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On the early stages of high purity iron boriding with crystalline boron powder

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Metallographic analyses and surface Mössbauer measurements were carried out on high purity iron borided in a mild boronizing medium. It was found that, irrespective of the preliminary iron treatment such as annealing, carburizing or cold rolling, only a fraction of the exposed surface reacts with boron at 1000° C. The stratified arrangement and the average thicknesses of the different reaction products within the iron boride isles were determined. These results, as compared with those previously obtained for borided Armco iron, allowed the hypothesis of a mechanism for the thermal growth of iron borides.

1. Introduction

Cementation by boron has been the subject of interest for a long time, but only recently has it been adopted as a technically useful process. Significant developments on the basic knowledge of the matter are still more recent. In a preceding paper [1], a scattering technique for X-ray and electron Mössbauer spectroscopy [2] has been utilized for the first time to analyse boride layers thermochemically grown on Armco iron. This technique adequately demonstrated its capability to provide qualitative and quantitative information about phase composition, structure and average thickness of thin surface layers, operating in a completely non-destructive way. With respect to this, one of the more powerful features of the technique is the possibility of analysing layers of different depth by detecting both the electromagnetic radiation and the electrons emitted as a consequence of the γ-resonant absorption, with a very high energy resolution.

For iron, by detecting the 14.4 keV γ-radiation, the 6.4 keV X-rays and the emitted electrons, one can obtain information about surface layers ~ 30, $\sim 20\,\mu$m and ~ 300 nm thick, respectively. Moreover, by selecting the energy of the conversion electrons, Mössbauer spectra of surface layers with thicknesses ranging from 180 nm down to a value lower than 10 nm can be obtained.

In the present paper, this technique has been utilized together with metallography to point out differences in reactivity existing between Armco iron and high purity iron when these metals are placed in contact with a mild boronizing medium i.e. crystalline boron powder, with the major aim of understanding better the mechanisms of the thermal growth of iron borides.

2. Experimental details

Samples of about $20 \times 10 \times 1\,\text{mm}^3$ were drawn from hot-rolled sheets of iron 4N85 grade, supplied by the Metal Research Ltd, containing $\text{C} < 10$ ppm by weight, Mn 3, Ni 2, Si 2, $\text{N} < 1$, $\text{Ag} < 1$, $\text{Cu} < 1$ and $\text{Mg} < 1$ as main impurities. The samples were subjected to wet abrasion on SiC emery papers up to a 600 grit, annealed for 15 h at 1000° C under a vacuum greater than 10^{-3} Pa, mechanically polished again and finally boronized for times up to 24 h at 850° C and 15 h at 1000° C in contact with a crystalline boron powder. More details on boron powder properties and on thermal treatments are given elsewhere [1].

Some high purity iron samples were carburized prior to boronizing, with the aim of elucidating a possible role of carbon in iron reactivity. Carburizing was performed by a mixture of carbon and BaCO_3 10% by weight, at 900 to 950° C in argon for times up to 90 min. Carburized samples were

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annealed under vacuum for 8h at 1000° C, in order to obtain homogenized alloys with average carbon contents of 0.01, 0.15 and 0.30% by weight.

In another series of experiments, some iron samples were unidirectionally cold rolled with a final thickness reduction of 22%, or locally punched and then boronized, to elucidate the possible role of cold working on the reactivity between metal and boron powder.

The external surfaces of the boronized samples were examined at first under a Jeol SM-15 scanning electron microscope. Then, cross-sections were observed under a Reichert MeF optical microscope. Finally, Mössbauer spectra were carried out by utilizing the apparatus described elsewhere [2]. The detected radiations were: 6.4 keV X-rays, whose maximum penetration range for iron is ~ 20 μm; and the conversion electrons in the energy range from 6 to 7.3 keV and, therefore, originating from within a surface layer ~ 100 nm thick [3].

