Structural proprieties of the Al–Al_4C_3 nanocomposite produced via mechanical alloying and annealing

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The Al–Al_4C_3 nanocomposite was produced via mechanical alloying of Al 6 wt% C mixture for a predetermined time (up to 20 h), followed by annealing. The structural evolution was characterised via X-ray diffraction and transmission electron microscope equipped with electron energy loss spectrometer. In addition, focused ion beam–scanning electron microscopy was used for locating and analysing the reinforcing particles. During milling, the size of aluminium particles reached the nanometre scale with a 54 nm size. After annealing, carbide was homogeneously distributed in the nanostructured aluminium particles with an average size of 50 nm, result in an average hardness of 320 HV. This was observed for the powder that was mechanically milled for 20 h and that underwent annealing from room temperature to 540°C and was maintained at this temperature for 4 h.

1. Introduction: Aluminium is an abundant material with excellent proprieties, such as low density and good workability, which makes it the second most commonly used metal after iron. It is used in diverse industrial applications. However, its poor elevated temperature proprieties limit its application [1–3].

To solve this issue, researchers reinforce aluminium with nano-scale particles of oxides and carbides. This produces stronger, resistant and lighter multifunctional materials that fulfil the essential demands of the modern industry [4, 5].

These composites can be produced via different methods, among which the method of mechanical alloying flowed by annealing enables the production of reinforced particles with homogenous distribution, that overcome limitations associated with the melting and solidification processes [4, 6].

Nanocomposite offers significant enhancement properties of materials due to the non-metric reinforcement better than micro-composite. On the other hand, Al_4C_3 show a high-temperature strength, thermal cyclic resistance, wear resistance and low linear expansion coefficient [7]. Which make the production of the nano-composite of an aluminium matrix reinforced by Al_4C_3 very interesting.

Using mechanical alloying subsequent annealing process, Al_4C_3-reinforced aluminium was successfully fabricated [1, 3, 7–14]. It was noted that Al_4C_3 is the responsible of reinforcing [2, 13]. Once it inhibits the dislocation motion, good mechanical proprieties are achieved even at elevated temperature. However, the efficiency by which reinforcement particles strengthen the matrix depends on their type, size, morphology, volume fraction and overall distribution [11, 15]. With the development of advanced analytical methods in the recent years, enormous progress led to the identification and characterisation of particles at atomic levels.

The annealed mechanically milled Al–C mixture has not been significantly investigated. Therefore, the aim of this Letter was to produce the Al–Al_4C_3 nanocomposite via mechanical alloying of the Al 6 wt% C mixture, determine its structural evolution during milling and after annealing, and reinforcement investigation.

2. Experimental: Pure aluminium (PRS Panreac, 97.44%purity) was milled with 6 wt% graphite in a planetary ball mill (Retsch PM 400) with a hardened steel vial and a stainless steel ball (11 mm diameter) for various predetermined periods of time. The ball-to-powder weight ratio was 20:1. All preparations were performed under inert argon atmosphere in a glove box.

Phase identification and transformation and structural characterisation were determined via X-ray diffraction (xrd) using a Panalytical X'Pert PRO diffractometer (45 kV, 40 mA) with Cu Kα radiation ($k = 0.15406$ nm).

The crystallite size and lattice strain were calculated using the modified Williamson Hall method. These values were deduced from the obtained plot from the slope and intercept of the straight line, respectively.

The resulting powder after 20 h of milling was heat-treated under argon atmosphere. Then, various analytical techniques were used to analyse it. Specifically, XRD, transmission electron microscopy and electron energy loss spectroscopy (EELS). The focused ion beam (FIB) technique was carried out using a FIB-scanning electron microscope (FIB-SEM) ZEISS Crossbeam 540 with a high-resolution Gemini II column equipped with a standard Everhart Thornley secondary electron (SE) detector and an in-lens detector.

To evaluate the mechanical properties, for the product powder after milling and after annealing, it was cold mounted in resin and their section was polished, then hardness was performed by microhardness measurements using a Vickers indenter with a load of 0.098 N for 15 s.

3. Results and discussion: Fig. 1 shows the XRD patterns of the Al 6 wt% C powder mixture that was milled for different periods of time (up to 20 h). We can see that the diffraction peaks of Al and C are clearly visible for the raw materials. Then, when the sample was milled for longer than 0.5 h, the crystalline graphite peaks disappeared. In addition, the aluminium peaks broadened with increasing milling time during the initial stage of mechanical milling process. This indicates a continuous decrease in grain size due to the formation of new defects.

The evolution of the average grain size and the internal micro-strain of aluminium as a function of milling time are presented in Fig. 2. This figure shows that the crystallite size decreases with increasing milling time. The refining effect weakens when the milling time is longer than 4 h, and an equilibrium average value of 54 nm is attained.

