IN-SITU SYNTHESIS OF INTERMETALLIC AND CERAMIC COATING USING PULSE ELECTRODE SURFACING

Arvind Agarwal and Narendra B. Dahotre
Department of Materials Science and Engineering Center for Laser Applications, University of Tennessee Space Institute, Tullahoma, TN 37388, USA

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Introduction

Pulse Electrode Surfacing (PES) technique utilizes high current electrical pulses of short duration to modify the metal surface. A high current, short duration pulse via discharge capacitance and voltage circuit results in melting the electrode and depositing the material on the substrate (1–6). The primary requirement for the electrode material is that it should be electrically conductive and thus capable of melting in an electric arc. The main advantage of this process is its ability to apply metallurgically bonded coatings with low heat input to the substrate at ambient temperature. Since the process requires very little total heat input, it reduces heat affected zone (HAZ) and minimizes the chance of thermal distortion (4). Substrate material acts as huge heat sink leading to rapid solidification of the molten pool. This results in an extremely fine-grained coating of high density, hardness and strength. Coatings deposited using PES process are used for several applications such as nuclear, fossil and geothermal energy environment (4,6–7), high temperature turbine coatings (8), industrial cutting tools such as milling cutters and drills (9), wear resistant surfaces on large agricultural and textile equipment, high temperature sensors, systems used in petrochemical and pharmaceutical industry and for modern sport equipment (4). In the earlier studies based on PES process, ultrahard ceramic and intermetallic coatings have been deposited using an electrode of same material as that of coating (6–7,10–12). However, in the present study an attempt has been made to synthesize intermetallic and ceramic coating using reactive synthesis during PES process. Such an approach may eliminate the need of using electrodes of intermetallic and ceramic materials for coating, as often it is very difficult and expensive to produce electrodes from these materials without any impurities. Fe₃Al based intermetallic and AlN based ceramic coatings have been synthesized using PES process.

Iron aluminate (Fe₃Al) based intermetallics are well known for their excellent resistance to high-temperature sulfidizing and oxidizing environment (13). Moreover, they have high hardness with an excellent wear and erosion resistance (14). However, environmental effect such as hydrogen embrittlement [HE] causes brittle failure of the intermetallic and limits processing of this alloy into useful shapes and components (15). Though several have been made in Fe₃Al alloy development using alloying and thermomechanical treatments, it is still far from being used as commercially available structural material (15–17). It is envisaged that coating structural steel with Fe₃Al based intermetallic would allow the effective usage of its environmental and wear resistant properties. Fe₃Al based coating would also obviate the problems faced in fabrication of these alloys into useful shapes.
Aluminum Nitride (AlN) has been of prime importance to electronic industry due to its electrical insulating characteristic at high temperatures and high thermal conductivity (18). AlN also possess corrosion resistance properties against molten aluminum and can be used as an anti-corrosive coating for liquid aluminum handling tools and sensors (19). AlN has a considerable high oxidation resistance upto 700°C and can be used as a coating on cutting tools and heating elements (19).

In the present study, Fe3Al and AlN coatings have been synthesized using reaction synthesis during PES process in nitrogen and ammonia environment. Thermodynamic feasibility of such coating synthesis has been addressed. Characterization of these coatings has been performed using various tools such as x-ray diffractometer, microhardness tester and scanning electron microscope (SEM).

**Experimental Procedures**

**Coating Process**

Coupons of AISI 1018 steel of dimensions 25 mm × 10 mm were mechanically polished on emery paper of grit 240 and then rinsed with acetone. Aluminum electrode (99.99% purity) was used to deposit coating on these steel coupons. Deposition was done using a hand held electrode gun in localized nitrogen (N2) and ammonia (NH3) environments provided around the region of deposition at room temperature. Pulsed electrode deposition was carried out at 100 volts and a spark time of 10 μs. The discharge capacitance used for the PES process was 300 μF with a current of 50 amperes.

**Characterization**

ISI Super III-A scanning electron microscope coupled with EDAX was employed for investigation of microstructural morphology and chemical characterization of the coating and interface. Structural characterization for phase(s) identification was carried out on a Philips Norelco x-ray diffractometer with CuKα radiation operating at 40kV and 20 mA. Microhardness measurements were performed on Buehler Micromet II microhardness tester using a Knoop indenter with a load of 200 gm applied for 15 seconds.

