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PHYSICAL PROPERTIES AND STRUCTURE OF MELT-QUENCHED AND VAPOR-QUENCHED Mn-Bi ALLOYS

The regularities of formation of metastable structures of Mn-Bi alloys obtained by quenching methods from the liquid and vapor state are investigated. It is established that the freshly-deposited Mn-Bi films in the initial state represent a mixture of the β-Mn, Bi_2O_3 and Bi phases of a rhombohedral and bcc modification analogous to the phase formed in pure bismuth at a pressure of 7.75 GPa. After heating above 670 K, in addition to the indicated phases, Bi_2Mn and MnO traces appear instead of Bi bcc modifications. Analysis of the demagnetization curves of films quenched from the vapor state showed that the hard-magnetic properties are observed only in films containing the Bi_2O_3 phase. In quenched from the liquid state Mn+(25-41) ат.% Bi foils, the peritectic phase of α-MnBi with γ-Mn was formed or with practically pure Bi in Mn+61 ат.% Bi. It is shown that the coercive force in the Mn-Bi alloy can be increased upon quenching from the liquid state due to an increase in the tempering temperature of the melt up to 1923 K and the formation of nanoscale α-MnBi phase crystals.

Keywords: quenching from the liquid and vapor state, Mn-Bi films, ion-plasma sputtering, hard magnetic materials, metastable state.

1. Introduction

It is known that alloys and chemical compounds of manganese with non-ferromagnetic elements can exhibit ferromagnetic properties. Therefore, the immiscible Bi-Mn system was chosen. In the case of nonequilibrium crystallization from a vapor state and melt in these alloys, the primary structure can be an amorphous or nanocrystalline one. During subsequent annealing, a structure from nanocrystalline ferromagnetic regions surrounded by interlayers of a diamagnetic matrix can be formed. If the dimensions of the ferro-regions are less then 40 nm, the alloy films show high magnetic properties. When obtaining films with the required structure by quenching from a liquid, the melt temperature is of great importance, especially for systems that do not mix in the liquid state. It is an important task in terms of developing new technologies and practical application of quenching products [1].

The decision of these problems is important not only from the point of deepening existent ideas in relation to conformities of objective laws of phase transformations in nonequilibrium conditions but also for optimizing the melt-quenching modes and ion-plasma sputtering (IPS) with the purpose of improving the properties of traditional and new melt-quenching materials and coatings.

This paper is concerned with the study of regularities that affect the formation of nonequilibrium nanocrystalline and amorphous structures under the conditions of quenching from a liquid (QLS) or from a vaporous state (QVS) in Mn-Bi alloys. The forming of the metastable crystalline phases and amorphous ones in Mn-Bi films, which are obtained by the modified method of the three-electrode ion-plasma sputtering of alloys and by the quenching from a liquid state, was the investigation object. The establishment of connections between the processes of film crystallization and the conditions of QLS and QVS, the film structure, the next stages of passing to the equilibrium state, and physical properties of quenched foil materials was the task of our research.

2. Materials and Methods

To produce foils 5-20 microns in thickness from high-temperature alloys, the water-cooled Tamman furnace was used, which allowed melting alloys with a melting point up to 2300 K and a splat-cooling method on the inner surface of a copper (heat-conducting) cylinder of radius 135 mm with a rotation frequency n ~ 125 s^{-1}. Systematic data were used to estimate the cooling rates along the thickness of the obtained samples [2]. Estimated cooling rates of foils were in the range (10^6 - 10^8 K/s). Preparation of thin films by a three-electrode ion-plasma sputtering [3] makes it possible to increase the purity films by reducing the operating pressure of the gas (argon) to (0.013 - 0.053) Pa, enables change of energy of the sputtered atoms by increasing the energy and flux of inert ion intensity gas. The calculated values of the energy of argon atoms as a function of the degree of ionization for an improved sputtering method from independent sources with an accelerating voltage of 2 kV are from 100 to 300 eV [3]. Under conditions of ordinary ion-plasma sputtering, this energy is only 3-5 eV. Thus, the high values and the dispersion of the energies of the condensed atoms provide non-equilibrium conditions for the formation of homogeneous films, even in immiscible systems in the liquid state. In the process of film formation by this method, the effective relaxation rates due to the condensation of atoms from the vapor state under different deposition regimes, according to different theoretical estimates, are ~ 10^{12}-10^{14} K/s. This is 5-7 orders of magnitude higher than the maximum cooling rates of the samples that can be obtained upon QLS [4] and allows us to speak of quenching from the vapor state (QVS).

