Combined Chromium–Boride Coatings on Oxide Ceramics

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Abstract

The possibilities for obtaining hard and corrosionresistant combined chromium-boride coatings on a cheap oxide ceramic base are investigated. Steatite and aluminium silicate (silimanite) ceramics are first thermodiffusively chromised and next boronised. A suitable chromising mixture is used for the chromising by packing it around the ceramic in a purified argon environment. During the chromising, an active chromium is formed which diffuses into the ceramic. The subsequent liquid boronising formed combined chromium-boride coatings. Their microhardness is high: 9000 and 9600 MN/m², respectively, for coatings on steatite and on aluminium silicate. The combined chromium-boride coatings are corrosion resistant in zinc melts at 650°C.

Die Möglichkeiten zur Erzeugung harter und korrosionsbeständiger Beschichtungen aus einer Verbindung von Chrom-Borid auf preiswerten Oxidkeramiken werden untersucht. Steatit und Aluminiumsilikat-(Silimanit) Keramiken werden zuerst durch Thermodiffusion kromiert und anschließend boriert. Zur Kromierung wird die Keramik in eine geeignete Mixtur eingebettet und in eine gereinigte Argonatmosphäre eingeschlossen. Während der Kromierung bildet sich aktives Chrom, das in die Keramik diffundiert. Die anschließende Flüssigborierung führt schließlich zu den kombinierten Chrom-Borid Beschichtungen. Ihre Mikrohärte ist hoch; 9000 und 9600 MN/m² für Beschichtungen auf Steatit bzw Aluminiumsilikat. Die kombinierten Beschichtungen sind in einer Zinkschmelze bei 650°C korrosionsbeständig.

On a étudié la possibilité d'obtenir des revêtements en borure de chrome, à la fois durs et résistants à la corrosion, sur un substrat céramique de type oxyde, peu onéreux. Des céramiques en stéatite et silicate d'aluminium (sillimanite) ont été d'abord chromés et ensuite borurés par thermodiffusion. Un mélange adéquat a été utilisé pour la chromuration en le compactant autour de la céramique dans une atmosphère d'argon purifié. Durant la chromuration, un chrome actif est formé et diffusé à l'intérieur de la céramique. Le liquide de boruration formé par la suite se combine en formant des recouvrements de borure de chrome. Leur microdureté est élevée: 9000 et 9600 MN/m^2 , respectivement pour les recouvrements sur stéatite et sur silicate d'aluminium. Les recouvrements combinés en borure de chrome résistent à la corrosion dans du zinc en fusion à 650°C.

1 Introduction

The borides, nitrides and carbides of the refractory metals chromium, titanium, zirconium and molybdenum are finding wide practical application as corrosion- and heat-resistant materials. The manufacturing of products from these materials is an expensive process associated with many technological difficulties. It is of great interest therefore to obtain hard, wear-, corrosion- and heat-resistant coatings on a cheap ceramic base.

The aim of the present work is to investigate the possibilities for producing chromium–boride coatings on steatite and aluminium–silicate (silimanite) ceramics.

2 Experimental

Thermodiffusive chromising by packing the ceramic in a solid saturation mixture in a purified argon environment followed by liquid boronising are used for the experiments. The main problem of the solid phase chromising is to find out an optimal compo-

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sition for the saturation mixture. The components must satisfy the following requirements:

- (1) to form at the saturation temperatures an active chromium, which can diffuse into the ceramics; and
- (2) to avoid chemical reactions with the ceramics.

A detailed thermodynamical analysis of the possible interactions between various components in model chromising mixtures and the ceramics has been made. On this base a chromising mixture, consisting of 41% Al₂O₃, 35% Cr₂O₃, 20% Al powder, 2% NH₄Cl and 2% NiO has been chosen.¹ The thermodynamic analysis of the interactions between this mixture and a steatite ceramic with composition based on MgO–SiO₂, involves the following basic chemical reactions:

$$Al + 3HCl = AlCl_3 + \frac{3}{2}H_2 (NH_4Cl = NH_3 + HCl)$$
(1)

