Influence of the heat treatment on the chemical composition of the ferromagnetic Ni-Mn-In thin film

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Abstract. The paper presents results of study of the dependence of the Ni-Mn-In film’s composition on the annealing parameters, data of scanning electron microscopy and energy dispersive analysis (EDX spectroscopy). The Influence of annealing of a film in vacuum on the chemical composition is shown. The content of manganese and indium decreases sharply with a rise in temperature up to 900 °C, and in a heating time up to 2 hours. The ferromagnetic Curie point in the investigated Ni-Mn-In films is observed. A decrease of the width of the ferromagnet-paramagnet transition results in the improvement of the crystallinity of the sample after annealing.

1. Introduction

The functional Heusler alloys of the Ni-Mn-In family are of great interest due to their inherent special effects based on a sharp change of the magnetization ΔM in the course of the first order phase transformation (PT) [1], such as a magnetic-field-induced shape memory effect (MSME), magnetocaloric effect (MCE), magnetoresistance. These effects are especially attractive in thin films produced by magnetron sputtering. The properties of such materials are highly dependent on the chemical composition and structural state, determined by the methods of preparation and further heat treatment. Management of the chemical composition and degree of crystallinity by annealing the film allow to be purposefully changed the parameters of these effects. The crystal lattices of the phases are strictly oriented relative to each other during thermoelastic martensitic PT, and at the reverse PT they give a single, initial position, which allows one to restore their shape. Materials with such properties find their application in medicine and energy, can be used as a working element of sensors, and also become the basis of a new principle in micromechanics [2-4]. Alloys of the Ni-Mn-X system (where X = In, Sn, Sb) belong to the family of Heusler alloys and they are of particular interest for creating magnetic-field-controlled microactuators due to the manifestation of MSME [5-7]. Such an effect of the magnetic field on the PT is determined by the strong coupling between crystallography and magnetic properties. The Heusler alloys of the Ni-Mn-X system exhibit structural transformation from ferromagnetic austenite to paramagnetic or antiferromagnetic martensite and, apart from MSME, the...
transformation results in the so-called reverse MCE (the sample is cooled when an external magnetic field is applied) [8]. This work is devoted to the study of thin films of the Ni-Mn-In system obtained by the method of magnetron sputtering. The properties of Heusler alloys strongly depend on the chemical composition and structural state, which are determined by the methods of preparation and further heat treatment. The goal of the work was to study the effect of annealing regimes on the chemical composition of thin films of Heusler alloy Ni - 44.4 %, Mn - 33.2 %, In - 22.4% weight percent.

2. Materials and Methods
The Ni-Mn-In films were obtained by magnetron sputtering (Shibaura, CFS-4ES) of the Ni$_{45}$Mn$_{40}$In$_{15}$ target. The intensity of spraying was set at 200 W [9]. The chemical composition of the films was determined using energy dispersive analysis (Scanning Electron Microscope JEOL JSM-6480LV), which showed the composition of the film in the initial state Ni - 44.4%, Mn - 33.2%, In - 22.4%. The films were deposited on a sacrificial water-cooled substrate (323 K) of polyvinyl alcohol (PVA). The separation of the substrate was carried out in distilled water at a temperature of 58–62 °C. The roentgenogram obtained at room temperature (figure 1) shows the structure of the original film which turned out to be amorphous with a small amount of the crystalline cubic phase Fm3m with the lattice parameter $a = b = c = 6.024$ [7]. The film thickness was determined by scanning electron microscopy (SEM) and it is equal to 1 μm (figure 2). Local EDX-analysis is depicted in blue on the figures 2 and 3.

![Figure 1](image1.png)  
**Figure 1.** The X-ray of the initial film shows an amorphous structure, but there are small inclusions of the crystalline phase with Fm3m crystal structure of the same composition (a narrow peak at the first halo).

![Figure 2](image2.png)  
**Figure 2.** The image of the SEM of the original film Ni-Mn-In, the film thickness is equal to 1 μm.

Rapid cooling during magnetron sputtering leads to the formation of an amorphous film structure. Heat treatment is necessary for crystallization of samples. In this case, geometrical features have a strong influence. A small film thickness leads to a change in the internal stress state, and, consequently, to the physical processes that take place. Thus, several approaches to solving this problem were identified: 1) assigning annealing modes according to literature data, 2) using differential scanning calorimetry (DSC) to determine the crystallization temperature, 3) empirical approach.

Samples of the Ni$_{44.4}$Mn$_{33.2}$In$_{22.4}$ thin films were also studied by the temperature dependence of the magnetization measurement in the temperature range 10–390 K in an external weak magnetic field $H = 100$ Oe in the ZFC-FH-FC measurement regime. Commercial installation Quantum Design PPMS-9T was used for this measurements.
3. Results and Discussions

The selected annealing regimes and chemical compositions, determined by the method of energy dispersive analysis, are presented in Table 1. For perception convenience the first line presents the initial chemical composition of the film.

Regimes 2 and 3 were chosen from literature data [7]. Annealing for 1 hour at a temperature of 900 °C (regime 2) and two step annealing of 750 °C and 900 °C with an exposure of 1 hour at each step (regime 3) led to a drastic change in chemical composition: almost complete evaporation of Mn and the significant change in the amount of In. In addition, active diffusion processes and evaporation of metals led to a violation of the integrity of the film sample, which was recorded using SEM (Figure 3). Such consequences of annealing are unacceptable.

