EFFECT OF CHROMIUM ADDITIONS ON THE STRUCTURE AND PHYSICAL PROPERTIES OF MANGANESE-BASED FILMS

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The formation of metastable structures of manganese films with chromium additions obtained by the method of modernized three-electrode ion-plasma sputtering is studied. It is shown that the deposition of pure manganese leads to the formation of nanocrystalline β-Mn and MnO oxide. Heating in vacuum above 700 K leads to the film oxidation. The addition of Cr to the composition of the films prevents the formation of MnO oxide. It is shown that the activation energy of structural changes decreases with an increase in the energy of deposited atoms for pure manganese and MnCr films. Magnetization hysteresis is observed only in freshly sprayed Mn and MnCr films.

Keywords: thin film, ion-plasma sputtering, coercive force, metastable state, nanocrystalline phase.

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1. Introduction

It is urgent to study magnetic samples obtained under nonequilibrium conditions in the form of a film. Such films are amorphous or nanocrystalline compounds, in which size effects play an important role, which directly affect the physical properties of the samples [1]. In addition to the MnBi system, a bimagnetic compound with chromium is known. The use of this compound is limited due to the complexity of the synthesis [2]. Chromium has a high melting point and CrO oxide prevents further oxidation of the surface. This component, reacting with low-melting bismuth, forms several intermediate phases with manganese. Chromium has similar magnetic properties to manganese. Mn and Cr are antiferromagnets even at relatively low temperatures.

In the MnCr system, there are two intermediate phases α-$CrMn_2$ and σ-$CrMn_3$, as well as solid solutions of chromium and various modifications Mn: (αMn), (βMn), (δMn), and (γMn). Phases α and σ undergo polymorphic transformations. The α-phase exists in two modifications: high-temperature α' and low-temperature α''. The polymorphic transformation temperature is ~ 870 K. The σ-phase exists in three modifications: high-temperature σ, medium-temperature σ' and low-temperature σ''. The polymorphic transformation temperature σ'↔ σ'' is ~ 1070 K. In this case, a high cooling rate (>10^7 K/s) makes it possible to stabilize metastable phases in alloys with a high Mn content.

One of the ways to increase the coercive force and magnetic energy of materials can be the refinement of the domain structure and the creation of thin diamagnetic layers between domains [3]. Potentially attractive materials with improved magnetic properties include a large group of alloys with a low-temperature ferromagnetic phase MnBi, which are known for their magnetic properties and are used in plastic magnets [2]. Of interest is the production of this magnetic material in the form of a film. The main advantage over bulk materials is the ability to produce films of any shape and size. In thin films, the content of the MnBi ferromagnetic phase decreases due to the formation of MnO oxides. By using chromium as an additional component that prevents oxidation, physical properties can be improved.

Known studies of the effect of paramagnetic and diamagnetic additives, which are practically immiscible with the main component even in the liquid state, on the magnetic properties [4–7]. Such alloys can be obtained in the form of films by the method of modernized three-electrode ion-plasma spraying (MTIPS) [4,8]. The modernized method of three-electrode ion-plasma sputtering of mosaic targets [9] increases the efficiency of traditional methods of ion-plasma deposition. This method provides an increase in the kinetic energy of the sputtered atoms over 100 eV prior to collision with the substrate [10]. This is

5-6 times more than with traditional methods of ion-plasma spraying. The effective cooling rates of such films, theoretically estimated considering the atomic relaxation time, are in the range from 10^{12} to 10^{14} K/s. Therefore, the structure of the films is formed under additional nonequilibrium conditions, that is, we can speak of quenching from the vapor state. The MTIPS method makes it possible to obtain homogeneous structures based on MnCr alloys. These alloys are promising because they have high uniaxial anisotropy energy and high coercive force. Interest in the study of compounds of this alloy with the addition of Cr is also because such a compound can combine the properties of magnetically soft and magnetically hard materials and opens possibilities for a wide range of applications.

The aim of this work is to obtain homogeneous films based on MnCr alloys by the method of modernized three-electrode ion-plasma sputtering and to determine the effect of alloying with Cr on the structure and properties of the sprayed coating.

2. Experimental procedure

To obtain Mn and MnCr films, we used the method of modernized three-electrode ion-plasma sputtering in vacuum of mosaic targets, which are a set of Mn and Cr squares (20x20 mm) placed directly on the sputtered surface [8].

The deposition of films was carried out under identical conditions on sitall substrates and on fresh cleavages of NaCl single crystals. Films deposited on NaCl were used to study the phase composition by X-ray diffraction analysis and transmission electron microscopy. Physical properties and thermal stability were studied on films deposited on sitall substrates. The electrical resistance of the films was measured by a four-probe method with continuous heating in a vacuum of ~ 13 mPa. The beginning and end of structural changes were determined from the temperature range of an irreversible decrease in electrical resistance in these dependences. The phase composition in the freshly sprayed state and after heating was determined from photometric X-ray diffraction patterns. X-ray diffraction patterns were obtained using a Debye camera in filtered Co-K_α radiation. With allowance for the extrapolation of the angle to 90°, the accuracy of the lattice parameter determination was ± 3×10^{-4} nm. The thickness of the films was determined by weighing the substrates before and after deposition with an accuracy of ± 20 nm. The coercive force H_c of the films was investigated using a vibromagnetometer in a maximum magnetizing field of 0.3 T, located parallel and perpendicular to the film surface. The calculation of the activation energy of the onset of structural changes was carried out by the Kissinger method [11].