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$$
⁽²⁾

$$MgO-SiO_2 + \frac{4}{3}AlCl_3 = \frac{2}{3}Al_2O_3 + MgO + SiCl_4$$
 (3)

$$MgO-SiO_{2} + \frac{4}{3}Cr = MgO + \frac{2}{3}Cr_{2}O_{3} + Si$$
 (4)

$$MgO-SiO_2 + 2Cr = Cr_2O_3 + Mg + Si$$
(5)

$$Na_2O-SiO_2 + \frac{4}{3}Cr = Na_2O + Si + \frac{2}{3}Cr_2O_3$$
 (6)

The thermodynamic potentials, $\Delta G_{\rm T}$, of these reactions are shown as a function of temperature in Fig. 1. The isobaric-isothermal potentials are calculated on the basis of the data in Refs 2-4. Practically, the chromising of the steatite is conducted at temperatures from 950 up to 1150°C for 4-20 h and that of the aluminium silicate (of a composition based on Al₂O₃-SiO₂) at temperatures from 1050 to 1250°C for 2-6 h. A liquid boronising is then carried out at 950°C with a 4 h duration. The boronising mixture composition is 60% BaCl₂, 18% NaCl and 22% ferroboron.

The microstructure of all the chromized and boronised specimens has been investigated. Specimen preparation requires diamond polishing and etching by a 1–2% aqueous solution of HF, $60^{\circ}C$, 10 min (Ref. 5) for the metallographic investigations.



Fig. 1. Isobaric-isothermal potentials (ΔG_T) of the reactions between the chromising mixture components and the steatite, dependent on the temperature (*T*). (The numbers of the lines correspond to the reactions numbers.)

The microhardness of the layer is measured with the help of a MICRO-DUROMAT 4000 unit (Firma Reichert Jung, Austria) at 30 g loading, 30 s duration and 10 g/s loading gradient. The reported microhardness value is an arithmetical mean of 30 measurements.

All specimens have been subjected to corrosion resistance tests in zinc melts at 650° C.

3 Results and Discussion

The X-ray structural analysis of the chromising mixture phase composition before and after treating the ceramics at saturation temperatures of 950–1250°C confirms the conclusions of the thermo-dynamical analysis (Fig. 2).

The microscopic investigations established that after the chromising a distinctly formed compact diffusive layer is observed on the surfaces of both steatite and aluminium silicate specimens (Figs 3 and



Fig. 2. Phase composition of the chromising mixture (a) before the saturation, and (b) after a saturation at 1050°C.





Fig. 3. Microstructure of the steatite, chromised for 6 h at 950° C.



Fig. 4. Microstructure of the aluminium silicate, chromised for 4 h at 1150°C.





(b)

Fig. 5. Microstructure of the chromium-boride layer on steatite (chromised for 10 h at 1100°C).

4). The microhardness of the chromium layer is (i) on the steatite, about 3900 MN/m^2 ; and (ii) on the aluminium silicate, about 4400 MN/m^2 .

Boronising of the chromium layers results in compact and well formed chromium-boride layers of high microhardness (Figs 5 and 6). Neither the steatite nor the aluminium silicate can be directly boronised.

New phases are observed at higher magnification in the chromium-boride coatings for both ceramics. The dendritic configuration of the phase in the onsteatite layer is clearly visible in Fig. 5. The microhardness of this coating is about 9000 MN/m^2 , while the microhardness of the chromium-boride layer on the aluminium silicate is about 9600 MN/m^2 .



Fig. 6. Microstructure of the chromium-boride layer on aluminium silicate (chromised for 3 h at 1200°C).



Fig. 7. Corrosion resistance, resp. weight losses (Δg), dependent on the zinc melt action time (t) at 650°C for silimanite: 1, without a coating; and 2, with a chromium-boride coating.

It is established that after corrosion resistance tests in zinc melts at 650°C the chromium-boronised steatite and aluminium silicate do not change while the uncoated ceramics dissolve (Fig. 7).

4 Conclusions

Chromising by the solid saturation mixture packing method in a purified argon environment followed by liquid boronising has been successfully used to obtain chromium-boride coatings on steatite and aluminium silicate (silimanite) ceramics.

The chromium-boride coatings are well formed and compact. Their microhardness is high: 9000 MN/m^2 on steatite and 9600 MN/m^2 on aluminium silicate. They are corrosion-resistant in zinc melts at 650° C.

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