Electrolytic processing of MgO coatings

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Abstract. MgO coating was formed on nickel superalloy substrate. The coating process consisted of two steps: cathodic electrolytic deposition of MgOH, and heat treatment. The heat treatment was necessary to calcinate and to sinter the deposit. The deposit morphology and composition, before and after heat treatment, were studied by X-ray diffraction and the scanning electron microscopy. The influence of deposition parameters on deposition yields and deposit morphology is studied and discussed.

1. Introduction
Metal ceramic coatings have played an increasing role in protecting metals from stresses, wear, chemical attack and high temperatures. The application of these coatings is growing continuously in the automotive, aeronautic and electro domestic industries. The most common methods used to fabricate metal ceramic coatings are: plasma spraying, CVD, sol gel and PVD.

Recently, the use of the electrolytic method to fabricate metal/ceramic coatings has been investigated. This is a low temperature method which provides coatings with a homogeneous microstructure and high sinterability. Gal-Or et al. [2][3] produced a ceramic composite coating of titanium oxide and zirconium oxide. The zirconia coat was deposited on a titanium substrate from an aqueous solution with zirconyl salt (ZrO(NO3)2). The deposited coat was amorphous and cracked. Sintering of the coatings in air at 780 °C caused crystallization of the tetragonal and monoclinic ZrO2 polymorphs phases having nanosize crystallites. Oxidation of the titanium substrate during heat treatment resulted in the formation of TiO2 at the site of cracks between the zirconia islands.

Aries [4] used the electrolytic method to fabricate an alumina barrier on stainless steel. The alumina barrier was obtained by thermal dehydration of aluminium hydroxide deposited from an aqueous solution of aluminium sulphate. Before deposition, the surface of the metal substrate was pretreated to form a functional conversion coating characterized by a strong adhesion to the substrate. The pretreatment involved a chemical treatment of the substrate or what is known as “anodizing process.” An anodic oxidation of the metal in an electrochemical cell with a suitable electrolyte leads to the formation of a homogeneous, rough-surface oxide layer with a thickness of about 200 nm. Alumina was then deposited by the electrochemical method to form a two-layer coat.

A great deal of research has been devoted to demonstrate the feasibility of electrolytic deposition of important ceramic materials like: Al2O3, ZrO2, CeO, TiO2, RuO2, PbO2, ZnO, Nb2O5, BaTiO3, PZT and YBa2Cu3O7. [1]
The present work investigates the possibility of magnesia electrolytic deposition and describes the formation of magnesia coating on nickel superalloy. Magnesia has the highest thermal expansion coefficient among ceramics, which is an important property for the application of metal ceramic coating.

2. Mechanism of Deposition

If two electrodes are immersed in an aqueous solution of magnesium nitrate (Mg(NO$_3$)$_2$) and connected to a source of current of a sufficiently high potential, there will be a passage of electric charge through the solution and at the same time various chemical reactions will take place at the electrodes. In an aqueous solution, the magnesium nitrate dissolves to give magnesium ions.

Mg(NO$_3$)$_2$ $\Rightarrow$ Mg$^{2+}$ + 2NO$_3^-$

During cathodic synthesis, the cathodic reaction is used to generate hydroxide ions at the electrode surface; created mainly by the electrolysis reaction of water.

2H$_2$O + 2e$^-$ $\Rightarrow$ H$_2$ + 2OH$^-$

The hydroxide ions may also be produced by other cathodic reactions that include the reaction of reduction of oxygen

O$_2$ + 2H$_2$O + 4e$^-$ $\Rightarrow$ 4OH$^-$

In the case of nitrate salts, the reduction reaction of nitrate produces hydroxide ions:

NO$_3^-$ + H$_2$O + 2e$^-$ $\Rightarrow$ NO$_2^-$ + 2OH$^-$
NO$_3^-$ + 6H$_2$O + 8e$^-$ $\Rightarrow$ NH$_3$ + 9OH$^-$

Mg$^{2+}$ ions are then hydrolyzed by the electro-generated hydroxide ions to form a cathodic deposit.

