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Surface structure of boride layers grown on Fe–C–Ni alloys

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Three Fe–C–Ni synthetic alloys differing in Ni content have been produced, powder borided for 15 h at 850° C with a B_4C-base mixture and then characterized by using surface Mössbauer spectroscopy, X-ray diffraction, metallography and microhardness measurements. The nature and disposition of the interaction products, boriding depths and hardness values of the predominant boride Fe_2B have been determined. The role of the Ni content in the alloy on the boriding process has been outlined.

1. Introduction

Thermochemical boriding of iron alloys is strongly dependent on the metal base composition. Alloying elements, in fact, can variously influence nature, disposition and properties of iron borides in the thermally grown surface layers, modifying in this way (i) diffusion paths and rates of the boriding species, (ii) nucleation characteristics of borides, borocarbides, etc., (iii) relative stability of reaction products, with particular reference to the FeB/Fe_2B ratio.

The increasing interest in boride Fe_2B as the main component of hard and wear-resistant surface layers has led to several fundamental and technological research programmes in the field. Blazon *et al.* [1] analysed the theoretical stability of the thermally produced $FeB/Fe_2B/Fe$ system starting from the configuration component of ion–ion interactions in the metal and concluding that Cr, Ni, Mo, Mn and W, as well as dissolved carbon, should have negligible effects on the boride layer structure. Cementite and other carbides, instead, should increase the relative stability of Fe_2B. Glukhov [2] tried to explain the mechanism of boriding with the aid of the concepts of stable electron configurations of atoms in solids, emphasizing the role of carbon in steels. Pradelli and co-workers [3–5] contributed widely to the knowledge of high-temperature Fe–Me–C–B phase diagrams (with Me = Mn, Cr, etc.). Technological efforts to improve boriding of commercial alloys have been pursued by many researchers.

Little attention, however, was devoted to synthetic alloys and to studies on the individual roles played in the process by each alloying element. Exceptions are the papers concerning the effects of V, Zr and Ti on growth kinetics and the hardness of boride layers on the corresponding binary alloys [6–8]. In the present work, synthetic Fe–C–Ni alloys differing in Ni content were powder borided and then examined to determine properties linkable to the presence of the alloying element.

2. Experimental details

Mixtures of Armco iron and pure nickel were melted in a middle-frequency induction furnace, then cast and homogenized by prolonged thermal treatments. In this way, three alloys were prepared containing 0.02 wt% C and, as for the main alloying element, 2.16, 4.59 and 8.85 wt% Ni, respectively.

Sheets of about 25 × 15 × 1 mm^3 were surface finished with emery papers up to a 600 grit and borided for times up to 15 h at 850° C in contact with a B_4C-base (20 wt%) powder mixture containing KBF_4 (2.5%) as activator and SiC as diluent.

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Surface Mössbauer measurements were performed using the experimental apparatus described by Carbucicchio [9] 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. As far as the electrons are concerned, regions of different depth were sampled by selecting electrons emerging from the surface with energies in the 5.5–7.3, 6–7.3 and 6.5–7.3 keV ranges. The thicknesses of the analysed surface layers were estimated using the method of Krakowski and Miller [10] with a correction for the escape of detected radiation for different phases [11]. A 40 mCi ^{57}Co(Pd) source was utilized. The spectra were measured at room temperature and computer-fitted to a series of Lorentzian lines. In all spectra shown, the isomer shifts were normalized with respect to the pure iron.

X-ray diffraction patterns of the borided samples have been recorded using the Cu$K\alpha$ radiation of 0.154 18 nm wavelength. Further information on thickness and arrangement of iron borides were achieved from samples abraded layer by layer. Metallographic sections were prepared to observe morphological details by means of optical and scanning electron microscopy. The hardness of different phases and regions in the borided coatings and substrates has been evaluated using a Vickers indenter with a 0.5 N load.