The radiations to be detected were chosen considering that (i) Armco iron boronized under the same conditions was covered by a surface boride layer not thicker than 20 μm, (ii) the Armco iron reactivity appeared to be much higher than that of high purity iron, and (iii) surface boride layers thinner than ~ 50 nm are of little practical interest. It is worth noting that equal layers at different depths do not contribute in the same way to a Mössbauer spectrum, owing to different escape probabilities of the detected radiation as a function of the crossed thickness [3–5]. As an example, the 50% of the conversion electrons leaving the iron surface with energies ranging from 6 to 7.3 keV, come from a surface layer with a maximum thickness of ~ 30 nm. In order to evaluate the escape depths for different phases, according to Cosslett and Thomas [6] one can assume that they can be obtained from phase-density ratios utilizing the mean free path of the conversion electrons in pure iron.

The source was a 15 mCi ^{57}Co diffused in a Rh matrix. The spectra were detected at room temperature and computer-fitted by least squares to a series of Lorentzian peaks.

3. Results

As described in a preceding paper [1], a treatment at 1000° C for 15 h in contact with a crystalline boron powder under vacuum produced boride layers ~ 20 μm thick on Armco iron. The Mössbauer measurements allowed the determination of a multi-layer structure of coating, consisting (from the inside to the outside) of Fe_2B, FeB and FeB_x crystals, with x greater than 1 and perhaps equal to 2 [1, 7]. The average thickness of each layer was determined to be ~ 15, ~ 5 μm and ~ 30 nm, respectively. After 24 h at 850° C, on the other hand, the Armco iron surfaces appear unchanged, although the formation of iron–boron solid solutions could not be excluded.

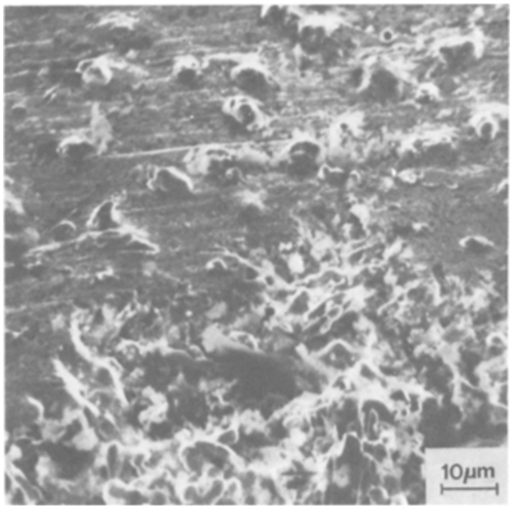

Figure 1 SEM of a pure iron surface boronized for 15 h at 1000° C, showing sparse islands of reaction products.

Under the same experimental conditions, high purity iron showed a much lower reactivity. At 1000° C, in fact, only sparse islands of reaction products have grown on boronized samples (Figs. 1 and 2), while no reaction product at all has formed at 850° C. At 1000° C a consistent layer of reaction products grew in the vicinity of edges and corners (Fig. 3) of the samples. Fig. 4 shows a SEM of the typical morphology of the outer crystals in the islands.

It is worth noting that neither the introduction of carbon up to 0.3 wt % in the starting metal nor a 22% thickness reduction by cold rolling markedly increased the reactivity at 1000° C between pure iron and boron powder. In no way, in fact, did the reaction products cover completely (or nearly) the metal surfaces. Much more abundant reaction products grew, instead, on the surface zones strongly work-hardened by punching, showing in the SEM a morphology somewhat different from that previously observed on annealed samples (Fig. 5). The Mössbauer measurements were in

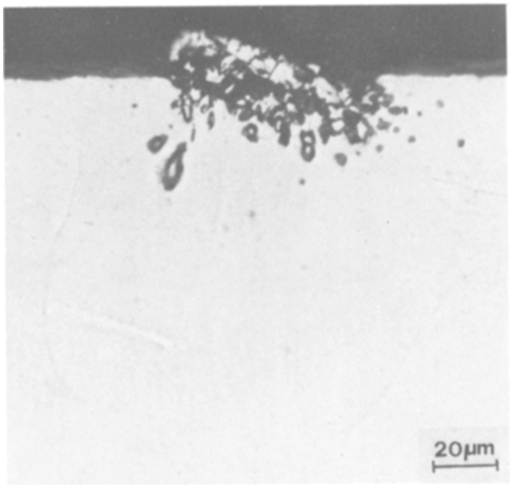

Figure 2 An optical micrograph of a cross-section of a pure iron sample boronized for 15 h at 1000° C, showing an island of reaction products.

