Synthesis and Characterization of Zirconium Oxide (ZrO$_2$) Films on AA5052 and Glass substrates

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Abstract: Aluminum alloy has gained lot of importance in Aerospace Industries and Engineering applications because of its strength, high resistance to heat, light weight and durability. In this paper we made an attempt to improve the AA5052 substrates properties by coating Zirconium Oxide (ZrO$_2$) by Sol-Gel Method. Glass substrates were also coated with Zirconium Oxide (ZrO$_2$) coating. The coated AA5052 and glass substrates will be annealed to check the thermal resistance for various time of thermal rig test. Micro crystalline properties and formation of ZrO$_2$ of the coated film is evaluated for surface morphological studies by using Scanning Electron Microscope (SEM) and the elemental composition studies done by EDAX (Energy Dispersive Absorption X-ray Spectrometer).

Keywords: Al alloy, Sol-Gel, Zirconium oxide (ZrO$_2$)

1. Introduction

Aluminum is one of the metals which are extensively used in day today lives from utensils to structural elements of airplanes. Pure aluminum is very soft and has no structural strength to manufacture the parts of an aircraft. It is also very ductile due to which it can be machined easily and strengthened further by alloying it with other metals such as copper, magnesium, manganese, zinc etc., for different application [1]. It is estimated that 75 to 80 percent of the materials used in modern-day aircraft is made up of aluminum alloy. Benefits of Aluminum alloy are it is extremely light weight material, high strength and has good corrosion resistance [2]. Different types of aluminum alloys are used for different applications. The commonly used Aluminum alloys in the aircraft industry are AA1050, AA 2024, AA 5052, AA6061, AA7050, AA7075 and AA7475 [8]. These alloys are used in the wing’s planes, rudder, doors and floors, exhaust pipes, engine turbines and the cockpit instrumentation [3,4].

Many products of today, ranging from refractory to medical products, pigments, electronics, coatings, and ceramics, have been based on zirconia due to its superior characteristics. Further, some of the other typical applications of zirconia include dies for hot metal extrusion, oxygen sensors, and membranes in fuel cells, deep well valve seats, and marine pump seals [5, 6].

ZrO$_2$ can be synthesized using several techniques i.e., Sol-Gel synthesis, Hydrothermal synthesis, Plasma sprayed deposition technique, and chemical vapor deposition etc. [7]. In our present work synthesis of the ZrO$_2$ is experimented using sol-gel technique; since it is economical, chemically pure, Nano-sized particles are formed with narrow sized distribution [8, 9].
2. **Experimental Details**

2.1 **Synthesis procedure for ZrO$_2$.**

In the present research work, Zirconium Oxide (ZrO$_2$) inorganic coatings are prepared by Sol-Gel method and coated on by dip and spin coating techniques respectively [10]. Here, Zirconium Oxide is used for the coating because it exhibits several excellent mechanical properties like strength, toughness, biocompatibility, high fatigue, high wear resistance, low thermal conductivity, high melting point and high resistance to corrosion. AA5052 substrate is used as it has high strength, high ductility and high corrosion resistance.

The prepared gel is coated on the substrates by Dip coating and spin coating technique. The coated specimen is subjected to structural, surface and elemental analysis to evaluate the improved properties. ZrO$_2$ solution is prepared for the coating using Sol-gel technique. Firstly, 40 ml of ethanol is taken in a beaker and kept for stirring at 500 rpm with a magnetic stirrer for uniform dissolution. 10 ml of Nitric acid is added together and stirred for 15 minutes. Then, 9 ml of Zirconium butoxide is added into the mixture and stirred for 30 minutes. A pale yellow ZrO$_2$ solution is obtained [1, 2].

In this experimentation, Aluminum alloy AA5052 and microscopic slides (glasses) are used as substrate materials. AA5052 substrate contains Al, Si, Fe, Cu, Mn, Mg, Cr, Zn, Ti in the ratio of 96.7, 0.25, 0.40, 0.10, 0.10, 2.2, 0.15, 0.10 respectively [10]. The surface of the aluminum alloy is made flat by using a scratch pad. Then both the substrates were cleansed in water and kept for ultra-sonication for 25 minutes. Later, the substrates were dried completely before the coatings were done [14].

