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# Influence of carbon ion implantation energy on aluminum carbide precipitation and electrochemical corrosion resistance of aluminum

Naveed Afzal<sup>a,\*</sup>, Mohsin Rafique<sup>a</sup>, Wajeeha Javaid<sup>a</sup>, R. Ahmad<sup>b</sup>, Ameeq Farooq<sup>c</sup>, Murtaza Saleem<sup>d</sup>, Zubair Khaliq<sup>e</sup>

<sup>a</sup> Centre for Advanced Studies in Physics, GC University, Lahore, Pakistan

<sup>b</sup> Department of Physics, GC University, Lahore, Pakistan

<sup>c</sup> Corrosion Control Research Cell, Department of Metallurgy and Materials Engineering, CEET, University of the Punjab, Lahore, Pakistan

<sup>d</sup> Department of Physics, SBASSE, Lahore University of Management Sciences, Pakistan

<sup>e</sup> Department of Polymer Engineering, National Textile University, Faisalabad, Pakistan

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### ABSTRACT

The effects of varying carbon ions (C<sup>+</sup>) implantation energies on Aluminum Carbide (Al<sub>4</sub>C<sub>3</sub>) precipitation, surface morphology and electrochemical corrosion resistance of aluminum (Al) were evaluated. The Al samples were implanted with C<sup>+</sup> of different energies of 0.25, 0.5, 1, 2, and 4 MeV at a constant dose of  $1 \times 10^{15}$  ions/ cm<sup>2</sup>. The X-rays diffraction (XRD) and field emission scanning electron microscope (FESEM) results showed Al<sub>4</sub>C<sub>3</sub> precipitates in the ion-implanted Al which were decreased at higher implantation energies ( $\geq 1$  MeV). The decrease in Al<sub>4</sub>C<sub>3</sub> precipitation was attributed to the lower chemical reactivity of C<sup>+</sup> with Al due to ion-induced lattice defects. The Al surface became rough, and micro-cracks appeared on it as the ion energy increased above 0.25 MeV. The electrochemical corrosion rate of Al decreased from 469.9 mpy to 70.32 mpy after C<sup>+</sup> implantation at 0.25 MeV. However, the corrosion rate increased with increasing ion energy above 0.25 MeV. This changes in corrosion rate were elucidated on the basis of Al<sub>4</sub>C<sub>3</sub> precipitation and lattice defects in Al created by C<sup>+</sup> implantation. The SEM analysis of electrochemically tested samples indicated lower pitting in the sample implanted with 0.25 MeV ions as compared to those implanted with higher energy.

## 1. Introduction

Aluminum (Al) is a commonly used metal in daily life which finds potential applications in aerospace, marine, and automotive industries because of its low density, high strength to weight ratio, and good corrosion resistance [1,2]. The corrosion resistance of Al is better than most of the other metals. This resistance is because of the formation of a passive oxide layer on its surface which restricts further corrosion. However, this passive layer dissolves quickly when Al is used in an acidic or alkaline environment. Also, this passive layer is not homogeneous which may cause localized corrosion and pitting on the Al surface [3,4].

The techniques such as nitriding and carburizing are used to improve the surface properties of Al and its alloys [5–10]. However, the generated nitride and carbide layers on the Al surface are rough and may contain cracks and groves [10,11]. Alternatively, ion implantation is a versatile technique for improving the surface properties of metals and alloys without affecting their bulk properties [12,13]. Researchers

improved the hardness, corrosion and wear resistance of Al by ions implantation [14-24]. Previous studies indicated that the nitrogen ion implantation in Al produced Aluminum Nitride (AlN) layer on its surface which increased its hardness. However, the AlN layer was not effectively resistant against corrosion and wear properties of Al due to rough surface morphology [11,19]. Carbon ion (C<sup>+</sup>) implantation in Al was used to improve the surface properties through the formation of Aluminum Carbide (Al<sub>4</sub>C<sub>3</sub>) precipitates [20–24]. Foerster et al. studied the effect of C<sup>+</sup> implantation in Al at room temperature (RT) and elevated temperature (400 °C) with doses up to  $2 \times 10^{21}$  ions/m<sup>2</sup> and ion energy of 25 keV [20]. They further reported that the carbon implantation at RT resulted in the formation of small sized Al<sub>4</sub>C<sub>3</sub> precipitates (2-4 nm), whereas the average size of these precipitates was increased to 20 nm at elevated temperature. In a later study, Foerster et al. showed that the  $Al_4C_3$  precipitation occurred in Al with 25 keV  $C^+$ implantation even at lower doses ranging from  $1 \times 10^{17}$  ions/cm<sup>2</sup> to  $20 \times 10^{17}$  ions/cm<sup>2</sup> [21]. The Al structure became amorphous with increasing the C<sup>+</sup> dose whereas the hardness of Al was increased. These

\* Corresponding author.

