film after annealing during 1 h at 240 °C and, yet before thinning (*i.e.* the film thickness was ≈ 48 nm), ring reflections of the polycrystalline type were observed, corresponding to the CuAuI, ordered phase, as well as the broadened ring reflections of the Cu-Au solid solution. The size of the crystallites estimated by the diffraction reflection broadening for the CuAuI ordered phase amounted to ≈ 5 nm, which corresponded to the size of the crystallites observed in the high resolution TEM image (Fig. 4a), obtained from the thinned film with the thickness of ≈ 10 nm. Thus, one could make a conclusion that after annealing the Cu/Au film during 1 h at 240 °C partially ordered CuAu crystallites with the size of 4–6 nm formed in the whole sample volume.

To explain the decrease of the gold concentration in the sample after thinning the film to ≈ 10 nm (the ratio of Cu:Au before thinning ≈ 48:52 at%, after thinning ≈ 60:40 at%) one could suggest the following schematic model (Fig. 5) of the concentration distribution for copper and gold along the Cu-Au film thickness after annealing at 240 °C during 1 h (the shaded part shows the film area after thinning to ≈ 10 nm). As is shown in [28] in the Cu/Au films with the total thickness of 200 nm the interdiffusion of copper and gold results in the complete mixing of the layers only after annealing at 350 °C. Thus, there was a reason to assume that in the studied Cu/Au films after annealing at 240 °C during 1 h there was some distribution of the gold and copper concentration along the film thickness due to the lack of time or/and
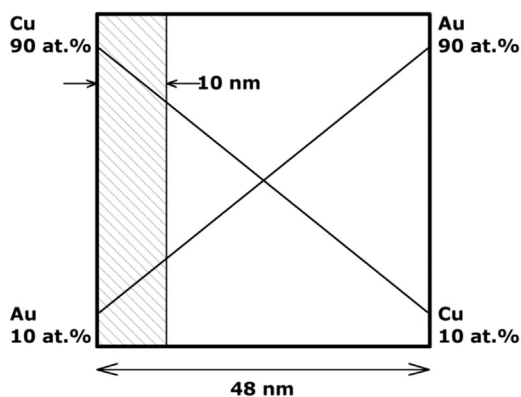
temperature of annealing. Since the film thinning was carried out on the side of the gold layer, it resulted in the decrease of the gold concentration in the thinned sample. Moreover, it is worth noting that the elemental composition of the crystallites with the size of 4–6 nm was close to the equiatomic one (Cu:Au ≈ 50:50 at%) along the whole film volume before thinning and the average copper and gold concentration in the matrix filling the space between the crystallites changed through the film thickness (see Fig. 5), however, totally, through the whole film volume it was also close to the equiatomic one.

Based on the obtained results the following mechanism of the solid state reaction between the copper and gold nanolayers could be suggested for the Cu/Au bilayer thin polycrystalline films. First, interdiffusion along the grain boundaries provided the transport of copper atoms to the gold layer and the transfer of gold atoms to the copper layer. Then, the volume diffusion of copper to the gold grains and of gold to the copper grains began resulting in the reduction of the grain size of the initial material. As a result of the interdiffusion and grain size reduction, nanocrystallites of the Cu-Au solid solution were formed in the film having the coherent scattering region ≈ 1 nm. As the size of the crystallites of the initial elements was reduced, the role of diffusion along the grain boundaries increased. Further interdiffusion resulted in the formation and growth of grains (with the size of 4–6 nm) of the partially ordered CuAu solid solution. Thus, one could make a conclusion that at the initial stages of the solid state reaction the mass transfer followed a combined mechanism including both the diffusion on the grain boundaries and volume diffusion, moreover, as the size of the copper and gold grains was reduced the contribution of diffusion on the grain boundaries increased.

