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Mössbauer study of titanium implanted α-Fe

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Abstract. Bulk α-Fe has been implanted with 200 keV Ti ions with doses ranging from 1×10^{17} to 8×10^{17} at. Ti cm^{-2} and characterized by conversion electron Mössbauer spectroscopy (CEMS). The CEMS spectra recorded for the low dose Ti implantation of the surface region reveal the formation of the crystalline phases (bcc-FeTi solid solution and FeTi intermetallic compound) and of the amorphous Fe–Ti–C phase. For Ti doses exceeding 4×10^{17} at. Ti cm^{-2} the amorphous FeTi phase is formed, whose relative spectral fraction saturates at about 40% of the total spectral area at 6×10^{17} at. Ti cm^{-2}. At high ion doses the amorphous Fe–Ti–C phase disappears but the bcc-FeTi and crystalline intermetallic FeTi phases persist, beside the amorphous FeTi phase, even at the highest Ti dose used.

1. Introduction

Ion implantation is a widely used technique for the modification of the surface-related properties of materials. The titanium implantation of iron [1–3] and steel [4] were carried out in order to improve the tribiological properties of implanted materials. It was shown that Ti-ion implantation of iron alloys leads to the formation of the bcc-FeTi and the amorphous Fe–Ti–C phases in the implanted layer [3]. The Fe–Ti system is interesting as regards the possibility of the formation of the amorphous FeTi phase. Its enthalpy of mixing is negative (-17 kJ mol^{-1} [5]) and is sufficient for amorphization over a wide composition range. The Fe–Ti system exhibits also wide stability ranges of the crystalline intermetallic FeTi and Fe_2Ti phases. It is, however, well known that the amorphous FeTi phase cannot be formed by the most common technique of rapid quenching from the melt [6]. The amorphous FeTi phases in a wide composition range were prepared by the sputtering method [7, 8] and by mechanical alloying [9]. The amorphous FeTi phase was observed also in Fe/Ti multilayers with small structural modulation wavelengths, which were deposited by rf sputtering [10]. The possibility of the formation of such a phase was studied for Fe/Ti multilayers exposed to Xe-ion irradiation. Contradicting results were reported by Brenier *et al*, who in some cases did not detect the amorphous FeTi phase [11], while in other cases the formation of the amorphous FeTi was well documented [6, 12]. Amorphization of Fe/Ti multilayers with various modulation wavelengths and compositions, induced by Ar- and Kr-ion-beam mixing, was reported recently [13].

In the previous experiments of Ti-ion implantation of iron a carbon-free FeTi amorphous phase was not detected, most probably because the Ti dose was too small (1–2×10^{17} at. Ti cm^{-2}) [3, 14]. The aim of the present study is an attempt to form the amorphous FeTi

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phase due to Ti implantation of the bulk α-Fe. Much higher ion doses up to 8×10^{17} at. Ti cm^{-2} were used. Since various crystalline FeTi intermetallic compounds (FeTi, Fe_2Ti), bcc-FeTi and amorphous phases were studied extensively by the Mössbauer technique it is fairly easy to identify phases formed in α-Fe due to Ti implantation by their characteristic hyperfine parameters, because the parameters of the crystalline compounds clearly differ from those characteristic for the amorphous phase [7, 8]. Therefore Mössbauer spectroscopy is a powerful analytical tool in such investigations.

2. Experimental details

The bulk samples of α-iron (Armco iron with the purity of 99.5%, from Goodfellow Ltd), 20 mm in diameter and 1.5 mm thick were implanted with titanium ions using a Balzers MRB 202 RP implanter. The samples were implanted at room temperature with Ti doses ranging from 1×10^{17} at. Ti cm^{-2} to 8×10^{17} at. Ti cm^{-2} with a beam current density of about 1 μA cm^{-2}. The energy of Ti ions was 200 keV. Their projected range in α-Fe, calculated with a TRIM program [15], was about 75 nm. After implantation the samples were characterized by conversion electron Mössbauer spectroscopy (CEMS). This technique provides structural information from the surface layer of the sample (about 100 nm thick) coinciding well with the range of the implanted titanium ions. The CEMS measurements were performed at room temperature by using a gas flow electron counter with He–6% CH_4 gas. The Mössbauer source was ^{57}Co in an Rh matrix. All isomer shift data are given with respect to the α-Fe standard.

The Mössbauer spectra were fitted using the NORMOS program [16]. The spectral parameters, such as the hyperfine fields, H_{hf}, quadrupole splittings, QS, isomer shifts, δ, and linewidths, Γ, were calculated. The relative spectral areas, A, of the subspectra corresponding to various phases formed in α-Fe due to Ti implantation allowed the determination of their relative fractions. These results were not corrected for the possible differences of the Debye–Waller factors of the relevant phases.

