Preparation of Silicon Monoxide Coatings on Aluminum Substrates

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SiO coatings on aluminum substrates were prepared using hard-facing performed at ambient conditions. Well-integrated SiO/aluminum interfaces are created via electrodiffusion that takes place during processing. Analysis of surfaces with scanning electron microscopy/EDS and nanoindentation confirm atomic stoichiometries and hardness values consistent with SiO. Hard-facing performed at ambient conditions is a way to coat aluminum with SiO that otherwise would decompose at elevated temperatures typically created using conventional hard-facing.

Keywords Silicon; Aluminum; Silicon oxides

I. INTRODUCTION

Hard-facing, is a low-cost metalworking process adopted across many industries including steel, cement, mining, petrochemical, power, and food, in which a harder or tougher material is welded to the surface of another metal. It is used to increase wear resistance of parts or restore worn surfaces. It is usually performed using specialized electrodes for arc welding, or filler rods for oxyacetylene and tungsten inert gas (TIG) welding [1]. Commonly applied materials include cobalt-based alloys, nickel-based alloys, chromium carbide alloys and NOREM, a complex alloy containing iron, chromium, manganese, nickel, silicon, molybdenum, and carbon. Use of SiO as a coating using this method has not been reported.

The ability to prepare SiO coated materials using a method economically competitive with ordinary hard-facing would enable the manufacture of a wide range of novel fire-resistant materials for industrial manufacturing use as well as novel electronic components [2]. Here, we characterize the surfaces of SiO surface-bonded aluminum prepared using a modified hard-facing method. In this method, SiO is synthesized in situ, at ambient atmospheric composition and pressure, and is bonded atomically to the underlying metal substrate without the use of flux or similar materials.

II. MATERIALS AND METHODS
A. Materials

Aluminum flat head rivets (99+%) about 5 mm in diameter were used as the substrate. Rivets were sonicated in acetone and ethanol to remove surface debris, then air-dried before use. Aluminum flat head rivets with surface-bonded SiO were supplied by Nanpol Technologies, Inc. (Salt Lake City, UT) for this study. They were produced by first mounting the aluminum rivets as the negative electrode in the device shown in Figure 1. A piece of silicon single crystal was placed in the opposing electrode mount. A voltage of +12 V (5.5 A-limit) was applied between the two electrodes and the distance between the two electrodes reduced until the two electrodes were touching. The positive silicon electrode was then moved slowly across the aluminum substrate to generate the SiO coating. The process was performed in air, at room temperature, without use of the gas/liquid injec-
tor (i.e., no additional reactive gases or liquids were used). The temperature of the aluminum substrate at the contact point of the silicon electron during operation was measured using an infrared thermometer to be approximately 250°C.

B. Analysis

The morphology, microstructure and atomic composition of the SiO surface layer was observed using a scanning electron microscope (SEM)/energy-dispersive X-ray spectroscopy (EDS) system (Quanta 600F-FEI, Oregon, USA) located at NanoFab Center at the University of Utah. Coating hardness was measured using a nanoindenter (TI 980 Nano-indenter-Hysitron, Minneapolis, MN). Additional compositional measurements were made using X-Ray photoelectron spectroscopy (XPS) (Axis Ultra DLD-Kratos, Manchester, UK). The X-ray source was monochromatic aluminum Kα with $hν = 1486.7$ eV. The energy resolution was 0.7 eV measured using a cleaned Ag standard sample. Binding energy calibration was referenced to the C−C peak from C 1s spectrum of adventitious carbon. The C−C peak was assigned a binding energy of 284.5 eV.

III. RESULTS AND DISCUSSION

Figure 2 shows a photograph of a 1-cm diameter aluminum rivet coated with a rough layer of SiO approximately 70 μm in thickness. Texture of the resulting SiO layer can be controlled using varying electrode sizes and process parameters.

Figure 3: SEM picture of A) clean aluminum rivet surface, B) coated with SiO. Images were obtained using an accelerating voltage of 15 kV, and beam spot size of 3.5 μm. Images were obtained at different zooms to show A) the smoothness of the underlying substrate and B) the large-scale continuity of the SiO layer.

Figure 4: Cross-section of SiO coating obtained using SEM. Average thickness is approximately 70 μm. The image shows evidence of electrodiffusion of SiO and aluminum at the substrate/coating interface. Light gray areas deeper in the aluminum substrate may indicate a developing phase change in the aluminum substrate as the SiO layer is established.

