JOURNAL OF MATERIALS SCIENCE 19 (1984) 4035–4039

# Composition and structure of boride layers grown on low-manganese ternary iron alloys

M. CARBUCICCHIO
*Institute of Physics, University of Parma, Italy*
G. PALOMBARINI, G. SAMBOGNA
*Institute of Metallurgy, University of Bologna, Italy*

Three Fe–C–Mn alloys containing 0.30, 0.60 and 1.35 wt % Mn, respectively, were laboratory cast and homogenized, borided for 4, 8 and 15 h at 850° C in contact with a $B_4C$-base powder mixture and then studied by using surface Mössbauer spectroscopy, X-ray diffraction, metallography and microhardness measurements. The boriding depth and the properties of the reaction products were determined and discussed with regard to the manganese content in the alloys. The comparison with the results previously obtained for borided Fe–C–Ni and Fe–C–Cr alloys allowed some general features to be determined with regard to the coatings which can grow on iron alloys in contact with high power boronizing media.

## 1. Introduction

Alloying elements are recognized to play an important role in the thermochemical boriding of laboratory and industrial iron alloys, in that they (i) appreciably influence both disposition and relative amounts of the reaction products in the boride coatings, and (ii) enter the coatings, modifying composition and properties of the iron borides.

To study the effect that each alloying element has individually on the boriding process and properties of the boride coatings, ternary alloys were laboratory prepared by adding different amounts of manganese to an iron–carbon base composition, and thermochemically powder borided. Only a few studies on the role of manganese are reported in the literature, and these generally deal with steels [1, 2].

The boride surface layers were studied with various experimental techniques and the results were discussed in comparison with those previously obtained for Fe–C–Ni and Fe–C–Cr alloys borided under the same experimental conditions [3, 4].

## 2. Experimental details

Mixtures of Armco iron and pure manganese were melted in a middle-frequency induction furnace, then cast and homogenized by prolonged thermal treatments. In this way, three alloys were prepared containing 0.30, 0.60 and 1.35 wt % Mn as the main alloying element; each alloy also contained 0.02 wt % C. The manganese content was selected on the basis of the usual composition ranges of steels.

Sheets of about $25 \times 15 \times 1\ \text{mm}^3$ were surface finished with emery papers up to 600 grit and borided for 4, 8 and 15 h at 850° C in contact with a $B_4C$-base (~ 20 wt %) powder mixture containing $KBF_4$ (~ 2.5%) as the activator and SiC as the diluent, following a pack-cementation procedure. This high power boronizing medium, which enables large amounts of active boron to be supplied, was chosen in order to obtain boride coatings containing reaction products richer in boron than $Fe_2B$.

Surface Mössbauer measurements were performed using the experimental apparatus described by Carbucicchio [5] and by detecting the *K* X-rays (6.4 keV) and the *K*-shell conversion electrons (7.3 keV) resonantly re-emitted by the $^{57}Fe$ atoms. Electron energies in the 5.5 to 7.3, 6 to 7.3 and 6.5 to 7.3 keV ranges were selected. The thicknesses of the corresponding surface layers were estimated according to Krakowski and Miller