Before the deposition the substrates were cleaned in a solution of acetone with ethyl alcohol. The substrates were placed at the distance of 70 mm from a target in the center of the substrate holder. Prior to the filling, the chamber with the working gas (Ar) was pumped out to 1.3×10^{-3} Pa. After that the chamber was filled with argon up to working pressure of $(1.3 - 5.3) \times 10^{-2}$ Pa. The ion current density to the target was j ≈ 3.1 – 3.2 mA/cm^2. Depending on the conditions of the experiment, the substrate temperature increased to 80 – 120°C and the rate of the coating increasing was 0.15–0.35 nm/s. The nominal thickness of the studied coatings was in the range from 0.34 – 0.88 μm. The deposition of the films was carried out on NaCl single crystals and pyroceramics (sitall) substrates. The films deposited on NaCl substrates were used for studying the phase composition in the initial and heat-treated states. The physical properties and thermal stability were examined for the foils and films deposited at pyroceramics substrates. The film resistivity was measured by four-probe method with continuous heating in a vacuum of about 10 mPa with controlled heating rates between 4 and 20 K/min. The activation energy calculation of phase transitions was conducted by the Kissinger method, i. e. by analyzing the phase transition temperature displacement with heating rate changing. The coercive force H$_c$ of the films was investigated by vibration magnetometer in the maximum magnetizing field about 0.3 T with orientations parallel and perpendicular to the film surface.

3. Results and Discussion

The transmission electron microscopy, XRD and CSR analysis showed in all samples obtained by quenching from the liquid state, formation of the peritectic phase of α-MnBi was observed: in alloys with a content of 25 and 40 at.% Bi, in addition to γ-Mn, and in the Mn-61 at.% Bi - together with the equilibrium Bi . The foils of the Mn-52 at.% Bi alloy showed the most complex phase composition. X-ray diffraction studies have shown that in the foils, in addition to the α-MnBi phase, there are phases γ-Mn and Bi (Fig. 1).

A probable reason for the formation of the peritectic phase of α-MnBi under the conditions of the QLS is the deep initial supercooling of the melt, characteristic of this process, which can reach 550 K at cooling rates of about 10^6 K/s. The samples studied in this work were obtained at higher cooling rates (~10^7 K/s), and, apparently, the melt refoldings achieved in these experiments were sufficient to initiate crystallization in the temperature range of the existence of the MnBi phase. Analysis of diffraction patterns of Mn-Bi foils showed that the phase α-MnBi formed at QLS has a lattice of NiAs type with periods $a = 0.450$ nm and $c = 0.581$ nm. Estimates of the sizes of the coherent-scattering regions L of this phase, estimated by the Selyakov-Scherer formula, were ~ 9-10 nm.
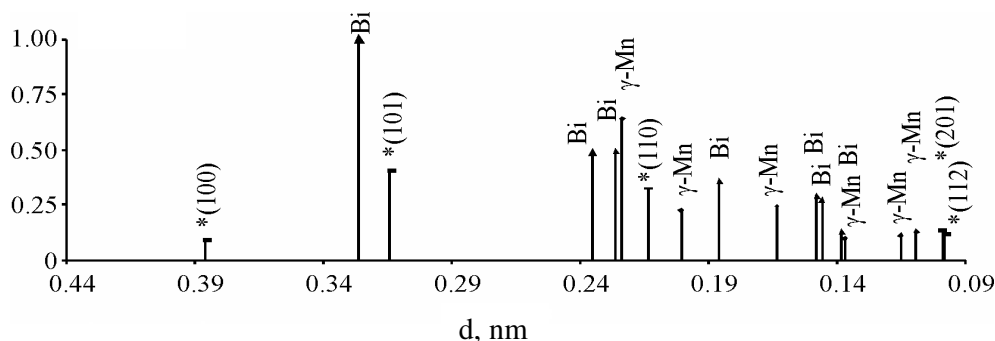