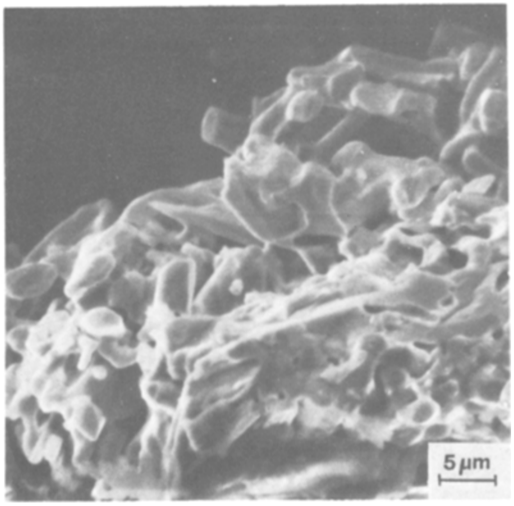

Figure 4 SEM of the outer boride crystals in an island of reaction products.

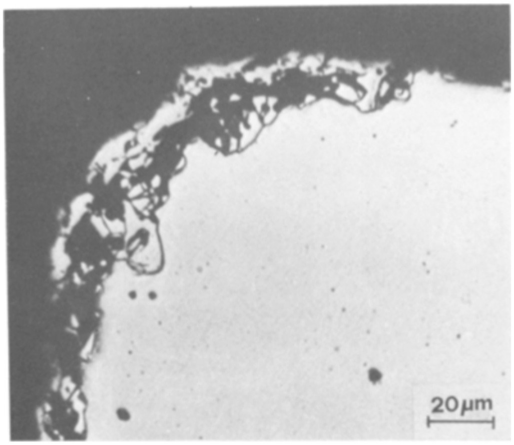

Figure 3 The same as in Fig. 2, showing a corner of the boronized sample.

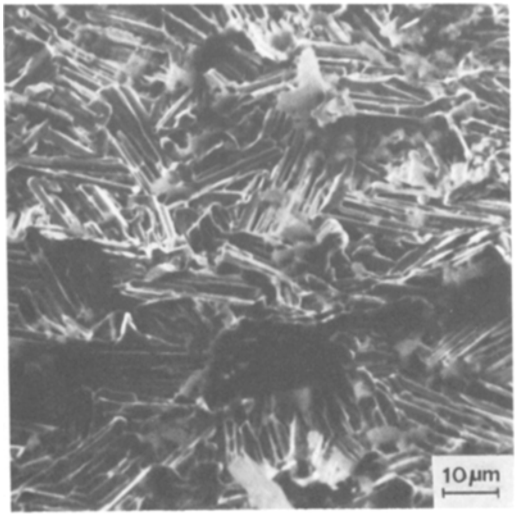

Figure 5 SEM of the outer boride crystals grown on a metallic zone previously work-hardened by punching.

agreement with the above metallographic observations and allowed the determination of the composition, the stratified arrangement and the average thicknesses of reaction products. Fig. 6 shows the Mössbauer spectra measured at room temperature on pure iron after thermal boronizing. As a rule, edges and corners of the boronized samples have been shielded.

