The surface composition of amorphous Finemet, Fe\(_{73}\)Si\(_{15}\)B\(_{8}\)Cu\(_{5}\)Nb\(_{x}\), was studied by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The as-received sample in the original state and after Ar\(^+\) sputter-cleaning was analyzed at room temperature as well as after cooling to \(-155^\circ\)C. In the cooled state, the surface oxide layer composed of oxides of the alloy constituents was found to be enriched with elemental iron and depleted of elemental silicon, boron, oxygen and carbon as compared to the state at room temperature. Interaction of residual water vapor and hydrogen with the complex oxide layer occurring at low temperatures is believed to be responsible for the enhanced formation of surface hydroxides of the alloy constituents. The processes resulting in the observed redistribution of the elements on the surface of Finemet at low temperatures are discussed.

Copyright © 2006 John Wiley & Sons, Ltd.

**KEYWORDS:** amorphous alloy; XPS; ToF-SIMS; low temperature; segregation

**INTRODUCTION**

Amorphous metallic alloys represent an important class of materials, with a number of their properties being often superior to those of their crystalline counterparts. Among them, ‘Finemet’-type alloys deserve special interest owing to their outstanding soft magnetic properties attained after partial crystallization.\(^1\) Finemet is a Fe–Si–B-based amorphous alloy containing additions of Cu and Nb, which develops a very fine nanocrystalline structure after annealing at moderate temperatures. As a result of thermal treatment, not only the magnetic property but also corrosion and catalytic properties of Finemet undergo essential alterations.\(^2\) Obviously, chemical and electrochemical properties of these alloys are determined to a significant extent by the structure as well as the elemental and phase composition of the surface layer. Both, preparation and annealing conditions play a dominant role in this respect. To monitor the physicochemical state of the surface layers, X-ray photoelectron spectroscopy (XPS) is the most frequently employed. In particular, XPS analysis has shown that the corrosion behavior of amorphous alloys Fe\(_{78}\)Cr\(_{10}\)Pt\(_{2}\)Cu\(_{5}\)\(^3\) Co\(_{0.1}\)Fe\(_{77.8}\)Si\(_{10}\)B\(_{16}\)\(^4\) and Finemet Fe\(_{76.5}\)Si\(_{15.8}\)B\(_{8}\)Cu\(_{5}\)Nb\(_{x}\)\(^5\) is related to the surface composition of the native oxide film formed in atmosphere on the alloy surface and modified by various pretreatments.

In contrast to extensive investigations of the structure, composition and properties of amorphous alloys annealed at moderate temperatures and temperatures close to the crystallization point, corresponding studies in the low-temperature region are rather scarce. In a pioneering work, Bayankin *et al.*\(^6\) investigated the effect of liquid-nitrogen temperature on the surface composition, corrosion and strength of amorphous alloy Co\(_{75}\)Ni\(_{10}\)Fe\(_{15}\)B\(_{7}\). A redistribution of elements in the surface layer caused by the low-temperature treatment was observed. It was also found\(^7\) that immersing amorphous alloys Fe\(_{71}\)Si\(_{6}\)B\(_{13}\) and Fe\(_{60}\)Co\(_{20}\)B\(_{14}\)Si\(_{1}\) into liquid nitrogen for 2–6 h resulted in irreversible changes of magneto-optical, magnetostatic, thermal and mechanical properties. This was suggested to be caused by a homogenization of the amorphous structure induced by thermo-elastic stress. Mild annealing of the Finemet alloy Fe\(_{74}\)Si\(_{13.8}\)B\(_{6}\)Cu\(_{5}\)Nb\(_{2}\) at 393 K prior to immersion into liquid nitrogen brought about changes in the coercive force which were dependent on the duration of both annealing and low-temperature treatment.\(^8\) In all these studies, the measurements were performed after withdrawal of the sample from liquid nitrogen, i.e. *ex situ*, at room temperature, yielding residual post-treatment effects. The aim of the present work was to study the surface composition of the Finemet Fe\(_{72}\)Si\(_{15.8}\)B\(_{8}\)Cu\(_{5}\)Nb\(_{2}\) at low temperatures *in situ*, using XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

**EXPERIMENTAL**

The sample used in the experiments was cut from an amorphous ribbon, 10-mm wide and 25-µm thick. The Finemet-type alloy of nominal composition Fe\(_{72}\)Si\(_{15.8}\)B\(_{8}\)Cu\(_{5}\)Nb\(_{2}\) was...

---

\(^1\) Institute of Metal Physics, National Academy Sciences of Ukraine, Blvd. Akad. Vernadsky 36, 03680 Kiev-142, Ukraine
\(^2\) Université Libre de Bruxelles (ULB), Chimie-Physique des Matériaux, CP243, Campus Plaine, B-1050 Bruxelles, Belgium
\(^3\) Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
produced using a single roller melt-spinning technique at the Institute of Metal Physics (National Academy of Sciences of Ukraine). The amorphous state of the as-quenched alloy was verified by X-ray diffraction analysis.

