HR AES AND XPS INVESTIGATIONS OF Fe-Si-B POWDERS

HR AES- IN XPS-PREISKAVE PRAHOV Fe-Si-B

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Fe-Si-B powders for soft-magnetic composite (SMC) materials were prepared by water-atomisation. The as-prepared powders were analysed using high-resolution Auger-electron Spectroscopy (HR AES). The powders were heat treated in a dry or wet hydrogen. X-ray photoelectron spectroscopy (XPS) was then used to analyse the ion-etched surfaces of untreated and heat-treated Fe-Si-B powders that were sputtered for times from 0 to 1200 s. Fe_2SiO_4, B_2O_3 and SiO_2 were identified as the main components of the oxide layers on the powder grains, their detailed compositions being strongly dependent on the sample's treatment and depth.

Key words: Key words: AES, XPS, Fe-Si-B, SMC, composite, oxide layer

Z vodno atomizacijo smo pripravili prahove Fe-Si-B za mehkomagnetne kompozite (SMC). Sveže pripravljene prahove smo analizirali z visokoločljivo spektroskopijo Augerjevih elektronov (HR AES). Prahove smo toplotno obdelali v suhem ali vlažnem vodiku. Nato smo z rentgensko fotoelektronsko spektroskopijo (XPS) analizirali ionsko jedkane površine neobdelanih in toplotno obdelanih prahov pri jedkalnih časih od 0 do 1200 s. Ugotovili smo, da so glavni konstituenti oksidnih plasti na zrnih prahov Fe_2SiO_4, B_2O_3 in SiO_2, da pa je njihova podrobna sestava močno odvisna od obdelave vzorca in globine.

Ključne besede: AES, XPS, Fe-Si-B, SMC, kompozit, oksidna plast

1 INTRODUCTION

Fe-Si-B powders in a dielectric matrix belong to the class of so-called dielectromagnetics. In the literature they are usually referred to as soft-magnetic composites (SMCs) consisting of a ferromagnetic material embedded in an inorganic or organic-dielectric matrix[1-3]. One of the most interesting features of these materials is the possibility to tailor their composition and processing to meet specific application requirements. In low-frequency applications it is possible to use coarser powdered soft magnetic material with thermoset resin, thus obtaining high permeability and low core losses. The SMC materials find a widespread applications as the cores in transformers, stators in electromotors, and they can also be used as condensers of electromagnetic fields for welding and quenching. They have a higher magnetic induction than ferrites and compared to electrical sheets their electromagnetic performances are isotropic.

Their magnetic properties depend mostly on the particles' size, shape and distribution in the dielectric matrix. Basically, they are soft-magnetic powder particles insulated from each other with either epoxy resin or some other dielectric. The insulation of individual particles is of great importance for the applicability of these materials. Oxides formed on the particle surface may act as an effective insulator providing that at a later stage some binder is applied to keep all the particles together.

In this work we present the results of an initial study of the surface properties of several Fe-Si-B powders that were produced at the IMT using the technique of water-atomisation. The microcrystalline powder alloys of Fe-Si-B were subjected to various heat treatments. During these processes an oxide layer was formed on the surface of each particle. It is the composition of this oxide layer as well as of the bulk of the particle that is the subject of this work. In order to obtain the desired information about the composition of the individual particles and their surfaces and about the averaged composition of the ensemble of particles as a whole we used the high-resolution Auger-electron spectroscopy (HRAES) and X-ray photoelectron spectroscopy (XPS). To the best of our knowledge, this is one of the first attempts to apply surface-spectroscopy techniques to the Fe-Si-B-based system[4-5].

2 EXPERIMENTAL PROCEDURE

The experimental Fe-Si-B powders were atomised using a David Mckee, type D5/2 pilot water-atomiser, resulting in a spherical particle morphology and broad particle size distribution. The composition of the powders was determined using chemical analysis to be: Fe 88,1 %, Si 6,84 %, B, 3,14 %, Ni 1,45 %, C 0,025 % and Al 0,12 %. The size distribution was analysed by a laser-diffraction technique and sieve separation. Only

particles less than 45 μm were selected for further experiments (sample A).