Fig. 3*c* presents the EELS spectra of the powder that was mechanically milled for 20 h after having been annealed from room temperature to 1000°C. For the three positions, the results display the K

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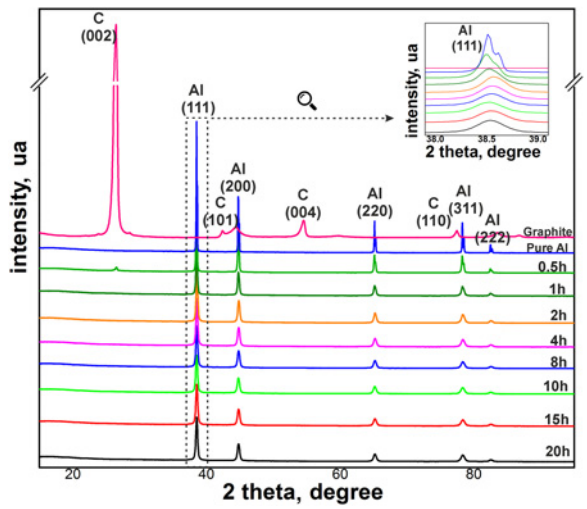

Fig. 1 *XRD patterns of the Al 6 wt% C powder mixture that was milled for various periods of time*

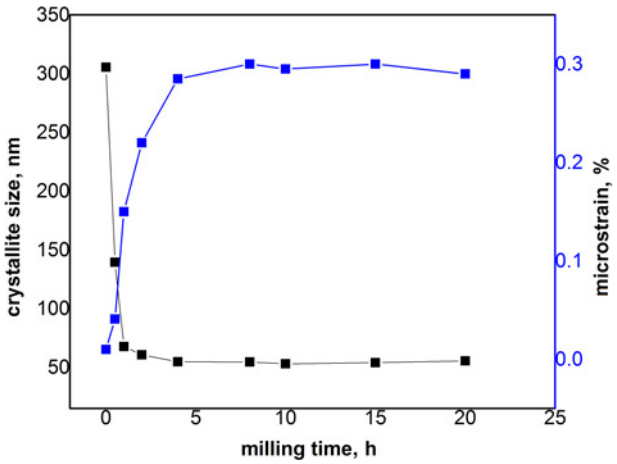

Fig. 2 *Variation of crystallite size and microstrain as function of milling time*

edge of aluminium but with three different spectral shapes. By combining the EELS database [16] and X-ray results (Fig. 3*a*), we identify the presence of aluminium (Fig. 3*a*), oxide of aluminium (Al_2O_3) (Fig. 3*c*) and carbide of aluminium (Al_4C_3), which is presented as a third structure of aluminium (Fig. 3*b*). These structures represent the phases formed after annealing.

Upon heating, the oxidation phenomenon occurs due to the impurity of argon gas. According to Coker [17], aluminium passes through four stages of oxidation during heating in the presence of oxygen, where amorphous alumina transformed to δ alumina when the stage II (550–650°C) is attained.

To avoid this oxidation, the powder that was milled for 20 h was annealed from room temperature to 540°C, and then, we maintained it at this temperature for 4 h. The XRD result presented in Fig. 4*b* confirms the formation of carbide (Al_4C_3), and no sign of oxidation is observed. In addition, aluminium preserves the nanocrystalline character and yields a crystallite size of 75 nm.

Fig. 4*c* shows the polished surface of the particle. This image was recorded using the InLens detector. This detector is more sensitive to the difference in the work function compared with the Everhart Thornley detector.

During the SEM analysis, when the incident beam inelastically interacts with the specimen, the incident electron transfers a part of its energy (which can be measured by the EELS detector) to an electron of the specimen, which results in its ejection. Hence, we can estimate that the work function can be referenced to the EELS measurements.

Fig. 3*c* shows that aluminium has a higher intensity (number of electrons) when it is in the carbide state. The higher intensity is attributed to the low work function. This results in a bright contrast appearance of the carbide of aluminium in SEM-InLens.

Using the ImageJ software, we estimated the particle size of carbide (Al_4C_3). Specifically, the average particle size is between 40 and 50 nm, with a surface fraction of 50.77%.

As presented in Fig 3*c*, we clearly observe the repartition of a homogenous nanoreinforcement of Al_4C_3 into the nanostructured aluminium matrix, results in an improvement of hardness, where it goes from an average of 195 HV for the product of milling after 20 h, to reach the 320 HV after annealing at 540°C and maintained for 4 h.