0022–2461/84 $03.00 + .12

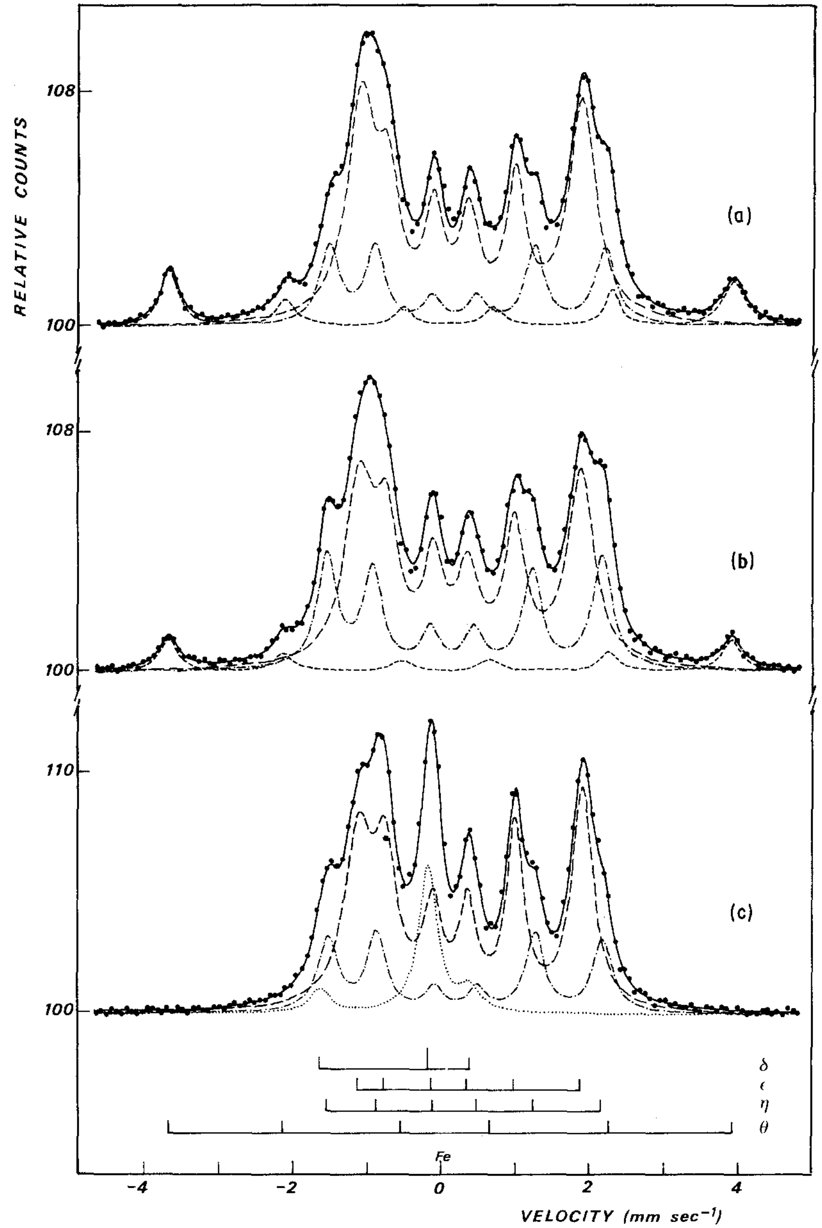

*Figure 1* Room-temperature surface Mössbauer spectra: (a) for the borided Fe–C–0.30 wt % Mn alloys (6.4 keV X-rays); and for the borided Fe–C–1.35 wt % Mn alloys, (b) 6.4 keV X-rays, (c) 6 to 7.3 keV conversion electrons.

[6] with a correction for the escape of detected radiation for different phases [7]. A 40 mCi $^{57}$Co(Pd) source was used. The spectra were measured at room temperature and computer-fitted to a series of Lorentzian lines.

X-ray diffraction patterns of the borided alloys were recorded using Co*Kα* radiation and a computer-controlled vertical goniometer. Further information on thickness and disposition of the reaction products was achieved from samples abraded layer by layer. Metallographic cross-sections of treated samples were prepared, observed under optical and scanning electron microscopes and, finally, utilized to measure thickness and microhardness of the boride coatings with the aid of a Vickers indenter with a 1.0 or 0.5 N load.

## 3. Results and discussion

Figs. 1a and b show the 6.4 keV X-ray Mössbauer spectra (estimated depth of analysis, ~ 25 μm) measured for the borided 0.30 and 1.35 wt % Mn alloys, respectively. For the same 1.35 wt % Mn sample, the 6 to 7.3 keV conversion electron spectrum (estimated depth, ~ 120 nm) is shown in Fig. 1c. All these spectra can be described in terms of various superimposed contributions:

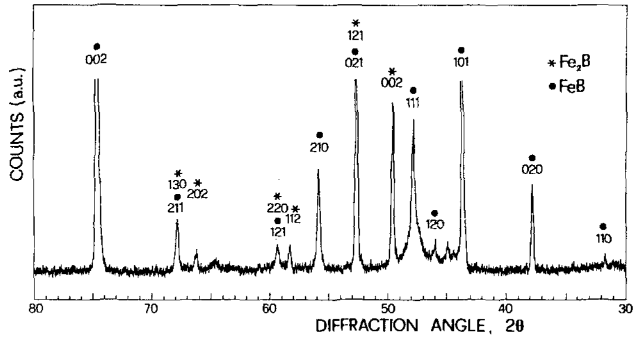

*Figure 2* X-rays diffraction pattern for the as-borided Fe–C–1.35 wt % Mn alloys (Co$K\alpha$).