Thermally treated Fe-Si-B powders were also prepared by heating sample A-type powders at 500 °C, and 600 °C in wet (100 ppm water) or dry hydrogen (samples B and C respectively).

AES and XPS analyses of the samples were performed by VG Microlab 310F instrument. The Eclypse v2.1 software package supplied by manufacturer was used for processing the measurements.

For the XPS analysis of the powder samples the powders were fixed on a silver adhesive tape and ion etched with Ar^+ ions at a current of 1.7 μA at 3 keV over the whole area (approx. 50 mm^2) for sputtering times between 0 and 1200 s. It was estimated that at these parameters the thickness of the removed layer fot the total sputtering time was below 0.1 μm.

Mg K_α radiation of 1253.6 eV at a 200 W output power was used for the XPS measurements.

3 RESULTS AND DISCUSSION

Figures 1a and **1b** show SEM and several AES spectra of the areas labelled A1-A4, each belonging to a different grain. The powder particles (grains) are simply pressed onto a silver-glue tape, i.e. the sample does not have any additional binder. This "as-received" sample shows intense Auger-electron signal originating from the oxide layers formed at the particle surfaces and a very intense carbon Auger intensity. Most of this carbon derives from the environmental exposure of the sample during preparation. All spectra show strong intensities of the signals associated with iron while those of silicon and boron are hardly discernible. This is a significant indication that the topmost oxide layer is primarily made up of some of the iron oxides, most probably Fe_2O_3.

In order to be able to explore this, it is necessary to remove surface contaminations, and under controlled conditions, also remove the oxide layer. This is usually done by depth profiling using argon-ion sputtering and Auger spectroscopy. In principle, this technique enables one to explore the chemical composition of the sample starting from the surface and going on ever deeper into the bulk. However, the quantification of the procedure depends critically on an exact knowledge of the sputtering parameters, sputtering cross-sections of the elements and on the effective sputtering current on the sample, and this in turn depends on the sample geometry. As this is extremely hard to achieve for the individual grains in our samples it was decided not to attempt depth profiling but to make use of another technique that enables one to study the interior of the individual grains. Briefly, the powder is pressed into a soft alloy surface, which is then mechanically polished. In this way a number of particles are cut and polished, randomly exposing their interior for the analysis. We have used HRAES to make line-scans across these newly produced surfaces. A detailed account of these experiments will be given elsewhere6. Here it is sufficient to say that the AES results indicate an oxide layer of 1-2 mm thickness. The nominal chemical composition of the particles was found about 5 mm from the surface. This, however, varied from particle to particle.