Experiments were performed in a combined ToF-SIMS/XPS instrument at a base pressure of 8.7 × 10^{-10} mbar. The ribbon was placed on a copper substrate 1-mm thick and fixed to 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 measured with a Ni–NiCr thermocouple. Prior to cooling, the original sample surface was sputter-cleaned by 500 eV Ar⁺ bombardment (current density ∼8 μA cm⁻²) for 10 min and SIMS and XPS spectra were collected. For the analysis, the outer surface of the ribbon was used that was not in contact with the wheel and therefore underwent a more regular uniform quenching (shiny side). This side is preferable because it is devoid of a considerable number of imperfections and corrugations that are inherent to the dull (contact) side. After ion bombardment, the sample was kept in vacuum for 22 h and then was cleaned again using 500 eV Ar⁺ ions for 1 min. Afterwards, the amorphous alloy was gradually cooled down to a temperature of −150 °C at an average rate of 2.4 °C/min. After holding for ∼45 min at −150 to −155 °C, XPS and static ToF-SIMS analyses were performed in sequence.

For XPS, a nonmonochromatic Mg Kα radiation was employed with the source operated at a power of 150 W. Photoelectron spectra were acquired with a hemispherical analyzer in the constant pass-energy mode at E₀ = 50 eV. The overall resolution of the spectrometer in this operating mode was 0.96 eV, measured as a full width at half-maximum (FWHM) of the Ag 3d₅/₂ line. The spectrometer was calibrated against E₀(Au 4f₇/₂) = 84.0 eV and E₀(Cu 2p₃/₂) = 932.4 eV.

Mass spectra of secondary ions were obtained with a pulsed (7.7 kHz) beam of 5 keV Ar ions, using a reflection analyzer. Positive secondary ions extracted at 1400 V were registered in the mass range up to m/z = 10² with a mass resolution of m/Δm = 1230 at an FWHM of m/z = 51. During spectra acquisition the ion dose was kept well below the static SIMS limit of 10¹⁵ ions/cm². The integral peak area was taken as a measure of the emitted intensity of corresponding secondary ions. Both XPS and SIMS spectra were taken in three different spots on an area of about 6 × 12 mm² of the sample and the data were reproducible.

RESULTS

XPS analysis

Figure 1 shows the Fe 2p, Si 2p, O 1s and C 1s XP spectra for as-received Finemet, FeₓSi₁₅₋ₓBₓ₂Cu₁Nb₂, in the initial air-exposed state (curves 1), after Ar⁺ sputter-cleaning at room temperature (curve 2) and at −155 °C (curve 3). After subtraction of the Shirley-type background, the core-level spectra were resolved into their components by mixed Gaussian–Lorentzian (G/L) lines with due account of the satellites, using a nonlinear least-squares curve-fitting procedure. The FWHM of the Fe²⁺ and Fe³⁺ components was constrained to be equal⁹ during deconvolution (as well as of the Si oxidized states¹⁰ and of components contributing to the O 1s and C 1s envelopes). Also, the G/L ratio for all the components in a given spectrum was constrained to be equal, except for the Fe 2p satellites where a pure Gaussian was used.¹¹

In the initial state, at room temperature, the peak intensities of the main constituents of the alloy are very low, in contrast to the intense carbon peak (Fig. 1(a) and (d), curves 1). In the Fe 2p spectrum (Fig. 1(a), curve 1), a tiny peak attributed to elemental iron Fe⁰ can be discerned. There are two more components at 710 and 711.6 eV corresponding to the Fe²⁺ and Fe³⁺ states,⁹,¹² respectively. The latter 3+ component is believed to represent a mixture of Fe₂O₃ and FeOOH¹³,¹⁴ and appears to be somewhat more abundant than the Fe²⁺ state originating most probably from Fe₂O₃. The Si 2p spectrum (Fig. 1(b), curve 1) indicates the trace of elemental silicon Si⁰, with the major component at 102.7 eV being related to the air-formed oxide SiO₂.¹⁰ The peaks of boron, copper and niobium were too small to be reliably identified.

The O 1s spectrum (Fig. 1(c), curve 1) is rather wide, thus pointing to a variety of different oxygen environments. A pronounced hump on the low-binding-energy side is formed by the O²⁻ species which yields a peak at 530.2 eV and originates largely from iron oxides.¹⁴ The major component at 532 eV, however, may be attributed to lattice and adsorbed OH⁻ species¹⁵,¹⁶ or to oxygen in FeOOH.¹⁶ The third component in the O 1s envelope located at 533.6 eV may be formed by contributions from carboxyl groups –O–C≡O¹⁷ and adsorbed water.¹⁵ The major component of the C 1s line located at 285.1 eV corresponds to hydrocarbon HC–CH bonds,¹⁸ while the minor components at 286.6 and 288.6 eV can be ascribed to C–O, C–OH¹⁹,²⁰ and O–C≡O¹⁷,²¹ groups, respectively (Fig. 1(d), curve 1). Thus, the original surface layer of Finemet is mainly composed of iron oxides/hydroxides and silicon oxide along with some elemental Fe and Si. Considerable contamination with hydrocarbons is also found. The relative fractions of the different chemical species at the initial alloy surface are presented in Fig. 2(a–d).

