Hyperfine Interactions of ^{57}Fe Nuclei in the Study of Interdiffusion Phenomena and Phase Formation*

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The effects of interdiffusion phenomena and reactions occurring in the early stages of the interaction at 1273 K between iron and chromium monoborides were studied by transmission Mössbauer and X-ray diffraction techniques, and modifications occurring in Fe/Al multilayers during both deposition and subsequent thermal aging at 400 K in vacuum or air were studied by conversion electron Mössbauer and Auger electron depth profiling techniques. In both cases the main objective of the work was to obtain a better understanding of the mechanisms of modification of the materials under examination with a view towards improving the properties of materials and coatings for specific applications.

1. Introduction

Diffusion phenomena and reactions occurring between compounds in the solid state and between reactive gases and solid surfaces are important for the preparation and in-service performance of innovative materials. Therefore, an understanding of the mechanisms of diffusion and reactions is required to optimise a material for a specific application [1, 2]. In this regard, Mössbauer spectroscopy proved to be a powerful technique of investigation [3, 4]. Useful information is obtained from the interactions occurring between Mössbauer nuclei and the surrounding charges, in particular those arising from the coupling of the nuclear magnetic dipole moment with the magnetic electrons or those due to the coupling of nuclear electric quadrupole moments with the crystalline electric field gradient.

The present work deals with diffusion phenomena and reactions occurring in the ternary system Fe-Cr-B and multilayers of thin films of Fe and Al. Knowledge of phase transformations and chemical reactions occurring at high temperatures in the Fe-Cr-B systems is essential to understand and control the technologically important treatment of chromium steels using boronising media to improve the surface hardness and wear resistance [1, 5, 6]. On the other hand, multilayers of a magnetic material intercalated with nonmagnetic films are applied in

fields as magnetic recording and storage. In particular, Fe-Al multilayers are studied with the aim of producing materials with improved soft magnetic properties [7–9], and their properties depend considerably on diffusion and reactions occurring during deposition as well as during their in-service life [10–12].

2. Experimental

2.1. Materials and Treatments

Powders of 99wt.% pure FeB and CrB were carefully mixed, cold compacted at 300 atm and then treated at 1273 K up to 32 h in crucibles of fused silica sealed under vacuum. Different compositions were prepared by increasing the Cr/(Cr+Fe) atomic ratio from 0.1 to 0.9 in steps of 0.1. The temperature for the isothermal treatments was in the range of interest for thermochemical boriding of iron alloys. This temperature is below the Fe-Fe$_2$B eutectic temperature but is high enough for kinetic processes. The lengths of treatment, in turn, were chosen short enough to allow study of the first stages of both diffusion and reaction phenomena.

The Fe-Al multilayers, coated for protection by an outer layer of Al 2 nm thick, were prepared by evaporation under ultra-high-vacuum (UHV) using electron beams as energy sources. The initial vacuum of $\sim 10^{-10}$ mbar changed to $\sim 10^{-8}$ mbar during evaporation. Ten layers of ^{57}Fe (each ~ 3 nm thick) were deposited on 7050 Corning glass at ~ 0.6 nm/min, intercalated with ~ 2 nm thick layers of Al deposited at ~ 2 nm/min (3Fe/2Al multilay-

ers). The samples were thermally aged at 400 K for times up to 50 h both under UHV and in air.

2.2. *Experimenal Techniques*

The effects of interdiffusion phenomena between Fe and Cr monoborides were investigated by means of room temperature transmission Mössbauer and X-ray-diffraction techniques. The Mössbauer measurements were carried out using a 10 mCi ^{57}Co/Rh source with detection of the 14.4 keV γ-rays. The XRD patterns were recorded by a computer-controlled goniometer and CrK$_\alpha$ radiation.

The Fe-Al multilayers were analyzed by conversion electron Mössbauer spectroscopy (CEMS) and Auger electron spectroscopy (AES). For the CEMS measurements, a 50 mCi ^{57}Co/Rh source was used. The AES measurements were carried out using a 2.0 keV electron beam energy and 2 µA beam current. AES depth concentration profiles were obtained using Ar$^+$ sputtering erosion (2 kV acceleration voltage and 80 µA sample current).

A least squares minimization routine with a combination of linear and nonlinear regressions allowed to fit the Mössbauer spectra and to obtain the distributions of hyperfine magnetic fields (H_{hf}) and quadrupolar splitting (ΔE_Q).

3. Results and Discussion

3.1. *Effects of Solid State Diffusion and Reactions between Compounds in the Fe-Cr-B System*

Among the surface modification technologies suitable to improve the in-service performance of iron alloys, boriding allows for coating consisting of the very hard products Fe$_2$B and FeB. During the treatment, diffusion occurs between the base alloys and the coatings which significantly modifies (i) the relative amounts, textures and morphology of the phases constituting the coatings, and (ii) hardness, compactness and toughness of the material.