In the real life we are interested in the properties of the whole ensemble of particles that compose the CMS product. These properties obviously depend on the averaged properties over all the grains. Therefore, it is important not only to study individual grains, like we discussed above, but also to make an analysis over a large number of particles at the same time. This can be achieved by using XPS on basically the same samples as above. In this case, where the sample is a flat surface of about 1 cm^2 (and not one single grain) it is easy to use depth profiling to make an in-depth characterization. Instead of AES we used XPS because in our experimental apparatus it collects photoelectrons from an area of aproximately 5 mm^2.
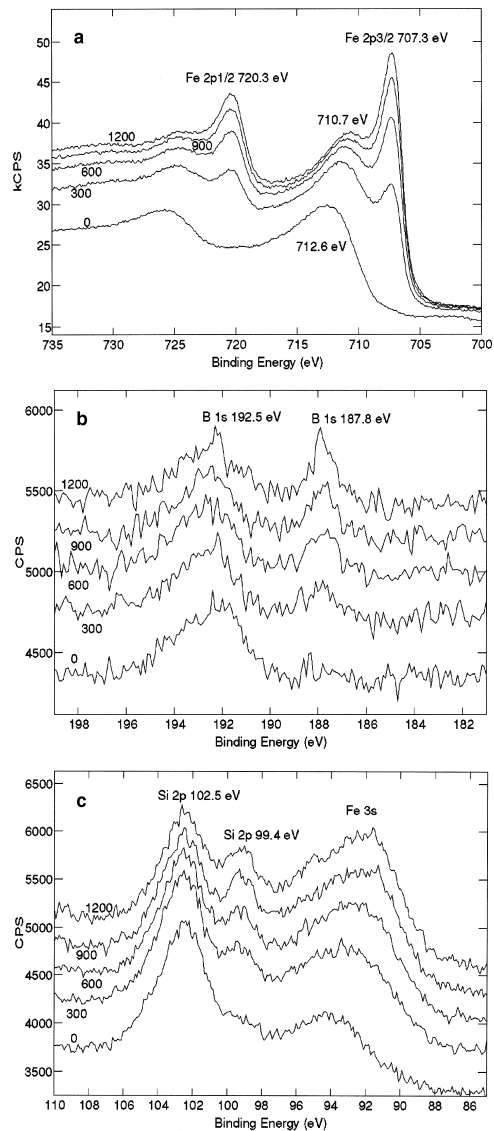
Figure 2 shows the XPS spectra of an untreated powder sample (sample A). Spectra were first measured over the non-sputtered surfaces and then over the progressively sputtered surfaces. In **Figure 2a** the binding energy values (uncorrected) for Fe $2p_{3/2}$ of 707.3 eV, 710.7-710.9 eV and 712.6 eV can be observed in the non-sputtered and sputtered sample. These values should be corrected for the charging effects produced by the ionisation of the sample grains and the silver-glue of the tape. It should be mentioned that both the X-rays and the argon-ion beam induce charging of the sample. Using the standard C 1s peak position at 284.7 eV (carbon contamination) as a reference to determine shifts due to the charging effects, the values of approximately 707 eV, 710.4-710.6 eV and 712.0 eV are obtained after the charge-shift correction. The first two can be interpreted as mainly metallic Fe with some Fe boride and Fe_2SiO_4[7,8], while the last (measured on a non-sputtered surface) may belong to thin Fe2O3 layer on Fe2SiO4 substrate. The supposition that at least partially the intensity of Fe $2p_{3/2}$ at 707 eV in **Figure 2a** is due to the existence of the Fe boride is corroborated by the B 1s peak at 187.8 eV[7,8] in **Figure 2b**. The B 1s peak at 192.5 eV in **Figure 2b** corresponds to B_2O_3[7,8]. **Figure 2c** shows the spectra of Si 2p after different sputtering times where the initial peak at 102.5 eV corresponds to Fe_2SiO_4[7,8], thus corroborating the identification of the Fe $2p_{3/2}$ peak at approximately 710.5 eV in **Figure 2a** as corresponding to Fe_2SiO_4, and an additional peak at 99.4 eV, which develops with sputtering. This additional peak corresponds to photoemission from neutral silicon atoms[7,8].