Fig. 1. Barcode X-ray diffraction pattern of QLS-foil Mn-52 at% Bi: * - α-MnBi phase, ♦ – γ-Mn, ▲ – Bi

(d – interplanar distance)

The periods of the crystal lattice of the α-MnBi phase obtained in this study differ from the results of [5]. Thus, in Ref. [5] it is said that during quenching from the solid state of the Mn-50 at. % Bi alloy from 673 K, the period of the lattice of the α-MnBi phase changes: an increase in the a axis from 0.426 to 0.433 nm and a decrease along the axis c from 0.608 to 0.584 nm in comparison with the equilibrium values for α-MnBi. An increase in the cooling rate of the melt to 10^7 K/s is accompanied by a more significant change in the periods of the crystal lattice of α-MnBi in comparison with the equilibrium values and is, as indicated earlier, $a = 0.450$ nm, $c = 0.581$ nm. A possible reason for this is a higher melt temperature before quenching from the liquid state, compared to a temperature of 1150-1200 K, from which the foils studied in [5] were obtained. In the present study, the temperature of the melts of the Mn-Bi system was maintained at ~1923 K. This temperature is much higher than the liquidus temperature (T_c), which reduces the size of clusters of all phases existing in the melt. The latter circumstance made it possible to obtain in the QLS-foils investigated a more dispersed structure in the form of a mixture of γ-Mn, Bi and the nanosized phase α-MnBi. It is known that, among pure elements, Bi is the most pronounced diamagnet, and the ferromagnetic phase of α-MnBi is considered in the technique of magnetic information carriers as a very promising magnetically rigid material. If the coercive force H_c for massive samples with an elemental content of ~ 50:50 is 88-270 kA/m [6], then for QLS samples obtained in this work by quenching the melt from 1923 K, it changes from 10 to 400 kA/m, depending on the Bi content, reaching a maximum in the Mn-52 at.% Bi foils (Fig. 2).

In this work, the QVS films of the Mn-Bi system of compositions (at. %) were

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studied: $Mn_{59}Bi_{41}$; $Mn_{56}Bi_{44}$; $Mn_{49}Bi_{51}$; $Mn_{42}Bi_{58}$. In this case, films of $Mn_{49}Bi_{51}$ composition were obtained at different working gas pressures, and their thickness is also 340 and 880 nm.

The phase diagram of the binary MnBi system is well studied, but even to date, the structure of the alloys of this system cannot be considered fully established. According to the data of [7], the region of fibration in the liquid state at 1255 °C is in the range from 30 to 93% by weight Mn. As is known, in this system there are chemical compounds Bi_2Mn and $BiMn_2$, formed by the peritectic reaction. Both modifications of the chemical compound MnBi have a hexagonal structure of the NiAs type. The constants of the crystal lattice of this compound for high-temperature modification vary from a=0.4341 nm, c=0.5975 nm, c/a=1.376 to a=0.433 nm, c=0.596 nm, c/a=1.376. For low-temperature modification, the parameters remain unchanged: a=0.4287 nm, c=0.6118 nm, c/a=1.427. At a temperature of ~633 K, a discontinuous change in the constants of the crystalline lattice occurs.
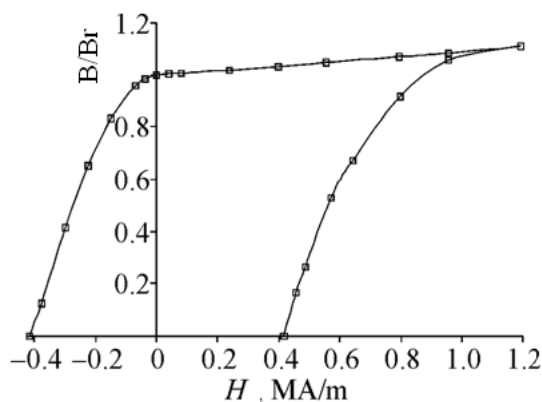