3. Results and discussion

Fig. 1a shows the 6.4 keV X-ray Mössbauer spectrum (surface layer ~ 25 μm thick) measured for the borided 8.85 wt % Ni alloy. This spectrum can be interpreted as the superposition of the following contributions (Table I):

(i) the sextets α and β, whose Mössbauer parameters agree with those reported in the literature for Fe_2B [12]:

(ii) the sextet η, which can be attributed to FeB [13];

(iii) the sextet ϵ, which was also found to contribute to surface Mössbauer spectra of Armco iron borided 15 h at 1000° C in contact with crystalline boron powder [14]; it was tentatively ascribed to an FeB_x compound with $x > 1$;

(iv) the quadrupole doublet δ and the single line indicated with an arrow in the figure, whose parameters agree with those reported in the literature for a solid solution of Fe in B: $(B, Fe)_{ss}$ [15].

It is worth noting that Ni (as well as other alloying elements) can diffuse in iron borides substituting Fe up to several tens at. %. Therefore, the above borides could be, in effect, Ni-containing iron borides. However, (i) Ni concentrations in the base alloys were relatively low, and (ii) analytical checks performed by the electron microprobe technique have shown a tendency for Ni to accumulate in the matrix near the boride layer. Then the amounts of Ni in the borides ought to be very small and this should correspond to variations in the Mössbauer parameters well within the experimental uncertainty.

For the same sample, surface layers ~ 90, ~ 120 and ~ 180 nm thick were analysed. Owing to the close similarity between the measured spectra, only the 6–7.3 keV conversion electron spectrum (estimated depth, ~ 120 nm) is shown in Fig. 1b. The lack of sextets α and β suggests that Fe_2B was the innermost reaction product grown after boriding. The other products FeB, FeB_x and $(B, Fe)_{ss}$ contribute to both X-ray and electron spectra (Fig. 1a, b). However, area measurements of the contributions to the spectra suggest that the relative amounts FeB_x/FeB and $(B, Fe)_{ss}$/FeB_x increase when passing from the Fe_2B layer to the external surface.

X-ray diffraction patterns recorded on the same sample showed FeB reflections together with some unresolved peaks lying within the 20°–24° and 36°–40° ranges of diffraction angle, θ (Fig. 2a). Any attribution of these peaks to the FeB_x compound was prevented by the lack of references in the literature to the subject. In considering the Fe_2B reflections, a masking effect by both FeB peaks and ground ought to be admitted.

Fig. 1c shows the 6.4 keV X-ray Mössbauer spectrum for the same sample as in Fig. 1a and b, whose outermost layer (~ 5 μm thick) was cautiously removed by abrasion. The lack of the single line and δ doublet indicates that the B–Fe solid solution was localized within the first 5 μm of the borided layer. The increase in the value of the Fe_2B/FeB ratio confirms the inner disposition of the Fe_2B product. As no contribution due to the matrix is detectable in this case either, one can deduce that the inner Fe_2B layer extends beyond 30 μm in depth. A lowering of the FeB_x/FeB ratio, in its turn, confirms the observation that products richer in boron are more abundant outwards.

By concluding this point, the borided coatings on the 8.85 wt % Ni alloys appear to be constituted

