Mössbauer studies of the effect of swift heavy ion irradiation on electrodeposited Sn-Co-Fe coatings

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Abstract. 57Fe and 119Sn conversion electron Mössbauer spectroscopy was used to study the radiation effect of 246 MeV Kr and 710 MeV Bi ions on electrochemically deposited amorphous Sn-Co-Fe coatings. The ion dependent changes induced by the swift heavy ion irradiation in the chemical short range order of these amorphous thin films regarding Fe and Sn atoms are discussed within the framework of the transient thermal spike model.

1. Introduction
Recently there has been a resurgence of interest in the use of electrochemical deposition to achieve compositionally modulated alloys, which provide an attractive range of properties through changes of the structure. In our previous research [1, 2] we were able to produce a new range of good quality Sn-Co-Fe ternary alloys using an environmentally acceptable electrolyte based on sodium gluconate. These novel ternary alloys have metastable structures which do not exist in the thermal equilibrium diagrams. 57Fe and 119Sn Mössbauer investigations supported by XRD analysis confirmed the amorphous nature of the coatings. Swift heavy ion irradiation is a well known method to modify the chemical short range order in solids resulting in materials with more favourable properties regarding technological applications. The aim of the present work was to study the effect of swift heavy ion irradiation on these novel Sn-Co-Fe coatings.

2. Experimental
The coatings were deposited on Cu substrates using a constant current technique in a static flow plating system using the following electrolyte composition: 0.02M SnSO4, 0.09M CoSO4, 0.09M FeSO4, 120 g/l Na-gluconate and 0.1 g/l peptone, at a cathode current density of 1 A/dm², an electrolyte temperature of 60 °C and pH=7.0. The deposition time was 20 min and the thickness of the resulting coatings was 3.96 µm. The composition of the deposits was 47.56% Sn, 22.89% Co and 29.55% Fe.

The irradiation of the samples was carried out with 246 MeV energy Kr and 710 MeV energy Bi ions at room temperature in a vacuum of about 10⁻³ Pa at the U-400 cyclotron of the Flerov Laboratory
of Nuclear Reactions, JINR, Dubna, Russia. The ion fluences applied were $5 \times 10^{13}$ ion/cm$^2$ in the case of Kr ions and $1 \times 10^{13}$ ion/cm$^2$ in the case of Bi ions.

$^{57}$Fe and $^{119}$Sn conversion electron Mössbauer (CEM) spectra of the samples were recorded by a conventional Mössbauer spectrometer (WISSEL) working in constant acceleration mode at room temperature. The conversion electrons were detected by a flowing gas (96% He, 4% CH$_4$) proportional counter (RANGER). A 50 mCi activity $^{57}$Co/Rh source supplied the gamma rays for the $^{57}$Fe measurements, while a 16 mCi activity Ca$^{119m}$SnO$_3$ source was used in the case of the $^{119}$Sn measurements. The velocity calibration was performed by $^{57}$Fe measurements. The evaluation of the Mössbauer spectra was performed by least-square fitting of the lines using the MOSSWINN code [3].

3. Results and discussion
The $^{57}$Fe CEM spectrum of the as-deposited sample (Fig. 1.1) exhibits an envelope of magnetically split spectrum with broad lines. Such spectra are typical for amorphous alloys and can be considered as a superposition of a large number of elementary spectra belonging to slightly different microenvironments of iron atoms having various alloying elements in their neighbourhoods. In accordance with our previous research [1, 2], the spectrum was decomposed into a dominant magnetically split sextet with broad lines and a minor doublet (Tab. 1), which were attributed to a ferromagnetic and a paramagnetic Sn-Co-Fe alloy respectively.

![Figure 1](image.png)

Figure 1. $^{57}$Fe and $^{119}$Sn CEM spectra of the as-deposited (1, 2), irradiated with 246 MeV energy Kr ions (3, 4) and irradiated with 710 MeV energy Bi ions (5) Sn-Co-Fe coatings.
Similarly to the $^{57}$Fe CEM spectrum, the $^{119}$Sn spectrum of the as-deposited sample (Fig. 1.2) exhibits a magnetically split envelope with very broad lines and was decomposed into a dominant sextet and a minor doublet (Tab. 1). Since Sn is nonmagnetic, the magnetic splitting is probably due to a transferred hyperfine field, which originates from the neighbouring magnetic atoms.

Table 1. $^{57}$Fe and $^{119}$Sn Mössbauer parameters of the as-deposited and irradiated Sn-Co-Fe coatings.

| Mössbauer parameters | As-deposited | 246 MeV Kr, $5 \times 10^{13}$ ion×cm$^{-2}$ | 710 MeV Bi, $1 \times 10^{13}$ ion×cm$^{-2}$ |
|----------------------|--------------|---------------------------------------------|---------------------------------------------|
| $^{57}$Fe (doublet), mm/s | 0.30         | 0.41                                        | 1.87                                        |
| $^{119}$Sn (doublet), mm/s | 2.00         | 0.77                                        | 0.51                                        |
| $^{57}$Fe (sextet), mm/s | 0.93         | 0.77                                        | 0.47                                        |
| $^{119}$Sn (sextet), mm/s | 0.55         | 0.51                                        | 0.47                                        |
| $^{57}$Fe (sextet), T | 0.15         | 0.13                                        | 0.75                                        |
| $^{119}$Sn (sextet), T | 1.92         | 1.82                                        | 1.75                                        |
| $^{57}$Fe (doublet), % | 28.7         | 29.4                                        | 5.37                                        |
| $^{119}$Sn (doublet), % | 5.37         | 4.69                                        | 5.58                                        |
| $^{57}$Fe (sextet), % | 76.3         | 72.2                                        | 92.4                                        |
| $^{119}$Sn (sextet), % | 92.4         | 85.6                                        | 90.8                                        |

Along with Mössbauer spectroscopy, the samples were also investigated by X-ray diffraction. In the X-ray diffractograms of the as-deposited samples [2] the main peaks, except the lines belonging to the Cu substrate, are very broad, reflecting the amorphous character of the coatings, which is in good agreement with the CEMS results. No changes could be observed in the crystalline structure of the deposits after the irradiation with 246 MeV Kr or 710 MeV Bi swift heavy ions, the X-ray diffractograms of the irradiated samples reflect essentially the same amorphous character of these thin films as in the case of the as-deposited sample.