Sputter-cleaning of the surface with Ar ions caused an efficient removal of hydrocarbons and uncovered the oxide layer. As a result, the peaks of the alloy constituents, including oxygen, appreciably increased, while the carbon peak strongly decreased (Fig. 1(a–d), curves 2). Now, the peak at 706.9 eV corresponding to elemental iron⁷,¹³ is clearly seen (Fig. 1(a), curve 2). The ratio of the Fe²⁺ and Fe³⁺ components located at 709.9 and 711.6 eV, respectively, has changed in favor of Fe²⁺. The predominance of the Fe²⁺ species in the oxide layer is also evidenced by the appearance of a pronounced characteristic peak at 715.4 eV ascribed to the Fe²⁺ shake-up satellite,⁹,¹²,¹⁴ with a satellite-to-Fe²⁺ intensity ratio (0.24) close to that reported in the literature¹¹ (0.2). Besides, the Auger parameter determined for the principal iron peak a(Fe) = KE (Fe L₃VV) + BE (Fe 2p₃/₂) = 1411.3 eV (KE stands for the kinetic energy of emitted Auger electrons, BE is the binding energy of core-level electrons) is intermediate between the values of 1409.7 eV for pure
Figure 1. The photoelectron Fe 2p (a), Si 2p (b), O 1s (c), C 1s (d) spectra of as-received amorphous Finemet in the initial state (1), after 500 eV Ar⁺ sputter-cleaning at room temperature (2) and in the cooled state at −155°C (3). Chemical species identified by deconvolution of the spectra are indicated. The spectra are displaced vertically for clarity.

elemental Fe²⁺ and 1412 eV for an iron oxide film with prevailing Fe³⁺ state. This points to the Fe²⁺ species as a major component in the alloy oxide layer.

On the sputter-cleaned surface of Finemet, the Si 2p peak at 99.6 eV, attributed to elemental silicon, becomes rather distinct and, in addition to the major component at 102.8 eV related to air-formed silicon oxide, a new species at 104 eV arises which can be attributed to SiO₂. This is in accordance with work in Ref. 23, in which a nonstoichiometric oxide SiOₓ (x ≈ 1.3) was studied. After low-energy (500 eV) Ar⁺ ion bombardment of this oxide, in addition to the dominating component at 102.5 eV in the Si 2p spectrum ascribed to the Si³⁺ species, a higher oxidation state of silicon, Si⁴⁺, associated with SiO₂ was observed to emerge at 104.1 eV. Besides, the SiO₂ species were found to arise after 3-keV Ar⁺ ion sputtering of as-received Finemet Fe₇₃Si₁₅B₇Cu₃Nb₃, in addition to elemental silicon and oxide SiO₂. Similar components (Si⁰, SiO, and SiO₂) in the Si 2p spectra have also been reported for amorphous alloys CoₓFe₆₀₋ₓSi₁₈B₁₀.

In the O 1s band of sputter-cleaned Finemet (Fig. 1(c), curve 2) the main peak is located at 531.2 eV. It can be ascribed to O⁻ species, which bear an electron density lower than that of the O²⁻ ions. These species are associated with low-coordinated oxygen ions, which may exist in the amorphous oxide layer, and form M–O bonds with a higher covalence. The smaller component at 532.3 eV may result from adsorbed OH⁻ species, and the tiny peak at 533.4 eV is attributed to adsorbed water. Similar components located at 532.1 and 533.3 eV were found to arise in the O 1s spectrum of iron exposed to water vapor and were therefore assigned to adsorbed OH and H₂O species, respectively. According to a study, adsorption of water on the preoxidized iron surface at room temperature proceeds via hydrogen transfer from the water molecule to the surface oxygen atom to form a hydroxyl group.
Figure 2. The relative fractions of the different chemical species present on the surface of Finemet in the initial state, after Ar$^+$ sputter-cleaning at room temperature and in the cooled state at $-155\, ^\circ C$ derived from deconvolution of the Fe 2p (a), Si 2p (b), O 1s (c), and C 1s (d) XP spectra (Fig. 1). To make the trends more demonstrative, the shown fractions of some species with low content ($Fe^0 \, a$, $Si^0 \, b$, $H_2O \, c$) are multiplied by a certain factor.

Dissociative adsorption of water on silicon can produce the hydroxyl Si–OH groups. 29 In the C 1s spectrum of sputter-cleaned Finemet a new component arises at 284.6 eV (Fig. 1(d), curve 2) which corresponds to carbon impurity in a graphitelike form. 12 Another peak at 285.4 eV can be related to the remnant dehydrogenated hydrocarbons 12 and/or to chemisorbed C–H species. 38 A very low contribution of ether C–O and/or carbonyl C=O groups at 287.5 eV 20 is identified. Note that sputter-cleaning efficiently destroyed and removed carboxyl groups, so that the pronounced peaks at 288.6 eV in the C 1s band and at 533.6 eV in the O 1s spectrum for initial-state Finemet (Fig. 1(c) and (d), curves 1) have practically vanished. These bands have formerly been attributed to O–C=O groups.

