Phase composition and morphology as a function of depth for boride coatings grown on Fe-Ni alloys

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Abstract. Two Fe-Ni alloys very differing in Ni content, Fe₆₄Ni₃₆ and Fe₂₀Ni₈₀, were borided at 850°C for 8 h using a high boron potential powder medium. On both alloys ~150 µm thick boride coatings grew in the form of two stratified sublayers of different thickness depending on the Ni content of the metal substrate. The outer sublayer mainly consisted of a ternary (Fe,Ni)B compound with small amounts of Ni borides in its outermost region, the inner by a ternary (Fe,Ni)₂B compound. It is shown and explained how the same (Fe,Ni)B compound could form on both high-Ni alloys in spite of the considerable difference in Ni content.

1. Introduction

A considerable interest is addressed to iron-nickel alloys as candidate materials for the production of structural components displaying a satisfactory resistance to chemical corrosion, as well as to surface treatments suitable to improve their performance to stress corrosion cracking, fatigue and wear [1]. In this regard, coatings of iron borides display hardness values in excess of 20 GPa, as well as good resistance to wear under both sliding and abrasive conditions [1-2]. Borided steel components display excellent performance in several tribological applications in the mechanical engineering and automotive industries. The composition, growth rate and properties of the boride coatings are dependent on type and behaviour of the alloying elements to an extent requiring further investigation and clarification.

In the present work attention has been addressed to the role of Ni. Two binary Fe-Ni alloys with Ni contents of 36 at.% and 80 at.%, respectively, were borided by means of a pack-cementation process under conditions (boron potential of the medium, exposure time) selected in order to produce protective coatings with a thickness of practical interest.

2. Experimental

1 mm thick sheets of two commercial Fe-Ni alloys, Fe₆₄Ni₃₆ and Fe₂₀Ni₈₀, received in an annealed state, were surface finished with SiC emery papers up to 600 grit and then thermochemically borided at 850°C for 8 h using a powder mixture consisting of amorphous boron (boronizing agent) and KBF₄ (10 wt.%, activator). The treatments were carried out in crucibles of refractory steel filled with the boriding medium and tightly sealed in order to avoid undesired oxidizing reactions. The analyses were carried out on as-grown coatings as well as at different depths after layer-by-layer abrasions performed parallel to the external surface. X-ray diffraction (XRD) was performed using a computer-controlled...
goniometer and CoKα radiation with 0.02 20 degrees step size and 1 s scan step time. The Mössbauer measurements were carried out by detecting the 6.4 keV X-rays in scattering geometry (CXMS) using a 40 mCi $^{57}$Co(Rh) source. A least squares minimization routine with a combination of linear and non linear regressions was used to fit the spectra as a superposition of Lorentzian lines. The isomer shifts are referred to α-Fe. The metallographic analyses were performed on cross sections of borided samples by means of optical microscopy (OM) and scanning electron microscopy (SEM) and, for elemental compositions, by energy dispersive spectrometry (EDS).

3. Results and Discussion

Figure 1(a) shows a metallographic cross section of the borided Fe$_{64}$Ni$_{36}$ alloy. A coating ~150 μm thick grew on the substrate in the form of two sublayers (A and B in figure) almost equal in thickness. EDS analyses carried out on the cross section at different depths from the external surface show that the reaction products contain Fe and Ni in an atomic ratio which everywhere in the coating is only slightly lower than that measured for the base alloy (Ni/Fe $\approx$ 0.53). In addition, the coating contained boron in amounts decreasing on going towards the coating-alloy interface.

![Figure 1](image1.png)

**Figure 1.** Cross sections of (a) Fe$_{64}$Ni$_{36}$ and (b) Fe$_{20}$Ni$_{80}$ samples borided at 850°C for 8 h with a powerful boriding medium: A: outer sublayer; B: inner sublayer;

The XRD pattern measured on the external surface of the coating [figure 2(a)] shows contributions of FeB phase displaying a strong (002) preferred crystallographic orientation, Ni$_2$B and Fe$_2$B, the last only contributing with its (002) reflection. A diffraction peak at 46.80 2θ might be attributed to the (501) reflection of orthorhombic Ni$_2$B$_3$, other peaks of this compound being masked by overlapping to peaks of the above phases in the coating, or missing at all as the consequence of crystallographic texturing effects.

The CXMS spectrum measured for the same sample [figure 3(a)] shows a quadrupole doublet, (Table 1) which can be attributed to an (Fe,Ni)B compound [3]. It is to be noted that the diffraction peaks for this ternary compounds are almost coincident with those of pure FeB because of the isomorphism existing between orthorhombic FeB and NiB compounds. (Fe,Ni)B could form due to the powerful reactivity between the base alloy and the adopted boriding medium, whose boronizing potential is very high. The effects of the boron reactivity, which are different for iron and nickel when lower boron potential media such as a B$_x$C-base powder mixtures are used, vanished and the active boron reacted without selectivity between Fe and Ni giving rise to a ternary (Fe,Ni)B compound. On the basis of the Ni/Fe atomic ratio evaluated by means of the above mentioned EDS analysis, the formula of this compound might be (Fe$_{1-x}$Ni$_x$)B with x slightly lower than the Ni at.% in the base alloy, taking into account that a small amount of nickel borides is present in the outermost part of the coating.