Fig. 2. The hysteresis loop QLS-foil Mn-52 at.% Bi

The initial structure of the films (Fig. 3) is a mixture of equilibrium Bi grains with a rhombohedral lattice and the Bi_2O_3 phase (bright regions) located in the oxide matrix MnO_2 (dark intergranular areas).
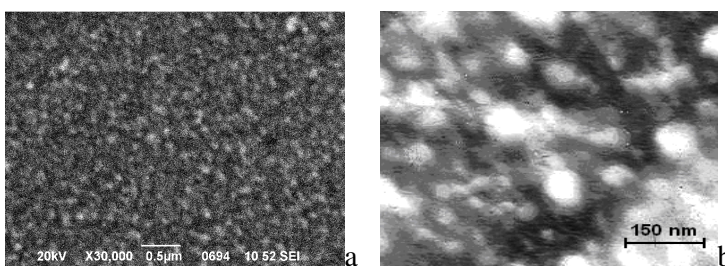

Fig. 3. Microstructure of MnBi films: a) $Mn_{49}Bi_{51}$; b) $Mn_{59}Bi_{41}$

X-ray phase analysis of the films showed that in the initial state there is formed a mixture of Bi phases with a rhombohedral lattice (a = 0.4533 nm) and Bi_2O_3 oxides with a monoclinic (a=0.58486, b=0.81661, c=0.75097 nm) and MnO_2 with orthorhombic lattice (a=0.92734, b=0.28638, c=0.45219 nm) (Fig. 4). The heating of the films to a temperature of ~ 943 K leads to an increase in the size of the CSR phase of the

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rhombohedral Bi from 6-8 to 9-14 nm and a change in the lattice period to values close to equilibrium. A characteristic feature of $Mn_{49}Bi_{51}$ films, irrespective of their thickness and atom energy, is a significant increase in the size of CSR in heat treatment, as compared to other samples. At the same time, the highest values of the dimensions of the CSR phase of rhombohedral Bi are noted in films with an increased content of Bi ($Mn_{49}Bi_{51}$ and $Mn_{42}Bi_{58}$). Films with thicknesses of ~360 nm obtained at the energy of deposited atoms of about 200 eV ($Mn_{59}Bi_{41}$ and $Mn_{49}Bi_{51}$) are characterized by the stability of the lattice parameter of the rhombohedral Bi phase during heat treatment and the closeness of its values to the equilibrium ones (0.4533 nm). In turn, the films $Mn_{56}Bi_{44}$ and $Mn_{42}Bi_{58}$ have an increased (0.462 nm) and a lowered (0.432 nm) value of this parameter, respectively. In the first case, the difference in the lattice parameter may be due to the increased pressure of the working gas (53 mPa). In films obtained at relatively high energy of the depositing atoms, the decrease in the parameter is associated with high atomic mobility during deposition. For the $Mn_{49}Bi_{51}$ film obtained under identical conditions, the lattice parameter is also increased (0.458 nm), however insignificantly, which is explained by the large film thickness ~880 nm and correspondingly by the different contribution of mechanical stresses.
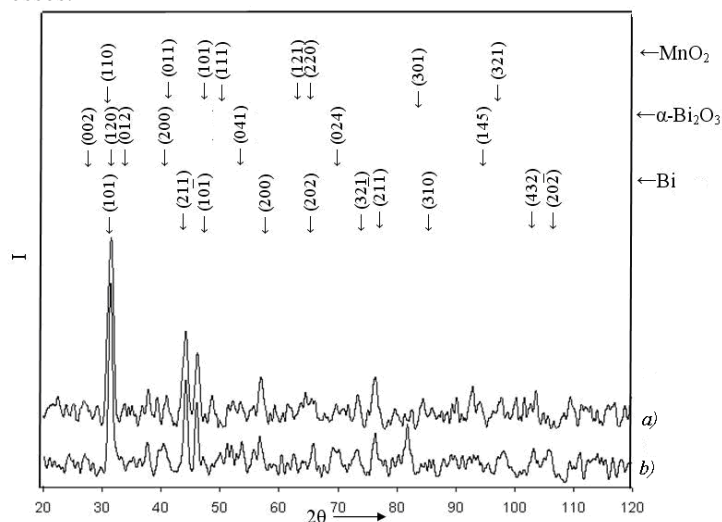

