ENERGY RESEARCH CENTER

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BETHLEHEM, PA

Cermet Composite Thermal Spray Coatings for Erosion and Corrosion Protection in Combustion Environments of Advanced Coal-Fired Boilers

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by

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EXECUTIVE SUMMARY

Research is presently being initiated to determine the optimum ceramic/metal combination in thermally sprayed metal matrix composite coatings for erosion and corrosion resistance in new coal-fired boilers. The research will be accomplished by producing model cermet composites using *powder metallurgy and electrodeposition methods* in which the effect of ceramic/metal combination for the erosion and corrosion resistance will be determined. These results will provide the basis for determining the optimum hard phase constituent size and volume percent in thermal spray coatings. Thermal spray coatings will be applied by our industrial sponsor and tested in our erosion and corrosion laboratories.

In the first six months of this project, *bulk powder processed* Ni-Al_2O_3 composites were produced at Idaho National Engineering Laboratory. The results of microstructural characterization of these alloys were presented in the last semi-annual report. The composite samples contained 0, 21, 27, 37, and 45 volume percent Al_2O_3 with an average size of 12 um. An increase in volume fractions of alumina in the nickel matrix from 0 to 45% led to significant increase in hardness of these composites.

During the last six months model Ni-Al_2O_3 cermet *coatings* with various volume fractions of alumina were produced. To deposit Ni-Al_2O_3 coatings, an electrodeposition technique was developed and coatings with various volume fractions (0-35%) of Al_2O_3 were produced. The effect of processing parameters such as current density on coatings microstructure was analyzed. An increase in current density lead to a decrease in volume fraction of alumina in these composites. The experimental procedure and microstructural characterization of Ni-Al_2O_3 electrodeposited cermet coatings are presented in this progress report along with plans

for research in the coming year.

I. INTRODUCTION

Present coal-fired boiler environments remain hostile to the materials of choice since corrosion and erosion can be a serious problem in certain regions of the boiler. Recently, the Clean Air Act Amendment is requiring electric power plants to reduce NO_x emissions to the environment. To reduce NO_x emissions, new low NO_x combustors are utilized which burn fuel with a substoichiometric amount of oxygen (i.e., low oxygen partial pressure). In these low NO_x environments, H_2S gas is a major source of sulfur. Due to the sulfidation process, corrosion rates in reducing parts of boilers have increased significantly and existing boiler tube materials do not always provide adequate corrosion resistance. Combined attack due to corrosion and erosion is a concern because of the significantly increased operating costs which result in material failures.

One method to combat corrosion and erosion in coal-fired boilers is to apply coatings to the components subjected to aggressive environments. Thermal spray coatings, a cermet composite comprised of hard ceramic phases of oxide and/or carbide in a metal binder, have been used with some success as a solution to the corrosion and erosion problems in boilers. However, little is known on the effect of the volume fraction, size, and shape of the hard ceramic phase on the erosion and corrosion resistance of the thermally sprayed coatings. It is the objective of this research to investigate metal matrix composite (cermet) coatings in order to determine the optimum ceramic/metal combination that will give the best erosion and corrosion resistance in new advanced coal-fired boilers.

II. EXPERIMENTAL PROCEDURE

II.A. Electrodeposition Method

Electrodeposition is the application of a coating on a substrate by passing a current through an electrolytic solution. The electrolytic solution is a conducting fluid in which the flow of current is accompanied by the movements of ions from an anode to a cathode. A schematic of the electrodeposition cell can be seen in Figure 1. When electric current passes between anode and cathode, metal ions in the electrolytic solution become positively charged and attracted to the cathode surface to form a coating. Processing parameters that affect electrodeposition include current density, type of electrolyte solution, cathode and anode material, time of deposition, and agitation of the electrolyte. Optimization of these parameters is required to produce quality protective coating.

II.B Alloy System

Ni-Al_2O_3 electro-composite coatings were produced with 0 to 34 volume percent hard phase (Al_2O_3) in a nickel matrix. Variation in the volume fraction of the hard phase provides a systematic change in the mechanical properties of the composites, and therefore, the effect of mechanical properties on erosion resistance can be analyzed.

II.C. Electrodeposition Procedure

The coatings were deposited on Nickel 200 substrates (99.61% nickel) with an approximate area of 450mm^2. Substrate material was ground to a 600 grit finish using silicon carbide paper and polished to 0.04μm finish using colloidal silica. The plating electrolyte was a nickel sulfamate bath with composition listed in Table I.

Table I. Electrolyte composition.