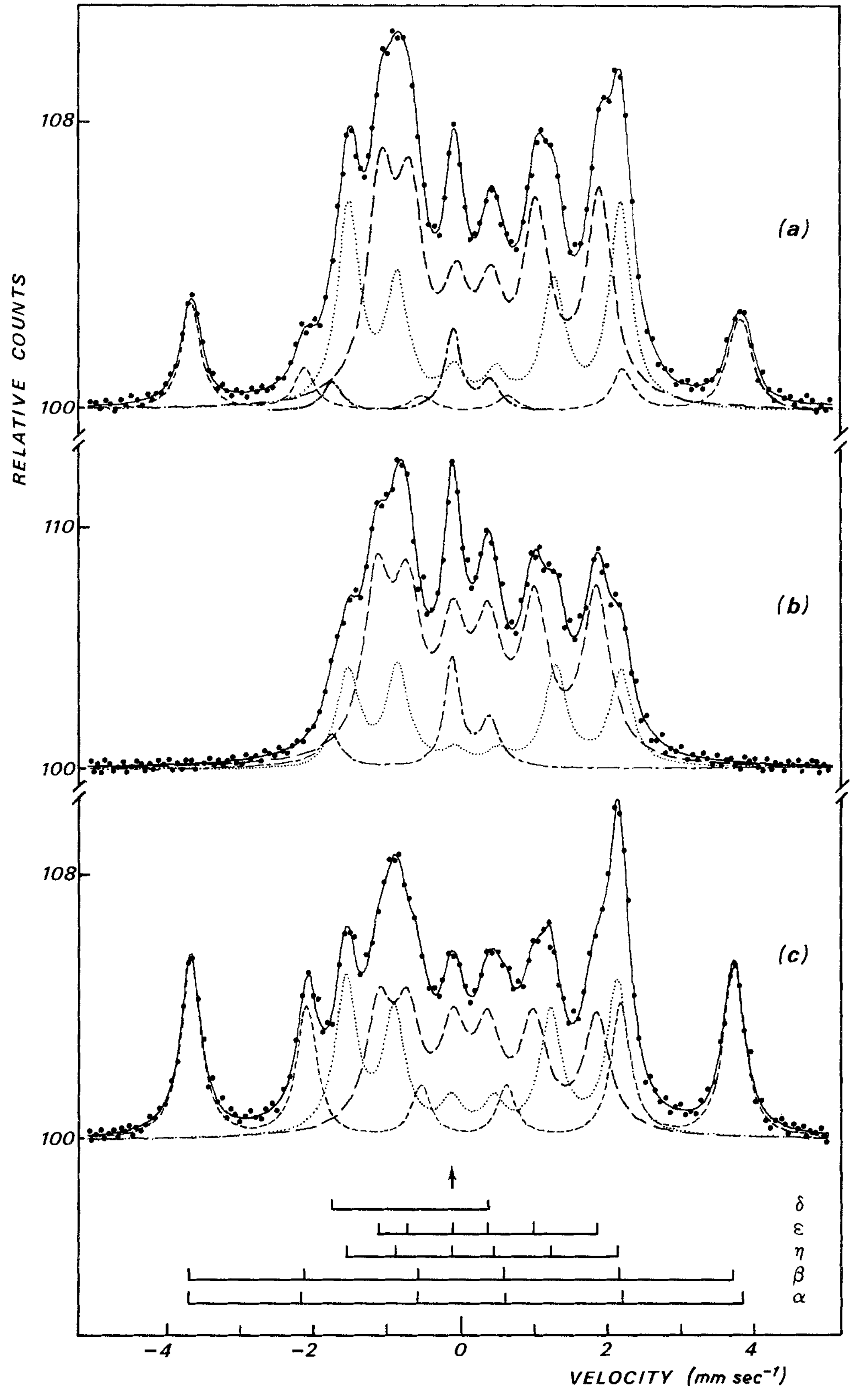

Figure 1 Room-temperature surface Mössbauer spectra for the borided Fe–C–Ni 8.85 wt% alloys: (a) 6.4 keV X-rays; (b) 6–7.3 keV conversion electrons; and (c) 6.4 keV X-rays after abrasion of a ~ 5 μm thick surface layer.

TABLE I Mössbauer parameters for the contributions to the spectra measured for borided Fe–C–Ni alloys: hyperfine magnetic fields (H_{hf}) in kOe, quadrupolar splittings (QS) and isomer shifts, against pure iron, (IS) in mm sec^{-1}

Contribution	H_{hf} (± 3 kOe)	QS (± 0.02 mm sec^{-1})	IS (± 0.03 mm sec^{-1})
Sextet α	235	0.07	0.06
Sextet β	231	0	0.03
Sextet η	116	0.13	0.25
Sextet ϵ	93	0.24	0.27
Doublet δ	–	2.14	−0.69
Single line	–	–	−0.13

by an innermost Fe_2B single-phase layer, an intermediate region containing FeB and FeB_x and a less than 5 μm thick outermost region containing FeB, FeB_x and $(B, Fe)_{ss}$.