The other alloy constituents are identified as low-intensity peaks at 192.4 eV (B 1s), 207.6 eV (Nb 3d$^{5/2}$) and 933.1 eV (Cu 2p$^{3/2}$), indicating their presence in oxide form as boron oxide, 24 Nb$_2$O$_5$, and CuO. 31

Cooling of Finemet to $-155\, ^\circ C$ does not result in the modification of the set of chemical species; only the relative abundance of those identified for the clean surface at room temperature changes (Fig. 1(a–d), curves 3). Also, a slight variation of the peak position for some species is observed. In particular, the Fe$^{2+}$ and Fe$^{3+}$ peaks have moved to lower BEs of 709.7 and 711.4 eV, respectively (characteristic for $Fe^0$ and FeOOH 14), indicating a decrease in ionic bond character, which is probably associated with lower oxygen coordination. No noticeable changes in the Auger parameter $\alpha(Fe)$ and in the XPS valence band of Finemet at $-155\, ^\circ C$ are detected as compared to those at room temperature.

Figure 2(a–d) allow the comparison of the relative abundance of the different chemical species on the surface of Finemet at room temperature and at $-155\, ^\circ C$. It is seen that in the cooled state the fraction of elemental Fe$^0$ increases (from 7.2 to 9.5%), while the Si$^0$ fraction decreases (from 6.9 to 3.5%). Cooling reduces the abundance of the Fe$^{2+}$ species (and intensity of the Fe$^{3+}$ satellite decreases); instead, the population of the Fe$^{3+}$ states increases (Fig. 2(a)), so that the ratio Fe$^{2+}$/Fe$^{3+}$ drops from 3.2 to 2.4. This appears to be associated with an enhanced formation of FeO–OH on the surface due to adsorption of water vapor.
and hydrogen at low temperatures and is consistent with the growth of the fraction of oxygen species related to \( \text{OH}^- \) and \( \text{H}_2\text{O} \) (Fig. 2(c)). By contrast, the fraction of \( \text{O}^- \) species decreases. In addition, the interaction of water with Si might also produce surface Si–OH bonds and SiO-type species\(^{29}\) which would increase the respective fraction (Fig. 2(b)). Adsorption of residual hydrocarbons and hydrogen occurring at low temperatures causes the growth of the fraction of C–H species; at the same time, contamination of the surface by elemental carbon decreases (Fig. 2(d)).

**ToF-SIMS analysis**

In Fig. 3(a–d) are plotted the intensities of the peaks of selected secondary ion species (most abundant isotopes) emitted from the surface of Finemet in the initial state, after sputter-cleaning at room temperature and in the cooled state at \(-155^\circ\text{C}\). The mass spectrum of the initial surface of Finemet (as-received, air-exposed) is dominated to a great extent by the peaks of hydrocarbons \( \text{C}_x\text{H}_y \) (Fig. 3(d)). Because of a considerable contamination of the surface, the peaks of the main alloy components are strongly suppressed (Fig. 3(a–c)); in particular, no \( \text{Nb}^+ \) emission is detected. Cleaning of the surface by 500-eV Ar\(^+\) bombardment for 10 min has, however, resulted in an effective removal of hydrocarbons so that all ion peaks related to the main components appear with higher intensity. The native oxide/hydroxide layer on the alloy surface appears to be rather thick because sputtering has not removed it completely: indeed, the ratio of the peak intensities \( \text{FeOH}^+ / \text{FeO}^+ \) and \( \text{SiOH}^+ / \text{Si}^+ \) for the clean surface has not significantly changed as compared with the initial state (Fig. 3(c), open bars). According to the literature, the thickness of the oxide layer on Finemet is between 2.5–4\(^{24}\) and 5–10 nm.\(^5\)

Cooling of Finemet down to \(-155^\circ\text{C}\) causes alterations of the surface elemental and phase compositions. Note the striking conformity in the trends of changes in the surface composition revealed by both XPS and SIMS when decreasing the temperature from ambient to \(-155^\circ\text{C}\) (Figs 2 and 3). In the cooled state, a somewhat higher Fe\(^+\) emission is observed (Fig. 3(a)). On the contrary, the Si\(^+\) and B\(^+\) peak intensities at \(-155^\circ\text{C}\) have decreased by about 15 and 27%, respectively (Fig. 3(a)), thus indicating a noticeable depletion of these elements at the surface as compared to room temperature. The Cu\(^+\) peak has diminished by about 30%, while the Nb\(^+\) peak shows little variation. The intensity

![Graphs showing the intensity of selected peaks in the mass spectra of secondary ions emitted from Finemet in the initial state, after Ar\(^+\) sputter-cleaning at room temperature and at \(-155^\circ\text{C}\).]

**Figure 3.** Intensity of some selected peaks in the mass spectra of secondary ions emitted from Finemet in the initial state, after Ar\(^+\) sputter-cleaning at room temperature and at \(-155^\circ\text{C}\). The ratio of ion peaks \( \text{FeOH}^+ / \text{FeO}^+ \) is also shown (c).
ratios $\text{Si}^+/\text{Fe}^+$ and $\text{B}^+/\text{Fe}^+$ have changed from 1.05 and 0.035 at room temperature to 0.88 and 0.025 at $-155^\circ\text{C}$, respectively.

