Boride coatings on non-ferrous materials in a fluidized bed reactor and their properties

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Abstract

Fluidized bed technology has been successfully used in the formation of different types of coatings, e.g. aluminizing [Surf. Coat. Technol. 120 (1999) 151; Steel Res. 66 (1995) 318; J. Mater. Sci. 35 (2000) 5493], chromizing [Surf. Coat. Technol. 120 (1999) 151; Steel Res. 66 (1995) 318; J. Mater. Sci. 35 (2000) 5493], nitriding [Heat treatment in fluidized bed furnaces, 1993], carburizing [Heat treatment in fluidized bed furnaces, 1993], carbonitriding [Heat treatment in fluidized bed furnaces, 1993]. Recently, this technology has been used for the deposition of hard boride layers onto ferrous substrates [Mater. Lett. 51 (2001) 156; Fifth International Conference on Heat Treatment Materials, Budapest, Hungary, vol. 3, 1986]. In the present paper, we used fluidized bed technology to deposit boride coatings onto non-ferrous metals and alloys. The coatings were examined by means of optical microscopy, Vickers microhardness and X-ray diffraction, to determine thickness and morphology, phase formation and properties. The properties of dry wear and thermal cycling oxidation of the coatings were evaluated. The as-produced coatings were characterized by adequate thickness and improved wear and oxidation resistance.

Keywords: Boriding; Fluidized bed; Non-ferrous substrates

1. Introduction

Heat treatments of alloys in fluidized bed reactors have been carried out for more than 25 years. Recently, this technology has been used for surface engineering applications in the deposition of hard and/or corrosion resistant layers onto ferrous and non-ferrous materials [1,2,4,5,6]. On the other hand, very little information exists on boride coatings obtained on non-ferrous metals and alloys using the fluidized bed technology, although the method is simple, efficient and environmentally friendly. Boride coatings on nickel have been reported to have high hardness and an excellent wear resistance [7] and titanium borides are well known for their high hardness and excellent corrosion, wear and oxidation resistance [8].

Nickel alloys are extensively used as high temperature corrosion resistant materials and improvements in their wear resistance could further increase the potential use of these alloys. Surface hardening treatments such as carburizing and nitriding cannot be used in nickel because Ni has very low solubility for carbon [9] and nitrogen [10] in the solid state. Boronizing of nickel has been achieved using the pack cementation method [7]. The layer obtained was thick and consisted mainly of Ni3B. Boronizing in fluidized beds is a promising method to improve the wear and corrosion properties of nickel and its alloys.

Ti and its alloys, especially with Al, are attracting considerable attention because of their potential use as low-density and high-temperature structural materials [11–13]. Their inadequate oxidation resistance at elevated temperatures (>700 °C), however, limits their practical applications. Addition of alloying elements such as Nb, Si, C, B do improve the oxidation resistance of these alloys, but the amounts of these additives should be controlled at low levels [14]. Use of surface modification techniques such as ion implantation of Al ions in to Ti–Al alloys, produce a high oxidation resistant TiAl3 coating, whose final overall oxidation resistance is nevertheless mitigated by the inherently developed cracks and voids in the coating [15,16]. Thermochemical diffusion processing such as boronizing in fluidized beds is a promising method for...
improving the oxidation resistance of Ti and its alloys, as it is a flexible and low cost method, yielding boride layers of excellent quality and uniformity.

Little information exists on boride coatings obtained on Co and its alloys by any method [17] and no information exists on the boriding of Mo or Cr substrates in a fluidized bed reactor.

The main advantage of fluidization is the high rate of mass and heat transfer, which results in a uniform temperature throughout the volume of the reactor and a flash mix of all compounds contained in it, thus yielding high quality coatings [18–20]. Additional advantages arise from, the process capability for quick parameter adjustment, the relatively low capital and operation costs and the fact that is environmentally friendly. Some of the main parameters affecting the quality of the fluidization process and that of the produced coatings, obviously are the properties of solids and fluids used, bed geometry, gas flow rate, type of gas distributor and overall reactor design.

This paper presents some of the results produced by a study of boride coatings applied onto Ni metal and nickel alloys, Ti metal and titanium alloys, Co metal, Mo metal and Cr metal substrates, by the fluidized bed process.

2. Experimental procedure

Coating process. Samples were prepared using a typical fluidized bed reactor system which is shown schematically in Fig. 1. The system consists of five main parts:

- the fluidized bed reactor unit;
- the gas preheating and providing system;
- the furnace for heating the reactor;
- the control panels and measuring instruments;
- the trapping of hazardous substances unit.

