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# Carbon ion implantation into pure aluminium at low fluences

C.E. Foerster[a,*], T. Fitz[b], T. Dekorsy[b], F. Prokert[b], U. Kreißig[b], A. Mücklich[b], E. Richter[b], W. Möller[b]

[a]Depto. de Física-UEPG, Ponta Grossa, Pr 84030-900, Brazil
[b]Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, D-01314 Dresden, Germany

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**Abstract**

This work presents selected results from carbon ion implantation into pure Al matrix. The carbon ions were implanted with an ion energy of 25 keV and fluences of $1\times10^{21}$ and $2\times10^{21}$ $C^+/m^2$ at room temperature (RT) and elevated temperature of 400 °C. Elastic recoil detection analysis (ERDA), grazing incidence X-ray diffraction analysis (GIXRD), Raman spectroscopy and high resolution electron microscopy (HRTEM) show the formation of embedded $Al_4C_3$ precipitates with carbon concentrations below its stoichiometric level. At RT ion implantation, the $Al_4C_3$ precipitates have an average grain size in the order of 2–4 nm. For carbon ion implantation at 400 °C, the precipitates grow up to approximately 20 nm in diameter and are randomly distributed in the implanted region. The carbon excess, not bound in the $Al_4C_3$ precipitates, forms highly disordered C–C clusters of approximately 0.2–0.4 nm in size. Implantation at a temperature of 400 °C reduces drastically the carbon clusters content due to the growth of the $Al_4C_3$ precipitates.


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## 1. Introduction

Aluminium is a material with wide potential for industrial application due to its high strength to weight ratio, good corrosion resistance and formability. However, even in alloyed form, it presents poor mechanical and tribological properties, i.e. low hardness and wear resistance in comparison to the most common iron alloyed materials. It is well known that processes like nitriding, oxidizing and carburising can be used to improve the mechanical and tribological surface properties of metals. In recent years, nitriding has been intensively investigated as a promising method for surface modification of aluminium, improving the mechanical surface properties by the formation of an AlN layer [1–10]. However, the surface of the aluminium nitride layers is often morphological rough containing deep grooves and cracks [11,12], and therefore, it is not satisfactory for industrial application. Carburising of iron and steels is also well studied and often applied as an alternative to nitriding [13]. Consequently, in similarity to these materials, carburising can also be an alternative to improve aluminium mechanical and tribological surface performance. However, hitherto there are only a few publications on this subject.

Recently, Uglov et al. [14] reported a study on the structural and phase composition changes in aluminium induced by carbon ion implantation. The experiments were done at 20 keV and carbon fluences ranging from $4\times10^{20}$ to $4\times10^{21}$ $C^+/m^2$ at RT condition. The authors observed that the carbon implantation leads to the formation of $Al_4C_3$ precipitates after a fluence of $2\times10^{21}$ $C^+/m^2$. However, for the higher used fluence ($4\times10^{21}$ $C^+/m^2$), the carbon concentration was 1.5 times greater than the stoichiometric level in the $Al_4C_3$ phase. Despite the experimental difficulty to observe carbon clusters, as a result of the carbon excess, the authors suggested that besides $Al_4C_3$ synthesis, carbon

* Corresponding author. Tel.: +55 42 220 3044; fax: +55 42 220 3042.
*E-mail address:* carlosef@uepg.br (C.E. Foerster).

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cluster formation also takes place in the near surface region. Other authors also worked with the formation of Al–C with different purposes. Ham et al. [15] performed plasma immersion ion implantation (PIII) in aluminium using methane plasma at 40 kV with an estimated fluence of $4\times10^{21}$ $C^+/m^2$. This process resulted in the formation of an aluminium carbide interlayer that enhances the adhesion between an aluminium substrate and a post-deposited diamond-like carbon (DLC) coating. Fariaut et al. [16,17] reported formation of $Al_4C_3$ surface layers grown on aluminium substrate using excimer laser irradiation. During this process, an excimer laser beam is focused onto the surface modified in a cell containing methane gas. As result, the vapour plasma expands from the surface and a shockwave dissociates and ionizes the gas that reacts with the aluminium surface. It was observed by the authors that the surface wear resistance increased after the treatment. Ning et al. [18] relate synthesis and structural properties of Al–C–N–O thin films produced by RF reactive diode sputtering of aluminium target in plasma of $N_2$, $O_2$ and $CH_4$ gas mixtures. The aim of the work was the production of a hard composite material by selecting appropriate components, their proportions and the results showed the formation of C–N, Al–N and Al–C bonds.