Pure iron boronized for 24 h at 850° C was analysed by detecting both X-ray and electrons. The electron Mössbauer spectrum is shown in Fig. 6a. Within experimental error, the spectra do not display any appreciable change compared to the pattern obtained before boronizing. From this result it follows that, in agreement with metallographic observations, no reaction product has formed on pure iron boronized for 24 h at 850° C with crystalline boron powder, at least for surface layers thicker than ~ 15 nm. Such a depth has been deduced from escape-depth probability calculations for iron [3], which indicate that for the detected electrons, a 15 nm thick surface layer gives a ~ 20% contribution to the spectrum.

Pure iron samples boronized for 15 h at 1000° C gave the X-ray Mössbauer spectrum shown in Fig. 6b. This spectrum is due to contributions arising from a ~ 20 μm thick surface

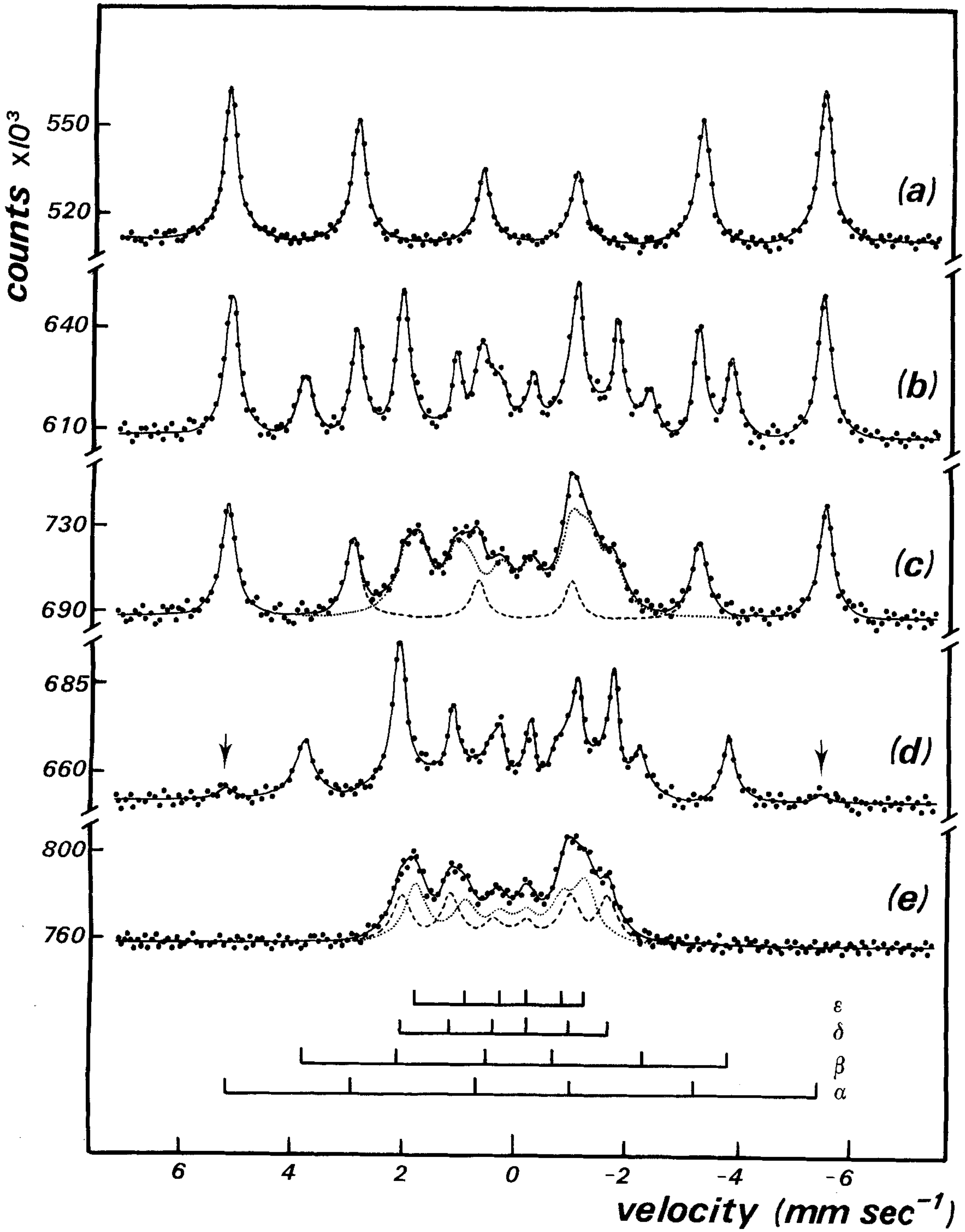

Figure 6 Room-temperature Mössbauer spectra for pure iron boronized: (a) for 24 h at 850° C (6 to 7.3 keV electrons), (b) for 15 h at 1000° C (6.4 keV X-rays), (c) for 15 h at 1000° C (6 to 7.3 keV electrons), (d) for 15 h at 1000° C (6.4 keV X-rays), (e) for 15 h at 1000° C (6 to 7.3 keV electrons). Zero velocity is referred to Rh.

TABLE I Hyperfine magnetic fields, H_{hf}, quadrupolar splittings, Q_S, and isomer shifts referred to Rh, I_S, for the samples analysed.

Sample	Detected radiation	Sextet α			Sextet β			Sextet δ			Sextet ϵ		
		H_{hf} (± 3 kOe)	Q_S (± 0.03 mm sec^{-1})	I_S (± 0.05 mm sec^{-1})	H_{hf} (± 3 kOe)	Q_S (± 0.03 mm sec^{-1})	I_S (± 0.05 mm sec^{-1})	H_{hf} (± 3 kOe)	Q_S (± 0.03 mm sec^{-1})	I_S (± 0.05 mm sec^{-1})	H_{hf} (± 3 kOe)	Q_S (± 0.03 mm sec^{-1})	I_S (± 0.05 mm sec^{-1})
Pure iron boronized 24 h at 850° C	6-7.3 keV electrons	330	0.00	−0.11									
Pure iron borided 15 h at 1000° C	6.4 keV X-rays	328	0.00	−0.12	236	0.06	−0.03	117	0.13	0.06			