E-mail address: Naveed.phys@gmail.com (N. Afzal).

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results were ascertained by Uglov et al. who reported the formation of Al<sub>4</sub>C<sub>3</sub> precipitates in Al implanted with 20 keV C<sup>+</sup> at low doses of  $0.4 \times 10^{17}$  ions/cm<sup>2</sup> to  $4 \times 10^{17}$  ions/cm<sup>2</sup> [22]. However, the Al<sub>4</sub>C<sub>3</sub> layer was observed by transmission electron microscope (TEM) only, and it could not be detected by the X-ray diffraction (XRD). Meunier et al. reported C<sup>+</sup> implantation effects in Al, cobalt (Co) and tungsten (W) in the dose range of  $10^{16}$  ions/cm<sup>2</sup> to  $10^{18}$  ions/cm<sup>2</sup> at constant ion energy of 1 MeV [23]. The carbide layer formation was significant in Al than that in Co and W. Also, the carbide precipitation increased with an increase of the ion dose. Similarly, Fariaut et al. reported the surface carburization of AlSiMg alloy by 2.4 J/cm<sup>2</sup> excimer laser that resulted in the formation of the Al<sub>4</sub>C<sub>3</sub> layer which increased the wear and corrosion resistance of the alloy [24].

Previous studies indicated that the C<sup>+</sup> implantation in Al had been investigated at different doses while keeping the ion energy constant. However, the energy of C<sup>+</sup> can play a significant role in the formation of carbide precipitates in Al. The energy variation can alter the penetration depth of ions in Al which may influence the carbide formation in it. In this study, the effects of varying C<sup>+</sup> energy on Al<sub>4</sub>C<sub>3</sub> precipitation and electrochemical corrosion resistance of Al have been investigated. The C<sup>+</sup> of different energies ranging from 0.25 MeV to 4 MeV are implanted in Al at a constant dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. Also, the C<sup>+</sup> dose used in this work is lower than that used in the previous studies [20–23].

#### 2. Methodology

Carbon ions (C<sup>+</sup>) of different energies were implanted in Al (99.9% pure) to investigate the ion-induced structural and surface morphology in it. The Al samples (20 mm  $\times$  20 mm) were mechanically grinded and polished by grinding and polishing machines. The grinding was carried out using emery papers of different grits. Afterward, the samples were polished to a mirror finish using diamond pastes (down to 3 µm). Then the samples were cleaned in an ultrasonic bath. A Pelletron Accelerator at Centre for Advanced Studies in

Physics (CASP), GC University Lahore, Pakistan, was used for C<sup>+</sup> implantation in Al [25,26]. The schematic diagram of the Pelletron Accelerator is shown in Fig. 1. The working principle of Pelletron Accelerator is based on the production of charge using a source of negative ions by cesium sputtering (SNIC) and then the acceleration of the charge through a chain of steel pellets by applying high electrostatic potential difference. The accelerated ions are then focused on the target material in a vacuum sealed chamber. In this work, a carbon cathode was used to produce C<sup>+</sup>. The Al samples were fixed on a holder inside the accelerator chamber. Initially, the samples were exposed to 0.25 MeV C<sup>+</sup> at the dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. The ion implantation was performed in vacuum at room temperature. Similarly, the Al samples were implanted with 0.5, 1, 2, and 4 MeV C<sup>+</sup> with a constant ion dose. The range of C<sup>+</sup> inside Al was studied using Stopping and Range of Ions in Matter (SRIM) software [27]. The range was found to be 0.5, 0.8, 1.38, 2.21, and 3.73 µm for 0.25, 0.5, 1, 2, and 4 MeV ion-implanted samples respectively. In other words, the range of C<sup>+</sup> in Al increases with increasing the implantation energy. The structural study was carried out using XRD operating at 40 kV with Cu-ka radiations. The XRD measurements were taken in glancing incident mode, and the diffraction patterns were recorded in the  $2\theta$ range of 20°-80° with a step size of 0.02°. The surface morphology of Al was studied by field emission scanning electron microscope (FESEM). The energy dispersive X-ray spectrometer (EDS) analysis (mapping and line) was carried out to detect the presence of carbon inside the Al. The electrochemical measurements were made using Gamry potentiostat 1000E connected with three electrode cell setup [28]. The un-implanted and  $C^+$  implanted samples (2 × 2 cm<sup>2</sup>) were used as working electrodes. The graphite acted as counter electrode whereas the reference electrode was made up of Ag/AgCl. The NaCl (3.5%) was used as an electrolyte for the electrochemical measurements at 35 °C. The potentiodynamic polarization tests for un-implanted and C<sup>+</sup> implanted samples were performed to evaluate the electrochemical corrosion rate of Al in 3.5% NaCl solution. The potential was varied from -0.5 to 1.5 V with a scan rate of 2.5 mV/s.



Fig. 1. Schematic diagram of pelletron accelerator.

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