Fig. 4. Photometric X-ray diffraction pattern of $Mn_{49}Bi_{51}$ films: a) initial state; b) after heat treatment at 963 K

The thermal stability of the films was investigated by plotting the curves of the temperature dependence of the electrical resistivity of the films at different heating rates. Thus, for $Mn_{49}Bi_{51}$ films, the first temperature range from 295 K to 530 K is characterized by a smooth decrease in the electrical resistivity, which indicates the absence of structural changes. A further increase in temperature leads to a sharper decrease in the electrical resistivity in the temperature range from 530 K to 640 K and is characterized by a change in the structure of the film due to the melting of the rhombohedral Bi phase and recrystallization processes. Above the temperature of ~800 K the sample is strongly oxidized by reaction $Bi \rightarrow Bi_2O_3$. In the cooling process, at a temperature of ~ 490 K, as in the Bi films, a sharp increase in the resistance occurs due to the crystallization of Bi in the matrix consisting of a mixture of Bi_2O_3 and MnO_2 crystalline phases.

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Investigations of the temperature shifts of the onset of phase transformations with an increase in the heating rate of the films made it possible to calculate the activation energy of the onset of phase transformations (E_A) by the Kissinger method. The activation energy of phase transformations in MnBi films is in the range of $E_A \sim 24 - 41$ kJ/mol, and the larger the higher the energy of the atoms deposited on the substrate.

Analysis of magnetization-demagnetization curves showed that MnBi films are characterized by anisotropy of magnetic properties. When the film is perpendicular to the orientation relative to the magnetic field, the samples exhibit weak hysteresis properties. In the initial state, the coercive force does not exceed 2 kA/m. Heat treatment at 720 K leads to an increase in the coercive force to 32 kA/m. As was established in the phase analysis, there is no intermediate phase α-MnBi in the films under study, which is responsible for the ferromagnetic properties of the material. Nevertheless, manifestations of hysteresis properties are due to the formation of the α-Bi_2O_3 phase, which also led to ferromagnetic behavior in the Bi films. Thus, the increase in the coercive force during heat treatment, in this case, is explained not only by the enlargement of the structure, but also by an increase in the content of the α-Bi_2O_3 phase because of the $Bi \rightarrow Bi_2O_3$ transformation. In turn, films with a high Mn content ($Mn_{59}Bi_{41}$ and $Mn_{56}Bi_{44}$) have a sufficiently low coercive force value (<0.5 kA/m).

4. Conclusions

It was shown that the formation of nanoscale (9-10 nm) crystals of the α-MnBi phase in the foils of the Mn-52 at.% Bi alloy obtained by quenching the melt from the temperature of 1923 K leads to an increase in the coercive force by 60% compared to the H_C of foils obtained by quenching from a temperature of 1175 K, in which the dimensions of the ferromagnetic inclusions were 5-10 μm.

It was found that the hysteresis properties in the sputtered films of the MnBi system is due to the non-low-temperature intermediate phase of α-MnBi, as in the QLS samples ($H_c \sim 10$-400 kA/m), and the formation of the α phase Bi_2O_3 ($H_c \sim 2$ - 32 kA/m).

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