In the case of boriding chromium steels, the modifications induced by the redistribution of Cr can be studied by experiments with powder mixtures of controlled composition selected within the Fe-Cr-B ternary system [13]. Because of its affinity to B, Cr, which diffuses within the coating during the boriding treatment could react with active B to give CrB which, in turn, might react with iron borides and modify the structure and properties of the coating.

Indeed, studies on the reactivity at high temperature between FeB and CrB powders showed that, during the early stages of the interaction, FeB is able to take Cr atoms from CrB with formation of (Fe,Cr)B. The Fe atoms liberated by the substitutional entering of Cr, in turn, preferentially react with nearby crystals of FeB to give Fe$_2$B. Figure 1a shows the Mössbauer spectrum measured for a mixture of FeB and CrB with Cr/Cr + Fe) = 0.1, treated for 8 h. The best fitting of the spectrum was obtained by superimposing the following contributions:

  – sextets β_1 and β_2 due to iron atoms in the two distinct sublattices of Fe$_2$B;
  – sextet η due to iron atoms in the pure FeB lattice;
  – a family of sextets (ζ contribution) with a distribution of hyperfine magnetic fields (H_{hf}) lower than that of FeB; the distribution shows two maxima at 102 ± 3 kOe and 90 ± 3 kOe. This contribution can be ascribed to Fe atoms which, in the (Fe, Cr) B lattice, differ in the number of Cr atoms as neighbours.

Figure 2a shows the XRD pattern recorded for the same sample. It is due to contributions from FeB, CrB, and Fe$_2$B. Boron liberated by the interaction between FeB and CrB does not contribute to the pattern because it is either in an amorphous state or in the form of small particles. The presence of Cr atoms in the FeB lattice, shown by Mössbauer measurements, could have been confirmed by XRD analyses only through very accurate measurements of the lattice parameters.

When the same treatment (8 h at 1273 K) is carried out on samples with higher values of the ratio Cr/(Cr+Fe), a higher number of FeB particles come in contact with CrB particles and, consequently, higher amounts of (Fe,Cr)B are formed. The higher amount of Fe atoms liberated in this way, in turn, also allows higher amounts of Fe$_2$B to form at the expense of the residual FeB. These effects are shown, for example, in the Mössbauer spectrum measured for an FeB-CrB mixture with Cr/(Cr + Fe) = 0.4 reported in Fig. 1b together with the distribution of H_{hf} relative to the series of sextets attributed to (Fe,Cr)B (ζ contribution). The similarity between the distributions of H_{hf} reported in Fig. 1 suggests that, when mixtures with increasing percentages of CrB are treated under the same conditions of temperature and time of exposure, comparable percentages of Cr atoms substitutionally enter an increasing number of FeB particles. It is to be noted that also an increase up to 16 h in the time of treatment at the same temperature allows higher amounts of both (Fe,Cr)B and Fe$_2$B to form.

When the Cr/(Cr+Fe) ratio was further increased, Cr also entered the Fe$_2$B lattice, giving (Fe,Cr)$_2$B, while Fe

entered the CrB lattice to give (Cr,Fe)B. Figure 3a shows the Mössbauer spectrum measured for a sample with Cr/(Cr + Fe) = 0.8 and treated for 8 h. It shows:

– a main contribution due to Fe$_2$B (sextets β_1 and β_2);

– a small contribution from (Fe,Cr)B (ζ contribution), that is an alloyed residual of the initial amount of FeB;

– a family of sextets (ψ contribution) with a distribution of H_{hf} values which are lower than those of Fe$_2$B. This contribution can be attributed to Fe atoms in (Fe,Cr)$_2$B;

– a paramagnetic contribution (δ), which can be ascribed to Fe atoms located in the CrB lattice.

