INVESTIGATION OF A CERAMIC-METAL INTERFACE PREPARED BY ANODIC SPARK DEPOSITION
K. Koshkarian, W. Kriven

To cite this version:
K. Koshkarian, W. Kriven. INVESTIGATION OF A CERAMIC-METAL INTERFACE PREPARED BY ANODIC SPARK DEPOSITION. Journal de Physique Colloques, 1988, 49 (C5), pp.C5-213-C5-217. 10.1051/jphyscol:1988522. jpa-00228019

HAL Id: jpa-00228019
https://hal.archives-ouvertes.fr/jpa-00228019
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
INVESTIGATION OF A CERAMIC–METAL INTERFACE PREPARED BY ANODIC SPARK DEPOSITION

K.A. KOSHKARIAN and W.M. KRIVEN

Department of Materials Science and Engineering, Ceramics Division, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, U.S.A.

ABSTRACT

Al₂O₃ coatings were deposited on Nb substrates using a process known as anodic spark deposition. Characterization was performed by scanning electron microscopy, X-ray diffraction, and electron beam microprobe analysis. Decreasing concentration of electrolyte solution, in which the coatings were deposited, was found to qualitatively lower the adherence. Solution concentration also affected the incorporation of Nb in the coating.

INTRODUCTION

In the broad field of coating technology, processes such as vapor deposition (CVD, PVD), and plasma spraying have received a great deal of attention in recent years. Overshadowed by these more popular and already commercially adapted techniques, anodic spark deposition is a unique process that has undergone only limited investigation.

Anodic spark deposition is a process by means of which ceramic coatings can be formed on conductive substrates. The process involves application of a high potential (on the order of hundreds of volts) to an electrolytic cell. The substrate material, typically a barrier or depletion layer forming metal such as Al, Ta, Nb, Ti, Ni or Cu, is positioned as the anode in an electrolytic cell. The precursor to spark deposition is anodization. As the voltage is raised, an anodic oxide film is induced to grow. However, above a certain applied potential, film thickness no longer increases uniformly and dielectric breakdown occurs. The breakdown of the initial barrier layer is seen in the form of many freely moving sparks. The movement of the sparks is attributed to the deposition of material and localized healing at one spot with subsequent sparking at nearby weak spots in the coating. The applied voltage sufficient to cause dielectric breakdown varies with the anode material, and electrolyte composition and temperature.

The anodic sparking phenomenon was first described in detail in a work by Guntherschulze and Betz. They noted that sparking reactions occurred due to dielectric breakdown.

Gruss and McNeill further studied the spark reaction by examining a wide variety of substrate materials in aluminate, tungstate and silicate solutions. Examination of reaction products showed that sparking resulted in the formation of chemical compounds comprised of the electrolyte ions and oxide of the anode.

More recently a detailed study was performed by Brown and Van in which various processing parameters were examined in order to determine their effect on adhesion, porosity, and surface area. Additionally, current decay at constant voltage was studied during a multiple spark reaction and the behavior of most systems fit the relation:

\[ e^{-kt} = \frac{\mathcal{I}_t}{\mathcal{I}_0 e^{t_0}} \]

where \( \mathcal{I}_t \), \( \mathcal{I}_0 \) and \( \mathcal{I}_e \) are current densities at time \( t \), at the start of decay, and at the steady state respectively. \( K \) is a voltage and system dependent constant. The latest study by Kurze and co-workers details a brief investigation of the mechanical, thermal and electrical properties of Al₂O₃ spark coatings on aluminum substrates and examines process parameters.

Commercial applications for sparked coatings have been demonstrated in the medical field as stomatological implants and in the electronics field as heat sinks. It has also been shown that through the addition of metal salts to the electrolyte, it is possible to produce colored spark coatings. Color shades are dependent on concentration and...
deposition parameters. This coloring technique is analogous to coloring of anodized layers, commonly performed on aluminum.

In light of previous research, the scope of this study was to characterize the niobium/alumina substrate/spark layer system. The microstructure of the coating in general and its metal/ceramic interface were specifically examined. The Nb/Al₂O₃ system was chosen for its high temperature compatibility. Comparison with similar interfacial studies making use of alternate bonding mechanisms is also possible. [9,10]

EXPERIMENTAL

Figure 1 shows the arrangement of the experimental apparatus used in this investigation. This arrangement is commonly applied to both laboratory anodization and electropolishing.

A dc power supply with voltage and current ranges of 0-1500V and 0-1.25A, respectively, was utilized. This power supply is capable of maintaining constant voltage or current within a ±4% accuracy.

Electrolytic solutions were contained in a 2000ml glass containment cell which was magnetically stirred to maintain homogeneity and avoid temperature differentials. The temperature was maintained at 17°C through use of a constant temperature water supply running through copper coils immersed in the solution. The maximum temperature fluctuation was 3°C for extended sparking time at high sparking voltages. Technical grade NaAlO₂ was used to make all solutions. Solutions of 0.1N, 0.05N and 0.10N were prepared fresh for each coating trial from the crushed salt. No more than three substrates were coated in each trial.

A Platinum cathode was used in all cases due to its inert nature with respect to reaction with the solution. The surface area of the cathode was approximately on an order of magnitude greater than that of the anode. However, its size was not rigidly controlled since variation has been shown to produce no effect. [1]

The anode material was 99.9% pure niobium (columbium) in the form of rods 1.29mm in diameter. The surface of the rods was prepared by successive polishing with 400 and 600 grit SiC paper followed by an ultrasonic rinse in acetone and final rinse in deionized water. Surface preparation was performed just prior to immersion in the electrolyte.