	6-7.3 keV electrons	330	0.00	−0.11				116	0.12	0.08	94	0.24	0.02
Pure iron borided 15 h at 1000° C (shielded)	6.4 keV X-rays				234	0.08	−0.03	118	0.14	0.06			
	6-7.3 keV electrons							115	0.10	0.08	94	0.24	0.03

layer, and it can be interpreted as the superposition of three sextets: α, β and δ. By comparing their Mössbauer parameters (given in Table I) with those quoted in the literature [8–13], it follows that the α, β and δ sextets are due to metallic iron, Fe_2B and FeB, respectively. By detecting the conversion electrons from the same sample, the spectrum of Fig. 6c was obtained, which appears to be due to the superposition of the three sextets α, δ and ϵ, whose parameters are given in Table I. Sextets α and δ can be attributed to metallic iron and to FeB, respectively. With regard to the sextet ϵ, it should be noted that a sextet with the same parameters was found to contribute to the room-temperature spectrum measured on Armco iron borided under identical experimental conditions by detecting the 6 to 7.3 keV electrons [1]. It was hypothesized that this sextet was due to a FeB_x boride, with $x > 1$ and perhaps equal to 2 [1, 7]. From a comparison between the spectra of Fig. 6b and c, obtained for an ~ 20 μm deep (X-ray spectrum) and an ~ 100 nm deep (electrons spectrum) surface layer, respectively, it follows that:

(i) the external regions of the samples borided at 1000° C do not contain Fe_2B compound, as the lack of sextet β in the electron spectrum (Fig. 6c) demonstrates;

(ii) the FeB compound grew between the inner Fe_2B and the outer FeB_x. In fact, as sextet ϵ (Fig. 6c) does not significantly contribute to the spectrum relative to a ~ 20 μm thick surface region (Fig. 6b), it must be concluded that FeB_x grows as the outermost very thin boride region. Moreover, both electron and X-ray measurements display a contribution from sextet δ, while sextet β contributes only to the X-ray spectrum (Fig. 6b).