Sulfamate Bath	
$Ni(NH_2SO_3)_2$	400g
Boric acid	30g
Nickel Chloride	5g
Sodium Laurel Sulfate	0.5g
Coumarin	0.1g
Distilled Water	1*l*

The sulfamate bath was chosen because of its ability to withstand high current densities during deposition without burning. Therefore, coatings produced from sulfamate bath have low residual stresses [1]. The high purity α-alumina particles with a nominal size of 0.6-0.8μm were co-deposited with nickel. For co-deposition, 150g/l of the alumina particles were added to the nickel sulfamate electrolyte and suspended in solution by a magnetic stirrer at 400 rpm. The pH of the solution was maintained at 4.0 ± 0.1 at a temperature of 50°C. To produce composites with different volume fractions of alumina particles, the current density was varied from 0.5 A/dm^2 to 25 A/dm^2. In addition, deposition times were altered to provide coating thicknesses of approximately 100μm.

III.B. Microstructural Characterization

Microstructural characterization of the coatings was conducted using Light Optical Microscopy (LOM). To reveal the grain structure of the coatings, an etching solution of 25% H_2O, 25% acetic acid, and 50% nitric acid was used. The volume percent of alumina particles in

nickel matrix was determined through quantitative image analysis on a LECO 2001 Image Analysis System. Microhardness measurements were performed on LECO-MFT Microhardness tester by using Knoop indenter with a load of 25g and dwell time of 15 seconds. All measurements were conducted according to ASTM E-384 standard.

III. RESULTS

III.A. Microstructure

III.A.1. Pure Ni coating

Pure nickel electrodeposits (100%Ni-0%Al_2O_3) were produced from the sulfamate bath (i.e., no alumina particles in solution). Figure 2 shows microstructure of these coatings consist of columnar grains. Also, an increase in current density during deposition leads to an increase in columnar grains width as shown in Figure 2.

III.A.2. Ni-Al_2O_3 composite coatings

Ni-Al_2O_3 composite coatings were produced from a sulfamate bath that contained suspended alumina particles. An unetched microstructure of the typical Ni-Al_2O_3 coating is shown in Figure 3. Most of the alumina particles (dark phase) are uniformly distributed within the Ni matrix (white phase). However, some agglomeration of the particles can be seen. The composite coatings contained 11, 15, 18, 21, 31, and 34 volume percent alimina. Current density has a strong influence on the volume fraction of alumina deposited in the coating. Figure 4 shows that the amount of alumina in the composites increased with a decrease of plating current density. With a slower plating rate, i.e., lower current density, the number of collisions between the particles and the cathode surface (Ni substrate) per unit volume of deposited matrix increases,

thus allowing more particles to be incorporated into the coating [2,3]. The incorporated alumina particles significantly increased hardness of the cermet coatings. An increase in volume fraction of alumina in the nickel matrix from 11 to 34 % led to an increase in hardness of these composites from 380 to 750 HK_{25}. Hardness measurements show that variation in alumina volume fraction produces significant change in mechanical properties of the composites. The effect of the mechanical properties on erosion resistance will be analyzed in the following progress reports.

IV. PLANS FOR COMING YEAR:

In the next six months, the powder and electrodeposited cermet alloys will be tested in our erosion simulator at different velocities. From these results we expect to determine the effect of hard phase constituent size and volume percent on the steady-state erosion rate. These results will form the basis for determining thermal spray coating hard phase constituent size and volume percent.

V. REFERENCES

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3. Brandes, E.A. and Goldthorpe, D. 1967. Metallurgia, 76 (457): 195-8.