From subsequent layer by layer analyses, the FeB-base region appeared to extend down to ~ 40 μm depth. The Fe_2B layer, in its turn, appeared to extend down to ~ 90 μm. It is worth noting that, on the abraded samples, both FeB and Fe_2B displayed (002) preferred X-ray diffractions, particularly strengthened near the FeB/Fe_2B and Fe_2B/alloys interfaces (Fig. 2b, c). Similar results have been reported in literature. Lyakhovich *et al.* [16] observed textured boride layers on Armco iron treated in the 600–1050° C range with strong boriding media (borax melts with an applied e.m.f., borax and boron carbide molten mixtures, or NH_4Cl-activated amorphous-boron powders). The same textures have been found by Casadesus *et al.* [17] in boride layers grown on Armco iron and carbon steels by means of ionic bombardment with diborane at 850° C, and by Galibois *et al.* [18] in layers grown at 900° C on an SAE 1095 high-carbon steel by means of a paste containing boron carbide and cryolite or a B_4C-base powder activated with KBF_4.

Metallographic cross-sections allowed the columnar morphology of the Fe_2B/alloy interface to be shown (Fig. 3), and the thickness values of the boride coatings to be confirmed.

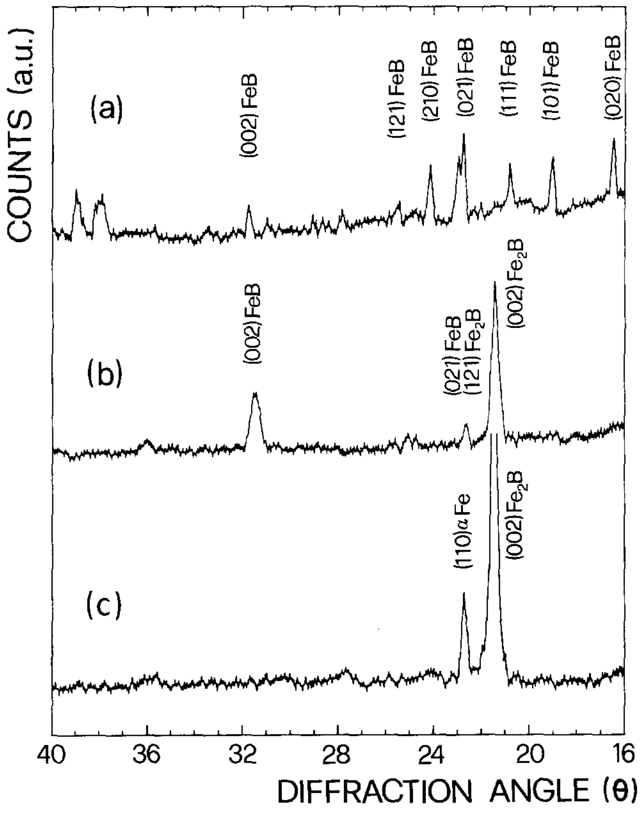

Figure 2 X-ray diffraction patterns for the borided Fe–C–Ni 8.85 wt% alloys: (a) as borided; and (b), (c) after abrasion of surface layers ~ 30 and ~ 85 μm thick, respectively.