It is to be noted that, in the XRD pattern recorded for the same sample (Fig. 2b) the contributions from Fe$_2$B and FeB are too small to give information on the presence of Cr in their lattice. On the other hand, the positions of the CrB peaks in the spectrum coincide with those of pure CrB; this means that the amount of Fe in the CrB lattice is very small.
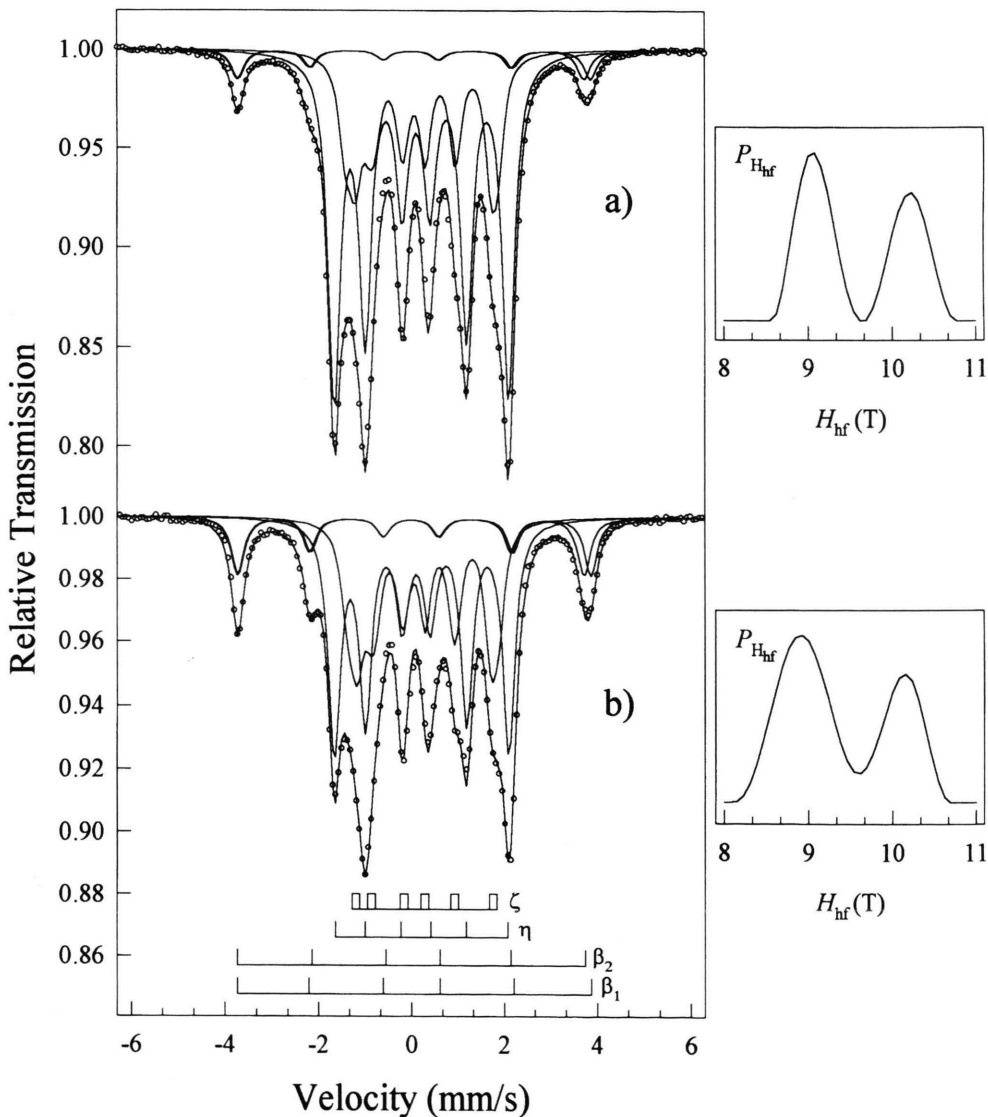

Fig. 1. Mössbauer spectra and hyperfine magnetic field (H_{hf}) distributions of ζ contribution for FeB-CrB powder mixtures thermally treated for 8 h: Cr/(Cr+Fe) = 0.1 (a) and 0.4 (b).
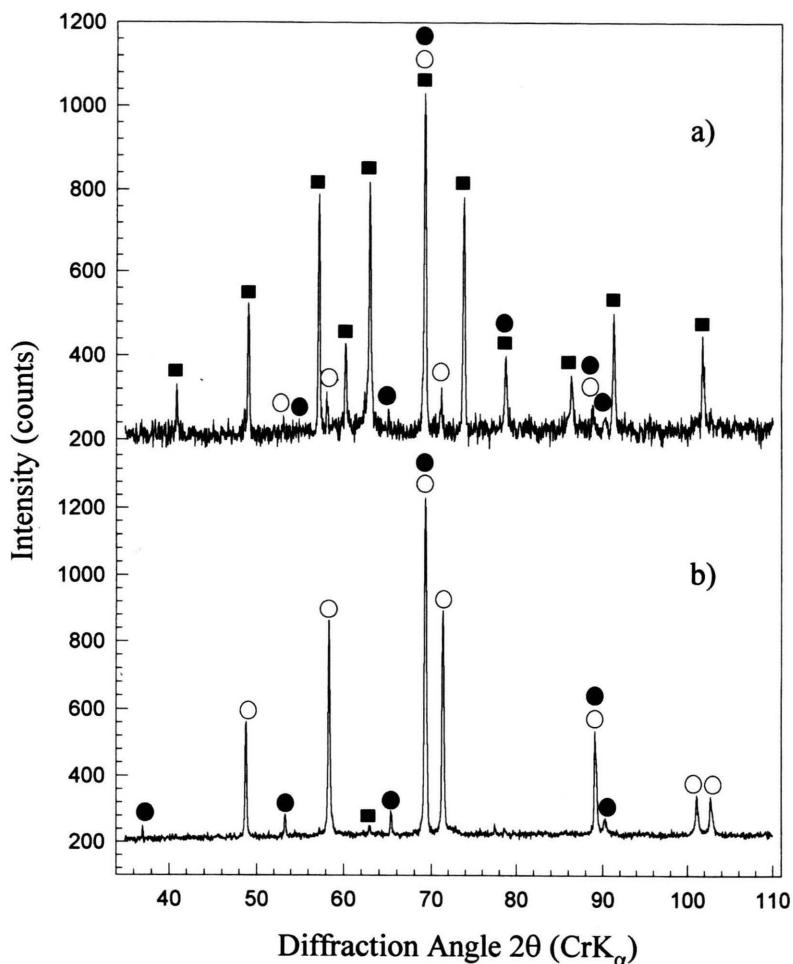
Fig. 2. X-ray diffraction patterns for FeB-CrB powder mixtures treated for 8 h: $Cr/(Cr+Fe)=0.1$ (a) and 0.8 (b) (○) CrB, (■) FeB and (□) Fe$_2$B.

