Nuclear Instruments and Methods in Physics Research B xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

# Transformation of amorphous alloy surface and thin film under impact of slow heavy ions

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ARTICLE INFO

*Article history:*
Received 20 October 2016
Received in revised form 11 April 2017
Accepted 11 April 2017
Available online xxxx

*Keywords:*
Amorphous alloys
Ion implantation
Surface sputtering
Surface crystallisation
Conversion electrons Mössbauer spectroscopy – CEMS
Particle induced *X*-ray emission – PIXE

ABSTRACT

In this work thin foils of amorphous alloys VP800 ($Fe_{73}Si_{16}B_7Cu_1Nb_3$) and VV8025X ($Fe_4Co_{66}B_{14}Cu_1Nb_2Mo_1$) maintained at the onset point temperature for primary crystallisation were irradiated with slow heavy ions (100–300 keV Ar and Xe) at the fluence changing from $10^{10}$ to $10^{13}$ ions/cm$^2$. The preferential surface modification during ion implantation-sputtering was analysed with SRIM and PIXE. With the use of CEMS Fe and Fe(Si) clusters accompanied by $Fe_3Si$ and even $Fe_{23}B_6$ nanocrystals were found in the films irradiated at a lower fluence, whereas rather amorphous structure was found in surfaces more heavily implanted.



## 1. Introduction

Amorphous alloys, far from thermodynamic equilibrium, undergo stress relaxation and partial crystallisation if some amount of energy is supplied [1–4]. These transformations under a single ion impact are related to thresholds, either in the potential energy, ~ 10 keV deposited by a highly charged ion (HCI) or with the threshold in electronic energy loss, ~ 5 keV/nm transferred by a swift heavy ion (SHI). This energy is $10^2$ times faster deposited to the electronic system of the material through electronic excitations ($\tau_e \sim 10^{-15}$ s), than subsequently transferred to the lattice through the electron–phonon coupling ($\tau_a \sim 10^{-13}$ s) [5–9]. The damage creation can be described within Thermal Spike [5,6] or Coulomb Explosion models [8,9]. The pulse of energy and shock wave can cause rearrangement of target atoms and relaxation of internal stresses. The process is governed by mobility, or by thermal conductivity of electrons, which may be substantially reduced in amorphous alloys, in comparison to metals, due to some clustering in the alloys, which introduces borders.

An elemental composition of the alloy is also important for structural and magnetic transformations, but preferential sputtering under the impact of heavy ions (HI) can change the content of the surface. In case of $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ (called Finemet) Cu drives crystallisation acting as a nucleation centre, whereas Nb retards a crystal growth process, producing a large number of small crystallites instead of a small number of larger ones [1]. An important task is to produce nano-crystals of a radius smaller than the exchange–correlation length.

Recently, a crystallization induced by GeV Pb ions at low fluences in amorphous alloys, which exhibit a two steps thermal crystallisation (like Finemet) was reported [10], as opposed to the absence of this crystallisation in alloys going through a single step thermal crystallisation, like $Fe_{40}Ni_{35}Si_{10}B_{15}$. In this case, only the secondary (without primary) crystallisation phase was observed, probably in some correlation with the absence of Cu [10].

Crystallities of 1–4 nm were formed around an amorphous ion track of 6–8 nm in diameter, thus a single ion converts material from initially amorphous to other amorphus and crystalline structures roughly within 100 nm$^2$ area. The fluence of $10^{11}$ ions·cm$^{-2}$ gives on average 1 ion per 1000 nm$^2$ area, so the places where ions hit the surface are well separated. The energy deposition from 5 GeV Pb ions to the Finemet through electronic stopping is 40 keV/nm [12] which is sufficient for activation of crystallisation [2,3]. The two-step crystallisation process (Fe(Si) and Fe(B)), which is characteristic for a thermally treated bulk Finemet, after the irradiation was converted into a single-step crystallisation, where the only one became the secondary crystallisation (Fe(B)). The alloys

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http://dx.doi.org/10.1016/j.nimb.2017.04.039
0168-583X/

with one-step crystallisation did not crystallise in response to irradiation [10].

In this paper it was shown that the impact of relatively slow and relatively heavy ions can also cause structural and magnetic transformations of the amorphous alloys surface, monitored by Mössbauer spectroscopy, the phenomenona up to now reserved only for slow HCI and fast HI and restricted by the energy thresholds.

## 2. Theoretical

### 2.1. Analytical approach – Thermal Spike Model

The impact of an energetic ion on the surface transfers locally an enormous amount of energy to the electron–phonon system. The description of the process within the thermal spike model [5,6] is based on the differential equations:

$$\partial_t T_e = \frac{1}{r}\cdot\partial_r[rD_e\cdot\partial_r T_e] - g(T_e - T_i) + S \tag{1}$$

$$\partial_t T_i = \frac{1}{r}\cdot\partial_r[rD_i\cdot\partial_r T_i] - g(T_i - T_e),$$

where $T$'s are the temperature distributions for electrons $e$ and ions $i$ respectively, $D$'s are diffusivities, $g$ is the electron–phonon coupling constant of the order of $5\times10^{18}$W/K/m$^3$ [11] and $S$ is the source of energy.