(i) a ferromagnetic spectrum, $\theta$, which contributes to spectra 1a and 1b;

(ii) two sextets, $\eta$ and $\epsilon$, which contribute to all the spectra reported in Fig. 1;

(iii) a central peak and the quadrupole doublet, $\delta$, which contribute only to spectrum 1c.

The analysis of their Mössbauer parameters suggests that: the $\theta$ contribution is due to $Fe_2B$ [8], sextet $\eta$ to FeB [9] and sextet $\epsilon$ to $FeB_x$ with $x > 1$ [3, 4]. The central peak and quadrupole doublet, $\delta$, can be ascribed to iron in solid solution with boron, $(B,Fe)_{ss}$ [10].

By comparing Mössbauer spectra relative to surface layers of different thickness (Figs. 1b and c), it follows that the coatings are constituted by an inner $Fe_2B$ single-phase layer (absence of the $\theta$ contribution to spectrum 1c) and an outer FeB-base polyphase region containing $FeB_x$ (presence of $\eta$ and $\epsilon$ sextets in both the spectra 1b and 1c) and an iron–boron solid solution located very close to the external surface ($\delta$ contribution to spectrum 1c only).

The X-ray diffraction patterns of the same samples showed resolved peaks of only FeB and $Fe_2B$ (Fig. 2). As already observed in the case of borided nickel- or chromium-containing ternary alloys, this type of analysis appears to be unable to reveal $FeB_x$. Since the solid solution $(B,Fe)_{ss}$ is very close to the external surface of the coatings, it could not be detected by X-ray diffraction.

Hardness values up to 16 kN mm$^{-2}$ were measured on metallographically prepared cross-sections of the coatings. Subsequent layer by layer X-ray diffraction analyses showed that both the outer FeB and the inner $Fe_2B$ display (002) preferred crystallographic orientations, particularly strengthened near the FeB–$Fe_2B$ and $Fe_2B$–alloy interfaces.

Similar compositions and structures were found in the case of Fe–C alloys containing 2.16 to 8.85 wt % Ni or 1.26 to 5.65 wt % Cr, borided under the same experimental conditions.

From area measurements of the contributions to the spectra relative to different depths of analysis for the same borided manganese-containing sample (Figs. 1b and c), it results that the FeB/$FeB_x$ ratio decreases as the external surface of the sample is approached. This result differs from that previously obtained for the boride coatings grown on Fe–C–Cr alloys, where the ratio increased through the coatings [4].

As expected, therefore, the relative concentration of $FeB_x$ in the FeB-base polyphase regions increases on going towards the external surface, with the important exception of the borided chromium-containing ternary alloys. To explain this exception, an hypothesis was advanced involving a progressive transformation of $FeB_x$ into $(B,Fe)_{ss}$ towards the external surface of chromium-containing boride coatings, due to an enhanced inwards diffusivity of boriding species allowed by a chromium-induced embrittlement and cracking of the outer part of these coatings [4].

From the comparison between the 6.4 keV X-ray Mössbauer spectra measured for borided 0.3 and 1.35 wt % Mn alloys (Figs. 1a and b), it follows that, as the manganese content increases in the base alloys:

1. The thickness of the outer FeB-base region of the boride coatings increases, since the relative $\theta$ contribution to the spectra (i.e. the $Fe_2B$ within the first 25 μm of thickness) decreases. A similar effect is played by chromium in boriding treatments of Fe–C–Cr alloys [4]. On the contrary, an increase of the nickel content in Fe–C–Ni alloys leads the thickness of this outer region to decrease in the boride coatings [3].
2. Within the FeB-base region, the FeB/$FeB_x$

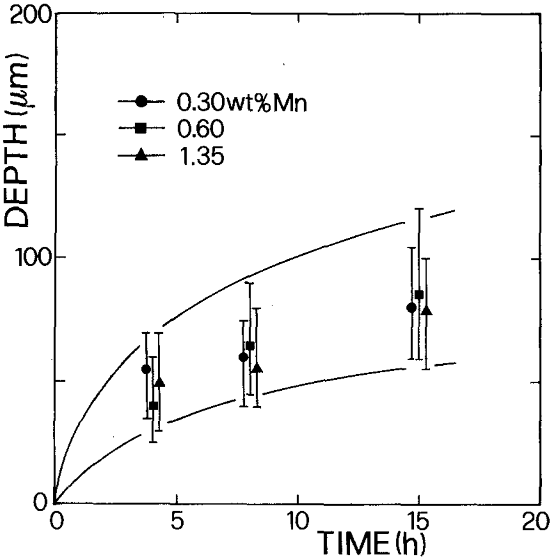

*Figure 3* Maxima, minima and average metallographically determined values of boriding depth for different lengths of treatment.