As it can be seen, only limited information on the topic of aluminium carburising and Al–C bonds formation can be found in the literature. Therefore, there is the necessity of a systematic study, independent of the used surface-modifying process (glow discharge, ion implantation, plasma immersion ion implantation, etc.), to understand the mechanism involved in the Al–C bond formation. As an instance, for aluminium carburising by ion implantation, parameters such as ion energy, fluence, current density and substrate temperature, as well as their influence on the surface properties, need to be better understood and correlated.

With the objective to contribute to the aluminium carburising, the present study reports selected results of carbon ion implantation into aluminium substrate. Complementary surface analysis methods were used in order to correlate the substrate temperature and the ion fluence dependence on the $Al_4C_3$ synthesis and the carbon excess distribution in the near surface region.

## 2. Experimental procedure

Aluminium samples in foil shape and thickness of $2\times10^{-3}$ m were mechanically polished to mirror finish surface and then cleaned by ultrasound. The implantation was carried out by the Rossendorf 200 keV Danphysic implanter fed with $CO_2$ gas with $^{12}C^+$ at ion energy of 25 keV and current density of 3 $\mu A/cm^2$. The samples were implanted at fluences of $1\times10^{21}$ and $2\times10^{21}$ $C^+/m^2$. Under these implantation conditions, the substrate heating was limited to about 50 °C by a backside sample cooling. Some samples were also implanted at the same implantation parameters but at a higher substrate temperature of 400 °C by using additional heating. The pressure in the vacuum chamber during the implantation was less than $1\times10^{-4}$ Pa.

Elemental depth profiles were obtained by ERDA using 35 MeV $Cl^{7+}$ ions at a scattering angle of 30° supplied from the Rossendorf 5 MeV Tandem accelerator.

GIXRD with Cu Kα radiation at an incidence angle of 0.5° was used to identify the phases formed in the near-surface region due to the carbon implantation. At this condition, the estimated X-ray (1/e)-penetration depth amounts to approximately 700 nm. Grain size estimation was performed by use of the Scherrer formula.

In order to observe the formed chemical bonding, the samples were analyzed by Micro-Raman spectroscopy (Jobin-Yvon LabRam HR) using an incident wavelength of 532.14 nm in the range from 500 to 2200 $cm^{-1}$. To estimate the penetration depth of the incident Raman wavelength, ellipsometry measurements were performed to assure that the resulting spectra are representative in respect to the modified region.

HRTEM was applied to observe the precipitate size and their distribution in the near surface region. For this purpose, cross-section samples have been prepared. The analysis was carried out using a Philips CM300 electron microscope, operated at 300 kV.

## 3. Results and discussion

Fig. 1 shows the elemental profiles of carbon and oxygen obtained by ERDA at fluences of $1\times10^{21}$ $C^+/m^2$ (Fig. 1a)) and $2\times10^{21}$ $C^+/m^2$ (Fig. 1b)), respectively. The substrate temperature during the implantation is indicated in the figures. As expected, the carbon profiles have a typical Gaussian shape and it should be noted that the obtained profiles are slightly distorted by the depth resolution of the

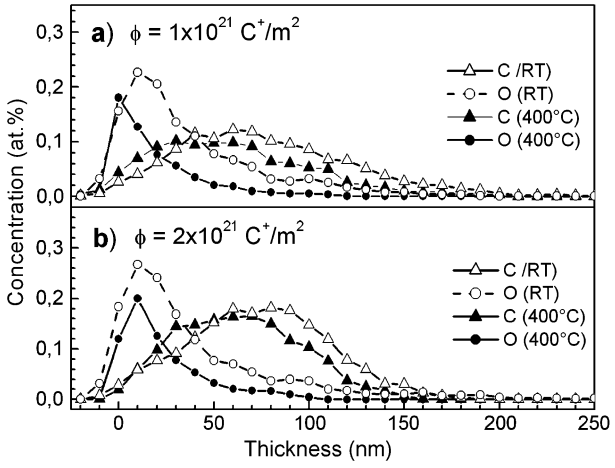


Fig. 1. ERDA profiles for C and O obtained after carbon implantation into Al at fluences of (a) $1\times10^{21}$ $C^+/m^2$ and (b) $2\times10^{21}$ $C^+/m^2$ at RT and 400 °C. (△) Carbon, RT; (▲) carbon, 400 °C; (○) oxygen, RT; (●) oxygen, 400 °C.