When the time of treatment of the same mixture is increased over 8 h, the Mössbauer spectra show a decrease in the contribution due to Fe$_2$B and an increase in the paramagnetic contribution due to (Cr,Fe)B which, after 32 h of treatment, becomes the main contribution to the spectrum (Figure 3b).

Fig. 3 also shows the quadrupole splitting distributions relative to the paramagnetic contribution attributed to the (Cr,Fe)B phase. The distribution relative to the spectrum in Fig. 3a shows a maximum at 0.52 ± 0.03 mm/s which vanishes as the length of treatment is increased, and a maximum at 0.22 ± 0.03 mm/s which, as the length of treatment is increased (Fig. 3b), becomes the only contribution to the distribution. This suggests that the peak at 0.22 mm/s is due to those Fe atoms in the (Cr,Fe)B lattice which preferentially have other Fe atoms as neighbours in addition to Cr atoms. From the above results it can be concluded that, at 1273 K, the boride CrB

is (i) less stable than FeB to which, consequently, it yields Cr atoms with formation of (Fe,Cr)B, but (ii) more stable than Fe$_2$B from which it is able to take Fe atoms with formation of (Cr,Fe)B. Therefore, during the thermochemical growth of polyphase boride coatings on Cr steels, Cr reacting with active boron to give CrB destabilizes FeB with formation of Fe$_2$B and (Fe,Cr)B. CrB can also interact with Fe$_2$B, formed either by direct reaction between Fe and B or by destabilization of FeB, to give (Fe,Cr)$_2$B and (Cr,Fe)B.

3.2. Effects of Interdiffusion and Oxidation Phenomena in Fe-Al Multilayers

The possibility of optimising the performances of Fe-Al multilayers mainly depends on careful characterization of the composition and microstructure which, in turn, can be significantly modified by interdiffusion and reac-
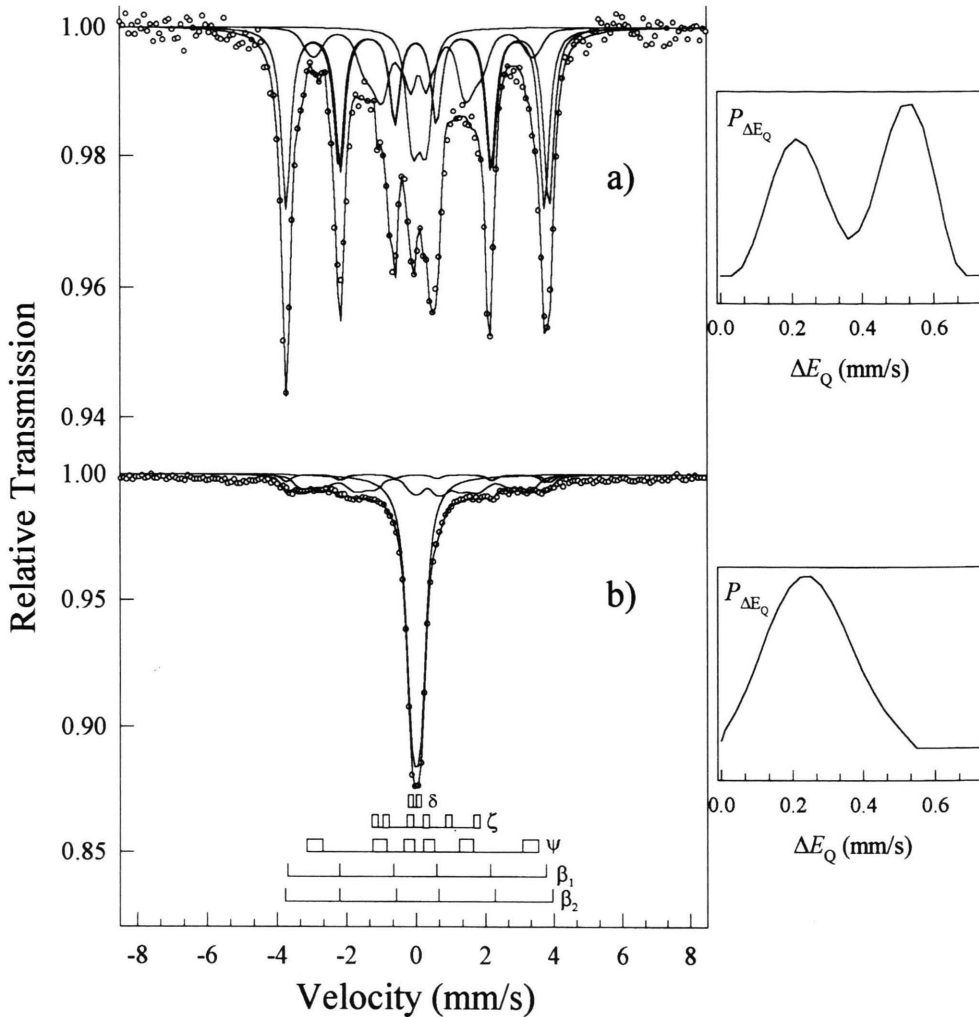
Fig. 3. Mössbauer spectra and quadrupole splitting (ΔE_Q) distributions of δ contribution for FeB-CrB powder mixtures with Cr/(Cr+Fe)=0.8, thermally treated for 8 h (a) and 32 h (b).