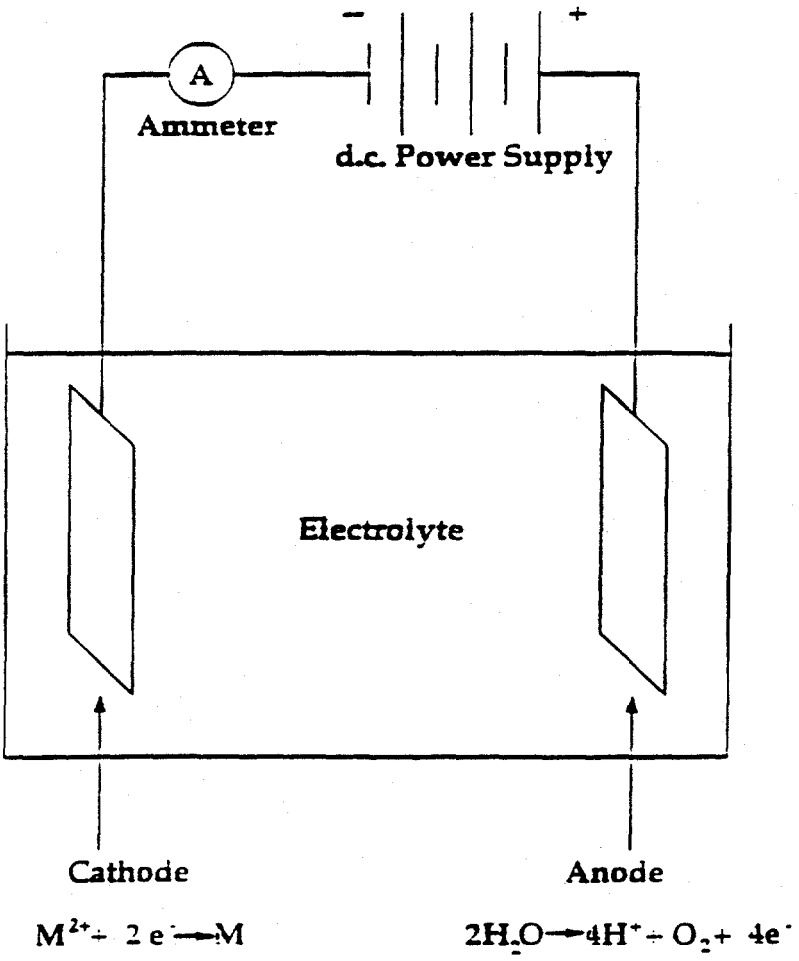

Figure 1. Schematic diagram of the electrodeposition set-up.

