Study of layered system $\text{Fe}_3\text{Sn}_2-\alpha$-$\text{Fe(Sn)}$ obtained by ion-plasma sputtering and thermal annealing

A K Zhubaev$^1$, S K Yerezhepova$^1$, A A Karassayeva$^1$ and Ye A Kantarbay$^2$

1 Physics Department, Aktobe Regional University, 34 Aliya Moldagulova av., Aktobe, 030000, Kazakhstan
2 International IT University, 34/1 Manas str., Almaty, 050040, Kazakhstan

mosslab.kz@mail.ru

Abstract. Thin Armco Iron foils with a Tin coating deposited by ion-plasma sputtering and subjected to isothermal annealing at 650°C have been studied by Mössbauer spectroscopy. The formation of intermetallic compounds $\text{FeSn}$ and $\text{Fe}_3\text{Sn}_2$, as well as a solid solution of Tin atoms in $\alpha$-$\text{Fe(Sn)}$, was revealed. The possibility of obtaining a thermally stable layered spatially inhomogeneous $\text{Fe}_3\text{Sn}_2-\alpha$-$\text{Fe(Sn)}$ system is shown.

1. Introduction
As shown in [1-2], the mutual diffusion of the coating components and the base material determines the processes under the influence of high temperatures on the coatings. In this case, all phases of a given binary system are detected in the near-surface layers. The thermodynamic approach [3] for solving the problem of chemical compatibility of heat-resistant surface layers with high-temperature alloys involves determining the composition and phase-structural states for the substrate and coating, which ensures the absence of chemical potential gradients for all alloy components at a given temperature. In this case, the coating and the base are in an equilibrium state and have different functional properties.

The presence of regions of existence of a solid solution of Tin in Iron $\alpha$-$\text{Fe(Sn)}$ with various intermetallic compounds on the state diagram of the binary Fe-Sn system is a distinctive feature of this binary system [4]. For this reason, based on the Fe-Sn system, it is possible to create models of layered systems consisting of a thermally stable coating (intermetallic compound) and a substrate that is a solid solution.

In this paper, the thermally induced phase formation processes in two-layer Sn-Fe systems were studied by the methods of Mössbauer spectroscopy on $^{57}$Fe and $^{119}$Sn nuclei.

2. Experimental
The substrates for the studies were prepared from a bar of armco iron (99.8% Fe) by rolling on a roll to a thickness of $\approx 8 \pm 1 \mu$m and subsequent homogenizing annealing at a temperature of $850^\circ$C for 2 hours. The deposition of Tin on Iron foil substrates was carried out by method of ion-plasma sputtering. The layer thicknesses were selected so that the average concentration of tin atoms over the entire sample volume was in the two-phase region of the phase diagram, which consists of a solution of $\alpha$-$\text{Fe(Sn)}$ and an intermetallic compound. The temperature of thermal annealing ($T_{\text{ann}}=650^\circ$C) was...
chosen based on the results of studies [5] of a layered system Sn(4 μm)-Fe(10 μm) subjected to isochronous thermal annealing in a wide temperature range. Sequential isothermal annealing of two-layer Sn(4 μm)-Fe(8 μm) systems was carried out at a temperature of 650°C up to 20 hours in a vacuum furnace with a residual pressure of 6×10⁻⁶ mm Hg. Samples were studied by Mössbauer spectroscopy (MS) methods on ⁵⁷Fe and ¹¹⁹Sn nuclei at room temperature. The fitting of the experimental spectra was carried out using the DISTRI program by reconstructing the distribution functions of the hyperfine parameters of the partial spectra and SPECTR program by model decoding [6].

3. Results
Layered system Sn(4 μm)-Fe(8 μm) have been studied using Mössbauer spectroscopy on ⁵⁷Fe nuclei. Figure 1a shows the spectra of the layered system after successive isothermal annealing at a temperature of 650°C. It can be seen (Fig.1a) that after 0.5 h of annealing, partial spectra of another magnetically ordered phase appeared against the background of intense six lines from α-Fe. At the next stage (after annealing for 1 h), the spectrum shows some growth of satellite lines near the intense extreme reflexes from α-Fe and the disappearance of the resonant lines of the newly formed phase. With an increase in the duration of annealing, the picture practically does not change. The experimental spectra of this layered system in the first approximation correlate well with the model spectra of the Sn(4 μm)-Fe(10 μm) layered system [7].