Figure 2: 1-cm diameter aluminum rivet coated with a rough layer of SiO approximately 70 μm in thickness. Texture of the resulting SiO layer can be controlled using varying electrode sizes and process parameters.

70 μm in thickness. Electrode size and process parameters were selected to intentional create a highly-textured surface for photograph visibility. By reducing electrode dimensions and adjusting process parameters smoother surfaces can be obtained.

Low resolution SEM imaging in Figure 3 shows the surface structure of the starting aluminum substrate (left) and coating (right) in greater detail. The starting aluminum substrate is smooth, with occasional defects, and very fine concentric circular texture arising from the machining process. The coated substrate is rough and covered with a continuous layer of material possessing amorphous characteristics. Some underlying aluminum substrate surface imperfections can still be seen in the right image.
Figure 4 shows the cross-section of SiO coating obtained using SEM. The average coating thickness is approximately 70 μm. The image shows evidence of electrodiffusion or interdiffusion of SiO and aluminum at the substrate/coating interface. Light gray areas deeper in the aluminum substrate may indicate a developing phase change in the aluminum substrate as the SiO layer is established. EDS analysis of the surface yielded atomic weight percent ratios consistent with SiO (Table 1).

In Figure 5A is shown Si 2p high resolution region spectrum, and in Figure 5B the O 1s high resolution region spectrum. The binding energy of Si 2p at ~102 eV suggests the presence of a monoxide of Si. In contrast, Si 2p from SiO₂ has a binding energy of ~103–104 eV. The above data suggests a predominance of the SiO compound (silicon monoxide). The analysis of available literature confirms the above statement [3]. The color of the coating is black, consistent with that of SiO. Coating characteristics were unchanged following immersion in HF overnight.

Figure 5: A) Si 2p high resolution region spectrum; B) O 1s high resolution region spectrum. The binding energy of the Si 2p at ~102 eV suggests the presence of a monoxide of Si. Si 2p from SiO₂ has a binding energy of ~103–104 eV. The above data suggest predominance of the SiO compound (silicon monoxide). The analysis of available literature confirms the above statement [5]. The color of the coating is black, consistent with that of SiO. Coating characteristics were unchanged following immersion in HF overnight.

Figure 5 shows the cross-section of SiO coating obtained using SEM. The average coating thickness is approximately 70 μm. The image shows evidence of electrodiffusion or interdiffusion of SiO and aluminum at the substrate/coating interface. Light gray areas deeper in the aluminum substrate may indicate a developing phase change in the aluminum substrate as the SiO layer is established. EDS analysis of the surface yielded atomic weight percent ratios consistent with SiO (Table 1).

Table 1: EDS analysis of SiO Surface. Element ratios are consistent with SiO.

| Element | wt%  | at%  |
|---------|------|------|
| O (K)   | 35.65| 36.1 |
| Si (K)  | 32.95| 33.2 |
| Al (K)  | 31.4 | 30.4 |
An important difference between our method and the conventional PECVD method is the use of a positively charged single crystal silicon electrode in contact with the aluminum substrate as the atomic source.

Another factor that likely influences the stability of the SiO layer is the depth of penetration of the SiO species into the aluminum substrate (Figure 4). While aluminum crystals are face-centered cubic with a lattice constant of 4.046 Å at 25°C, and SiO is cubic with a lattice constant of 7.09 Å, the fact that the SiO layer produced is amorphous and well-anchored in the aluminum reduces excess energy in the form of lattice strain that may be present on more superficially deposited SiO surfaces.

The materials characterized in this work represent the first time pure and stable SiO coatings have been created using a hard-facing method. Because this method was performed under ambient conditions, it allows the SiO layer to form well-anchored, and maintain phase stability during growth. The resulting coating is stable in contact with harsh solvents, including hydrofluoric acid. The obtained SiO layers also provide good mechanical protection for the coated substrate. Variation of voltage, electrode substrate difference temperature and atmosphere can be used to adjust the interface thickness and composition between the two materials and thereby allowing further control over coating hardness and temperature stability. Strength and stability-tailored coatings will find use for aluminum parts used as heat or radiation shields, to interface with ceramic glass and conductive glass materials.

IV. SUMMARY

An ambient condition hard-facing process was applied for the production of SiO layers on aluminum metal. This method is an alternative to expensive vacuum methods. The coating can be made smooth or coarse enough to generate significant tribological alteration of the working metal surface.

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