Characterization of an iron boride coating produced by pack boronization of low carbon steel

The formation of iron boride conversion coatings on ferrous substrates is attractive for a wide range of applications. Significant features are their high melting points (1540° C for FeB [1, 2] and 1390° C for Fe_2B [1–4]), their metallic resistivities at 20° C (80 μohm cm for FeB and 38 μohm cm for Fe_2B [1–2]), their hardness [5–7] and potential low cost. Although in the past the principal application of iron boride coatings has been the surface hardening of steels for improved wear resistance, recent work has explored their potential as a protective coating in corrosive environments [7–11]. This paper describes an iron boride conversion coating on low carbon steel that was prepared and characterized during the course of a programme directed at identifying a corrosion resistant coating for positive electrode current collectors of high temperature molten salt batteries.

Iron boride conversion coatings can be prepared in numerous ways, including gas boronizing, molten salt boronizing, with and without electrolysis, and pack boronizing [4, 12]. In this work, the iron boride coatings were prepared using pack boronization techniques.

Most pack boronization mixtures consist of a boron compound as a source of boron, an activator and a filler. The composition of the pack mixture used in this work was [12]: boron compound: 20 mol % B_4C (Cerac, −325 mesh); activator: 5 mol % KBF_4 (Alpha Products); and filler: 75 mol % graphite (Fisher, Acheson No. 38). Samples to be boronized were 2 cm × 1.5 cm rectangular plates of 0.46 mm thick AISI 1008 steel. Sample pretreatment consisted of a 5 min wash in 5 M HCl followed immediately by a methanol rinse. Boronization was carried out in covered alumina or 304 stainless steel containers with the steel samples submerged in the pack mixture. Samples were inserted into and removed from the furnace at a furnace temperature of 960 ± 10° C. Steel samples were removed from the pack mixture and scraped clean.

Heating times were varied from 1 to 5 h with the change in surface composition being followed by powder X-ray diffraction (XRD) and the coating thickness by optical microscopy of polished cross-sections. Table I lists the XRD results obtained from the surfaces of boronized samples over the range of heating times.

TABLE I Effect of boronization time on surface composition (temperature = 960° C)

Sample	Heating time (h)	XRD of surface
7b	1	Patterns ill-defined, Fe_2B immerging, strong graphite, probable weak Fe.
8b	2	Fe_2B pattern prevalent, graphite strong, FeB immerging, no Fe detected.
9b	3	Fe_2B and FeB about equally well-defined and strong, graphite strong, no Fe detected.
10b	4	FeB strong, Fe_2B fading, graphite strong, no Fe detected.
6	5	FeB strong, Fe_2B weak, graphite strong, no Fe detected.

Samples of known composition were run as standards for identification purposes. These included the pack mixture materials (graphite, KBF_4, B_4C), AISI 1008 steel and the iron borides (FeB, Fe_2B). As Table I indicates, the coating developed a good crystalline structure only after heating times greater than 1 h and for longer periods consisted of a combination of FeB and Fe_2B.

As expected, the iron-rich boride Fe_2B appeared first and reached a maximum surface coating concentration between 2 and 3 h. At times greater than 2 or 3 h, the FeB phase began to dominate the surface layer. The presence of a strong graphite pattern throughout indicates a problem with the pack boronization technique used, i.e. its inability to completely remove the surface residue left by the pack mixture. Several stronger lines were not identified. Compounds such as Fe_3C (cementite), $Fe_{23}(C,B)_6$, and KF were considered, but no match could be made. Many possibilities exist; for example, other residual pack mixture debris or mixed-phase species.

Examples of cross-sectional views of the boronized steel for two different heating times are shown in Fig. 1.

The characteristic dentate structure of iron boride coatings on low carbon steel reported in the literature [7, 8] is evident. Because of the

