

TITLE: IMPROVED CORROSION PROTECTION by IN-SITU INTERMETALLIC COMPOSITE COATINGS

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GRANT NO.: DE-FG2698-FT-40118

PERIOD OF PERFORMANCE: June 1, 1998 – June 1, 1999

DATE: April, 1999

### ABSTRACT

Ni-Al intermetallic alloys are of interest as structural components in applications involving high temperature oxidation due to their ability to form protective, Al-rich oxide scales. The use of Ni-Al intermetallic coatings is a cost effective means of providing oxidation resistance at the surface while maintaining the mechanical properties of the underlying substrate. The composite electrodeposition technique offers a unique way to deposit Ni-Al coatings while avoiding microstructural problems associated with other coating techniques such as thermal spray. The objectives of this project are to deposit Ni-Al based composite coatings and develop an understanding of their high temperature corrosion behavior. To accomplish these goals, Ni-Al coatings were oxidized in a thermogravimetric analyzer (TGA) along with bulk Ni-Al alloys obtained from Oak Ridge National Laboratory. The microstructures of the as-plated, heat treated, and oxidized Ni-Al based coatings were characterized by light optical microscopy (LOM), scanning electron microscopy (SEM), quantitative image analysis (QIA), electron probe microanalysis (EPMA) and x-ray diffraction (XRD).

### RESEARCH ACCOMPLISHMENTS

#### Coating Composition

Through image analysis, it was found that increasing Al particle loading in the electrodeposition bath increases Al content in the coatings up to a maximum of 20-25 vol. %. After heat treatment at 825°C, the coatings contain a two phase mixture of Ni<sub>3</sub>Al ( $\gamma'$ ) blocks in a matrix of  $\gamma$  solid solution, with small voids also present. EPMA shows the  $\gamma$  and  $\gamma'$  phase compositions are in agreement with the Ni-Al phase diagram.

### Oxidation Behavior

The heat treated coatings were oxidized in air at 800 and 1000°C using TGA and a tube furnace for long-term testing up to 2000 hours. Coating oxidation resistance depends on the ability to form a protective Al<sub>2</sub>O<sub>3</sub> blanket layer beneath an outer scale layer. At 1000°C, an α-Al<sub>2</sub>O<sub>3</sub> layer forms below an outer spinel (NiAl<sub>2</sub>O<sub>4</sub>) layer. In addition, at 1000°C a single phase γ layer is produced beneath the scale indicating that dissolution of Ni<sub>3</sub>Al acts as an Al reservoir for growth of the protective Al<sub>2</sub>O<sub>3</sub> surface layer. At 800°C, the inner layer is γ-Al<sub>2</sub>O<sub>3</sub> and the outer layer was identified as NiO using X-ray diffraction. To compare the two-phase composite coatings to bulk Ni-Al alloys, single phase Ni<sub>3</sub>Al (γ')(13 wt. % Al), two-phase γ + γ' (9.5 wt. % Al), single phase γ (6.2 wt. % Al), and pure Ni alloys were also tested. The results indicate that coating oxidation behavior is similar to or better than bulk γ + γ' and single phase γ' alloys. Bulk two-phase γ + γ' and single phase γ' alloy oxidation kinetics are also controlled by Al<sub>2</sub>O<sub>3</sub> scale growth. In contrast, the γ phase (6.2 wt. % Al) bulk alloys showed much higher weight gains at 800 and 1000°C. At 800°C, the γ alloy had even higher weight gain than pure nickel due to extensive internal oxidation.

### Coating Lifetime

Recent work has focused on EPMA analysis of the coating and substrate after long time exposure at high temperatures. The objective of this work is to understand Al depletion and diffusion into the substrate which can be used as an estimation of coating lifetime. Interdiffusion coefficients for Al at 800 and 1000°C were used in an error function solution to Fick's second law for the geometry of a coating of finite thickness on a substrate of infinite depth. The concentration of Al at the coating surface as a function of time was successfully modeled using this technique. The results indicate that, if a protective Al<sub>2</sub>O<sub>3</sub> layer is formed at the surface, the coating lifetime is governed by diffusion of Al into the nickel substrate. When the Al level at the surface drops below a critical level, the coating is no longer able to form an alumina scale during isothermal exposure. The Al surface content needed for protective scale growth is estimated from the TG and long-term oxidation tests to be 6-9 wt.% depending on oxidation temperature. Thus, at 1000°C, a 100 um coating has a lifetime of about 1000 hours. At 800°C, due to the slower Al diffusion rate, the coating lifetime exceeds 20,000 hours. Work is currently underway to show the effect of ternary Si additions on the oxidation behavior and resultant lifetime of electrodeposited composite coatings.

### **SUMMARY**

The results of this project show that the oxidation resistance of Ni-Al electrodeposited composite coatings is comparable to bulk γ' and γ + γ' alloys. The γ' phase acts as an Al reservoir to produce a slow-growing Al<sub>2</sub>O<sub>3</sub> surface layer at 800 and 1000°C. In addition, if a protective Al<sub>2</sub>O<sub>3</sub> scale is formed, coating lifetime depends on diffusion of Al into the substrate. The lifetime for binary Ni-Al coatings can be estimated using EPMA data combined with a simple diffusion analysis. The accomplishments of this project demonstrate the feasibility of the Ni-Al composite technique as an alternative method for coating applications involving oxidizing atmospheres at moderate temperatures.

## **ARTICLES, PRESENTATION, AND STUDENT SUPPORT**

### **Journal Articles**

- D.F. Susan, K. Barmak, and A.R. Marder, "Electrodeposited Ni-Al Particle Composite Coatings", *Thin Solid Films*, Vol. 307, pp. 133-140, Oct. 1997.
- K. Barmak, S.W. Banovic, C.M. Petronis, D.F. Susan, and A.R. Marder, "Structure of Electrodeposited Graded Composite Coatings of Ni-Al-Al<sub>2</sub>O<sub>3</sub>", *Journal of Microscopy*, Vol. 185, Pt. 2, 265-274, Feb. 1997.

### **Student Support**

- Donald Susan, Ph.D. student in materials science and engineering, Lehigh University