This experimental set up is simple and flexible and allows to deposit a wide range of single and multielement coatings. A detailed description of the experimental set up has been given in a previous publication [3]. In the present study boriding was carried out in such a system on nickel metal and nickel alloys, titanium metal and titanium alloys, cobalt, molybdenum and chromium.
metal, at temperatures between 900 and 1000 °C. Argon was used as a fluidizing gas \( (Q = 1.4 \text{ m}^3/\text{h}) \), while fluidizing media were composed of \( \text{Al}_2\text{O}_3 \), \( \text{B}_4\text{C} \) and sodium or ammonium fluoride or chloride.

Coating properties and characterization. The thickness of coatings and their morphology were examined using optical microscopy. Hardness was measured by a Vickers microhardness tester. The phases formed in the coating were identified by X-ray diffraction (XRD) measurements which were performed using monochromatic Fe K\( \alpha \) radiation.

The tribological properties of the coating were evaluated using a pin on disc type equipment under dry wear conditions. Test conditions: pressure 15 kP, SiC paper 220 grit, testing time 4 min, velocity 30 rev./min. The experimental set up for tribological testing has been described in a previous publication [21].

Fig. 5. XRD results of the boride coating on pure nickel indicating the presence of Ni\( _3\text{B} \).

![XRD results of the boride coating on pure nickel indicating the presence of Ni\( _3\text{B} \).](image1)

Fig. 6. Effect of the boride coating on dry wear resistance of Ni. Test conditions: pressure 15 kP, SiC paper 220 grit, testing time 4 min, velocity 30 rev./min.

![Effect of the boride coating on dry wear resistance of Ni. Test conditions: pressure 15 kP, SiC paper 220 grit, testing time 4 min, velocity 30 rev./min.](image2)

Fig. 7. Typical morphology of the boride coating on nickel alloy INCONEL obtained in a fluidized bed reactor at 975 °C after 5 h.

![Typical morphology of the boride coating on nickel alloy INCONEL obtained in a fluidized bed reactor at 975 °C after 5 h.](image3)
The oxidation resistance properties of the coatings were evaluated using a cycling oxidation testing system. Test conditions: maximum heating temperature 750 °C, cooling temperature 25 °C, heating time 30 min, cooling time 15 min, and total number of 600 cycles.

3. Results and discussion

In Fig. 2 a typical morphology of the boride coating obtained on nickel, after 5 h of treatment is shown. This coating has average thickness of 35 μm, Vickers microhardness values of 870 HV (Fig. 3) and it is characterized by good uniformity.

The boride coating thickness versus time at 950 °C is shown in Fig. 4. During the boriding process two types of reactions have been reported [22]. The first reaction takes place between the boron-yielding substance and the component surface. This produces a thin, compact boride layer (see Fig. 4 1, 5 h point). The second reaction is diffusion controlled. A concentration gradient provides the driving force for diffusion-controlled boride layer growth [22]. The thickness of the boride layer growth during this second stage can be calculated by a simple parabolic relation: \( d = k \sqrt{t} \), where \( d \) is the boride layer thickness, \( k \) is a constant and \( t \) is time (Fig. 4 shows the 3 and 5 h experimental and theoretical points).

The overall reactivity of boriding in the fluidized bed has to do with the temperature, time and chemical composition of the fluidizing media and more specifically with the amount of boron supply and the nature and amount of the activator used [22,23]. For process time of 2 h at 950 °C boride layer thickness reported [23] was in the range of 20 μm for steel for low activator content. In the present paper both theoretical and experimental results give a similar type of result (18–22 μm, see Fig. 4) but on Ni substrate. XRD patterns (Fig. 5) indicated that the as prepared coating consisted of Ni2B.

The tribological properties of pure and borided Ni for different times (1, 5 and 3 h) are shown in Fig. 6. In the tribological tests under dry wear conditions the Ni2B (35 μm) layer showed an approximately 50% increased resistance to wear compared to the untreated Ni. A thinner Ni2B (10 μm) layer also provided protection against dry wear, but for a shorter period (1–2 min). When the layer was removed (after approximately 3–4 min of testing) the wear performance was similar to that of Ni metal.