Note that the increase in the $\text{Fe}^+$ ion yield at $-155^\circ\text{C}$ seems to reflect mainly the variation of the elemental iron concentration on the surface rather than results from the so-called chemical ion emission associated with chemisorption of reactive species. Indeed, the Finemet was already covered with an oxide layer and negligible content of the reactive species in the residual atmosphere could not change the degree of oxidation of the surface during extremely low exposures. Besides, if it had been the effect of the adsorbed species, this would have caused the enhancement of the ion yield for all the components of the alloy, particularly, of those with a high affinity to electronegative species. However, this is at variance with the experiment: while the $\text{Fe}^+$ yield rises, the emission of $\text{Si}^+$, $\text{B}^+$ and $\text{Cu}^+$ drops.

The FeO$^-$ emission decreases when Finemet is cooled to $-155^\circ\text{C}$ (Fig. 3(b)). At the same time, the emission of FeOH$^+$ ions increases (Fig. 3(c)), so that the ratio FeO$^-$/FeOH$^+$ drops from 0.5 to 0.3, i.e. by a factor of 1.67. This is clearly consistent with a decrease in the Fe$^{2+}$ fraction (related to oxide FeO) and with an increase in the Fe$^{3+}$ fraction (attributed mainly to hydroxide FeOOH) observed by XPS (Fig. 2(a)). The lowering of the FeO$^-$ emission is caused by a diminution of the oxygen coordination in iron oxide (which would result in a decrease of probability of ejecting Fe$^{3+}$ ions), while the growth of the FeOH$^+$ emission is induced by the hydroxylation of the surface due to enhanced adsorption of water and hydrogen at low temperatures. This is corroborated by the increase in H$_2$O$^-$ emission (Fig. 3(c)) resembling the growth of the H$_2$O fraction in XPS (Fig. 2(c)) and a higher H$^+$ emission (Fig. 3(d)). Besides, the chemisorption of hydrogen at low temperatures is accompanied by a ~50% rise in the FeH$^+$ emission. Hydroxylation of the surface at $-155^\circ\text{C}$ is also responsible for the reduced emission of SiO$^-$ and NbO$^-$ species (Fig. 3(b)) and for the enhanced emission of SiOH$^-$ (Fig. 3(c)) and NbOH$^-$.

In accordance with XPS data (Fig. 2(d)), SIMS reveals the increase in emission of C$_2$H$_7^+$ (Fig. 3(d)) associated with some low-temperature adsorption of residual hydrocarbons. At the same time, the C$^+$ peak slightly decreases (Fig. 3(d)), thus implying that the C$^+$ species arise from adventitious impurity carbon rather than from hydrocarbons (though the latter cannot be completely excluded).

However, the compositional changes revealed by SIMS in Finemet after cooling to $-155^\circ\text{C}$ differ quantitatively from those found with XPS, which appear to be associated with different information depths of the methods. In SIMS, secondary ions originate mainly from the top one to two atomic layers, while XPS probes larger depths, up to about threefold photoelectron mean free path (roughly, for Finemet $3\lambda_{mm} \sim 3$ nm for the Fe 2p and $\sim 4.7$ nm for the Si 2p photoelectrons). Thus the greater cooling-induced changes observed by XPS (about +32% for the elemental Fe and $-49\%$ for the elemental Si content) might indicate a stronger enrichment with Fe and depletion in Si of the subsurface region. Iron in metallic form appears to be present on the surface in very small quantities. Upon cooling, it segregates from the bulk most likely at the metal–oxide interface, yet diffusing through oxide to the surface, which yields some increase (about $+2\%$) in the Fe$^+$ emission detected by SIMS.

**DISCUSSION**

It has been shown$^{33}$ that oxide scale formed at 350°C in air on amorphous alloy Fe$_{70}$Si$_{15}$B$_{15}$ consists of many relatively large oxide particles, mainly Fe$_{2}O_{3}$ and Fe$_{3}O_{4}$, embedded in a thin continuous layer of a fine oxide matrix rich in silicon oxide. As follows from our XPS data, similar structure and composition of the native oxide layer can be expected to form on the surface of Finemet, with some FeOOH added. The sputter-cleaned surface of Finemet, according to the XPS and SIMS data, is composed of oxides of the alloy constituents including the presence of elemental forms of Fe and Si. The availability of elemental Fe and Si may result from the formation of the Fe–Si chemical bonds preventing complete oxidation of these elements. The principal component of the layer is iron oxide represented by the Fe$^{2+}$ and Fe$^{3+}$ states, with the Fe$^{2+}$ species being dominant and yielding the specific Fe$^{2+}$ satellite. The same chemical species of close binding energies and similar phase composition were reported$^4$ for the native oxide layer formed on amorphous alloys Co$_x$Fe$_{50-x}$Si$_{15}$B$_{15}$ ($x = 0, 15, 70, 80$). So, iron and silicon were observed to be present in both elemental and oxidized forms. The iron oxide was also composed of the major Fe$^{2+}$ (indicated by the Fe$^{2+}$ satellite) and minor Fe$^{3+}$ states, and the silicon oxide was a mixture of the suboxides SiO$_2$ and SiO$_2$. Hence, neither substitution of Fe atoms with Co in the above alloy nor the presence of Nb and Cu in Finemet noticeably influences the binding energies of the other components. The obtained characteristics of the surface oxide layer on Finemet in the as-received state and after sputter-cleaning are also in many respects similar to those observed in a previous work$^{34}$ on Finemet of nearly the same composition, Fe$_{73}$Si$_{15}$B$_{12}$Cu$_{1}$Nb$_{3}$. The Fe$^{0}$, Fe$^{2+}$, Fe$^{3+}$ components were also resolved in the Fe 2p spectrum of the native oxide of amorphous alloy Fe$_{70}$B$_{30}$. While oxide film of the as-received Fe$_{70}$B$_{30}$ was represented mainly by the Fe$^{2+}$ species, after 3-keV Ar$^+$ sputtering for 4 min the Fe$^{3+}$ species grew in abundance and the Fe$^{2+}$ satellite at 715.8 eV appeared.