**Results and Discussion**

Figure 1(a) shows x-ray diffraction spectrum of the coated surface in N2 environment. Fe3Al is the major phase present in the coating. However, few peaks of non-stoichiometric phase(s) such as FexAly are also indicated. Figure 1(b) is x-ray diffraction spectrum of the coated surface in NH3 environment. Though Fe3Al is still the major phase in the coating, characteristic peaks of AlN are also observed between 30 and 40 degree values of two theta. AlN peaks are further resolved in a low speed x-ray scan shown in Figure 1(c). Fe2N and Fe3N peaks are also observed apart from AlN peaks. It is an interesting observation that both Fe3Al and AlN peaks are observed in the coating synthesized in NH3 environment whereas only Fe3Al peaks are present in the coating synthesized in N2 environment. Such behavior can be understood by the thermodynamic nature of reacting species. Equation 1 represents dissociation of NH3 (20).

\[
NH_3 = N + 3/2 H_2; \quad \Delta G = 45.46 - 0.11T \text{kJ/mol}
\]

Pulse electrode surfacing is a high energy density process, which appears to provide sufficient energy input to cause dissociation of NH3. Nascent N reacts with Al electrode to form AlN. Formation of AlN from its parent elements is represented by equation 2 (21).
Adding equation (1) and (2) provides synthesis of AlN by PES process in NH₃ environment, which is represented by equation (3)

\[ \text{Al} + \text{N} = \text{AlN}; \quad \Delta G = -322.17 + 0.093T \text{kJ/mol} \]  

Equation 3 is a thermodynamically feasible reaction and ceases AlN formation at 2387°C ($\Delta G = 0$). During PES process, consumable Al electrode with a positive polarity is brought close to the substrate having a negative polarity, which results in arc formation of microsecond duration. Though temperature
measurement during arc formation is a debatable issue, it has been successfully argued that material transfer from electrode tip to substrate occurs in liquid state (3). Hence, it is reasonable to assume that arc temperature is higher than melting point of Al. Liquid Al drop reacts with nascent N atom from dissociated NH₃ to form AlN as represented by equation 3.

\[
N_2 = N_{\text{gas}} + N_{\text{gas}}; \quad \Delta G = +473.39 - 0.061 T \text{kJ/mol} \quad (100 \text{ K} \leq T \leq 1300 \text{ K})
\]

Although PES is a high energy density process, due to its relatively inefficient mode of energy transfer, energy input is not high enough to cause dissociation of nitrogen (12). On the contrary, nitrogen dissociation has been observed during laser material processing which has very high energy input in comparison with PES process (12,23). Since nitrogen does not dissociate during PES process, liquid Al drop impinges on to 1018 steel substrate and forms Fe-Al based intermetallic. Fe₃Al is the most prominent phase formed represented by equation 4 (24–25).

\[
3Fe + Al = Fe_3Al; \quad \Delta H_f = 18.0 \text{ kJ/mol}
\]

Formation of Fe₃Al is an exothermic reaction, which occurs after melting point of Al is achieved (24–25). The presence of Al rich liquid causes a rapid increase in the reaction rate resulting in heat evolution, which further increases reaction rate leading to synthesis of Fe₃Al within few seconds (25). A similar reaction mechanism occurs during PES process where liquid Al droplet reacts exothermically with steel substrate to form Fe₃Al based intermetallic coating. EDS analysis suggests 13–16 wt % Al within the coating region. Such composition is further indicative of Fe₃Al formation within the coating (25).

Microhardness values within the coating, interface and substrate are elucidated in Figure 2. Coating synthesized in NH₃ environment has a higher hardness (774 Knoop) than coating formed in N₂ environment. This is attributed to the presence of AlN in addition to Fe₃Al intermetallic within the coating. AlN is a hard ceramic (1200 kg/mm²) compared to Fe₃Al based intermetallic which has hardness in the range of 380–620 kg/mm² (18,26). Presence of this hard phase causes an increased hardness in coating produced in NH₃ environment. On the contrary, coating produced in N₂ environment does not have AlN phase. Hardness (592 Knoop) of the coating produced in N₂ environment is mainly due to Fe₃Al.

Figure 3 shows an SEM micrograph of the cross section of the coating produced by PES process in NH₃ environment. Coating is metallurgically bonded and adherent to the substrate. There are few vertical cracks within the coating, which could be due to differential thermal conductivity of Fe₃Al and
AlN (18,26). Similar morphology was observed for the coating deposited in N\textsubscript{2} environment except with an absence of cracks.

**Conclusions**

Fe\textsubscript{3}Al based intermetallic and AlN based ceramic coatings have been successfully synthesized using PES process in N\textsubscript{2} and NH\textsubscript{3} environment. AlN is synthesized only in NH\textsubscript{3} environment due to availability of N atoms from dissociated ammonia. Fe\textsubscript{3}Al formation is exothermic in nature and occurs in both, N\textsubscript{2} and NH\textsubscript{3} environment. Hardness of coating synthesized in NH\textsubscript{3} environment is higher due to presence of AlN apart from Fe\textsubscript{3}Al.

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