The most striking changes induced by the swift heavy ion irradiation in these Sn-Co-Fe coatings are reflected by the changes in the values of the hyperfine field of the sextets. The field increases in the case of $^{57}$Fe (Fig. 1.3) and, at the same time, decreases in the case of $^{119}$Sn (Fig. 1.4) after the irradiation with 246 MeV energy Kr ions (Tab. 1). These changes can be associated with a decreased number of ferromagnetic Fe and Co atoms in the neighbourhood of paramagnetic Sn atoms in the case of irradiation with Kr ions. On the other hand, the value of the hyperfine field increases after the irradiation with 710 MeV energy Bi ions in the case of $^{119}$Sn (Fig. 1.5). This can be attributed to an increased number of Fe and Co atoms in the neighbourhood of Sn atoms in the case of Bi ion irradiation.

Calculations made with the SRIM 2008 code [4] show that both, Kr and Bi ions deposit their energy in the samples via inelastic collisions with the electrons in the medium and the respective values of the electronic stopping power for the 47.56% Sn-22.89% Co-29.55% Fe alloy are 19.98 keV/nm and 48.86 keV/nm. Since these values are several orders of magnitude higher than those of the nuclear stopping power, the thermal spike mechanism [5] can be considered as the main driving force responsible for the changes in the chemical short range order of these amorphous thin films observed in the Mössbauer spectra. In this case, the observed changes in the chemical short range order can be attributed to the effect of the additional mixing of the elements due to the swift heavy ion irradiation, which occurs as a consequence of a transient molten state diffusion [6]. Studies conducted on pure crystalline metals irradiated at low temperatures show that in the case of low velocity ions as in our case, thermal spikes occur only above a threshold value of 24 keV/nm [7]. In the case of Bi irradiation the value of the electronic stopping power highly exceeds this threshold value, consequently the Bi ions induce a considerable mixing effect resulting in a more disordered amorphous state, which corresponds to a more random distribution of the constituent elements as compared to the as-deposited amorphous state. This would result in an increased number of Fe and Co atoms in the neighbourhood of Sn atoms as we observed on the basis of the Mössbauer spectra. Similar effects were observed in the case of Fe$_{40}$Ni$_{30}$B$_{20x}$Si$_{x}$ and Fe$_{x}$Ni$_{80-x}$P$_{20}$ amorphous alloys in which the degree of the disorder increased upon swift heavy ion irradiation [8]. However, in the case of Kr
ions the value of the electronic stopping power is under the threshold value of the thermal spike initiation, consequently one would expect a different effect than in the case of Bi ions. Although, the thermal spike mechanism cannot be entirely excluded as it was pointed out that in the case of amorphous materials and irradiations performed at room temperature the threshold value can be reduced [9]. In this case, the changes caused by Kr ions could be mainly attributed to irradiation induced defect creation as well as partial segregation and rearrangement [10] of the constituent elements from the amorphous towards an ordered state. This could easily result in a decreased number of Fe and Co atoms in the neighbourhood of Sn atoms, accordingly, the average value of the hyperfine field increases at the Fe sites and decreases at the Sn ones as we observed.

4. Conclusions
Swift heavy ion irradiation of electrodeposited Sn-Co-Fe coatings induces ion dependent changes in the chemical short range order of these amorphous thin films regarding Sn and Fe atoms. The observed changes can be explained by the mixing of the elements within the thermal spikes as a consequence of a transient molten state diffusion in the case of Bi ions and irradiation induced defect creation as well as partial segregation and rearrangement in the case of Kr ions.

References
[1] Kuzmann E, Stichleutner S, Doyle O, Chisholm C U, El-Sharif M, Homonnay Z and Vértes A 2005 AIP Conf. Proc. 765 99
[2] Chisholm C U, Kuzmann E, El-Sharif M, Doyle O, Stichleutner S, Sólymos K, Homonnay Z and Vértes A 2007 Appl. Surf. Sci. 253 4348
[3] Klencsár Z, Kuzmann E and Vértes A 1996 J. Radioanal Nucl. Chem. 210 105
[4] Ziegler J F, Biersack J P and Littmark U 1985 The Stopping and Range of Ions in Solids (Pergamon, N. Y.)
[5] Toulemonde M, Dufour Ch and Paumier E 1992 Phys. Rev. B 46 14362
[6] Wang Z G, Dufour C, Euphrasie S and Toulemonde M 2003 Nucl. Instr. Methods B 209 194
[7] Wang Z G, Dufour C, Cabeau B, Dural J, Fuchs G, Paumier E, Pawlak F and Toulemonde M 1996 Nucl. Instr. Methods B 107 175
[8] Kuzmann E and Spirov I N 1985 J. Nucl. Mater. 135 22
[9] Gupta A 2000 Vacuum 58 16
[10] Nolfi F V 1983 Phase transformations during the irradiation (Applied Science Publishers, London)