3. Results and discussion

The conversion electron Mössbauer spectra recorded for the α-Fe samples implanted with Ti ions with doses ranging from 1×10^{17} to 8×10^{17} at. Ti cm^{-2} are shown in figure 1. The spectrum of the unimplanted Fe sample (not shown here) consists exclusively of a well known characteristic sextet with $H_{hf} = 32.95$ T, $\delta = 0.00$ mm s^{-1} and $\Gamma = 0.28$ mm s^{-1}. Implantation with Ti ions induced changes in the material which can be easily seen in the CEMS spectra in figure 1. At the lowest Ti dose (1×10^{17} at. Ti cm^{-2}) the implanted titanium forms a bcc solid solution in the α-Fe lattice. The Ti atoms are located in the first and the second coordination spheres which leads to the reduction of the hyperfine field at the iron sites. A reduction of the hyperfine field (ΔH) due to the Ti impurity in the first ($\Delta H_1 \approx 2$ T) and the second ($\Delta H_2 \approx 2$ T) coordination spheres was observed for the dilute FeTi alloys [17]. The spectrum in figure 1(a) was fitted with three sextets: (i) one corresponding to the α-Fe phase ($H_{hf} = 32.95$ T, $\delta = 0.00$ mm s^{-1}) and (ii) two sextets due to Ti atoms in the bcc structure with the hyperfine fields of about 30 T and 26 T, and the isomer shifts of -0.005 and -0.010 mm s^{-1}, respectively. Such a strong reduction of the hyperfine field suggests that several Ti atoms are located in the nearest and next nearest neighbour positions in the bcc-Fe structure especially since even at the lowest implantation dose of 1×10^{17} at. Ti cm^{-2} the Ti concentration, calculated by the TRIM program [15], is already fairly high (about 15%).

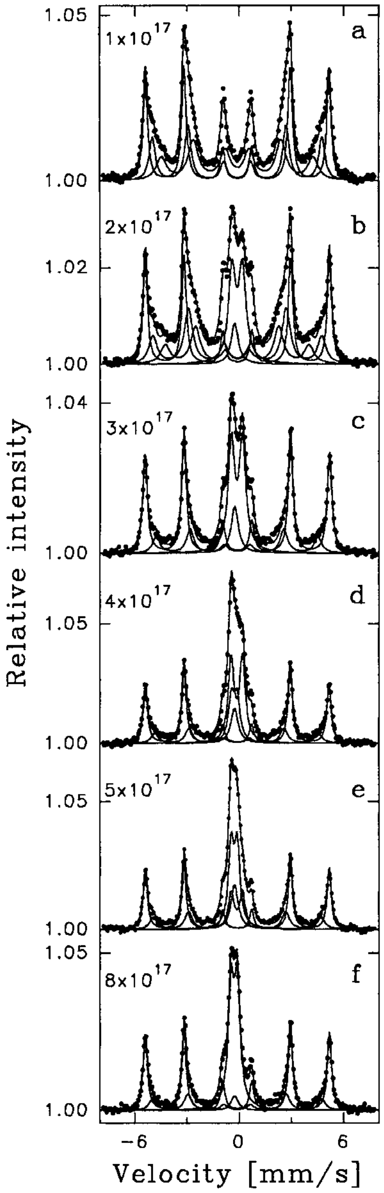

Figure 1. CEMS spectra recorded for the bulk Fe samples implanted with 200 keV Ti ions with doses ranging from 1×10^{17} to 8×10^{17} at. Ti cm^{-2}.

The bcc-FeTi phase (figure 1(a)) has a broad distribution of Ti content, ranging from Ti-poor regions (corresponding to the sextet with $H_{hf} \approx 30$ T) to Ti-rich ones (corresponding to the sextet with $H_{hf} \approx 26$–27 T). The relative content of the bcc-FeTi phase is high; it contributes about 60% to the total spectral area. The increase of Ti dose to 2×10^{17} at. Ti cm^{-2} causes the formation of other Ti-containing phases (figure 1(b)). In addition to the α-Fe sextet (relative spectral contribution $A = 32\%$) and the previously observed sextets corresponding to the bcc-FeTi solid solution ($A = 44\%$), paramagnetic spectral components are clearly seen in