Ar$^+$ ion bombardment at 500 eV of $\alpha$-Fe$_2$O$_3$ crystal was reported$^{35,36}$ to produce a disordered, oxygen-deficient surface exhibiting several Fe valence states, Fe$^{3+}$, Fe$^{2+}$, Fe$^{0}$, with a major contribution from Fe$^{2+}$ cations. The reduction of iron oxides $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO under Ar$^+$ ion bombardment has been shown$^{37}$ to occur owing to preferential sputtering of oxygen. Ion sputtering is the routine to clean the original surface of amorphous alloys. Obviously, 500 eV Ar$^+$ sputter-cleaning of Finemet also caused some reduction of the native iron oxide$^9$ and thereby increased the abundance of the Fe$^{2+}$ state. Preferential sputtering of oxygen appears to be responsible for the emergence of the oxygen-deficient species O$^{2-}$ and OH$^{-}$ revealed by XPS in the cleaned Finemet at higher binding energies than those corresponding to O$^{2-}$ and bulk OH$^{-}$ species in the original oxide (Fig. 1(c)). The surface of the ion-bombarded $\alpha$-Fe$_2$O$_3$ could be restored to its
initial stoichiometry by annealing in vacuum at 820°C or in \(5 \times 10^{-6}\) Torr of oxygen at 330°C.\(^{38}\) Annealing of the damaged Fe\(_2\)O\(_3\) in vacuum brought about a rapid change (occurring within ~1 min) in the surface state of the oxide followed by a much slower alteration.\(^{38}\) In particular, after annealing at 100°C for ~30 min, the degree of restoration of the oxide surface could reach ~30%. However, annealing of the ion-bombarded amorphous alloys is an undesirable procedure inasmuch as it will cause structural and compositional changes in the metastable material. In this respect, Finemet is even more susceptible to heat treatment because it develops a nanostructure already at moderate temperatures. Therefore, to restore at least partly the surface after Ar\(^+\) ion cleaning, we held the Finemet sample in vacuum at room temperature for 22 h. Subsequent Ar\(^+\) bombardment for 1 min employed to remove adsorbed species prior to cooling could only slightly affect the oxidation state of the surface.\(^{30}\)

Annealing of Finemet Fe\(_{76}\)Si\(_{13}\)B\(_{13}\)Cu\(_1\)Nb\(_3\) in vacuum at temperatures 500–600°C was reported\(^{2}\) to cause enrichment of the surface in silicon and boron and their oxidation with depletion of iron. Surface segregation of metalloid components and carbon under heat treatment was observed\(^{38}\) also for other amorphous alloys such as Fe\(_{86}\)B\(_{20}\), Fe\(_{86}\)Ni\(_{10}\)P\(_{14}\)B\(_{41}\). On the other hand, according to an Auger electron spectroscopy (AES) study,\(^6\) the low-temperature treatment of amorphous alloy Co\(_{57}\)Ni\(_{10}\)Fe\(_{5}\)Si\(_{11}\)B\(_{17}\) in liquid nitrogen (~196°C) for 10, 60 and 120 min also brought about an enrichment of the surface with silicon and boron and a depletion of cobalt, oxygen and carbon. Such redistribution of the components in the surface layer of the amorphous material was explained\(^{39}\) by the low-temperature diffusion of metal–metalloid clusters in the temperature gradient field. Also, the significant thermo-elastic and dynamic stresses (~10\(^7\) N/m\(^2\)) arising in the Fe\(_{75}\)Si\(_{13}\)B\(_{13}\) and Fe\(_{86}\)Co\(_{20}\)B\(_{13}\)Si\(_8\) ribbons as a result of quenching of as-quenched amorphous alloys in liquid nitrogen were assumed\(^7\) to be capable of causing surface segregation of metalloids and homogenization of the amorphous structure.