The problem of charging in these complex systems consisting of metallic grains covered by oxide layers and glued to an organic film containing silver particles for better conduction is illustrated in **Figure 3a**:
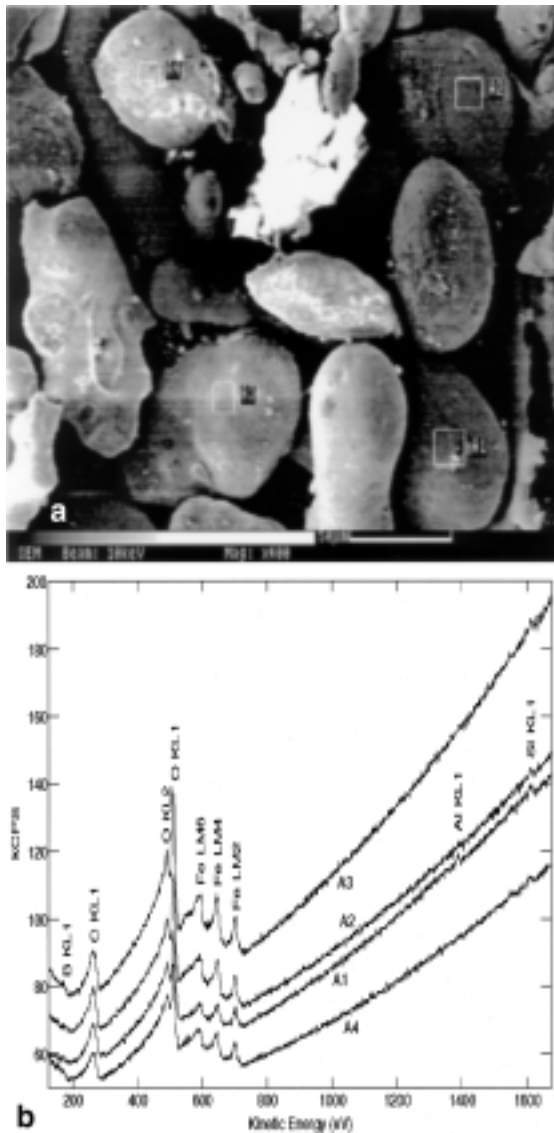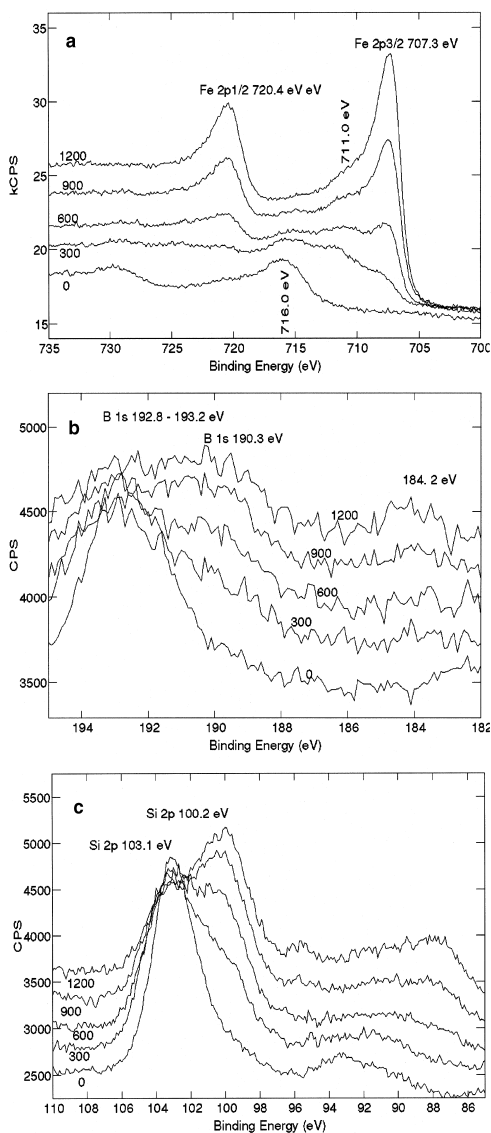
Figure 1: SEM of water-atomised Fe-Si-B powder (a); AES spectra measured from the areas labelled A1-A4 in **Figure 1a** (b)
Slika 1: SEM-posnetek prahu Fe-Si-B (a); AES-spektri, izmerjeni na področjih A1-A4 na **sliki 1a** (b)

Figure 2: XPS spectra of water-atomised Fe-Si-B powder (sample A) sputtered from 0 to 1200 s: Fe 2p (a), B 1s (b), Si 2p (c); spectra in (c) are not corrected for charge shift
Slika 2: XPS-spektri prahu Fe-Si-B (vzorec A) ionsko jedkanega od 0 do 1200 s: Fe 2p (a), B 1s (b), Si 2p (c); v (c) ni upoštevan premik energijske skale zaradi nabijanja vzorca

Binding-energy values (uncorrected) for Fe $2p_{3/2}$ of 707.3 eV, 711.0 eV and 715-715.5 eV can be observed in the spectra of a sample sputtered for 300, 600 and 900 s. Now, the last binding energy value suggests a large charge shift that is incompatible with the first binding-energy value. Possible solution would be to suppose two values for the charge shift deriving from areas of the sample with different properties. If corresponding values for the charge shift are evaluated by deconvoluting C 1s from carbon contamination the values of 0.2-0.6 eV and 3.8-4.2 eV are obtained. This means that three peaks can be interpreted as two peaks at approximately 707 eV and 711 eV, corresponding to smaller shift, and third peak corresponding to a larger shift, again at approximately 711 eV when corrected.