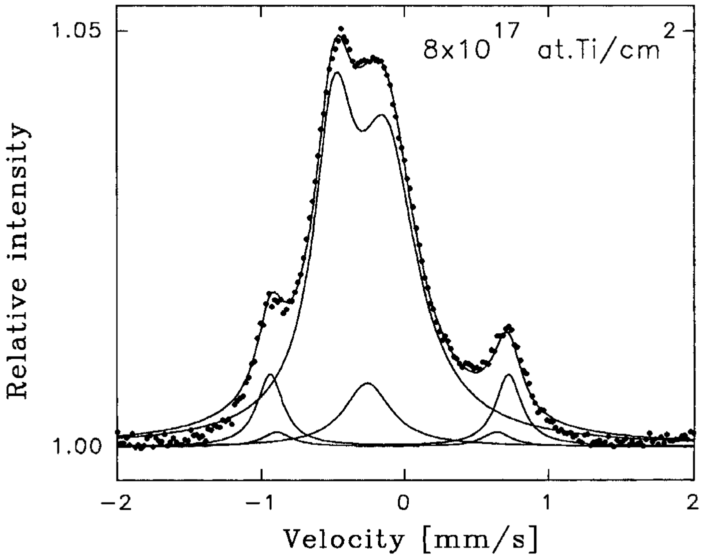

Figure 2. CEMS spectrum of the sample irradiated with 8 × 10^{17} at. Ti cm^{-2} recorded at the reduced velocity range.

the central part of the spectrum. They consist of a quadrupole doublet (QS = 0.64 mm s^{-1}, $\delta = 0.00$ mm s^{-1}, $A = 20\%$) and a single line ($\delta = -0.15$ mm s^{-1}, $A = 4\%$). The hyperfine parameters of the quadrupole doublet do not correspond to any FeTi crystalline or amorphous phases [7, 8]. However, the QS and δ values of this doublet correspond well to those of the amorphous Fe–Ti–C phase detected in α-Fe implanted with Ti and C by Williamson *et al* [3]. The isomer shift close to 0 mm s^{-1} suggests fairly low carbon content in this phase. Since our iron samples were implanted with Ti ions only, carbon contamination of the implanted sample could come from the residual carbon contamination in the vacuum of the target chamber rather than from the carbon impurity in the samples (Armco iron with the carbon content of about 0.1 at.%). The spectrum of the unimplanted sample did not show any traces of iron–carbon phases. A single line detected in the spectrum in figure 1(b) corresponds well to the crystalline intermetallic FeTi phase [8]. With increasing Ti dose the relative contents of the crystalline FeTi and amorphous Fe–Ti–C phases significantly increase at the expense of α-Fe and bcc-FeTi fractions (figure 1(c)).

At the dose of 4 × 10^{17} at. Ti cm^{-2} the shape of the central part of the spectrum changes significantly (figure 1(d)). In addition to the QS doublet characteristic for the amorphous Fe–Ti–C phase and a single line corresponding to the crystalline FeTi compound, a new QS doublet with considerably smaller quadrupole splitting and negative isomer shift appears. It contributes about 15% to the total spectral area. The hyperfine parameters of this doublet (QS = 0.33 mm s^{-1}, $\delta = -0.17$ mm s^{-1}) allow the identification of the new phase as the amorphous FeTi with Fe content of about 40–50% [7, 8]. Formation of the amorphous FeTi phase leads to a considerable decrease of the bcc-FeTi fraction to about 15%.

At 5 × 10^{17} at. Ti cm^{-2} the spectral contribution related to the amorphous Fe–Ti–C phase decreases and the amorphous FeTi fraction increases rapidly (figure 1(e)). At doses of about 6 × 10^{17} at. Ti cm^{-2} the spectral component related to the amorphous Fe–Ti–C phase disappears and the central paramagnetic component of the CEMS spectrum consists predominantly of the QS doublet characteristic for the amorphous FeTi phase. Implantation with doses 6–8 ×

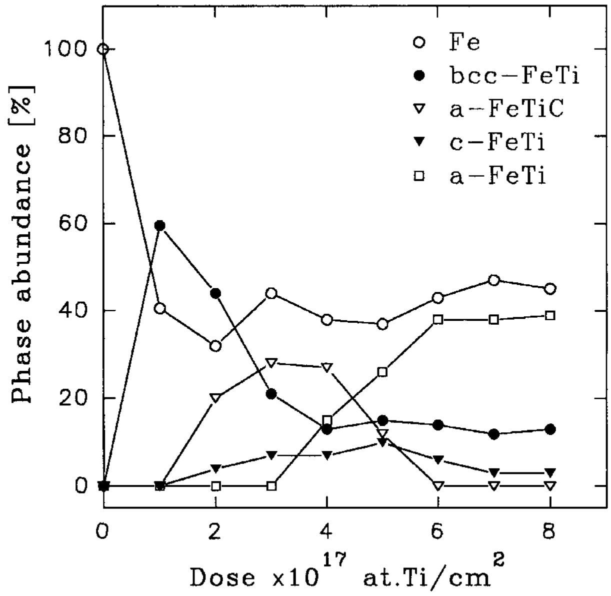

Figure 3. Relative abundance of various Ti-containing phases formed in α-Fe due to Ti implantation.