In the simplest case describing the time evolution of thermal spike temperature distribution $T_e(r,t)$ the Eqs. (1) can be replaced by the heat diffusion equations in the cylindrical reference frame

$$\partial_t T(r,t) = \frac{\lambda}{\rho c}\frac{1}{r}\partial_r(r\partial_r T(r,t)), \tag{2}$$

where: $r$ is the distance from $z$-axis selected along the ion track, $c$ is the specific heat, $\lambda$ is the heat conductance and $\rho$ is the volume density. Subjected to the initial condition: $|d_xE|\delta(r) = \rho cT(r,0)$, where $|d_xE|$ is the energy loss per unit distance, the analytical solution of Eq. (2) is

$$T(r,t) = \frac{|d_xE|}{4\pi\lambda t}\exp\left(-\frac{\rho cr^2}{4\lambda t}\right). \tag{3}$$

In Fig. (1) is presented the distribution of temperature $T(r,t)$ induced by 300 keV Xe ion which stops in Fe with $d_xE = 6$ keV/nm at depth of $R_{range} = 47$nm in $t_{stop} = 3*10^{-13}$ s. It shows that boiling of Fe is possible within a cylinder of the 3.5 nm radius and melting occurs within 4.5 nm.

The sputtering yield $Y$ from the thermal spike is determined by the evaporation flux $j(r,t)$ of $m$-mass atoms with a Maxwellian energy distribution, the energy of which exceeds the surface binding energy $U_s$

$$Y = \int \mathbf{d^2r}\int dtj(r,t) = \frac{\Gamma(3/2)}{24\sqrt{2}\pi^{3/2}}\frac{|d_xE|^2k_B}{\lambda\sqrt{m}U_s^{3/2}} \tag{4}$$

$$j(r,t) = n\sqrt{\frac{k_BT(r,t)}{2\pi\ m}}\exp\left(-\frac{U_s}{k_BT(r,t)}\right), \tag{5}$$

provided that $\rho c \approx 3nk_B$, where $k_B$ is the Boltzmann constant. The yield $Y$ is thus inversely proportional to the surface binding energy, $U_s^{3/2}$ (≈1 eV, different for atomic species in multicomponent material) which causes preferential sputtering.

Initially amorphous alloys exposed to energetic heavy ions suffer modification of subsurface properties. This is caused by the deposition of a large amount of energy accompanied by selective sputtering of surface elements and unavoidable implantation of the beam ions, leading to a local formation of new structural and magnetic phases. In simple terms, the 200 keV Ar ion, which statistically stops in $2\times10^{-13}$ s after travelling in an alloy a projected length equal to 100 nm, transfers to electrons the power of 0.15 W, $\sim M_i/Nm_e$ times more effectively than to ions, where $N$ is the ionization degree. If we accept that the thermal conductivity of the alloy is smaller than that of the iron, ~ 80 W/m/K, due to lower mobility of electrons caused by the presence of grains and boundaries closing atomic clusters, the temperature in the track centre will jump well above 3000 K, as shown in Fig. (1). This is higher than the melting points of all the components in the alloy, even if the sample, as a whole, is maintained in thermal contact with $LN_2$ cryostat. The track center is cooled at $10^{11}$ K/s and solidified in the secondary amorphous phase by transferring heat to a

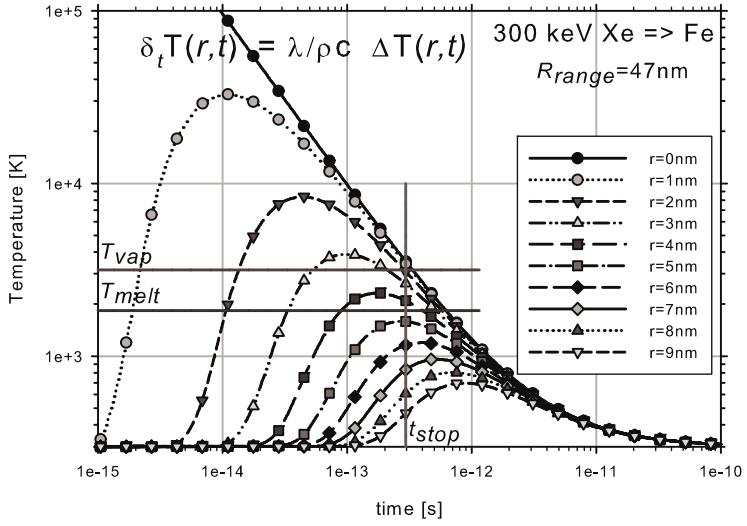


**Fig. 1.** Temperature as a function of distance $r$ and time $t$ from the ion track induced by impact of 300 keV Xe ion on Fe surface. The iron specific heat $c$ = 440 J/kg/K, heat conductance $\lambda$ = 80 W/m/K and volume density $\rho$ = 7870 kg/m$^3$ are the data for bulk Fe. The Fe melting 1811 K and vaporizing 3134 K temperatures are shown by horizontal markers. The ion stops in $3\times10^{-13}$ s after passage of 50 nm [12].

Please cite this article in press as: R. Brzozowski, M. Moneta, Transformation of amorphous alloy surface and thin film under impact of slow heavy ions, Nucl. Instr. Meth. B (2017), http://dx.doi.org/10.1016/j.nimb.2017.04.039