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High temperature attack by SO₂ of laser boronized iron

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Abstract. — Laser alloying of boron predeposited on iron samples led to Fe-Fe₂B alloys, with composition and microstructure depending on the irradiation conditions. Three different surface alloys were prepared corresponding to hypo-, hyper- and eutectic microstructures. This last kind of surface alloy exhibited the best behaviour in static SO₂ between 400 and 600 °C. The parabolic rate law, tending to a 3rd and 4th power law at the highest temperatures was explained as the result of outward iron diffusion leading to a magnetite external sublayer and inward SO₂ and S₂ transport, allowing the formation of a FeS-B₂O₃ internal sublayer. In this sublayer, slowly reacting Fe₂B transforms to B₂O₃ leading to an increased blocking during the course of the reaction.

1. Introduction.

Laser alloying is a versatile way to produce surface alloys which can be used for corrosion protection. Classical techniques of boronization form generally FeB-Fe₂B layers, with a high hardness, and more suitable for tribologic purposes than for corrosion protection [1, 2]. This paper describes an attempt to elaborate more ductile alloys but containing sufficiently boron to afford an efficient protection against SO₂ attack.

2. Experimental.

Iron samples were cut (15 × 15 mm) in 1.5 mm thick iron foils with a purity of 99.5%, from Goodfellow Metals Ltd. Boron powder ($\phi \sim 10 \mu\text{m}$) was suspended in ethanol and sprayed onto the samples. After drying, the deposited mass was measured and fixed to 2.3 mg · cm⁻² for all the experiments.

Laser irradiation was performed with a YAG-Nd laser, guided with an optical fiber, delivering a maximum power of 350 W in a 1 mm circular spot. The samples were scanned at a 4 mm · s⁻¹ speed with parallel scans and 600 μm overlapping. Three different powers (120, 150, 175 W) were used, leading to power densities of 1.7, 2.1 and $2.5 \times 10^8 \text{ W} \cdot \text{cm}^{-2}$.

The kinetics of corrosion were followed continuously between 400 and 600 °C in 133 hPa static SO₂ by means of a quartz spring thermobalance. The maximum duration of the experiments was 25 h.

3. Characterization of the surface alloys.

After laser alloying, the samples were characterized by XRD, SEM, EPMA and microhardness measurements. The results on composition and microstructure are presented in table I.

Table I. — *Characterisation of the Fe-B surface alloys achieved for three different power densities (same amount of predeposited boron: $2.3 \text{ mg} \cdot \text{cm}^{-2}$, same scanning speed: $4 \text{ mm} \cdot \text{s}^{-1}$).*

Power density $\text{W} \cdot \text{m}^{-2}$	1.71×10^8	2.1×10^8	2.5×10^8
Average at. % boron in the alloy	24	18	10
Phases	Fe + Fe ₂ B	Fe + Fe ₂ B	Fe + Fe ₂ B
Microstructure	hypereutectic	eutectic	hypoeutectic

The three compositions achieved lie in the Fe-Fe₂B domain of the binary phase diagram [3]. The hypoeutectic alloy presents large iron dendrites, separated by the eutectic Fe-Fe₂B material (Fig. 1). The eutectic alloy is very fine-grained and homogeneous in composition (18 at. B%) from the external surface to the non-alloyed substrate (Fig. 2). The hypereutectic alloy presents angular Fe₂B grains (5-10 μm in size), embedded in the eutectic material (Fig. 3). The size of the Fe₂B grains diminishes when going outwards (influence of increasing solidification rate).

Fig. 1. — Cross-section of the Fe-Fe₂B hypoeutectic alloy.

Microhardness testing was performed on cross-sections in directions perpendicular to the scan axis, at different depths. The average maximum values obtained for the hypoeutectic, eutectic and hypereutectic microstructures at a depth of 20 μm are 500, 850 and 950 HV. As already shown for other laser-alloyed materials [4], the microhardness was influenced by the transverse position of the measurement, as, in the geometry used (diameter of the beam:

Fig. 2. — Cross-section of the Fe-Fe₂B eutectic alloy.

Fig. 3. — Cross-section of the Fe-Fe₂B hypereutectic alloy.

1 mm, overlapping: 600 μm), parts of the surface alloy were melted 2 or 3 times during processing. It was shown that the highest hardness was in the 2 times melted zones (Fig. 4).

4. Corrosion of the surface alloys by SO_2 .

4.1 KINETICS. — Kinetic experiments were firstly performed at 400 and 500 °C under 133 hPa static SO_2 with the three observed microstructures. All of them reduced considerably the corrosion in SO_2 , compared with pure iron but it was observed that hypoeutectic alloys exhibited the worse behaviour for low temperatures (Fig. 5). Eutectic and hypereutectic alloys seemed to corrode in the same manner, hypereutectic being less close to the parabolic law. This last fact appeared more evidently for higher temperatures (Fig. 6) where hypereutectic alloys corroded linearly and became the most corroded after 20 h.