Figure 1. Mossbauer spectra of ⁵⁷Fe (a) and ¹¹⁹Sn (c) nuclei, as well as the result of reconstruction (b) of the distribution functions of the effective magnetic field \( H_n \) (on ⁵⁷Fe nuclei) after consequent isothermal annealing

In one of the first works [8-9] on the study of the FeSn compound using the Mössbauer spectroscopy on ⁵⁷Fe nuclei, it was reported that the spectrum of this intermetallic compound is a single Zeeman sextet with an internal magnetic field of ~110 kOe. The data obtained for the isomeric shift \( \delta \) and the quadrupole shift \( \varepsilon \) are very different. This is due to both the quality of the experimental spectra and the insufficiently developed mathematical apparatus for processing the spectra. According to the authors of [10], the three equivalent positions (h1, h2 and h3) of Iron atoms in the Fe-Sn
compound correspond to three Zeeman sextets with the parameters: \( \delta=0.68\pm0.02\) mm/s (relative to sodium nitroprusside), \( \varepsilon=-0.45\pm0.02\) mm/s and \( H_1=120.9\pm1.5\) kOe, \( H_2=113.6\pm1.5\) kOe and \( H_3=101.4\pm1.5\) kOe, respectively.

Taking into account the type of experimental spectra, the processing was carried out by the method of reconstructing two distribution functions of the magnetic field \( H_\alpha \) in the intervals of \( 80\) kOe\( \leq H_\alpha \leq 220\) kOe and \( 260\) kOe\( \leq H_\alpha \leq 360\) kOe. Figure 1b shows that the reconstructed first distribution function for the layered Sn-Fe system after 0.5 h of annealing has a polymodal form. With an increase in the annealing time, the mode in the region of 100 kOe shifts and then disappears, and the type of distribution in the region of 160-220 kOe does not undergo significant changes. The arrows show the values of the fields specific to the FeSn [10]. It is obvious that the newly formed phase is the intermetallic compound FeSn.

Based on studies of the authors [11], in which by Mössbauer spectroscopy on \(^{57}\)Fe nuclei is defined connection parameters \( \text{Fe}_2\text{Sn}_2 \): \( \delta=0.37\pm0.01\) mm/s (relative to \( \alpha\)-Fe), \( \varepsilon=0.21\pm0.02\) mm/s, \( H_1=196\pm3\) kOe, and given the above, the modes in the range of 160-220 kOe were related to intermetallic \( \text{Fe}_3\text{Sn}_2 \).

The distribution in the range of 260-360 kOe fields has a two-modal form with local maxima of \(-310\) kOe and \(-330\) kOe, which correspond to Fe atoms in a solid solution of \( \alpha\)-Fe(Sn) with 1 Sn atom in the nearest environment and Fe atoms without impurity atoms in the first coordination sphere, respectively. According to the phase diagram [4] of the Fe-Sn binary system, the solubility of Tin in Iron at 650°C exceeds 3 at. %.

The study of this layered system have been performed using Mössbauer spectroscopy on \(^{119}\)Sn nuclei (Fig.1c). It can be seen that any diffusion processes were excluded during coating, and the Mössbauer spectrum of the two-layer sample is a singlet line from the \(^{119}\)Sn nuclei to \( \beta\)-Sn. Even after the first annealing, significant changes are observed in the spectrum, which occur up to annealing within 3 hours. The increase in the duration of heat treatment did not affect the appearance of the experimental spectrum.

The results of Mossbauer studies on \(^{119}\)Sn nuclei of the antiferromagnetic compound FeSn at temperatures from 77°K to the magnetic transition temperature are presented in paper [10]. The occupation of the Sn 1(a) and 2(d) positions is determined by the ratio 1:2. Mössbauer parameters of the intermetallic compound at room temperature is equal to \( \delta=1.97\pm0.05\) mm/s, \( \varepsilon=2.14\pm0.10\) mm/s and \( \delta_1=2.14\pm0.05\) mm/s, \( \varepsilon_1=2.82\pm0.10\) mm/s, \( H_1=14.4\pm1.5\) kOe. Thus, the Mössbauer spectrum of an intermetallic FeSn represents a superposition of a doublet and a sextet. The intermetallic compound \( \text{Fe}_3\text{Sn}_2 \) was studied by method of Mössbauer spectroscopy on \(^{119}\)Sn nuclei between 5 and 670°K [12]. It was found that at room temperature, the spectrum of this intermetallic compound consists of two sextets with parameters: \( \delta_1=1.92\) mm/s, \( \varepsilon_1=1.62\) mm/s, \( H_1=52\) kOe, \( \delta_2=1.79\) mm/s, \( \varepsilon_2=1.04\) mm/s, \( H_2=15.5\) kOe.