![Figure 3. The image of the SEM sample after annealing modes 2 (a) and 3 (b).](image)

The attempt to determine the temperature of the PT of the amorphous state to the crystalline one by the method of differential scanning calorimetry (DSC) did not show a result. No characteristic peaks were found on the DSC curves. The unsubstantiated DSC may be associated with a small sample mass and, accordingly, a small thermal effect. The presence of a small thermal effect in the temperature range of 255–280 °C may occur due to the relaxation of internal stresses, which is confirmed by the irreversibility of this process: no similar effect was observed on the cooling curve.

A series of heat treatments (4.1–4.4) were carried out, the parameters of which were chosen empirically in order to ensure diffusion processes and minimize the change in chemical composition. As can be seen from Table 1, annealing at 500 °C does not lead to a change in the composition of the film in the range of exposures 1–15 min. Micrographs of the film after annealing are shown on Figure 4. SEM images show that the surface of the films has inclusions of various sizes. EDX analysis showed that the films after annealing at regimes 4.1-4.4 have a homogeneous distribution of chemical elements over the surface. The integrity of the films is preserved. The black areas on Figure 4b correspond to areas with the maximum content of oxygen (12% wt.) in the sample. The key issue is the structural change during such treatments, since there is a possibility of incomplete diffusion processes. The samples annealed at regimes 4.1–4.4 turned out to be of very low mass, therefore, XRD and DSC measurements were impossible to held.

4. Magnetic Properties

For an amorphous film, the temperature dependence of the magnetization in the temperature range 10–390 K under magnetic field with $H = 100$ Oe in the ZFC-FH-FC regimes is presented on Figure 5. Measurement of the temperature dependence of magnetization for the annealed film is presented on Figure 6. For the amorphous sample with decreasing temperature from $T_{C1} \approx 200$ K smooth PT is observed to the state with higher magnetization. Such behavior of the sample, as well as the discrepancy between the measurement results in the FC and ZFC regimes, indicates the ferromagnetic nature of this PT. The nature of the low-temperature behavior of the sample changes dramatically after a brief annealing for 15 minutes in a static vacuum at 550 °C. Thus, the transition temperature shifts to
the high-temperature region $T_C = 315$ K, the PT becomes abrupt. The temperature dependence of the magnetization is non-monotonic at low temperatures and reaches saturation.

### Table 1. Annealing of film samples sealed in evacuated quartz ampoules.

| № | Ni, % wt.          | Mn, % wt.          | In, % wt.          | O, % wt.          |
|---|--------------------|--------------------|--------------------|-------------------|
| 1 | original film      |                    |                    |                   |
|   | 44.39 (43.70 – 45.69) | 33.18 (32.66 – 33.92) | 22.43 (20.39 – 23.64) | –                 |
| 2 | annealing for 1 hour at 900 °C + cooling the ampoule in air [7] | | | |
|   | 88.94 (76.44 – 97.00) | 1.19 (1.09 – 1.31) | 9.87 (1.84 – 22.38) | –                 |
| 3 | annealing for 1 hour at 750 °C + annealing for 1 hour at 900 °C + cooling the ampoule in air [7] | | | |
|   | 86.60 (79.71 – 92.48) | 2.94 (2.45 – 3.59) | 10.46 (4.78 – 17.84) | –                 |
| 4.1 | annealing for 1 min at 500 °C + cooling the ampoule in air | | | |
|   | 42.70 (42.65 – 42.75) | 32.27 (32.18 – 32.35) | 25.04 (24.90 – 25.17) | –                 |
| 4.2 | annealing for 2 minutes at 500 °C + cooling the ampoule in air | | | |
|   | 39.86 (36.98 – 42.75) | 31.11 (29.97 – 32.25) | 22.45 (20.94 – 23.96) | 6.58 (1.05 – 12.11) |
| 4.3 | annealing for 5 minutes at 500 °C + cooling of the ampoule in air | | | |
|   | 42.21 (41.27 – 43.06) | 32.01(32.11 – 32.62) | 22.49 (22.07 – 22.78) | 3.30 (1.84 – 5.56) |
| 4.4 | annealing for 15 minutes at 500 °C + cooling of the ampoule in air | | | |
|   | 43.13 (43.90 – 42.12) | 32.17 (31.38 – 32.91) | 24.70 (24.42 – 24.97) | –                 |

### Figure 4. SEM images of the film after annealing according to regimes 4.1 (a), 4.2 (b), 4.3 (c) and 4.4 (d).

Since the chemical composition of the sample after annealing has not changed significantly, the shift of the PT to the high-temperature region, as well as a decrease in the PT width may indicate the improvement of the crystallinity of the sample after annealing. The non-monotonic nature of the magnetization below the PT may indicate clusterization of the sample into areas with similar chemical compositions, or spin-glass effects.
5. Conclusions
The study of the Ni-Mn-In thin films has shown that the technological parameters of annealing have a strong influence on the chemical composition of the samples. The high temperatures (750–900 °C) and the long exposure (1–2 hours) lead to undesirable evaporation of Mn and In, which, in turn, separates the composition from the region of existence of the magnetostructural PT. The violation of the integrity of the film leads to its unsuitability for the further manufacture of microactuators. The empirically selected regimes 4.1 - 4.4 do not change the chemical composition of the film, but the question of the crystallization of samples remains open. In the Ni-Mn-In films under study (an amorphous film and an annealed film for 15 min at 550 °C), a ferromagnetic Curie point is observed. A decrease in the width of the ferromagnet-paramagnet PT and the shift of the Curie point result from an improvement in the crystallinity of the sample after annealing.

Acknowledgments
The reported study was funded by RFBR and Moscow city Government according to the research project No. 19-37-70012 and partially was carried out within the framework of the state task. The authors are grateful to Prof. M. Ohtsuka from Tohoku University for the preparation of the original samples, as well as to N.Yu. Tabachkova and A.V. Irzhak from NUST "MISiS" for assistance in conducting experiments.

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