The dehydration of magnesium hydroxide to form MgO occurs during heat treatment.

Mg(OH)$_2$ $\Rightarrow$ MgO + H$_2$O

In the following sections the effects of electrochemical deposition parameters on the deposit morphology and the microstructure evolution in the as-deposited and sintered coatings will be analyzed.

3. Experimental Procedure

Nickel superalloy (Inconel 600) was used as a substrate. The substrate specimen has dimensions of 2x1.5x0.6 cm$^3$. The electrochemical bath consisted of a 250ml beaker. The electrolyte was composed of 0.5M Magnesium Nitrate (Mg(NO$_3$)$_2$), dissolved in 50% water and 50% ethanol. The substrate was the cathode and the anode material was graphite with a distance of 2 cm between them. The source of current was (EG&G Instruments Potentiostat) rectifier. Deposits were obtained on the cathode with current densities ranging from 2.5-20 mA/cm$^2$, and duration from 5 to 60 minutes. All experiments were performed without stirring. The cell Voltage and current density were measured with AVOmeters. The deposits were dried in air at room temperature. The coating weights were measured before and after the deposition. Specimens were fired at 700 °C and 1100 °C in air; TGA was used to study the weight change during firing. The microstructure of the deposit was characterized after different stages of the process, using the optical and scanning electron microscopy (SEM). The phase composition and the crystallization state were determined by X-ray diffraction (XRD).

4. Results and Discussion

Figure 1 shows a SEM image of the deposited coat; the obtained deposit was a gel-like transparent solid deposit with a homogeneous coverage of the substrate. The color of the deposit depended on the current density. The deposit color was yellow at low current density, yellow-orange at intermediate current density and brown at high current density. No visible change was observed when the deposit was removed from the bath, which indicates that the Mg(OH)$_2$ deposit did not dehydrate with drying.
Both the deposit quality and quantity depended on the current density. The amount deposited in the same period of time increases with increasing current density. High deposition rates can be obtained at high current densities; but the deposit quality is best at low current density. At a current density greater than 5 mA/cm$^2$, the deposit forms cracks after drying. However, at low current density, the deposit is homogeneous without any cracks.

The dependence of the deposited weight on deposition time at constant current density of 2.5 mA/cm$^2$ is linear. During deposition, the thickness of the coat increases. As this is a non-conductive deposit, the resistance to current increases, and since we are working at a constant current density the voltage across the cell increases with time.

The weight of the deposited Mg(OH)$_2$ decreases rapidly with time as temperature increases. This decrease in weight is related to the evaporation of the co-deposited solvent, which was about 20% of the deposit weight. At a temperature of 200 °C the nickel superalloy substrate started to oxidize and the sample weight started to increase, but at around a temperature of around 300 °C the weight of the sample decreased. This decrease is expected to be the result of the calcination reaction of Mg(OH)$_2$ to form MgO.

Figure 2 shows the change in morphology of the deposit with heat treatment. The calcination process used to form MgO, the crystallization process of MgO and the sintering of the MgO all these processes occur during the heat treatment.

Figure 2. Morphology of the deposit after different heat treatment:
1. Sintered at 700 °C for ½ hr.
2. Sintered at 1100 °C for 1 hr.
5. Summary

Electrolytic coating of ceramics is a simple process that can be used to produce ceramics and ceramic coatings. In this work MgO coating was produced using the electrolytic technique. The main problem that has to be overcome when using this technique is the cracking of the coating, which results from the shrinkage that takes place during the drying process. A crack-free coating of magnesium oxide on nickel superalloy substrate was produced in this work by depositing magnesium hydroxide from magnesium nitrate aqueous solution. The magnesium hydroxide was then calcinated to produce MgO.

References

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