tion phenomena occurring during both preparation and in-service life. In effect, it was observed that interdiffusion phenomena between iron and aluminium occur during the deposition process of Fe-Al multilayers by thermal evaporation. As a consequence, regions of solid solutions $Fe(Al)_{ss}$ form at the interfaces between Fe and Al films. In zones of $Fe(Al)_{ss}$ richer in Al, Fe-Al intermetallic compounds can also form.

Fig. 4a shows the conversion electron Mössbauer spectrum measured for a 3Fe/2Al multilayer. The spectrum can be interpreted as due to:

– a broad ferromagnetic contribution, which can be described as the superposition of the sextet due to α-Fe (α) and a series φ of sextets with a distribution of H_{hf} (re-

ported beside) attributable to a solid solution of Al in Fe, $Fe(Al)_{ss}$;

– a paramagnetic contribution (δ doublet, $\Delta E_Q = 0.51 \pm 0.03$ mm/s and $IS = 0.22 \pm 0.02$ mm/s with reference to α-Fe) attributable to the Fe_2Al_5 intermetallic compound. It is to be noted that in the Al-rich zones of $Fe(Al)_{ss}$, Fe_4Al_{13}, richer in Al than Fe_2Al_5, did not form. This has been explained on the basis of the "effective" heat of formation of the two compounds [14, 15].

The diffusion of Al into Fe films during deposition, gave rise to a concentration gradient, as shown by the H_{hf} distribution. Reasonably, the diffusion occurred mainly along preferential paths, such as grain boundaries, giving rise to regions of pure iron surrounded by regions of
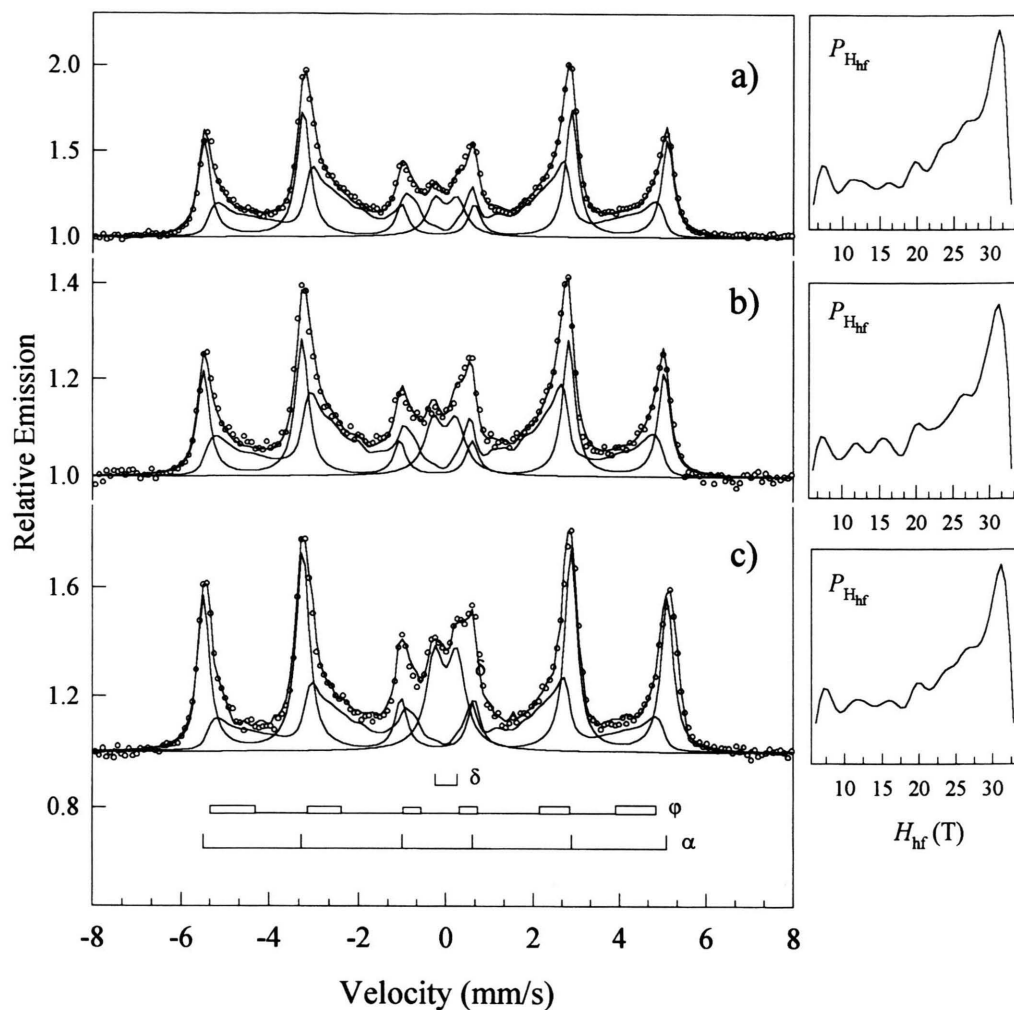
Fig. 4. Conversion electron Mössbauer spectra and hyperfine magnetic field (H_{hf}) distributions of φ contribution for 3Fe/2Al as deposited (a), treated at 400 K for 50 h in UHV (b) and in air (c).