Figure 1c shows the positions of the spectral lines for FeSn and \( \text{Fe}_3\text{Sn}_2 \). The positions of the spectral lines for the \( \alpha\)-Fe(Sn) solid solution [13] are also presented. It can be seen that the newly formed phases can be identified as the intermetallic compounds FeSn and \( \text{Fe}_3\text{Sn}_2 \) and the solid solution \( \alpha\)-Fe(Sn).

Based on the results of processing the Mossbauer spectra, the dependences of the relative intensities of the partial spectra of samples of different phases on the annealing time were obtained (Fig.2). For sufficiently thin samples, the intensity of the spectrum is proportional to the number of Mossbauer nuclei. Then, assuming that the probability of the Mössbauer effect is equal for different phases, it follows that Figure 2 shows the dependence of the relative content of the phases in the atomic units of Iron and Tin.

Figure 2a shows that after 0.5 h of annealing, the relative content of intermetallics FeSn and \( \text{Fe}_3\text{Sn}_2 \) is \( \approx7\%\) and \( \approx17\%\), respectively. Subsequent annealing leads to the decomposition of the intermetallic compound FeSn and an increase in the relative contribution of the second intermetallic compound. Further, the contributions of the \( \text{Fe}_3\text{Sn}_2 \) intermetallic compound and the \( \alpha\)-Fe(Sn) solid
solution are stabilized. This trend of the appearance, followed by the decay of the Fe-Sn intermetallic compound and the stabilization of Fe$_3$Sn$_2$ with $\alpha$-Fe(Sn) also occurs for the dependences of the relative intensities $I$ of the partial Mossbauer spectra of $^{119}$Sn nuclei (Fig.2b).

![Graphs showing the relative intensities of $^{57}$Fe and $^{119}$Sn nuclei in the formed phases on the time of thermal annealing at 650°C]

**Figure 2.** Dependences of the relative intensities $I$ of the partial Mossbauer spectra of $^{57}$Fe (a) and $^{119}$Sn(b) nuclei in the formed phases on the time of thermal annealing at 650°C

Thus, after isothermal annealing of the layered system Sn(4 $\mu$m)-Fe(8 $\mu$m) at 650°C, first, as a result of mutual diffusion, the dissolution of Tin atoms in the Iron matrix takes place and the formation of intermetallic compounds FeSn and Fe$_3$Sn$_2$, as well as a solid solution of tin atoms $\alpha$-Fe(Sn). With an increase in the duration of heat treatment, the stabilization of the resulting layered spatially inhomogeneous Fe$_3$Sn$_2$–$\alpha$-Fe(Sn) system is observed.

4. Conclusions
As a result of the studies carried out, a sequence of phase transformations in layered Sn-Fe systems subjected to isothermal annealing was established; the relative content of formed phases in the sample at each annealing step is obtained; the formation of a thermally stable spatially inhomogeneous Fe$_3$Sn$_2$–$\alpha$-Fe(Sn) system is revealed.

References
[1] Novikov I I 1986 *Theory of thermal treatment of metals* (Moscow, Metallurgiya) (in Russian)
[2] Kolomytsev P T 1991 *High-temperature protective coatings for nickel alloys* (Moscow, Metallurgiya) (in Russian)
[3] Kadyrzhanov K K 2001 *Physical fundamentals of ion technologies for creating stable multilayer metal materials* (Almaty) (in Russian)
[4] Lyakishev N P 1997 *Diagrams of the state of double metal systems* (Moscow, 1997) (in Russian)
[5] Zhubaev A K et al 2019 *J. Phys.: Conf. Series* 1393 012155
[6] Rusakov V S 2000 *Mossbauer spectroscopy of locally inhomogeneous system* (Almaty, INP NNC RK) (in Russian)
[7] Zhubaev A K et al 2019 *J. Phys.: Conf. Series* 1281 012097
[8] Yamamoto H 1966 *J. Phys. Soc. Japan* 21 1058
[9] Djega-Mariadassou C et al 1966 *Nuovo Cimento* 46 35
[10] Kulshreshta S K and Raj P 1981 *J. Phys. F: Metal Phys.* 11 281
[11] Ichiba S et al 1968 *Bull. Chem. Soc. Japan* 41 2791
[12] Le Caer G et al 1979 *J. Phys. F: Metal Phys.* 9 1905
[13] Vincze I and Aldred A T 1974 *Phys. Rev.* 9 3845