After removing from the coating an ~11 μm thick external layer of reaction products, the XRD pattern only shows the contribution of FeB, together with the (002) reflection of Fe$_2$B [figure 2(b)].
This result indicates that nickel borides only formed in the outermost part of the coating. The CXMS spectrum for the same sample only shows the quadrupole doublet attributed before to the (Fe,Ni)B ternary compound. Similar XRD and CXMS results were found after layer-by-layer analyses carried out at different depths within the outer sublayer of the boride coating [figure 1(a), zone A].

![Figure 2](image_url)

**Figure 2.** XRD patterns for borided samples: Fe\textsubscript{64}Ni\textsubscript{36} (a) as-borided and after removal of (b) 11 µm and (c) 75 µm outer layers; (d) Fe\textsubscript{20}Ni\textsubscript{80} as-borided.

After removing practically the whole outer sublayer of the coating, i.e. the zone A in figure 1(a), the XRD pattern shows a very intense (002)-Fe\textsubscript{2}B reflection, together with some relatively low intensity peaks due to both FeB and Fe\textsubscript{2}B [figure 2(c)]. The CXMS spectrum for the same sample [figure 3(b)] shows a prevailing ferromagnetic contribution (\(\beta_1\) and \(\beta_2\) sextets), whose parameters are reported in Table 1, which can be attributed to a (Fe,Ni)\textsubscript{2}B ternary compound. The spectrum also shows the contribution of the \(\delta\) doublet indicating the presence of small amounts of the (Fe,Ni)B ternary compound.

**Table 1.** Hyperfine parameters of the contributions to the CXMS spectra in figure 3.

| Contribution | IS (mm/s)    | \(\Delta E_Q\) (mm/s) | \(H_{hf}\) (kOe) |
|--------------|--------------|----------------------|------------------|
| \(\delta\)   | 0.21 ± 0.01  | 0.50 ± 0.01          | -                |
| \(\beta_1\)  | 0.17 ± 0.02  | -0.14 ± 0.03         | 184              |
| \(\beta_2\)  | 0.07 ± 0.01  | -0.04 ± 0.02         | 210              |

In conclusion, the coating grown on the Fe\textsubscript{64}Ni\textsubscript{36} alloy using a very powerful boriding medium consists of an outermost thin region of nickel borides and two main sublayers [zones A and B in figure 1(a)] containing respectively the (Fe,Ni)B and (Fe,Ni)\textsubscript{2}B ternary compounds. The hypothesis on the stoichiometry of the (Fe\textsubscript{1-x}Ni\textsubscript{x})B compound with \(x \approx 0.36\), was proposed considering that no preferred reaction could occur between boron and iron or nickel under the adopted boriding conditions. Under this hypothesis, (Fe,Ni)B ternary compounds differing in stoichiometry might form in boride coatings grown under the same conditions on binary alloys differing in the Ni content. Figure 1(b) shows a metallographic cross-section of a ~150 µm thick boride coating formed on the Fe\textsubscript{20}Ni\textsubscript{80} alloy. It consists of an ~5 ÷ 20 µm thick fine-grained sublayer grown on an inner ~130 µm thick coarse-grained sublayer of reaction products. The EDS analysis shows that, also in this case, the Ni/Fe ratio in the coating was everywhere similar to that in the base alloy. XRD measurements
confirmed that a FeB phase is the main component of the outer sublayer whose more external part, as shown by layer-by-layer analysis, consists of nickel borides Ni$_2$B and Ni$_4$B$_3$ [figure 2(d)].

The CXMS spectrum measured for this sublayer shows the $\delta$ quadrupole doublet due to the same (Fe,Ni)B ternary compound already found in the outer part of the boride coating grown on the Fe$_{64}$Ni$_{36}$ alloy. This fact suggests that the same (Fe,Ni)B ternary compound can form in the boride coatings growing on high-Ni binary alloys irrespective of the Ni content when a medium with a powerful boriding potential is used.

4. Conclusions
The boriding treatments carried out at 850°C on two Fe-Ni alloys considerably differing in Ni content using a very high boron potential medium for an exposure time of 8 h allowed the following conclusions to be drawn:

- The boriding reactions strongly involved both iron and nickel leading to the formation of coatings consisting of Fe-Ni-B ternary compounds, together with nickel borides located in the outermost regions of the coatings.
- The coatings grew in the form of two stratified sublayers. The outer composed of an (Fe,Ni)B ternary compound containing a small amount of nickel borides in a few $\mu$m thick region of its outer border, while the inner consists of (Fe,Ni)$_2$B compound. The thickness of the (Fe,Ni)B-base sublayer was considerably lower for the alloy with the highest Ni content, i.e. the Fe$_{20}$Ni$_{80}$, while the total thickness of the boride coating was practically the same on both alloys.
- The Mössbauer spectra measured for the (Fe,Ni)B formed on both Fe-Ni alloys are characterized by the same hyperfine parameters, a result indicating that the same ternary compound formed in the coatings irrespective of the Ni content in the base alloy. According to EDS analysis and considering the presence of Ni borides in the coatings, the Ni fraction in (Fe,Ni)B was evaluated to be slightly lower that 0.36.

References
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