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Temperature-dependent modifications in the surface composition of Finemet: A ToF-SIMS study

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Abstract

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed as an *in situ* tool to study the temperature-induced alteration of the surface composition of amorphous Finemet, $Fe_{73}Si_{15.8}B_{7.2}Cu_1Nb_3$. Temperature was changed reversibly by cooling from room temperature to 118 K and warming back to room temperature. As a general result, the ion intensities and, consequently, the surface concentrations of the alloy constituents were found to vary non-monotonously. Therefore segregation processes were in operation the extent of which was element-specific. Most importantly, while cycling the temperature hysteresis behaviour was observed with concentration of Fe developing just opposite to that of the alloying elements. Accordingly, on cooling the alloy, the surface enrichment with B, Si, Nb, Cu attained first a maximum in the range of 248–193 K before the segregation changed the trend to establish appreciable depletion of these elements at 118 K (as compared to room temperature). By contrast, the surface iron content developed inversely and decreased first to a minimum at ~223 K before reaching enrichment at 118 K. During warming, a maximum segregation of boron and silicon was observed at about 223 K – similar as on cooling – so that this temperature can be considered characteristic of the segregation process. Dissociative adsorption of water from the residual atmosphere occurring at low temperatures was responsible for the formation of surface hydroxides of iron, silicon and niobium; an enhanced adsorption of molecular water was observed at temperatures below 153 K. The temperature-dependent segregation and adsorption–desorption processes were found to be largely reversible, so that the surface composition of Finemet was practically restored after finishing the cooling–warming cycle. The processes and factors governing the non-monotonous temperature dependence of the surface segregation in the amorphous alloy are discussed within the frame of segregation theory and the influence of temperature-induced tensile stress on segregation.

Keywords: Amorphous alloy; ToF-SIMS; Surface segregation; Low temperature

1. Introduction

Amorphous metallic alloys are typically produced by quenching of the melt and remain in this metastable glassy state at room temperature for a long period of time. Due to their special structure and corresponding novel properties, the interest in these alloys has increased rapidly during the past years [1]. Upon heating, rapidly solidified materials experience phase transformations involving structural relaxation and subsequent crystallization. Physico-chemical processes occurring in amorphous alloys Fe–B and Fe–Ni–P–B in the course of dynamic heating to temperatures above the crystallization point and subsequent cooling were studied [2] by SIMS and found to have a significant effect on the emission of secondary ions of the main constituents. Auger electron spectroscopy studies

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revealed a redistribution of elements and segregation processes to take place on the surface during annealing of Fe–Ni–P–B [3] and Co–B [4] amorphous alloys.

Some metallic glasses (in particular, Fe–Si–B-based alloys), when annealed at relatively low temperatures, yield nanometric precipitates dispersed in an amorphous matrix. These nanostructured materials, which were obtained in a controlled crystallization process and thus called 'Finemet', have found numerous practical applications due to their excellent soft magnetic properties. The magnetic properties, crystallization kinetics and structural changes of Finemet were studied extensively, but there is still a lack of data describing in detail the influence of the temperature on the surface composition. Recently, it was reported [5] that annealing of the initially amorphous Finemet Fe–Si–B–Nb–Cu in vacuum at temperatures ranging from 823 to 873 K caused an enrichment of the surface in silicon and boron and a depletion of iron.

In the low-temperature region, below room temperature, studies of the structure, composition and properties of amorphous alloys are rather scarce. Temperature dependent magnetic properties of Finemet-type alloys were measured between 300 and 2 K. It was found that coercivity, magnetization and magnetostriction of the amorphous state of Finemet $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ increased with decreasing temperature [6], with the trend of magnetization in this temperature region being indicative of the presence of spin wave excitations in the alloy [7]. Measurements of the magnetic properties of nanocrystalline $Fe_{73.5}Cr_5B_{16}$-$Cu_1Nb_{4.5}$ alloy showed [8] a strong magnetic hardening at low temperatures characterized by a rapid increase in the coercive field by nearly two orders of magnitude below ~30 K.