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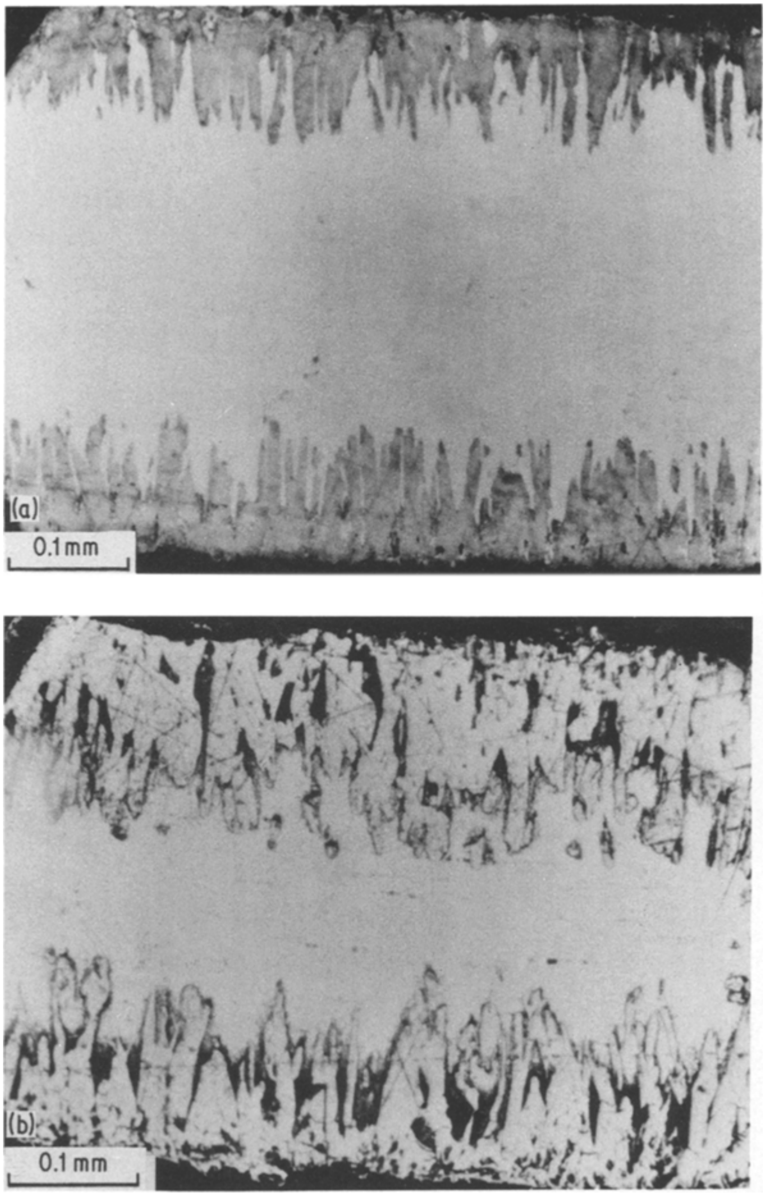

Figure 1 Magnified cross-sections of boronized AISI 1008 steel: samples heated at 960° C for (a) 2 h (Sample 8B) and (b) 4 h (Sample 10B).

dentate structure, the definition of coating depth is ill-defined. Two depths are defined here to be (a) complete coverage – the distance from sample edge to the point where any substrate fingers begin to appear, and (b) maximum depth – the distance from the sample edge to the end of the fingers of iron boride protruding into the substrate. The two distances are plotted as a function of boronization time in Fig. 2.

In summary, the pack boronization procedure described is useful for preparing coatings with a mixed composition of FeB and Fe_2B and with coating thickness in the range 0.050 to 0.100 mm where the presence of graphite can be tolerated.

Acknowledgement

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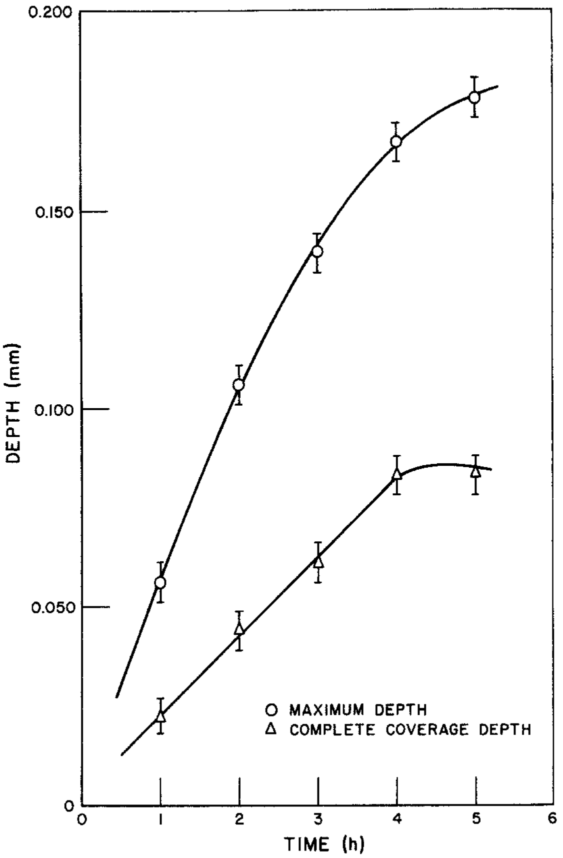

Figure 2 Boride layer depths as a function of time for AISI 1008 steel samples heated at 960° C in the pack mixture.

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MICHAEL R. ST. JOHN
ANTHONY F. SAMMELLS
*Institute of Gas Technology,
Chicago,
Illinois 60616,
USA*

The size of shear lips in polymers

Shear lips have been observed on the fracture surfaces of a number of polymeric materials, in particular polycarbonate [1–4], vinyl-urethane resins [5], polyphenylene oxide [6] and polyethylenes [7]. In other, more brittle materials such as polystyrene and polymethylmethacrylate (PMMA) shear lips are not observed. The normal equation used to estimate the width of a shear lip on a fracture surface, d, is that suggested by Irwin *et al.* [8, 9] for metallic materials

$$d = \frac{1}{2\pi}\left(\frac{K_{\mathrm{Ic}}}{\sigma_{\mathrm{y}}}\right)^2, \qquad (1)$$

where σ_{y} is the tensile yield stress and K_{Ic} is the plane strain fracture toughness. This equation cannot describe or explain the situation where shear lips are not observed. Also there is no direct evidence that it is correct, even in form, in the situations where the shear lips are visible in polymers. The aim of this note is to follow up an earlier suggestion that shear lips form in crazing materials only when the stress across a craze is