Firstly, AA5052 substrates were dip coated manually using ZrO$_2$ gel. The substrates were coated for 1, 3, 5, 7 number of times respectively. The substrates were immersed in the solution for 15 seconds and air dried for 1 minute after each coating. The coating deposited on the substrate is then air dried for 3 days and kept for annealing at 350 °C for 2 hours.

Further, the solution is aged for 3 days and then deposited on glass substrates following the same method as mentioned for aluminum alloy substrates. Spin coating is also carried out on the glass substrates using the same ZrO$_2$ solution which was kept for aging as the same number of times mentioned above. The substrates were coated using a spin coater at 340 rpm for 10 seconds. 2 drops of the solution were placed on to the substrate each time the coating was carried out and the substrates were annealed at 350 °C for 2 hours [1].

3. **Characterization Techniques**

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX) were used to analyze the coatings deposited on the substrates for surface morphology and elemental composition. Scanning Electron Microscope (SEM) is an electron microscope which scans the surface of any sample and produces the image by using electrons beam. It is used to analyze the surface morphology and the chemical composition of the sample.

Energy Dispersive X-ray Analysis (EDAX or EDX) is also called as Energy Dispersive X-ray spectroscopy (EDS) which is used to estimate the elemental composition of the sample using Scanning Electron Microscope (SEM). It also detects the elements having higher atomic number than boron even when it is in the concentration of 0.1%. Therefore, it also helps in evaluating and identifying the metal and in detection of the contaminants etc. [11, 13].

4. **Results and Discussions**

The scanning electron microscope (SEM) images of the coated AA5052 substrates (dip coated) and glass substrates (dip coated and spin coated) for different number of times are shown below. The thickness of the coating increases with increase in the number of dipping times [1].

We initially got the uniform coatings for each dip which were also homogeneous. But with respect to the above images obtained after annealing sintered structures, clusters, cracks were observed and the coatings were non uniform. Different structures are also observed. Bonding strength was poor between the coating and substrates which is evident from the spallation of coatings [15]. It may be caused due to excessive air drying and then heating [16].
Figure 1. SEM images of the coated AA5052 substrates with different dipping numbers (a) 1 (b) 3 (c) 5
The results obtained are dependent on a number of process parameters which includes roughness of the substrate, nature of the gel, number of dipping etc. Figure 1. (a) (b) (c) depicts the surface morphological images of 1,3,5 number of dipping respectively. It is evident that the coatings were uniform throughout before annealing the samples. After the samples were subjected to annealing time for 1 hour at a temperature of 350 °C, spallation of the coatings was observed. Crack initiation in the coatings of ZrO\textsubscript{2} was observed due to the penetration of heat until the substrate. In figure 2. (a) (b) (c) (d) (e) and (f) glass substrates which were dip coated as well as spin coated were subjected to thermal rig test for 2 hours respectively [12]. The coatings had a void at the center which indicated the epicenter of crack initiation as shown in figure 2. (e) and (f). Further in figure 2. (d) the structure indicated to be in the hexagonal shape.

Figure 3. EDX analysis of the coated AA5052 Substrates with different number of times (a) 1 (b) 3 (c) 5 (d) 7

Figure 3. (a) (b) (c) and (d) represents the elemental composition of ZrO2 dipping on AA5052 which indicates the presence of Aluminum, Zirconium, Oxygen and Bromine. The weight percentage of Al was 35, 35.4, 32.9, 43.5, the weight percentage of O was 22.3, 22.5, 20.7 and 21.5, the weight percentage of Br was 25.9, 19, 26.1 and 17.4 and the weight percentage of Zr was 10.5, 16.5, 14.2, 12.3 for 1, 3, 5,
7 number of times respectively. It showed an uncertain variation in the weight percentage of the ZrO2 due to the breakage of coatings.

5. Conclusions

ZrO2 coatings were successfully deposited on the AA5052 and glass substrates. Though the coatings were observed to be uniform and homogeneous initially, SEM images of the substrate depicted the cracks and spallation of the coatings occurred due to weak bond strength/adhesion between the film and the substrate. EDX analysis showed the elemental composition of the coated AA5052 substrate, which indicated an uncertain variation in the weight percentage of the Al, O, Br and Zr. Further, the morphological study revealed that the deposited films were initiated with cracks due to the exposure to thermal flux.

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