(iii) The reaction products did not form a continuous coating on the pure iron samples, in agreement with the metallographic observation. Like sextet δ, sextet α contributes both to the 20 μm (Fig. 6b) and to the 100 nm spectrum (Fig. 6c). The same considerations as in (ii) would imply the improbable presence of a layer of material not affected by the boriding process (i.e. pure iron) between two boride layers (Fe_2B and FeB_x). From Mössbauer measurements, therefore, one must once more conclude that a fraction of the sample surface did not react with boron.

It seemed useful to analyse separately the two morphologically different zones displayed by the surfaces of boronized pure iron. Fig. 6d and e show X-ray and electron spectra, respectively, detected at room temperature from pure iron samples boronized for 15 h at 1000° C after shielding the zones surrounding the islands of borides. The X-ray spectrum shown in Fig. 6d differs from that measured from the same sample before shielding (Fig. 6b) in that sextet α is reduced to only two small shoulders, indicated by arrows in the figure, and corresponding to the $\frac{3}{2} \rightarrow \frac{1}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$ transitions of metallic iron. As the electron spectrum for the shielded sample (Fig. 6e) does not display sextet α at all, one can conclude that this small contribution arises from the base metal areas underlying the boride islands. From area measurements, sextet ϵ was seen to give a 50% contribution to the electron spectrum. Therefore, an average thickness of ~ 35 nm has been estimated for the more external boride, FeB_x, that is responsible for sextet ϵ. When shielding boride islands, on the other hand, both X-ray and electron spectra only display the sextet α (metallic iron): thus in such a part of the surface no reaction product was formed between pure iron and boron, at least for regions deeper than 15 nm in the samples examined.

It should be noted that the room-temperature Mössbauer spectrum of pure iron is indistinguishable, within the experimental error, from the spectra of Fe–B solid solutions, owing to the very low solubility of boron in α iron [14]. Therefore, the possibility that boron has diffused into the metallic zones surrounding the islands of reaction products cannot be excluded on the basis of Mössbauer analyses.

4. Discussion

A few of the above results must be discussed in particular detail. First, the pure iron showed surface zones differentiated in reactivity towards boron, so that sparse boride islands were allowed to grow in 15 h at 1000° C. This behaviour of metal surfaces is well known, and its extent in the present case is not surprising when the low rate of boriding process in a crystalline boron powder is taken into consideration.

A second result to be discussed is that the islands of reaction products contained, in a stratified arrangement, crystals of the same borides which were singled out in the coatings previously produced on Armco iron under identical experimental conditions [1]: Fe_2B, FeB and FeB_x, in order from the base metal to the external surface. Furthermore, the average thicknesses of the boride regions grown on the more reactive zones of pure iron surfaces were equivalent to the thicknesses of the layers already observed on Armco iron. It is possible therefore to argue that nucleation of the compound less-rich in boron, Fe_2B, may be the limiting step in the studied boriding process. In other words, at 1000° C under vacuum, the boronizing medium assures availability of active boron, which can react with certain zones of the pure iron surface to give Fe_2B. At these preferred zones boriding proceeds in the same way and to about the same extent as it happened on Armco iron: Fe_2B nuclei grow in the form of large crystals (Fig. 4), owing to the low density of nucleation sites. The outer crystals of Fe_2B, being in contact with boron, become richer in this element and then change to FeB. The new boride, in its turn, grows and then FeB_x crystals are formed in its outer part.