![XRD results of the boride coating on INCONEL indicating the presence of Ni3B.](image1)

**Fig. 8.** XRD results of the boride coating on INCONEL indicating the presence of Ni3B.

![Typical morphology of boride coating on titanium alloy obtained in a fluidized bed reactor.](image2)

**Fig. 9.** Typical morphology of boride coating on titanium alloy obtained in a fluidized bed reactor.
Under dry wear conditions there is no unique wear mechanism operating over a wide range of conditions. The main factors controlling the importance of the underlying mechanism are mechanical stresses, temperature and oxidation phenomena [24].

In our wear testing results, the 3 h treatment simply had a thicker boride layer compared to the 1, 5 h treatment. This thicker layer provided protection against wear for a longer period of testing time.

In Fig. 7, a typical morphology of the boride coating obtained on nickel alloy INCONEL (72Ni–15Cr–13Fe), after 5 h of treatment at 975 °C, is shown. This coating had average thickness of 25 μm and it is characterized by very good uniformity. From X-ray patterns (Fig. 8) it was concluded that the as-prepared coating consists of a uniform compound which was found to belong to the Ni₄B₃ phase.

Addition of alloying elements in Ni, Co and Ti metals have been reported [22] to retard the rate of boride layer growth and in the case of multiphase alloys the proportion of boride layer with high boron content has been found to increase.

In the case of multiphase INCONEL alloy a similar tendency is observed, i.e. the formation of a thinner boride layer and with a higher boron content (Ni₄B₃) compared to the pure Ni metal where Ni₃B is formed.

In Fig. 9 a typical morphology of the boride coating obtained on Ti–6Al–4V alloy, after 6 h of treatment, is shown. This coating had average thickness of 10 μm and it is characterized by a partial tooth-shaped morphology. It is interesting to observe that some of the teeth formed extended as much as 2 times the average coating thickness. From XRD patterns (Fig. 10) it was concluded that the as-prepared coatings consisted mainly of TiB and TiB₂ with evidence of incorporation of V into the titanium borides. The typical morphology of the TiB coating obtained on 99.5% pure Ti after 5 h of treatment at 950 °C is presented in Fig. 11. The boride coating thickness versus time at 950 °C is shown in Fig. 12.
Fig. 12. Variation of the titanium boride layer thickness versus time at 950 °C.

Fig. 13. The cyclic oxidation resistance of titanium boride. Test conditions: maximum heating temperature 750 °C, cooling temperature 25 °C, heating time 30 min, cooling time 15 min, and total number of 600 cycles.

Fig. 14. XRD results of the boride coating on cobalt, indicating the presence of Co₃B and Co₄B.
The oxidation properties of the borided Ti were evaluated by means of cycling oxidation testing. A protective layer is produced during the first 100 cycles of the test and as a result of this the cyclic oxidation resistance of the coating substrate system is shown to be extremely good with no signs of cracking or any other form of spallation (Fig. 13).

For powder pack cementation boriding of cemented carbides containing a Co binder phase, treatment temperatures between 500 and 1100 °C and time of 90 min have been reported [17] producing \( \text{Co}_2\text{B} \) and \( \text{Co}_3\text{B} \) phases. Below these phases a Co impoverishment region of 10 \( \mu \text{m} \) thickness was detected.

Boriding pure Co metal in a fluidized bed reactor at 950 °C for 3 h resulted in the formation of \( \text{Co}_3\text{B} \) \( \text{Co}_4\text{B} \) phases of \( \approx 130 \mu \text{m} \) total thickness (Figs. 14 and 15).

Boriding of pure Cr metal in a fluidized bed reactor at 950 °C resulted in the formation of \( \text{Cr}_2\text{B}_3 \), \( \text{Cr}_2\text{B} \) and \( \text{CrB} \) phases (Fig. 16). The boride coating thickness versus time at 950 °C is shown in Fig. 17.

Boriding of pure Mo metal in a fluidized bed reactor at 950 °C for 5 h, resulted in the formation of \( \text{Mo}_2\text{B}_3 \) phase (Fig. 18) and a 15 \( \mu \text{m} \) coating (Fig. 19).

4. Conclusions

The fluidized bed technology has been successfully used to deposit good quality boride coatings on non-ferrous metals and alloys. The good quality and uniformity of coatings is mainly due to the high rate of mass and heat transfer taking place in the fluidized bed reactor, resulting in a uniform temperature throughout its volume, and a flash mix of all compounds contained in it. The method is simple, flexible, cost effective, environmentally friendly and constitutes a serious alternative for producing hard boride corrosion and wear resistant coatings on metallic substrates.
The properties of dry wear and thermal cycling oxidation of the coatings were evaluated. The as-produced coatings are characterized by adequate thickness and improved wear and oxidation resistance.

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