In the present experiments, the opposite pattern was observed, i.e. the surface content of elemental iron in Finemet was found to increase, while the concentration of silicon and boron decreased. The amount of elemental carbon impurity on the surface also decreased. However, in contrast to the studies\(^6,39\) of the surface composition of amorphous alloys performed \textit{ex situ} at room temperature, after termination of the low-temperature treatment, which was carried out by immersing the sample in liquid nitrogen (i.e. by quenching), we measured the surface content of the alloy constituents and impurities \textit{in situ}, after the gradual cooling of Finemet to −155°C and holding it at this temperature. Thus, the effect of thermo-elastic stress and temperature gradients can be excluded. The influence of mechanical bending deformation on the surface composition of amorphous alloy Fe\(_{70}\)Cr\(_{10}\)P\(_{13}\)C\(_{7}\) was studied in work described in Ref. 40 by AES. It was shown that under tensile stress the surface was enriched with iron and oxygen and depleted of carbon, while under compression, on the contrary, a strong segregation of carbon and a depletion of iron and oxygen occurred. The observed redistribution of the alloy constituents was explained by diffusion occurring in the field of elastic strain, which should result in the migration of large-size atoms toward the region of stretching and of small-size atoms toward the compression region. In view of the small thickness of Finemet ribbon and the prolonged holding at ~−155°C (for ~45 min), no appreciable stress gradient is expected to arise in our sample. However, in the cooled state, under equilibrium, the surface of Finemet was depleted of elements with small radius (Si, B, C) and enriched with a large-size component (Fe), as if the surface suffered tensile stress. Probably, such stress might arise in the course of cooling at the interface between the oxide layer and underlying alloy because of the different coefficients of thermal expansion.

Significant silicon segregation observed on the original surface of amorphous alloys Co\(_9\)Fe\(_{80}\)–Si\(_{13}\)B\(_{10}\), Fe\(_{75}\)Si\(_{13}\)B\(_{13}\) and Finemet Fe\(_{76}\)Si\(_{13}\)B\(_{13}\)Cu\(_1\)Nb\(_3\) seems to take place for our sample as well. During Ar\(^+\) ion cleaning of Finemet, silicon is preferentially sputtered from the surface so that the Si 2p/Fe 2p\(_{3/2}\) peak ratio decreases by a factor of 2.5. Note that cooling of the cleaned sample causes further depletion of the surface of silicon.

The surface enrichment in elemental iron at low temperature is accompanied by a depletion of the surface layer of oxygen and some reduction of the prevalent Fe\(^{2+}\) species (Fig. 2(a) and (c)), which might be caused by the migration of oxygen atoms into the oxide to recombine with oxygen vacancies produced by ion bombardment in the subsurface layers.\(^{36}\) This is supported by the observation\(^6\) that after the low-temperature treatment of the amorphous alloy Co\(_{57}\)Ni\(_{10}\)Fe\(_{5}\)Si\(_{11}\)B\(_{17}\) in liquid nitrogen, the surface oxygen concentration and the oxide layer thickness decreased.

Besides, iron oxide might be partially converted to the surface hydroxides FeO–OH/FeO–H because of adsorption of water and hydrogen. The adsorption of water at low temperatures on metallic surfaces, both clean and preoxidized, and on iron oxides was studied in a number of works. It was found\(^41\) that after a 10 Langmuir (L) exposure to D\(_2\)O at room temperature very little water or hydroxyls were present on the surface of the Fe\(_2\)O\(_3\)(111) and the biphase (FeO + Fe\(_2\)O\(_3\)) ordered overlayers which were formed on a sputtered and annealed α-Fe\(_2\)O\(_3\)(0001). However, dosing both the oxide structures with 3 L of D\(_2\)O at ~−188°C gave rise to a significant amount of adsorbed hydroxyls and molecular water, which was revealed by XPS through the appearance of the two new components in the O 1s spectrum at 531.6 and 533.2 eV, respectively. Note that the component corresponding to the adsorbed surface hydroxyl arose at a binding energy that was 0.3–0.5 eV higher than that of the lattice hydroxide component present on the clean surface.\(^41\) For Finemet, we observe a similar shift of 0.3 eV between the adsorbed OH\(^+\) and the lattice OH\(^−\) components (Fig. 1(c)). The fully oxidized stoichiometric α-Fe\(_2\)O\(_3\)(0001) surface is quite inert to H\(_2\)O adsorption. At room temperature, exposures greater than 10\(^3\) L were found\(^{42}\) to be necessary before any significant changes were apparent in the ultraviolet photoelectron spectra (UPS) spectra, which indicated disso- ciative adsorption of H\(_2\)O resulting in adsorbed OH\(^−\) ions. At low temperatures (~73 to ~123°C), only physisorption of
molecular water (ice condensation) was observed.\textsuperscript{36} On the other hand, water was reported\textsuperscript{40} to adsorb dissociatively at \(-153^\circ\text{C}\) on the \((1 \times 1)\) and \((2 \times 1)\) surfaces of \(\alpha\text{-Fe}_2\text{O}_3(012)\) to form terminal and bridging hydroxyl groups by proton transfer to oxygen anion sites, and only at large \(\text{H}_2\text{O}\) exposures bound molecular water was detected in addition; adsorption of water at low temperatures was accompanied by rising emission of the \(\text{FeOH}^+\), \(\text{FeH}_2\text{O}^+\) secondary ions measured by static SIMS. \(\text{Ar}^+\) ion sputtering of the \(\alpha\text{-Fe}_2\text{O}_3\) crystal results in the substantial change in the process of \(\text{H}_2\text{O}\) adsorption. Oxygen-deficient surface containing \(\text{Fe}^{2+}\) cations becomes very active, and at room temperature water dissociates to produce adsorbed hydroxyl species at much lower \(\text{H}_2\text{O}\) exposures than on the stoichiometric \(\alpha\text{-Fe}_2\text{O}_3\).\textsuperscript{42} It is claimed\textsuperscript{38} that water is strongly chemisorbed and dissociates only when reduced \(\text{Fe}^{2+}\) species are present in the outermost atomic plane of \(\alpha\text{-Fe}_2\text{O}_3\), since at low temperature \((-123^\circ\text{C})\) both adsorbed OH species and molecular \(\text{H}_2\text{O}\) species are formed. Similar processes of water adsorption are believed to occur at low temperatures on the sputter-cleaned surface of Finemet, as is evidenced by XPS–SIMS data which demonstrate increasing abundance of the adsorbed OH and \(\text{H}_2\text{O}\) species and rising emission of the \(\text{FeOH}^+\) ions (Figs 2(c) and 3(c)). As to the adsorption of hydrogen, which is the principal component of the residual atmosphere, it may dissociate on the oxidized surface and form \(\text{OH}^-\) radicals with oxygen anions.\textsuperscript{42}