3.3. Solid state reaction in the Fe/Pd films

To study solid state reaction processes in the Fe/Pd thin films the samples were heated from room temperature to 850 °C at a rate of 4 °C/min. At 390 °C the beginning of a solid state reaction was observed, as well as the formation of a Fe-Pd disordered solid solution which was accompanied by broadening the Pd and Fe reflections in the electron diffraction patterns. Similar results had been obtained earlier for Pd/Fe(001) films [18]. At 430 °C the beginning of the formation of a $L1_0$-FePd ordered structure is observed (the $L1_0$ type ordered structure, the space group $P4/mmm$ (123), lattice constants: a = b = 3.85 Å, c = 3.72 Å, PDF 4+ card #03-065-9971), which was accompanied by the appearance of superstructure diffraction reflections $L1_0$-FePd: d(100) = 3.85 Å and d(110) = 2.72 Å in the electron diffraction patterns. The ordered structure $L1_0$-FePd was formed with the orientation [001] relative to the film plane [22]. Based on the analysis of the

Fig. 5. Schematic model of the concentration distribution of copper and gold (in at%) through the thickness of the Cu-Au film after annealing at 240 °C during 1 h (the shaded area corresponds to the film after thinning to the thickness ≈ 10 nm).
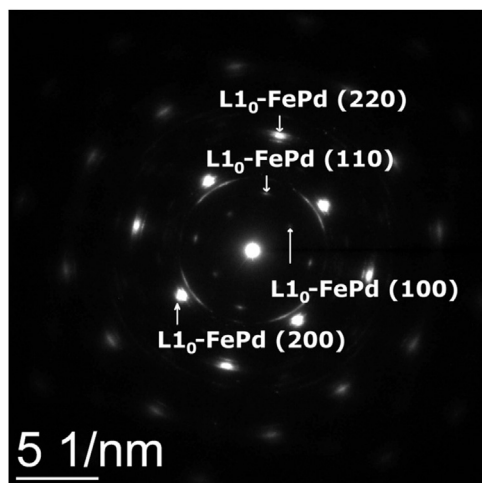
Fig. 6. SAED pattern of a Fe/Pd film at 600 °C.

changes in the diffraction reflections in the electron diffraction patterns obtained from the Cu/Au and Fe/Pd systems in the solid state reaction process one could assume that the solid state reaction mechanism in the Fe/Pd films was similar to the Cu/Au system, however, the ordering began in a thinner solid solution layer formed as a result of interdiffusion directly on the interface of the iron and palladium layers.

In the course of further heating to 600 °C (see Fig. 6) the growth of the $L1_0$-FePd ordered structure was observed which was accompanied with the intensity growth of the superstructure reflections in the electron diffraction patterns. At temperatures higher than 600 °C the intensity decrease of the superstructure reflections was observed which was due to the beginning of the order-disorder transfer. Upon reaching 690 °C the $L1_0$-FePd ordered structure was completely transformed into the FePd disordered solid solution.

3.4. Temperature dependence of the long-range order parameter value (S) of the $L1_0$ type ordered structures formed as a result of solid state reactions in the Cu/Au and Fe/Pd films

Based on the analysis of the electron diffraction patterns obtained from the samples in the process of heating the values of the long-range order (LRO) parameter (S) of the CuAuI and $L1_0$-FePd ordered phases were estimated. The method of estimating the LRO parameter value of the CuAuI and $L1_0$-FePd phases was similar to the one mentioned in [29]. The value of the LRO parameter for the CuAuI and $L1_0$-FePd ordered phases was estimated based on the analysis of the ratio of the intensities of the (110) type superstructure reflections and the (220) type structural reflections in the electron diffraction patterns obtained from the samples in the process of heating. To estimate the LRO parameter value the dependence of the reflection intensity ratio from the planes of the (110) and (220) $I_{(110)}/I_{(220)}$ type on the LRO parameter value S was calculated. The calculation was made using the software Crystal Impact Endeavour [30], which allows one to theoretically calculate diffraction reflections and their intensity values for the given structure taking into account the radiation type (X-ray, electrons) and the values of the accelerating voltage. The calculation was made for the atomic ratios of Cu:Au ≈ 48:52 at% and Fe:Pd ≈ 46:54 at%, corresponding to the samples studied in the present work. Though the long-range order parameter S cannot be used directly for the theoretical calculation of the electron diffraction patterns it can be introduced using the function of the distribution of A or B type atoms across the nodes of the crystal lattice which for the $L1_0$ type super-structure has the form [15]:

$$n(x, y, z) = c + S\frac{e^{i2\pi z}}{2}$$

where n is the distribution function of the A or B type atoms in the lattice $L1_0$, c is the concentration of the A or B atoms S is the long-range order parameter, z are the coordinates of the A or B type atoms.

Based on the comparison of the experimentally obtained values $I_{(110)}/I_{(220)}$ and calculated dependencies of the LRO parameter value S, one obtained temperature dependencies of the LRO parameter value of the ordered CuAuI (Fig. 7a) and $L1_0$-FePd (Fig. 7b) phases formed in the process of the solid state reaction occurring in the Cu/Au and Fe/Pd bilayer thin films in the process of thermal heating at a rate of 4 °C/min.

In the temperature dependence curve of the value of the LRO parameter for the CuAuI ordered phase (Fig. 7a) the growth of the LRO parameter value was observed up to 350 °C. This was due to the formation process of the CuAuI ordered phase from the CuAu solid solution as a result of the solid state reaction. In the temperature range of 350–390 °C the value of the LRO parameter did not change. Thus, at 350 °C the maximum value of the LRO parameter $S = 0.53 \pm 0.05$ was reached (for the given sample and experimental conditions) (Fig. 7a). In this case, the maximum calculation value of the LRO parameter for the given atomic ratio (Cu:Au = 48:52 at%) amounted to 0.96. A rather low value of the long-range order parameter obtained on the given experiment was accounted for by the lack of time for the formation of the CuAuI ordered structure and a big number of the lattice defects, first of all, on the grain boundaries. At a temperature higher than 390 °C, within the limits of the experimental error (± 5 °C) corresponding to the upper boundary of the temperature range for the existence of the CuAuI phase (See Fig. S1), the LRO parameter value sharply decreased, reaching zero at 410 °C (see Fig. 7a), which gave evidence concerning the transition to the disordered solid solution. The observed temperature of the transition to the disordered solid solution (410 °C) corresponded to the transition temperature according to the phase equilibrium diagram of the for the Cu-Au system (See Fig. S1).

In the curve (Fig. 7b) of the dependence of the LRO parameter value for the $L1_0$-FePd ordered phase the growth of the LRO parameter value was observed up to 605 °C. It was possible to assume that at this stage, near the interface between Fe and Pd there existed the interdiffusion of the materials with the formation of a layer of the Fe-Pd solid solution, where ordering occurred. At 605 °C the value of the LRO parameter of the $L1_0$-FePd ordered structure formed as a result of the solid state reaction reaches the value of 0.73 ± 0.05 in the process of heating. Similar LRO parameter values were obtained for $L1_0$-FePd single crystal films with the thickness of 40 nm, formed by annealing at 600 °C ($S = 0.6$–0.7) [31]; of the $L1_0$-FePd ordered structure formed as a result of annealing at 550 °C of Fe/Pd multilayer films with the thickness of an individual layer being 0.75–5.50 nm ($S \approx 1$) [32]; of the $L1_0$-FePd ordered structure formed by annealing Fe/Pd bilayer thin films at 500 °C (the total thickness being 200 nm) ($S = 0.8$) [33].