A third result, the marked difference in reactivity between high purity and Armco iron, should be further discussed. Experiments with iron samples carburized up to 0.3% C by weight prior to being boronized have shown that the higher reactivity of Armco iron towards boron powder at 1000° C cannot be attributed to differences in carbon levels, i.e. in the contents of interstitial carbon and possibly of cementite. By also taking into account the fact that the metals compared are about equivalent in grain size and have both been boronized in an annealed condition, the differences in reactivity might be due to different densities of lattice defects, and especially of dislocations. From internal friction measurements on Armco iron borided with amorphous boron powder, Chomka *et al.* [15] deduced that boron had diffused in iron along dislocations and grain boundaries. Krishtal and Grinberg [16], while studying the changes in the structure of iron during the diffusion of boron, observed by means of electron microscopy that dislocation density was an order of magnitude higher in the regions through which boron had passed than in the boron-free regions. These might be two good reasons for a greater penetration and reaction of boron in a more defective metal. Boronizing experiments with previously cold-rolled iron samples, however, lead us to discard this explanation. A very high increase in dislocation density, in fact, undoubtedly has ensued a 22% thickness reduction, without an equivalent increase in the surface reactivity of metal samples toward boron.

Now, it seems more plausible that the higher reactivity of Armco iron may be due to a greater lattice distortion, caused in this metal, for example, by a higher content of large-sized atoms in solid solution. To support this view, there is the reactivity towards boron displayed both by edges and corners of the samples, and by the pure iron surface zones heavily deformed by punching before boronizing. In these regions, cutting or punching gave rise to local concentrations of internal stresses and lattice distortions.

In conclusion, from the experimental results reported in the present paper one is allowed to think that thermal boriding of pure iron with crystalline boron powder may be controlled by Fe_2B nucleation. At Fe_2B nuclei, reaction can proceed thanks to constraint arising at the Fe_2B–Fe interfaces as a consequence of differences existing between the volume of the formed boride and the volume of the transformed metal. On preferred surface zones of pure iron, therefore, there is a growth of Fe_2B boride, followed by a successive formation of FeB and FeB_x borides.

The density of nucleation sites for Fe_2B is very high near wedges, corners, or other heavily deformed surface zones of pure iron samples, as well as at the surface of Armco iron. These zones or surfaces, therefore, become entirely covered by reaction products. Such a scheme has been built up for the boriding process of pure iron on the basis of these experimental results. Further work is being carried out to confirm this definitely.

5. Conclusions

Boronizing with crystalline boron powder of high-purity iron samples previously annealed, or carburized up to 0.3% C by weight, or cold rolled up to a 22% thickness reduction, has pointed out that only a fraction of the exposed surface reacts with boron at 1000° C, irrespective of the preliminary treatment. In no way were boronized samples covered by a continuous layer of reaction products, as happened to the Armco iron samples examined in a preceding paper [1]. On the contrary, pure iron surface zones heavily deformed by punching, or lying near wedges and corners of the samples, behaved at 1000° C like Armco iron surfaces.

X-ray and electron Mössbauer spectroscopy revealed, on pure iron, the same reaction products as on Armco iron, i.e. Fe_2B, FeB and FeB_x with $x > 1$ going from the base metal to the external surface. The technique also allowed a stratified disposition of borides to be determined and the average thickness of each boride region was found to be about the same on pure iron and on Armco iron: $\sim 20\,\mu m$ for the total thickness, and ~ 35 nm for the FeB_x region.

These results have been interpreted by assigning to the nucleation of the boride less-rich in boron, Fe_2B, the role of limiting step for thermal boriding of iron in boron powder. At Fe_2B nuclei, boriding should be aided by constraint at Fe_2B–Fe interface. In this way, differences between the two metals with regard to reactivity towards boron may be attributed to different densities of nucleation sites for Fe_2B.

Compared to high purity iron, Armco iron has a higher content of atoms which can be responsible for intensified internal stresses and distortions. These effects must reach the same order of magnitude as those induced in pure iron samples by cutting or punching. The effects of an increase of carbon content up to 0.3 wt% or of a 22% thickness reduction by cold rolling, proved to be insufficient to raise reactivity of pure iron to the same level as Armco iron.

Finally, crystalline boron powder, as expected, has proved to be too mild a boronizing medium to be of practical interest. The study of its interaction with iron, however, allowed significant information to be collected on the early stages of powder boriding.

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