Due to their best behaviour, the eutectic alloys were more extensively studied. In particular, the influence of temperature was carefully determined. The kinetics were shown to exhibit a decreasing rate shape (Fig. 7) but could be described as parabolic at 400 and 450 °C only,

Fig. 4. — Variation of the Vickers microhardness at two depths along a direction perpendicular to the scan axis (eutectic alloy).

for durations not exceeding 10 h. For longer times and at higher temperatures, a power law $\frac{\Delta M}{A} = kt^n$ fitted well the results with the exponent n increasing with time (Fig. 8). At 600 °C, for example, the rate law was rapidly cubic, tending towards a 4th power law after 20 h of corrosion.

4.2 FORMED PRODUCTS AND MORPHOLOGY OF THE CORROSION SCALE. — Over the entire temperature range, X-ray diffraction experiments showed the presence of Fe_3O_4 and FeS in the corrosion scales. No crystallized boron-containing compound could be identified.

Microscopic examinations showed that the corrosion scale was always constituted of 2 sublayers (Fig. 9). The external one was made of large grains of Fe_3O_4 , with scarce islands of FeS . The internal one was fine-grained and showed evidence of several phases. EPMA measurements allowed to detect B and O in this layer in addition to FeS (Fig. 10).

4.3 DISCUSSION.

4.3.1 Formed products. — The absence of boron in the external layer shows that this layer grows by outward iron diffusion. On the contrary, the internal layer grows inwards, including boron from the alloy. Such an observation corresponds exactly to what occurs during corrosion of low chromized steels by SO_2 [5]. The presence of oxygen in this layer is in agreement with SO_2 inward diffusion. This mechanism was largely discussed in the past [6, 7]. In the present experiments, it is possible that both SO_2 and S diffused inwards, leading to the observed S/O ratio in the internal layer near unity.

Fig. 5.

Fig. 6.

Fig. 5. — Gravimetric curves of SO₂ attack at 400 °C of the different surface alloys achieved compared to pure iron. $P_{\text{SO}_2} = 133$ hPa.

Fig. 6. — Gravimetric curves of SO₂ attack at 500 °C of the different surface alloys achieved. $P_{\text{SO}_2} = 133$ hPa.

The boron profile in this layer, opposite to that of sulfur, allows to think that B₂O₃ exists in addition to FeS. Indeed B₂O₃ and FeS have a large common domain in the P_{S_2} - P_{O_2} stability diagram for the temperature range explored.

In addition to FeS and B₂O₃, unreacted Fe₂B is also present in the internal sublayer.

4.3.2 Kinetics. — The general decreasing rate shape observed results from limiting solid state diffusion (although SO₂ slow decomposition should participate also, leading to non equilibrium Fe₃O₄ at the scale gas interface).

Compared to corrosion of pure iron, the presence of boron reduces markedly the iron diffusion through FeS. This fact is in contradiction with Wagner-Hauffe rules for vacancy diffusion, but the results of Chatterjee and Dowell [8] suggest predominant grain boundary diffusion under 700 °C (2 slopes Arrhenius' law). Sulfur and SO₂ diffusion along the grain boundaries of the FeS-B₂O₃ layer is not affected by boron. This layer is therefore thicker in the presence of boron compared to what observed for pure iron [9, 10].

At the metal-scale interface, the iron grains of the alloy are rapidly converted to FeS, whereas Fe₂B grains are slowly superficially transformed into B₂O₃. This fact was more easily detected on hypoeutectic alloys where large Fe areas exist (Fig. 11). B₂O₃ growing within previously formed FeS is probably responsible for the deviation from the parabolic law, as the

Fig. 7.

Fig. 8.

Fig. 7. — Influence on temperature on the corrosion of the eutectic surface alloy. $P_{\text{SO}_2} = 133 \text{ hPa}$.
 Fig. 8. — Log-log plot of the gravimetric curves of corrosion of the eutectic surface alloy showing the deviation from the parabolic law at high temperatures. $P_{\text{SO}_2} = 133 \text{ hPa}$.

Fig. 9. — Cross-section of the scale formed by SO_2 attack of the eutectic surface alloy. $P_{\text{SO}_2} = 133 \text{ hPa}$, $T = 600^\circ\text{C}$, $t = 25 \text{ h}$.

Fig. 10.

Fig. 11.

Fig. 10. — Electron probe microanalysis profiles through the corrosion scale of figure 9.

Fig. 11. — Cross-section of the internal part of the scale formed by SO_2 attack of the hypoeutectic surface alloy, showing preferential sulfidation of iron grains. $P_{\text{SO}_2} = 133 \text{ hPa}$, $T = 400^\circ\text{C}$, $t = 25 \text{ h}$.

diffusion area decreases during the course of the reaction. This influence is more sensible when B_2O_3 formation is rapid, i.e. at high temperatures, as experimentally observed.

5. Conclusion.

Laser alloying of boron into pure iron could be optimized to achieve homogeneous eutectic surface alloys, with a good hardness-brittleness ratio. These alloys exhibited parabolic or higher power rate laws of corrosion by SO_2 , leading to the formation of a duplex scale containing Fe_3O_4 in its external part and FeS in its internal part. In this part, B_2O_3 growing from unsulfidized Fe_2B grains is thought to account for the deviations observed from the parabolic law.

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