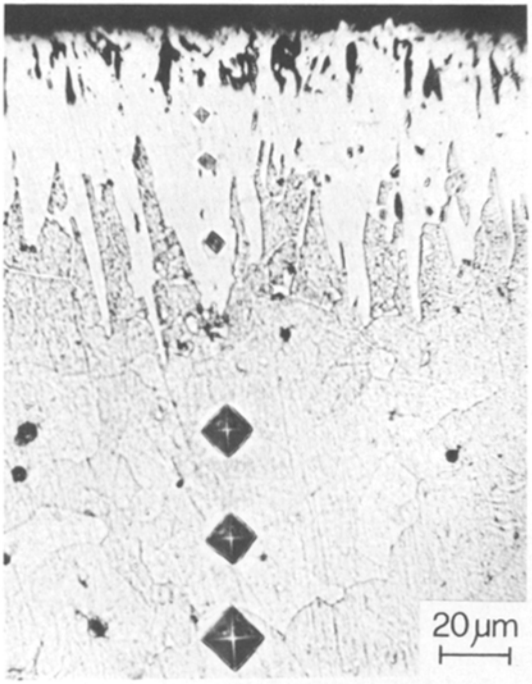

Figure 3 Optical micrograph of a cross-section of an Fe–C–Ni 8.85 wt% alloy borided for 15 h at 850° C, showing brittleness of the outer FeB-base region, tooth-like morphology of the Fe_2B/substrate interface and drastic change in hardness across the same interface.

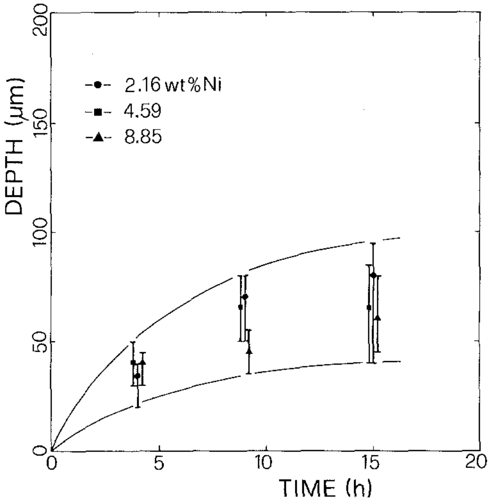

Figure 4 Maxima, minima and average metallographically determined values of boriding depths for different treatment times.

An appreciably different situation had been found for Armco iron borided for 15 h at 1000° C with crystalline boron powder, when Fe_2B, FeB and FeB_x were identified as the inner, the intermediate and the outer components of distinct layers ~ 15 μm, ~ 5 μm and ~ 30 nm thick, respectively [14]. In the present case, instead, the products richer in B than Fe_2B seem to be grown being characterized by higher permeability to boriding species, as a probable consequence of the remarkable differences existing between the boriding media, substrates and treatment temperatures adopted in the two types of experiments. Thus, nucleation and growth of high-B particles within the FeB phase should be facilitated in this case, and especially near the external surface.

The Mössbauer spectra of borided 2.16 and 4.59 wt%Ni alloys appeared to be due to the same products as those grown on the Ni-richer alloy. As the Ni content decreased, however, the 6.4 keV X-ray spectra displayed lower contributions from Fe_2B and $(B, Fe)_{SS}$. This indicates that (i) a concentration of the B–Fe solid solution occurred near the external surface, and (ii) the thickness of the products richer in B than Fe_2B increased.

Boriding depths, as determined from metallographic cross-sections, are reported in Fig. 4 for different length of treatment. Table II shows hardness values of the reaction product predominant in the coatings and more interesting for applications, Fe_2B. Maxima and minima measurements of boriding depth appear to be in accordance with an Fe_2B/alloy columnar interface (Fig. 3). A difference between maxima and minima of boriding depth which increases with treatment time in Fig. 4, should be noted. The minima are to be considered of particular importance with regard to a possible early emerging of metal zones at the external surface, e.g., as a consequence of wear or corrosion phenomena. A noticeable dispersion of results, moreover, is inherent to a metallographic technique of thickness measurement in that very hard and brittle surface products are likely to have undergone rounding and spalling effects.