Fe(Al)$_{ss}$ the extension of which decreased on going towards the centre of the Fe lattice. The peaks in the H_{hf} distribution can be correlated to Fe atoms which, in the Fe(Al)$_{ss}$, differ in the number of neighbouring Al atoms [16].

When the same sample is treated under UHV at 400 K for times up to 50 h, the Mössbauer spectra undergo small modifications: the contribution from α-Fe decreases, while that from the Fe$_2$Al$_5$ intermetallic compound increases (Figure 4b). The definition of the H_{hf} distribution is improved as the result of more ordered configurations that Al atoms assume as neighbours of the Fe atoms.

When the Fe-Al multilayers are exposed to oxidizing atmospheres at 400 K, oxygen first oxidizes the outer

layer of Al to Al$_2$O$_3$ and then, after longer times of exposure, diffuses within the Fe(Al)$_{ss}$, preferentially oxidizing Al. Consequently, Fe is protected from oxidation by the Al in solid solution.

Figure 5 shows the Auger concentration depth profiles of Fe, Al, and O, measured for the outer three bilayers of a 3Fe/2Al multilayer, before and after exposure to air for 50 h at 400 K.

The main consequence of the oxygen penetration was a loss of periodicity in the outer layers. This effect can be explained considering that the preferential reactivity between aluminium and oxygen caused a reduction in the Al content in the Fe(Al)$_{ss}$. Consequently, further migration of Al was promoted from the adjacent layers of Al
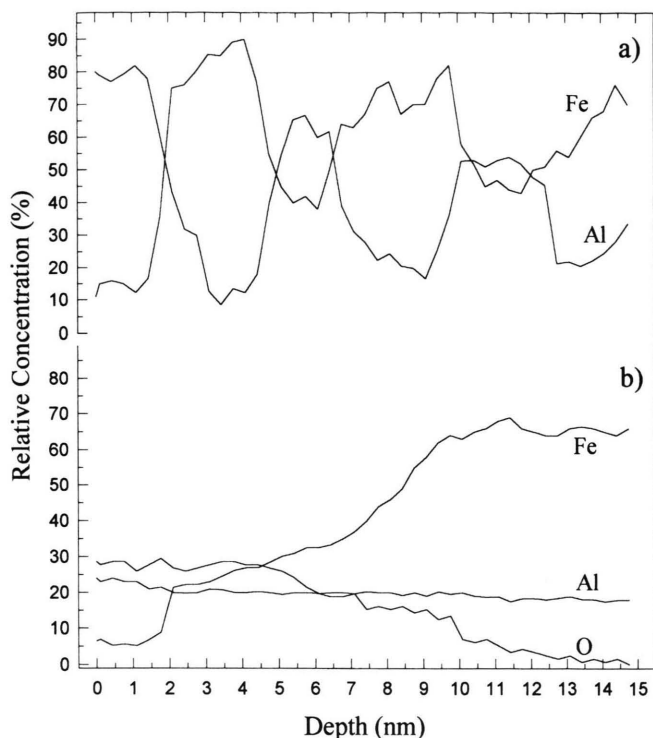
Fig. 5. Fe and Al Auger electron spectroscopy depth profiling of the three bilayers of 3Fe/2Al multilayer as deposited (a) and treated at 400 K for 50 h in air (b).