A number of questions for the structural and compositional changes in amorphous metallic alloys at low temperatures are still open. It was believed that no appreciable alterations in the structure and composition should occur because they require thermal activation. On the other hand, after immersion of the Fe–Si–B, Fe–Co–Si–B amorphous ribbons into liquid nitrogen for 2–6 h, irreversible changes in the magnetic properties were observed [9], which were assumed to be caused by a modification of the short-range order and a homogenization of the amorphous structure induced by thermo-elastic stress. Moreover, the low-temperature treatment of amorphous alloy $Co_{57}Ni_{10}Fe_5Si_{11}B_{17}$ in liquid nitrogen for 10–120 min was shown [10] to bring about a redistribution of the components in the surface layer of the amorphous material due to low-temperature diffusion of metal–metalloid clusters in the temperature gradient field.

In previous work [11], using X-ray photoelectron spectroscopy (XPS) and ToF-SIMS, we investigated *in situ* the surface composition of amorphous Finemet $Fe_{73}Si_{15.8}B_{7.2}Cu_1Nb_3$ held at a temperature of 118 K. It was found that the surface concentrations of the alloy constituents under these conditions noticeably differed from those at room temperature. The goal of the present work was to study in detail the variation of the surface composition of the $Fe_{73}Si_{15.8}B_{7.2}Cu_1Nb_3$ amorphous alloy in the course of dynamic cooling and subsequent warming. To monitor *in situ* the surface compositional changes, ToF-SIMS was employed.

2. Experimental

The sample was cut from an amorphous ribbon, 10 mm wide and 25 μm thick, produced by a single roller melt-spinning technique (Institute of Metal Physics of the National Academy of Sciences of Ukraine). Its nominal composition was $Fe_{73}Si_{15.8}B_{7.2}Cu_1Nb_3$ (Finemet-type alloy). X-ray diffraction analysis confirmed that the alloy was in the amorphous state. According to small-angle X-ray scattering data, inhomogeneities (precipitates) of ~2 nm in size were present at the most.

Experiments were performed in a combined ToF-SIMS/XPS instrument at a base pressure of 9.5×10^{-10} mbar. The ribbon was placed on a copper substrate 1 mm thick and fixed in a stainless-steel sample holder. The holder enabled cooling of the ribbon with a flow of liquid nitrogen through a cold finger pressed to the rear of the substrate. The temperature at the surface of the ribbon was monitored with a Ni–NiCr thermocouple. Prior to cooling, the sample surface was sputter-cleaned by 500 eV Ar^+ ion bombardment (current density ~2.6 μA cm^{-2}). For analysis, the outer surface of the ribbon (shiny side) was used, which was not in contact with the copper quenching wheel during rapid solidification of the melt and thus underwent a more regular quenching. The sample was gradually cooled down to a temperature of 118 K. In the range from room temperature to 153 K the cooling rate was ~2.4 K/min but decreased at lower temperatures. After holding the amorphous alloy at 123–118 K for ~45 min the liquid nitrogen flow was terminated and the sample was warmed up back to room temperature. The warming rate in the range from 118 K to 223 K was 2.7 K/min and then decreased. The overall cooling–warming cycle took 1100 min. During the cooling–warming cycle, the sample surface was analyzed *in situ* using static ToF-SIMS. Mass spectra of secondary ions taken sequentially at different temperatures were obtained with a pulsing (7.7 kHz) beam of 5 keV Ar^+ ions, using a reflectron analyzer (Kore Technology). At each temperature, a mass spectrum was acquired during 6 s that corresponded to an ion dose of about 2×10^{12} ions/cm^2 and was well below the static SIMS limit. Positive secondary ions extracted at 1400 V were registered in the mass range up to $m/z = 400$ with a mass resolution of $m/\Delta m = 1230$ at FWHM of $m/z = 51$. The analyzed area was about 1 mm^2. The integral area under a particular peak in the mass spectrum was taken as a measure of the emission intensity of corresponding secondary ions. Analysis of the residual gas atmosphere in the sample chamber was performed with a quadrupole mass spectrometer (Hiden Analytical).