The peak at 711 eV corresponds, most probably, to Fe in a thin layer of Fe_2O_3 being removed by the sputtering[7,8]. The peak at 707 eV may correspond to metallic Fe, however, its intensity may be partially due to Fe boride, since their binding-energy values overlap[7,8]. This is supported by the spectra in **Figure 3b** (charge-shift corrected) where an initial B 1s at approximately 193 eV after sputtering develops additional two peaks at 190.3 eV and 184.2 eV. The first of these values can be ascribed to B_2O_3, the second may be due to some organic boride, possibly produced by some sputter-induced reaction, and the third is too low for any boron compound unless a smaller charge shift is used and this peak gets shifted towards higher binding energies by a

Figure 3: XPS spectra of water-atomised wet-hydrogen annealed Fe-Si-B powder (sample B) sputtered from 0 to 1200 s: Fe 2p (a), B 1s (b), Si 2p (c); spectra in (c) are not corrected for charge shift
Slika 3: XPS-spektri prahu Fe-Si-B (vzorec B) ionsko jedkanega od 0 do 1200 s: Fe 2p (a), B 1s (b), Si 2p (c); v (c) ni upoštevan premik energijske skale zaradi nabijanja vzorca
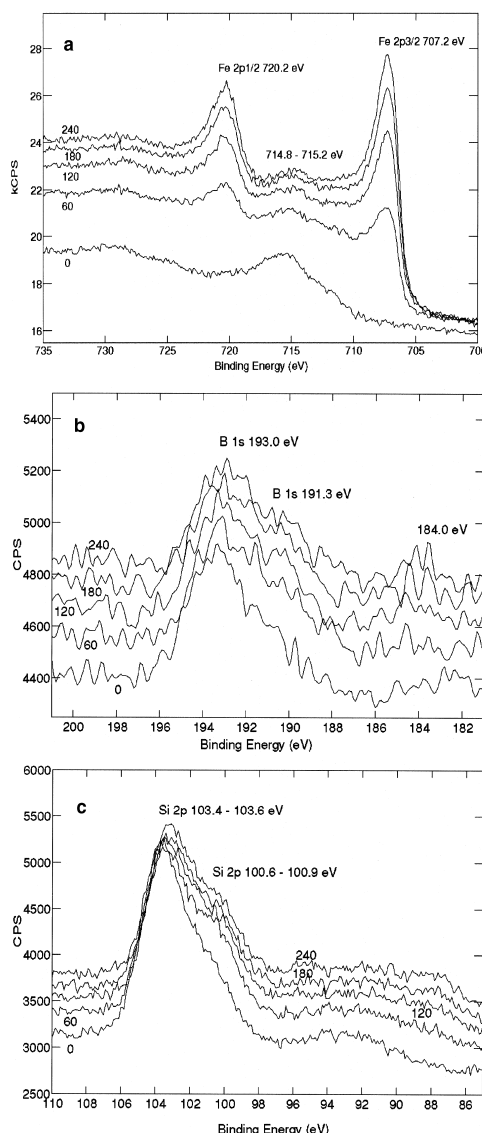
Figure 4: XPS spectra of water-atomised dry-hydrogen annealed Fe-Si-B powder (sample C) sputtered from 0 to 240 s: Fe 2p (a), B 1s (b), Si 2p (c); spectra in (c) are not corrected for charge shift
Slika 4: XPS-spektri prahu Fe-Si-B (vzorec C) ionsko jedkanega od 0 do 240 s: Fe 2p (a), B 1s (b), Si 2p (c); v (c) ni upoštevan premik energijske skale zaradi nabijanja vzorca

difference of two charge shifts to approximately 187.9 eV, which corresponds to Fe boride[7,8]. **Figure 3c** shows the spectra of Si 2p after different sputtering times where the initial peak at 103.1 eV corresponds to SiO_2[7,8]. and an additional peak at approximately 100 eV develops. This additional peak may develop due to some organic silicide, possibly produced by some sputter-induced reaction (sample B).