In the absence of the temperature-induced stress gradients, the driving force for segregation in alloys is the difference in the heats of vaporization or free surface energies of the constituents. However, there may be corrections due to relaxation of atoms in the surface layer and the strain energy arising from different atomic sizes of the components. In the cooled state, large Fe atoms may cause stronger distortions, so that the elastic energy may be minimized by driving them to the surface. Moreover, the surface segregation state of the alloy may be modified by adsorption of foreign species. In Ref.\textsuperscript{44} the heat of segregation of a solute was calculated for a large number of alloys with a clean surface and for a surface covered by chemisorbed \(\text{H}, \text{O}\) and CO species. It was shown that not only the magnitude but also the sign of the heat of segregation could change under chemisorption, and the result was strongly dependent on the nature of the adsorbed species. In case of a negative value of the heat of segregation, enrichment of the surface with atoms of the solvent should occur. Indeed, surface segregation in amorphous alloy \(\text{Ni}_{80}\text{Nb}_{20}\) was reported\textsuperscript{45} to be influenced by oxidation in 1 atm \(\text{O}_2\). In \(\text{Fe}_{80}\text{Ni}_{20}\text{B}_{20}\) metallic glass, at low oxygen exposures, boron was observed\textsuperscript{46} to segregate to the surface, while the concentration of iron and nickel decreased. An AES study of the annealing of amorphous alloy \(\text{Fe}_{75}\text{B}_{25}\text{Si}_{8.5}\) in nitrogen, argon, hydrogen and air has revealed\textsuperscript{47} an iron loss from the surface of the ribbon, whereas annealing in an \(\text{H}_2 + \text{H}_2\text{O}\) atmosphere produced a surface strongly depleted of boron but enriched in Si and Fe. In our experiments, the chemisorption of hydrogen and water vapor occurring on the surface of Finemet at low temperatures (Fig. 3(c) and (d)) could also alter the heat of segregation to a negative value\textsuperscript{44} which would stimulate the increase in the surface concentration of solvent (Fe) and decrease the surface concentration of solute components (B, Si, C) as compared to the surface composition at room temperature.

CONCLUSIONS

The native oxide layer formed on the surface of as-received Finemet \(\text{Fe}_{72}\text{Si}_{15}\text{B}_{12}\text{C}_{1}\text{Nb}_{5}\) is composed of oxides of alloy constituents, the major component being iron oxide (as \(\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4\)) and iron hydroxide. Sputter-cleaning of Finemet with Ar ions causes some reduction of the oxide layer. The ion-bombarded oxide is represented by dominant \(\text{Fe}^{2+}\) cations with an admixture of \(\text{Fe}^{3+}\) species; silicon oxide contains both \(\text{Si}_2\text{O}_3\) and \(\text{SiO}_2\) phases. Besides, iron and silicon are present in the surface region in elemental, non-oxidized form. Gradual cooling of Finemet to a temperature of \(-155^\circ\text{C}\) gives rise to an alteration of the surface composition as compared to that at room temperature. Atoms with a larger size migrate toward the surface, while smaller atoms move into the depth, so that in the cooled state the surface concentration of elemental iron increases and that of silicon, boron, oxygen and carbon decreases. Holding the amorphous alloy at low temperature results in an increased formation of the surface hydroxides of iron, silicon and niobium due to an enhanced adsorption of water and hydrogen. At the same time, some reduction of respective oxides accompanied by a lowering of oxygen coordination in the surface layer takes place.

Acknowledgements

The authors thank Dr V. V. Maslov and Dr V. K. Nosenko for the preparation and X-ray characterization of the amorphous alloy precursor.

REFERENCES