which, adding to the thermally induced migration of Al, caused a progressive flattening of the concentration profiles of both Fe and Al. In agreement, the Mössbauer spectrum measured for the same sample (Fig. 4c) shows an increase in the contribution from pure Fe (in addition to an increase in the contribution from Fe_2Al_5) with respect to that from $Fe(Al)_{ss}$. In particular, the ferromagnetic contribution to the spectrum is due to (i) α-Fe located in regions previously constituted by the $Fe(Al)_{ss}$ and then modified because of oxygen diffusion and preferential formation of Al_2O_3, and (ii) α-Fe and $Fe(Al)_{ss}$ located in the unoxidized part of the multilayer.

Under aging conditions leading to zones of pure iron no longer protected by metal Al, Fe can also be oxidized by gaseous oxygen. Figure 6 shows the Mössbauer spectra measured for ~8 nm thick films of ^{57}Fe evaporated on silica glass (one directly onto the substrate, 8Fe, the other with intercalation of ~1 nm thick film of Al, 8Fe/1Al) after exposure to air at room temperature for several months [17].

The spectrum in Fig. 6a was fitted by superimposing two single lines (α and β) to a set of doublets showing the quadrupolar splitting distribution reported beside the spectrum. The distribution displays a prevailing peak (δ)

at $\Delta E_Q \cong 1.1$ mm/s, and two small peaks (σ) at ~1.9 mm/s and 2.2 mm/s. The α, β, and δ contributions can be attributed to α-Fe, Fe_3O_4 and Fe_2O_3, respectively, all in the form of small particles showing superparamagnetic behaviour. The σ contribution, in turn, was ascribed to a very small amount of $FeSiO_3$, formed at the film-glass interface. These results indicate that iron grains become progressively smaller because of the preferential oxidation at grain boundaries, so that small particles of both iron and iron oxides can form.

The spectrum in Fig. 6b, measured for the Fe-Al bilayer, was fitted by superimposing the α, β, and δ contributions discussed above, and, moreover, two doublets ε and η which were attributed to $FeAlO_3$ and $FeAl_2O_4$, respectively. The formation of these ternary compounds can be ascribed to a high reactivity between iron oxides in the form of small particles and the previously formed Al_2O_3. Therefore, when Fe-Al multilayers are exposed to oxidizing environments under conditions allowing oxidation of Fe (because the oxygen potential of the gaseous atmosphere is high, or the films of protective Al are thin and the metal Al in the $Fe(Al)_{ss}$ is all oxidized), small and very reactive particles of iron oxides can react with Al_2O_3 to give Fe-Al-O ternary compounds.

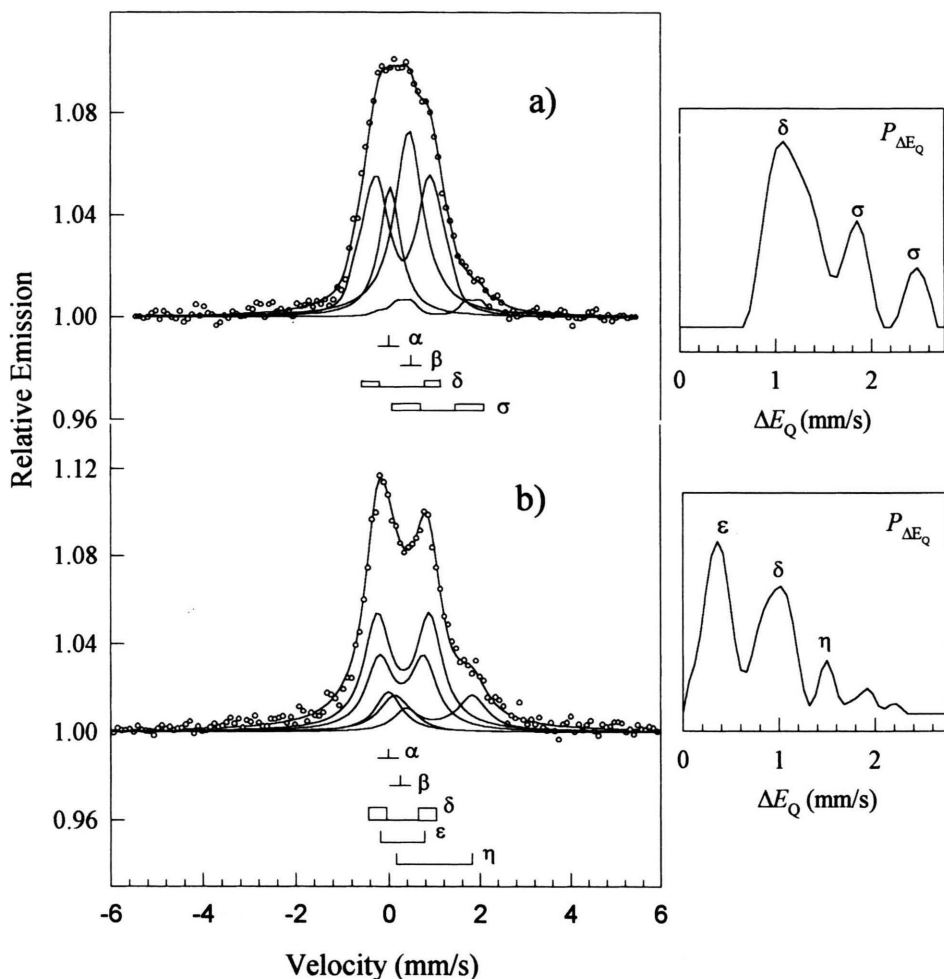Fig. 6. Conversion electron Mössbauer spectra and quadrupole splitting (ΔE_Q) distributions for 5Fe film (a) and 5Fe/2Al bilayer (b) aged at room temperature in air.