All coatings were deposited at constant voltage, using an initial current density of 1.0 amp/cm². Because the conductivity of the solution changed with concentration, higher voltages were successively needed for lower normality solutions. Voltages were chosen as 500V, 610V and 745 V respectively for the 0.1, .05 and .01N solutions. These voltages were chosen because they were sufficiently high enough to provide sparking for the desired time of 10 minutes.

Upon completion of each deposition experiment the substrate was removed from the cell, rinsed in deionized water and dried in a cold air-stream.

Characterization of the coating and the coating substrate interface was performed thorough X-ray analysis, scanning electron microscopy and electron microprobe analysis. Transmission electron microscopy is presently being carried out.

RESULTS AND DISCUSSION

The sparking reaction generally followed the description of previous investigators [1,3,4]. Coating deposition began with smaller more mobile sparks followed by larger sparks which appeared to be stationary. The color of the sparks varied with the electrolyte concentration. The 0.1N solution exhibited only orange colored sparks. However, some white sparks appeared, mixed with a heavy concentration of orange sparks, in the .05N solution. Reactions in the .01N solution resulted in only white sparks. The decrease in solution concentration produced spark reactions of higher temperature as evidenced by this change from orange to white sparks. This change in temperature is understandable in light of the increase in voltage necessary to initiate and maintain the reaction.

Gas bubbles were observed, in later stages of sparking (8 minutes), to emerge from isolated sites on the deposited coating where sparking was not occurring. Sparking very quickly followed at these sites. The release of gases evidently opened a path of dielectric weakness, which precipitated sparking. [11]

The coating was quite porous following only several minutes of sparking as evidenced by Figure 2. However, as Figure 3 illustrates, the coating becomes more uniform with time. All coatings were white in color. The surface texture of the coating becomes smoother as solution concentration decreased. The .01N solution produced a coating that was quite glassy looking in appearance.

X-ray diffraction analysis of the coating confirmed that it did indeed become more amorphous with decreasing electrolyte concentration and increasing voltage. Crystalline phases were detected in all cases. However, increased background intensity suggests amorphous phases.
The higher spark reaction temperature of white sparks, producing a greater quench rate in the solution, also tends to encourage amorphous coating formation. This relationship is in contrast to that found for reactions on aluminum substrates. [4] Also through X-ray analysis, the coatings were found to be primarily α-Al2O3 with minor amounts of β-Al2O3 incorporated. Trace quantities of Nb2O5 were also found. Detection of Nb2O5 likely occurred due to an anodic layer formed on the Nb substrate.

Adherence of the coating was greatly affected by change in electrolyte concentration. Figure 4 shows a polished cross-sectional view of the coating substrate interface produced by deposition in 0.01N electrolyte. The coating was separated from the substrate over most of the interface. In contrast, deposition in 0.1N solution produced the best adhesion. Figure 5 shows that the coating is generally attached along the entire length of the substrate. Only isolated regions exhibit non-uniform contact between the coating and substrate. These regions are likely due to gas entrapment.

Figure 6 shows a high magnification micrograph of a characteristic region where intimate contact exists between the coating and substrate. Both mechanical bonding, due to the surface roughness of the substrate, and chemical bonding is evident.

Electron beam microprobe analyses performed on cross-sectional surfaces produced typical traces shown in Figure 7. The .1N and .05N solution deposition traces showed evidence that Nb was incorporated in the coating. It is likely that this incorporation was in the form of metallic inclusions [11] An apparent trend of increasing relative intensity of Nb within the coating as electrolyte concentration increased was observed. This trend has basis in that the applied voltage, hence electric field strength, decreased with increasing solution concentration. The .01N solution reaction (Figure 7a.), sparked at 745V, showed little inclusion of Nb within the coating. Of interesting note is the fact that in the .05N and .1N traces (Figure 7b,c) Nb in the coating was not observed near the interface but only further into the coating. Similar observations have been made by others in alternate coating applications.[12,13] There was considerable diffusion of Al (in some form) into the Nb substrate in all cases. It is known that at elevated temperatures a chemical reaction can occur at the interface such that Al2O3 will form in the Nb. [9] Therefore, it is questionable whether the microprobe traces detected Al10 or Al2O3 precipitates. Future TEM work will help to clarify this question.

CONCLUSION

Anodic spark deposition proves to be an intriguing process for deposition of an alumina coating on a niobium substrate. Important process parameters such as, but not limited to, electrolyte concentration and sparking voltage critically affect the chemistry and structure of the coating and its associated substrate interface. However, further work (TEM) is necessary to determine more precisely the nature of the interaction between the substrate material, the electrolyte solution constituents, and the deposited coating.

ACKNOWLEDGEMENTS

The work of K.A. Koshkarian was supported by a General Telephone and Electric grant and that of W. M. Kriven was supported by the U.S. Department of Energy under contract DOE DEAC02 76 ER 1198.

REFERENCES

Fig. 1 Experimental apparatus arrangement

Fig. 2 Coating surface after 5 minutes 0.1 N solution.

Fig. 3 Coating surface after 10 minutes 0.1 N solution.
Fig. 4 Cross section of substrate/coating, 0.01 N solution.

Fig. 5 Cross section of substrate/coating, 0.10 N solution.

Fig. 6 Cross section of substrate/coating at high magnification, 0.10 N solution.

Fig. 7 Electron beam microprobe analyses.
  a) 0.01 N solution
  b) 0.05 N solution
  c) 0.10 N solution