A similar situation with double charge shifts can also be observed in **Figure 4,** which shows the XPS spectra of sample C. **Figure 4a** shows the spectra of Fe $2p_{3/2}$ with maxima at 707.2 eV and 714.8-715.2 eV. After the charge-shift correction the corresponding values are approximately 707 eV and 711 eV, corresponding to

metallic Fe or Fe boride and Fe_2O_3[7,8]. Fe boride formation is again supported by the B 1s peak at 184.0 eV in **Figure 4b**; its actual binding energy value (with smaller charge shift) is approx. 188 eV[7,8]. B 1s at approx. 193 eV corresponding to B_2O_3 and B 1s at approximately 191 eV, which may appear due to some organic boride, possibly produced by some sputter-induced reaction, can be observed in **Figure 4b**. **Figure 4c** shows the spectra of Si 2p after different sputtering times with a strong peak at approximately 103.5 eV corresponding to SiO_2[7,8] and an additional peak developing at approximately 100.5-101 eV. This additional peak may develop due to some organic silicide, possibly produced by some sputter-induced reaction.

Fe borides, at least in thermally treated samples, should come as no surprise, since they have been known to appear in similar systems, though at slightly higher temperatures (around 700 °C)[9].

As mentioned above, the thickness of the oxide layer is of the order of 1 µm, while the thickness of the removed layer is below 0.1 µm. (Even less for sample C where the total sputtering time is shorter.) At first glance this seems to be at odds with the intense Fe 2p peaks deriving mainly from the metallic Fe measured after finishing the sputtering cycles in all three samples. However, though the metallic Fe content significantly increases with the depth, there are still oxides present: B_2O_3 and Fe_2SiO_4 in sample A; B_2O_3 and SiO_2 in samples B and C but not any more Fe_2O_3 as found in all three samples on the very top surface (also suggested by AES of the non-sputtered surface of the untreated sample, as mentioned above), but removed after the first sputtering cycle. Thus, our results may be interpreted as if only part of the oxide layer has been removed and its composition varies with the depth. This was shown to be the case by the AES line-scans of the powder grains'cross-sections.[6] Also, the estimation of 0.1 µm thickness should not be relied upon since it was arrived at under the assumption of flat sample surface which is not true in the case of the powder sample.

As for the problem of the double charge shift observed in two of the samples, an attempt at an explanation may be presented along the lines of differences in surface roughness of the powder grains for the different samples observable in **Figure 1a**[7,8]. One can imagine that smoother grains are also better connected electrically, while grains with a high surface corrugation may exist such that their conductivity to ground is low. It is these areas that contribute a signal with a high charge shift. Also, sputtering may enhance the conductivity between grains by smoothing out the roughness of the grains in the surface layer and by redistributing the material.

4 CONCLUSIONS

Water-atomised Fe-Si-B powder particles with a regular round shape were produced. HR AES was used to investigate the surface of as-prepared powder particles while XPS spectroscopy combined with ion etching was used to study the surface as well as subsurface layers of untreated and thermally treated powder grains. As-prepared Fe-Si-B powders seem to have an Fe_2SiO_4 layer that changes with depth relatively slowly. Its insulating characteristics are also very favourable, not so, unfortunately, are its mechanical characteristics. In thermally treated Fe-Si-B powders B_2O_3 and SiO_2 appear on the surface. Their concentration decreases with depth relatively quickly compared to the Fe_2SiO_4 concentration in the untreated powder, however, they make for a better oxide layer from the point of view of mechanical characteristics and thus ease the manufacturing process of the SMC from the corresponding Fe-Si-B powder. As already mentioned, this study is an initial investigation of the oxide layers on the Fe-Si-B powder grains. In the future the optimisation of the oxide-layer properties will be attempted by varying the parameters of the powder's thermal treatment.

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