TABLE II Boriding depths and $HV_{0.05}$ hardness values of the Fe_2B layers grown on Fe–C–Ni alloys in 15 h at 850° C

Alloy	Thickness (μm)		Microhardness (X 10 N mm^{-2})
	min	max	
Fe–C–2.16 wt% Ni	40	95	1450
–4.59 wt% Ni	40	85	1550
–8.85 wt% Ni	45	80	1350

4. Conclusions

The following conclusions can be drawn from the preceding discussion:

(1) the boride coatings grown on Fe–C–8.85 wt% Ni alloys contain Fe_2B, FeB, FeB_x (with $x > 1$) and a B–Fe solid solution as interaction products. Borides are likely to contain a few at.% Ni. Studies on the boriding of iron alloys generally ignore the formation of FeB_x and $(B, Fe)_{ss}$;

(2) Fe_2B is the only reaction product arranged as a single-phase layer. FeB_x and $(B, Fe)_{ss}$ grew within an FeB matrix, admittedly as a consequence of a somewhat high permeability of FeB itself to the boriding species, and their concentrations increase as the external surface is approached. $(B, Fe)_{ss}$, in particular, is concentrated within the first 5 μm;

(3) on samples abraded layer by layer, both Fe_2B and FeB display (002) preferred X-ray diffractions which, moreoever, appear to increase in strength when approaching the Fe_2B/alloy and FeB/Fe_2B interfaces;

(4) the columnar morphology of the coatings grows with treatment time;

(5) as the Ni content decreases in the alloys, Fe_2B is detected at increasing depths, while $(B, Fe)_{ss}$ is concentrated closer to the external surface. As the total boriding depth undergoes no remarkable change (Table II), one can conclude that the relative amount of Fe_2B diminishes in the coating as Ni increases in the alloy.

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References

1. M. BLAZON, B. STANOJEVIC and V. VELIKOVIC, *Scripta Metal.* 9 (1975) 1153.
2. V. P. GLUKHOV, *Sov. Powder Met. Metal Ceram.* 4 (1969) 278.
3. M. LUCCO BORLERA and G. PRADELLI, *Met. It.* 63 (1971) 107.
4. G. PRADELLI and C. GIANOGLIO, *Atti Accad. Naz. Lincei* 57 (1974) 655.
5. G. PRADELLI, C. GIANOGLIO and M. VALLINO, *Met. It.* 70 (1978) 265.
6. V. G. PERMYAKOV, I. Kh. TRUSH, V. F. LOSKUTOV, V. N. PISARENKO and Yu. E. YAKOVCHUK, *Met. Sci. Heat Treat.* 15 (1973) 1005.
7. I. Kh. TRUSH, V. G. PERMYAKOV and B. S. KIRCHEV, *ibid.* 16 (1974) 270.
8. V. G. PERMYAKOV, V. F. LOSKUTOV, V. P. BELYAEVA, V. N. PISARENKO and I. Kh. TRUSH, *Zashch. Pokrytiya Metallakh* (Protective Coatings on Metals) 9 (1975) 50.
9. M. CARBUCICCHIO, *Nucl. Instrum. Meth.* 144 (1977) 225.
10. R. A. KRAKOWSKI and R. B. MILLER, *ibid.* 100 (1972) 93.
11. V. E. COSSLETT and R. N. THOMAS, *Brit. J. Appl. Phys.* 15 (1964) 883.
12. I. D. WEISMAN, L. J. SWARTZENDRUBER and L. H. BENNETT, *Phys. Rev.* 177 (1969) 465.
13. H. BUNZEL, E. KREBER and U. GONSER, *J. Phys. (Paris)* 35 (1974) C6.609.
14. M. CARBUCICCHIO, L. BARDANI and G. PALOMBARINI, *J. Mater. Sci.* 15 (1980) 711.
15. F. STANKE and F. PARAK, *Phys. Stat. Sol.* 52 (1972) 69.
16. L. S. LYAKHOVICH, F. V. DOLMANOV, V. V. SURKOV and Yu. V. TUROV, *Khim-Termich. Obrabot. Met. Splavov,* Russian Collection, Minsk (1971) p. 74.
17. P. CASADESUS, C. FRANTZ and M. GANTOIS, *Mém. Sci. Rev. Mét.* 76 (1979) 9.
18. A. GALIBOIS, O. BOUTENKO and B. VOYELLE, *Acta Met.* 28 (1980) 1765.

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