At temperatures higher than 605 °C the value of the LRO parameter began to decrease (Fig. 7b), which gave evidence concerning the beginning of the order-disorder transition. At 695 °C the value of the LRO parameter reached zero. A similar character of the temperature dependence of the LRO parameter value of the $L1_0$-FePd ordered structure was obtained in [34]: in the range of 380–580 °C the growth of the LRO parameter value was observed (the maximum value being 0.78), in the range of 630–700 °C one observed the decrease of the LRO parameter value to zero which was explained by the order-disorder transition and corresponded to the phase diagram for the ratio Fe:Pd ≈ 50:50 at% (see Fig. S2, the green lines).

According to the phase diagram (See Fig. S2, the red lines), the initiation temperature of the order-disorder transition for the Fe-Pd alloy with the atomic ratio of Fe:Pd ≈ 46:54 at% amounted to ≈ 740 °C, the temperature of the transition termination being ≈ 760 °C. The palladium concentration of 48.5 at% corresponded to the initiation temperature for the order-disorder transition (605 °C) observed in the present work (See Fig. S2, the blue line). The order-disorder transition in the ordered structures $L1_0 \rightarrow$ FCC is known to be the first type
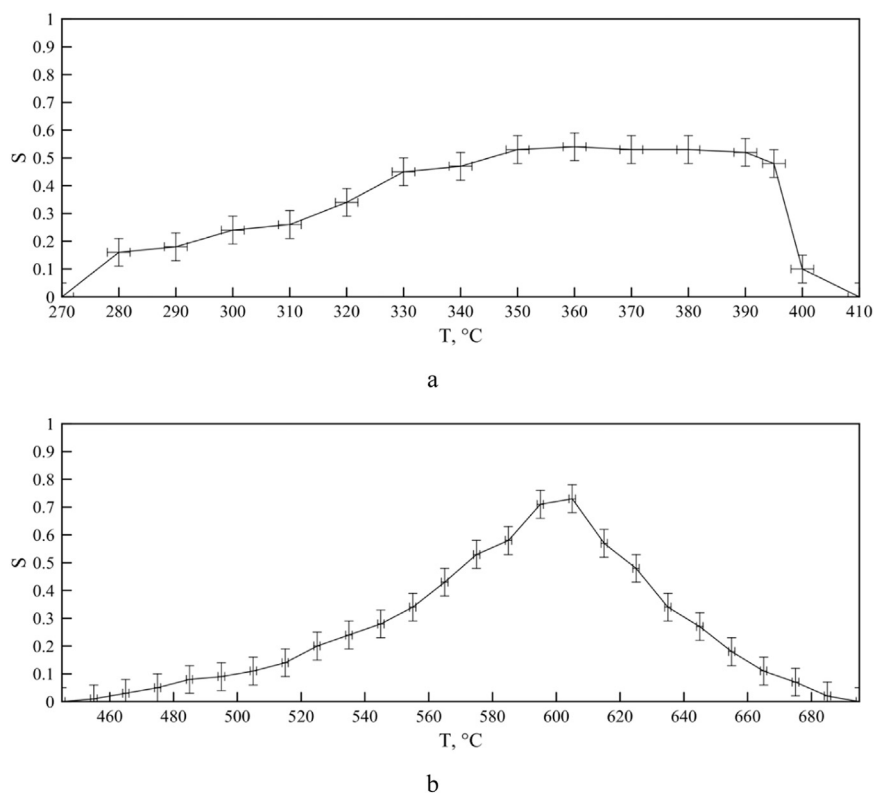
Fig. 7. Temperature dependence of the value of long-range order (LRO) parameter (*S*) for the ordered phases: CuAuI (a) and L1$_0$-FePd (b), formed during the heating of the Cu/Au and Fe/Pd films at a heating rate of 4 °C/min.