3. Results and discussion

In pure Mn films, in a freshly sprayed state, a nanocrystalline β-Mn phase is formed with a coherent scattering region (CSR) size *L* of about 7.5 nm. After heating in vacuum to 773 K, Mn is oxidized with the formation of MnO oxide, and the CSR size of the β-Mn phase increases to 10.5 nm. When samples are obtained by quenching from a liquid state, either a single-phase structure of nonequilibrium γ-Mn is formed (at $V_{cool} = 5\times10^7$ K/s), or a two-phase structure of α-Mn and γ-Mn (at $V_{cool} = 5\times10^6$ K/s) [12].

A mixture of phases of nanocrystalline β-Mn (*a* = 0.6315 nm) with CSR size 7.5 nm, chromium with a hexagonal lattice (hcp) (*a* = 0.2722; *c* = 0.4427 nm) and traces of the MnO_2 oxide phase with a rhombic crystal lattice (*a* = 0.92734; *b* = 0.28638; *c* = 0.45219 nm) are formed in the initial MnCr films. Heating the films in vacuum to a temperature of ~ 773 K leads to the formation of the MnO phase (Fig. 1.)

The $Mn_{93}Cr_7$ films deposited at φ = 100 eV was characterized by an increased β-Mn lattice parameter (*a* = 0.6359 nm), which can be explained by the removal of mechanical stresses in the film due to the higher atomic mobility and an increase in the substrate temperature. The lattice parameter β-Mn after heating becomes close to the tabular values (a = 0.6315 nm). (Fig. 1)

The obtained dependences of the electrical resistance during heating and cooling are characterized by a few characteristic sections. Thus, for pure Mn films, the first section (from 295 K to 600 K) is characterized by a reversible change in resistance. This indicates that phase changes do not occur in this temperature range and the structure of the sample remains stable. The second section is characterized by an irreversible decrease in the surface resistance in the temperature range from 620 K to 700 K, which indicates a change in the structure of the film associated with recrystallization processes. At a temperature of ~ 800 K, the sample undergoes strong oxidation. The third section is characterized by a reversible decrease in resistance upon cooling from 770 K to 295 K.

For MnCr films, as the temperature rises above ~ 620 K, an irreversible decrease in resistance occurs, which indicates the transformation $MnO_2 \rightarrow MnO$.

As a result of studies of the shift in the temperature of the onset of structural transformations with an increase in the heating rate of the films by the Kissinger method, the activation energy of structural transformations (E_a) was calculated.

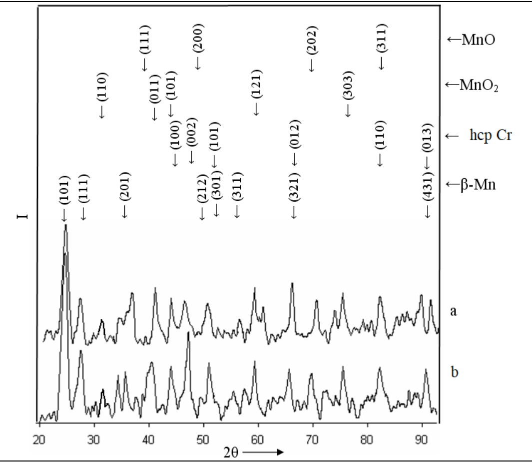

Fig. 1. X-ray diffraction patterns of $Mn_{93}Cr_7$ films after photometry in the initial (a) and heat-treated states (b).

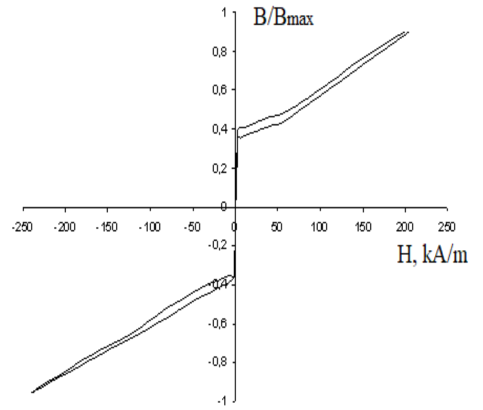

Fig. 2. Demagnetization curve of Mn film after heat treatment.

The activation energy of structural transformations for pure Mn films under conditions of a higher deposition rate and the energy of deposited atoms is ~ 17300 K and is 3 times higher than the activation energy for films obtained with a lower deposition rate (~ 0.1 nm/s) and the energy of deposited atoms (E_a~5000 K).

For $Mn_{93}Cr_7$ films obtained at a low energy of deposited atoms (φ ~ 20 eV), the activation energy of phase transformations is 3400 K. For $Mn_{90}Cr_{10}$ and $Mn_{85}Cr_{15}$ films obtained at a higher energy of deposited atoms (φ ~ 100 eV) E_a ~ 4700 K.

This indicates a more equilibrium structure. and can be explained by the greater heating of the surface layers due to the higher energy of the deposited atoms.

Investigation of the magnetic properties of the films shows the manifestation of anisotropy of properties. In the initial state, the coercive force of the samples is ~ 2.3-4.0 kA/m in a parallel field (Fig. 2). In a field perpendicular to the film, hysteresis properties are not fixed. In this case, it is necessary to consider the possibility of increasing the coercive force of the films when selecting the temperature and holding time.

4. Conclusions

As a result of the comparative analysis of the phase composition of Mn samples obtained under nonequilibrium conditions by quenching from liquid and vapor, it is found that a nanocrystalline nonequilibrium ß-Mn phase and MnO_2 oxide are formed in the initial Mn films. When samples are obtained by quenching from a liquid state, either a single-phase structure of nonequilibrium γ-Mn is formed (at $V_{cool}=5\cdot10^7$ K/s), or a two-phase structure of α-Mn and γ-Mn (at $V_{cool}=5\cdot10^6$ K/s). The regularity of an increase in the activation energy of the onset of structural transformations in manganese and MnCr films by a factor of 2–3 with an increase in the energy of deposited atoms from 20 to 100 eV is established.

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