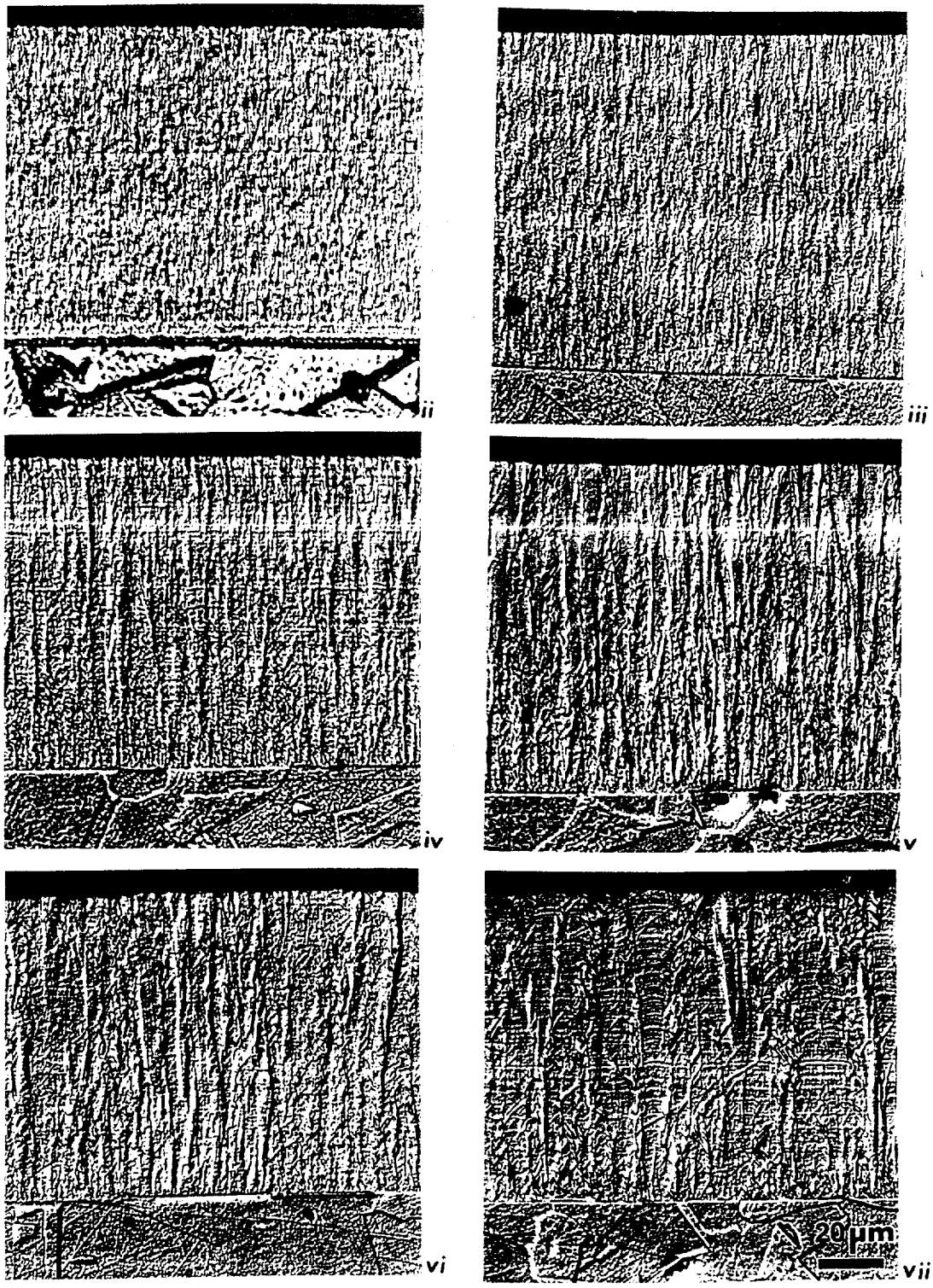

Figure 2. Etched cross-sections of electrodeposited nickel. Current densities: ii) 1A/dm^2, iii) 5A/dm^2, iii) 5A/dm^2, iv) 10A/dm^2, v) 15A/dm^2, vi) 20A/dm^2, vii) 25A/dm^2.

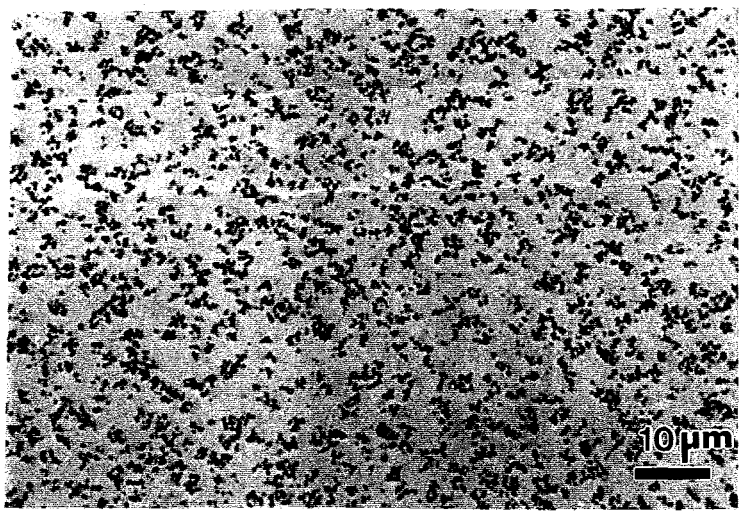

Figure 3. Polished cross-sections of Ni-Al_2O_3 electrocomposite (dark phase is Al_2O_3; white phase is Ni).

DISCLAIMER

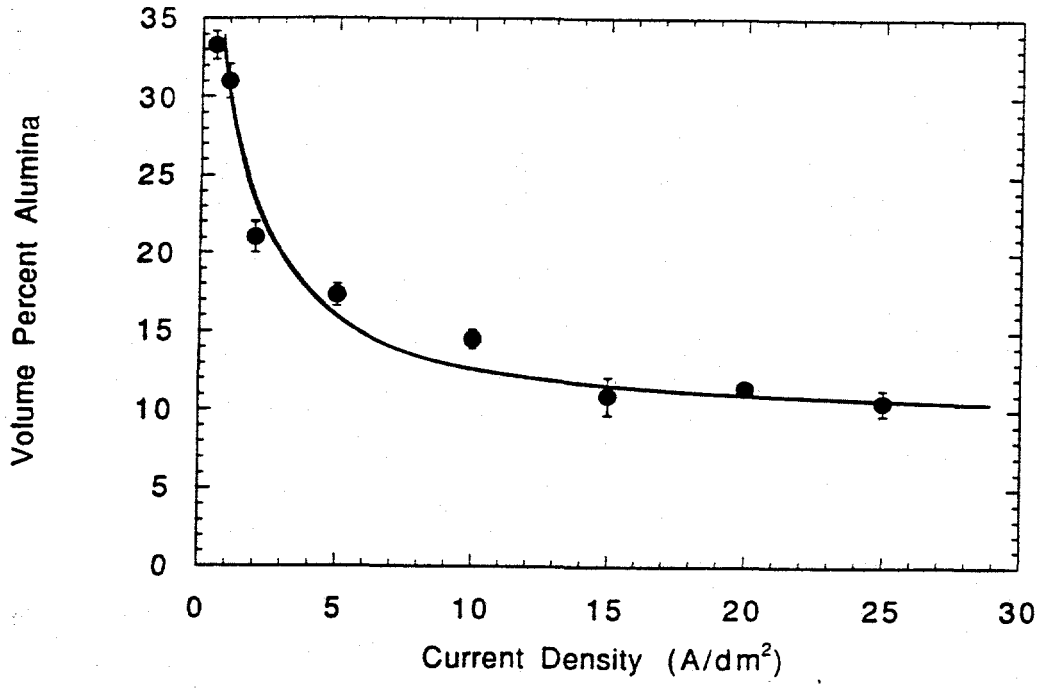

Figure 4. Volume fraction of alumina as a function of current density