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$L1_0$ 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 coercitive force H_c ~ 10 kOe and magnetic anisotropy constant $K_u \sim 10^7$–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 temperatures (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 ≈ 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 ≈ 48:52 at%, Fe:Pd ≈ 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 ≈ 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 ≈ 1 μm, 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*-3*m* (225), lattice constant a = 3.62 Å, PDF 4+ card #00-004-0836), and, Au (the space group *Fm*-3*m* (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*-3*m* (229), lattice constant a = 2.87 Å, PDF 4+ card #00-006-0696) and Pd (FCC lattice, the space group *Fm*-3*m* (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

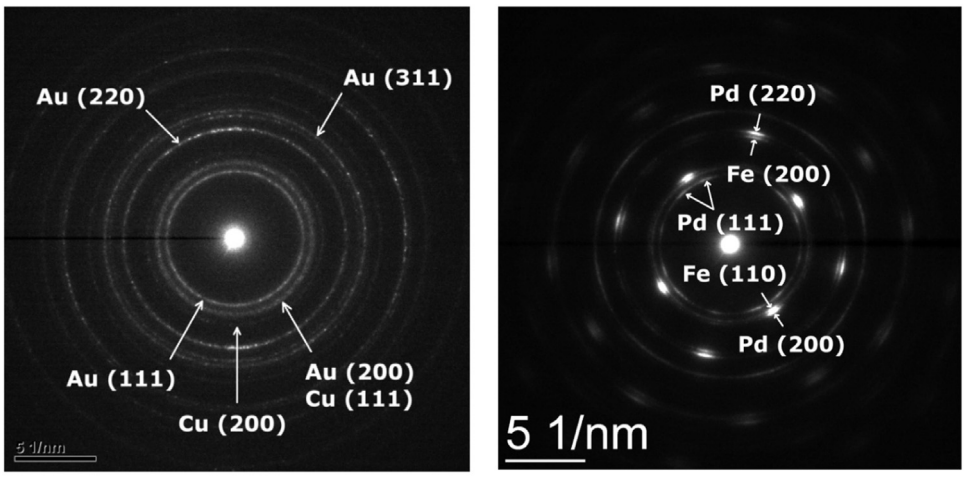

Fig. 1. SAED patterns of Cu/Au (a) and Fe/Pd (b) bilayer films at the initial state.