ratio increases, as determined by relative area measurements. Again, a similar effect was observed when the chromium content of the Fe–C–Cr alloys was increased [4], while the FeB/FeB$_x$ ratio was found to be only slightly affected by variations in the nickel concentration of Fe–C–Ni alloys [3].

In the boride coatings grown on manganese-containing alloys, the $(B,Fe)_{ss}$ is located within the first 100 nm of thickness. In the case of Fe–C–Cr alloys, the thickness of the $(B,Fe)_{ss}$-containing surface layers increased from 100 nm up to a few micrometres as the chromium content was increased from 1.26 to 5.65 wt% in the base alloy [4]. A similar increase of the relative $(B,Fe)_{ss}$ amounts in the surface layers of the coatings was observed for Fe–C–Ni alloys as the nickel content was increased from 2.16 to 8.85 wt% [3]. It is to be noted that (i) the maximum content of manganese (1.35 wt%) and minimum of chromium are almost coincident, and (ii) the concentration ranges of nickel and chromium are partially overlapping. This suggests that the commonly used iron-alloying elements are similar in promoting the formation of a reaction product particularly rich in boron (a solid solution of iron in boron) within the outer FeB-base regions of coatings grown on iron alloys.

The morphology of the coating–substrate interfaces appears to be strongly columnar for all the Fe–C–Mn alloys examined. The differences between maximum and minimum thicknesses of the coatings increase with the length of treatment (Fig. 3). It is worth noting that chromium, when increased in the Fe–C–Cr alloys, was able to induce an appreciable flattening of the coating–substrate interfaces, while nickel contents up to 8.85 wt% only slightly reduced the coating columnarity [3, 4].

The iron borides in the coatings grown on Fe–C–Mn alloys are in effect manganese-containing products. The manganese redistribution between coatings and substrates was studied by means of electron probe microanalysis carried out on metallographic cross-sections such as that shown in Fig. 4. Manganese concentration profiles, recorded about parallel to the external surface of a borided 0.60 wt% Mn sample across the columnar aggregates of the $Fe_2B$ boride, are shown in Fig. 5. These paths of analysis proved to be more effective in showing redistribution phenomena of alloying elements than were paths perpendicular to the external surfaces. The profiles clearly indicate the

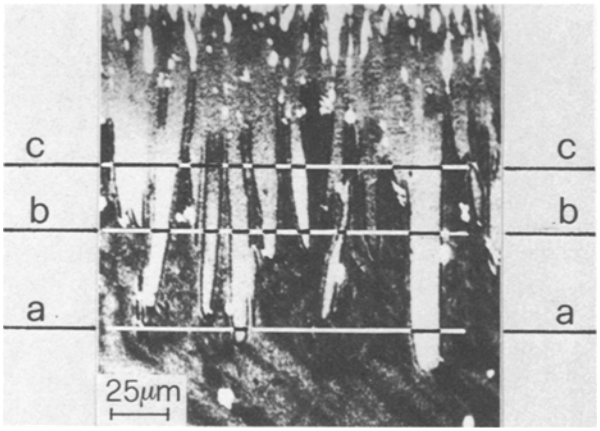

*Figure 4* Optical micrograph of a cross-section for an Fe–C–0.60 wt% Mn alloy borided for 15 h at 850° C, showing the lines selected for manganese microanalysis.