transition [15,35], *i.e.* the LRO parameter value upon reaching the transition temperature abruptly drops to zero. The temperature range for the order-disorder transition observed in this work (605–695 °C, see. Fig. 7b) can be explained in the following way. At 605 °C in the electron diffraction patterns obtained from the sample it is still possible to observe the reflections of iron and palladium which gives evidence to the fact that not all the iron and palladium present in the sample reacted entirely. One can assume that at the initial stage of the solid state reaction, on the interface of iron and palladium, due to the interdiffusion a layer of the Fe-Pd solid solution was formed with the palladium content of ≈ 48.5 at%. Upon reaching the temperature of 605 °C the transition order-disorder began, however, in the process of further heating the interdiffusion of iron and palladium was still in progress which resulted in the change of the atomic ratio of Fe:Pd in the layer of the ordered solid solution, and, as a consequence, in the order-disorder transition temperature broadening, which stopped upon reaching 695 °C, which corresponded to the concentration of Fe:Pd ≈ 50.2:49.8 at% (See Fig. S2, the green lines). Since the initial concentration amounted to Fe:Pd ≈ 46:54 at%, a small amount of palladium was unlikely to have reacted upon heating. This assumption, explaining the shift of the initiation and terminating temperatures of the order-disorder transition, is confirmed by the results given in [36], which demonstrate that the duration of the order-disorder transition in the L1$_0$-FePd nanoparticles is determined by the deviation of the atomic ratio of Fe:Pd from the stoichiometric one.

4. Conclusions

In the present work the formation processes of CuAuI and L1$_0$-FePd ordered structures in the course of the solid state reaction in Cu/Au and Fe/Pd bilayer thin films were investigated by the method of *in situ* electron diffraction.

It is established that in the Cu/Au thin films (the crystallite size being 10–20 nm, Cu:Au ≈ 48:52 at%) the solid state reaction began with

the interdiffusion along the grain boundaries at 180 °C in the process of thermal heating at a rate of 4 °C/min. Then, the volume interdiffusion of gold and copper began resulting in the size reduction of the grains of the initial materials. As the crystallite size of the initial materials was reduced, the role of diffusion along the grain boundaries increased. As a result, nanocrystallites of the Cu-Au solid solution were formed with the coherent scattering region ≈ 1 nm. Further, the grain formation and growth of the CuAu partially ordered solid solution occurred. In the case of the Fe/Pd films (the crystallite size being 10–20 nm, Fe:Pd ≈ 46:54 at%) the solid state reaction began at 390 °C in the process of thermal heating at a rate of 4 °C/min. Based on the analysis of the changes in the diffraction reflections in the electron diffraction patterns obtained from the Cu/Au and Fe/Pd systems in the solid state reaction process it is assumed that the solid state reaction mechanism in the system Fe/Pd was similar to the one in the system Cu/Au, however, the ordering began in a thinner layer of the solid solution formed as a result of the interdiffusion directly on the interface of the iron and palladium nanolayers.

The value of the long-range order (LRO) parameter was estimated for the CuAuI and L1$_0$- FePd ordered structures formed in the process of the solid state reaction. The maximum reached value of the LRO parameter for CuAuI amounted to 0.53, L1$_0$-FePd – 0.73. It is assumed that a rather low value of the LRO parameter for CuAuI was due to a big number of the lattice defects, primarily on the grain boundaries. The temperatures of the order-disorder transition in the CuAuI and L1$_0$-FePd thin films were determined. It was established that the initiation temperature of the order-disorder transition in the Cu-Au system corresponded to the upper boundary of the temperature range for the existence of the CuAuI ordered phase according to the phase equilibrium diagram for the Cu-Au system. At a temperature of 410 °C, which, according to the phase equilibrium diagram of the Cu-Au system, corresponded to the temperature of the transition to the disordered solid solution, the LRO parameter value reached zero. In contrast to the Cu-Au system, the initiation and termination tempera-

ture of the transition for the Fe-Pd system did not correspond to the phase equilibrium diagram for the given iron and palladium concentration; in this case a considerable order-disorder transition temperature broadening was observed (from 605 to 695 °C). A mechanism was suggested which explained the shift of the transition temperature and the observed order-disorder transition temperature broadening.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2018.09.009.

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