4. Conclusions

Mössbauer spectroscopy proved to be a very useful technique to study the effects of interdiffusion phenomena and phase formation occurring both in metallic and ceramic systems.

In the case of a study on the interactions between iron and chromium monoborides, bulk information on the modifications occurring at high temperature was obtained by combining transmission Mössbauer and X-ray diffraction analyses.

In the case of multilayers constituted by thin films of Fe and Al, information on the modifications occurring at the interfaces during both deposition and subsequent thermal aging in vacuum or air was obtained by combin-

ing conversion electron Mössbauer and Auger electron depth profiling analyses.

In this way, it was possible to study the complex mechanisms of modification of the materials under examination. Knowledge on mechanisms and effects of these modifications allows the properties of both materials and coatings to be significantly improved for specific applications.

[1] "Surface Modification Technologies", T. S. Sudarshan Ed., M. Dekker, New York, USA 1989.

[2] D. Gupta and P. S. Ho, in "Diffusion Phenomena in Thin Films and Microelectronics Materials", Noyes ed., Park Ridge, New York, USA 1988.

[3] M. Carbucicchio, Mössbauer Spectroscopy, in "Physics of Metals", E. S. Giuliano and C. Rizzuto eds., World Sci. Pub. Co. Pte. Ltd., Teaneck NJ, USA 1988, pp. 108–138.

[4] M. Carbucicchio, Backscattering Mössbauer Spectroscopy, in "Magnetic properties of matter", G. Asti, D. Fiorani, and F. Lucari eds., World Sci. Pub. Co. Pte. Ltd., River Edge NJ, USA 1991, pp. 500–518.

[5] M. Carbucicchio and G. Sambogna, Thin Solid Films **126**, 299 (1985).

[6] M. Carbucicchio and G. Palombarini, J. Mater. Sci Letters **6**, 1147 (1987).

[7] M. Matsumoto, T. Haeiwa, and S. Sakguchi, IEEE. Transl. J. Magn. Jpn. **5**, 583 (1990).

[8] A. Fuß, S. Demokritov, P. Grünberg, and W. Zinn, J. Magn. Magn. Mater. **103**, L221 (1992).

[9] F. Pan, B. X. Liu, and K. Tao, Phys. Stat. Sol. (a) **151**, 407 (1995).

[10] M. Carbucicchio, G. Palombarini, R. Bertoncello, A. Glisenti, E. Tondello, and G. Sberveglieri, Hyp. Int. **92**, 1249 (1994).

[11] M. Carbucicchio, G. Palombarini, R. Bertoncello, A. Glisenti, E. Tondello, G. Sberveglieri, and S. Groppelli, J. Magn. Magn. Mater. **133**, 504 (1994).

[12] J.-F. Bobo, P. Delcroix, J.-C. Ousset, M.-F. Ravet, and M. Piecuch, J. Magn. Magn. Mater. **93**, 452 (1991).

[13] M. Carbucicchio, G. Palombarini, and G. Sambogna, Hyperf. Interactions **92**, 993 (1994).

[14] R. Pretorious, A. M. Vredenberg, F$_{FF}$. W. Saris, and R. De Reus, J. Appl. Phys. **70**, 3636 (1991).

[15] J. L. Alexandre, M. A. Z. Vasconcellos, S. R. Teixeira, and I. J. R. Baumvol, Appl. Phys. A **56**, 113 (1993).

[16] M. Carbucicchio, G. Palombarini, M. Rateo, and G. Ruggiero, Phil. Mag. B **76**, 425 (1997).

[17] M. Carbucicchio, G. Palombarini, R. Bertoncello, A. Glisenti, E. Tondello, and G. Sberveglieri, Hyp. Int. **78**, 327 (1993).