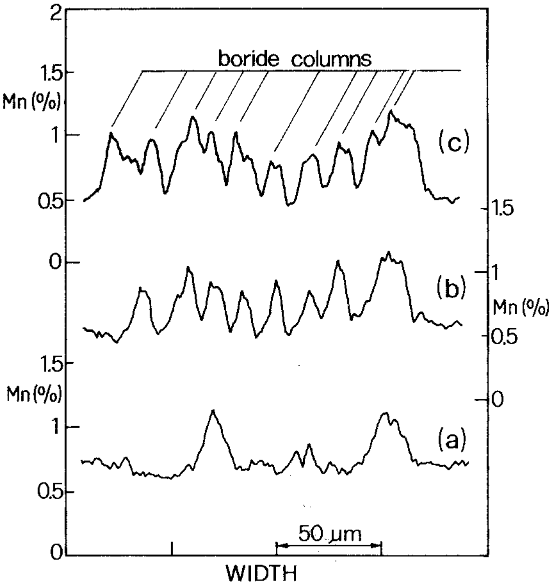

*Figure 5* Manganese concentration profiles measured along the lines a, b and c shown in Fig. 4.

tendency of manganese to concentrate within the boride, with the consequent depletion of the underlying unborided matrix. Manganese redistribution is qualitatively similar to that pointed out for chromium [4]. Nickel, on the contrary, showed the tendency to concentrate beneath the coatings, allowing borides to be grown which are low in nickel as compared with the base alloys [3].

## 4. Conclusions

Phase composition and structure of boride layers thermochemically grown on Fe–C–Mn laboratory prepared alloys containing from 0.3 to 1.35 wt% Mn, at 850° C in contact with a high power boronizing medium, were studied and compared with the results previously obtained for coatings grown on Fe–C–Ni and Fe–C–Cr alloys borided under the same experimental conditions. The following conclusions can be drawn.

1. The boride coatings grown on the ternary iron alloys are generally constituted by an inner $Fe_2B$ single-phase layer and an outer FeB-base polyphase region containing $FeB_x$ with $x > 1$ and, close to the external surface, an iron in boron solid solution.

On going towards the external surface of the coatings grown on Fe–C–Mn alloys, the FeB/$FeB_x$ ratio decreased similarly to what occurred for Fe–C–Ni alloys, while it was found to increase for Fe–C–Cr alloys.

2. With increasing contents of the third alloying element in the alloys, both the thickness of the FeB-base region and the FeB/$FeB_x$ ratio increased in the case of manganese- or chromium-containing alloys; in the case of nickel-containing alloys, that thickness decreased while the ratio appeared to be only slightly affected.

The content of the third alloying element, moreover, considerably influences the amounts of the iron–boron solid solution within the surface layers of the boride coatings.

3. All the alloying elements examined enter iron borides, substituting for iron. Manganese and chromium, however, tend to concentrate within the coatings, depleting the underlying unborided matrix, whereas nickel concentrates beneath the boride coatings, allowing low-nickel borides to be formed.

4. Borides generally grow as columnar aggregates of ordered crystals; the extent of columnarity increases with length of treatment.

The preferred crystallographic orientation is (002) for the main reaction products and it is particularly strong near the FeB–$Fe_2B$ and $Fe_2B$–substrate interfaces.

In the coatings, the hardness reaches values up to 16 kN mm$^{-2}$.

## Acknowledgements

This work was carried out with financial support from the CNR, Italy, under the "Progetto Finalizzato Metallurgia".

## References

1. V. I. POKHMURSKII, V. G. PROTSIK and A. M. MOKROVA, *Sov. Mater. Sci.* 16 (1980) 185.
2. J. VILSMEIER, P. CASADESUS, Kh. G. SCHMITT-THOMAS and M. GANTOIS, *Hart.-Tech. Mitt.* 35 (1980) 24.
3. M. CARBUCICCHIO, G. MEAZZA and G. PALOMBARINI, *J. Mater. Sci.* 17 (1982) 3123.
4. M. CARBUCICCHIO, E. ZECCHI, G. PALOMBARINI and G. SAMBOGNA, *ibid.* 18 (1983) 3355.
5. M. CARBUCICCHIO, *Nucl. Instr. Meth.* 144 (1977) 225.
6. R. A. KRAKOWSKI and R. B. MILLER, *ibid.* 100 (1972) 93.
7. V. E. COSSLETT and R. N. THOMAS, *Brit. J. Appl. Phys.* 15 (1964) 883.
8. I. D. WEISMAN, L. J. SWARTZENDRUBER and L. H. BENNET, *Phys. Rev.* 177 (1969) 465.
9. H. BUNZEL, E. KREBER and U. GONSER, *J. Phys. (Paris)* 35 (1974) C6.609.
10. F. STANKE and F. PARAK, *Phys. Status Solidi* 52 (1972) 69.

*Received 6 February*
*and accepted 21 February 1984*