10^{17} at. Ti cm^{-2} does not affect the phase structure of the samples. The shapes of the CEMS spectra do not change significantly (figure 1(f)). The relative fractions of the amorphous FeTi and of the bcc-FeTi phases saturate at about 42% and 13%, respectively, at 6×10^{17} at. Ti cm^{-2}. They do not change with increasing Ti dose. The amount of the crystalline FeTi phase gradually decreases, but the single line spectral component is still clearly seen in the spectrum recorded for the highest implanted Ti dose ($A \approx 3\%$). The saturation of the phase abundance is most probably related to the sputtering of the sample surface by high dose of Ti ions.

In order to check for the presence of other than amorphous FeTi, bcc-FeTi, crystalline FeTi and retained α-Fe phases in the high-dose implanted samples (6–8 × 10^{17} at. Ti cm^{-2}) the CEMS spectra were recorded in a reduced velocity range. A spectrum of the sample implanted with 8×10^{17} at. Ti cm^{-2} is shown in figure 2. The fit with the QS doublet characteristic for the amorphous FeTi, the single line related to the crystalline FeTi, two inner lines of the α-Fe sextet and traces of two inner lines of the bcc-FeTi sextet is almost perfect and does not leave any spectral intensity for additional spectral components. This shows that a high dose Ti implantation of α-Fe leads to the formation of the amorphous FeTi phase, dominating in the implanted layer, with some retained crystalline phases such as the bcc-FeTi solid solution and the intermetallic FeTi phase formed already at lower Ti dose.

The results discussed above are summarized in figure 3 which shows the ranges of the relative abundance of various phases formed in α-Fe due to Ti implantation. The bcc-FeTi phase dominates at low Ti dose. The amorphous Fe–Ti–C phase is observed only in the dose range of 1–5 × 10^{17} at. Ti cm^{-2}. The intermetallic FeTi compound is formed at doses exceeding 2×10^{17} at. Ti cm^{-2} with the maximum abundance at 5×10^{17} at. Ti cm^{-2}. Formation of the amorphous FeTi phase requires high Ti doses, exceeding 4×10^{17} at. Ti cm^{-2}. Its relative abundance saturates at about 40% for the dose of 6×10^{17} at. Ti cm^{-2}.

The present study of Ti-ion implanted bulk α-Fe clearly shows that all CEMS spectra contain a significant α-Fe component, whose spectral contribution decreases with increasing ion dose. It remains almost constant ($A \cong 45\%$) for Ti-ion doses exceeding 4×10^{17} at. Ti cm^{-2} (figure 3). This means that in the implanted layer, whose thickness coincides well with the depth sensitivity of the CEMS technique [4], a substantial fraction of α-Fe is not transformed into Ti-containing phases and remains unaffected. A part of the spectral intensity related to α-Fe may come from deeper Fe layers beyond the range of Ti ions. This contribution is, however, too small to account for the almost 45% spectral contribution of the α-Fe sextet. Similar behaviour was observed in our earlier studies of N-implanted [14, 18, 19] and B-implanted [20] bulk α-Fe. In spite of the formation of various crystalline nitride phases [14, 18] or amorphous FeB [20] the spectral contribution due to α-Fe was always substantial; it was close to 50% and 40% for N- and B-implantation, respectively. The reasons for the incomplete transformation of a near surface region of α-Fe during ion implantation seems to be related to the impurity redistribution during the cooling phase of the cascade evolution and were discussed earlier [19, 20]. On the other hand, ion-beam mixing of nanoscale multilayer structures (Fe/Zr [21], Fe/Ti [13]) induced by ion irradiation leads to almost complete conversion of Fe layers to new phases. The dependence of phase transformations in the implanted layer on the thickness of the implanted material is still not fully explained and requires further studies. Some aspects of the dependence of ion-beam mixing on the substrate thickness in Fe/Zr bilayer system were discussed recently [22, 23].

4. Conclusions

Our results show that titanium ion implantation of bulk α-Fe leads to the formation of the amorphous FeTi phase providing that the Ti dose is sufficiently high (exceeding 4×10^{17} at. Ti cm^{-2}). At low doses the Ti-implanted ions are located in the bcc structure of α-Fe and form the bcc-FeTi solid solution. Also at low Ti doses the crystalline FeTi intermetallic compound is formed. At high Ti doses (exceeding 6×10^{17} at. Ti cm^{-2}) the relative abundance of the amorphous FeTi and bcc FeTi phases saturates, which is most probably related to the saturation of the Ti content in the near surface region of the sample due to the sputtering effect.

The CEMS technique allowed the study of the phenomena occurring due to titanium implantation of iron. It permitted phase identification and the quantitative evaluation of the phase abundance and their evolution as a function of the implanted Ti dose.

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