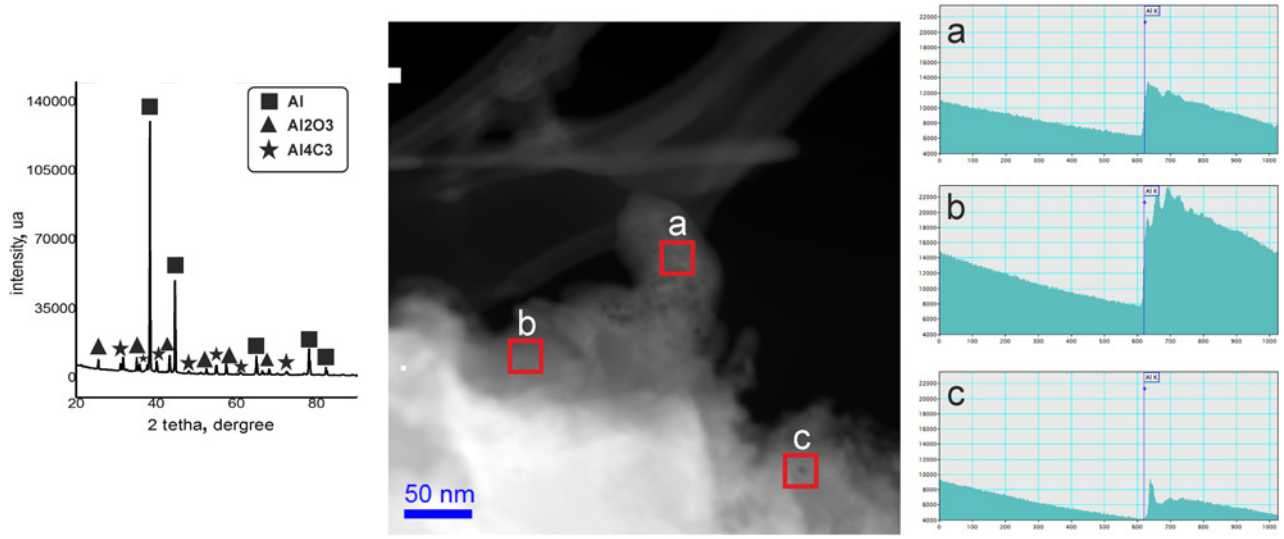

Fig. 3 *(a) XRD pattern after annealing at 1000°C. (b) TEM image of the powder milled for 20 h after annealing at 1000°C. (c) EELS spectrum at various location presented in (b)*
a Al
b Al_4C_3
c Al_2O_3

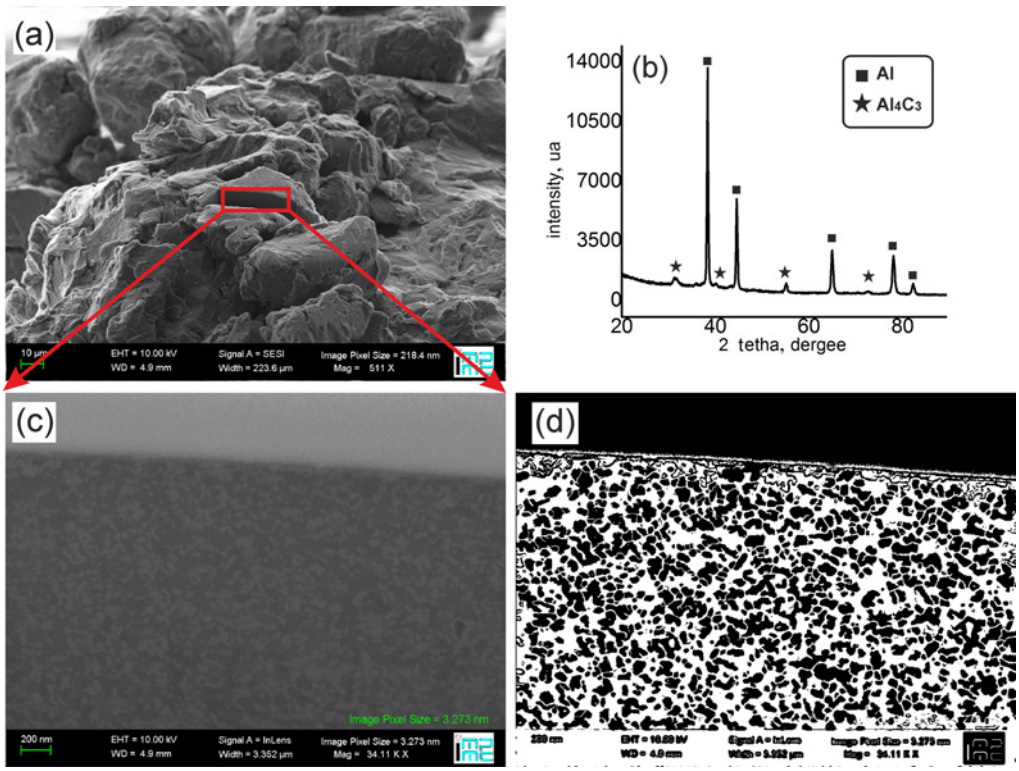

Fig. 4 *Phases and microstructures of the powder that was milled for 20 h after annealing at 540°C for 4 h*
a SEM image of the FIB-milled surface
b XRD pattern
c SEM image of the polished surface acquired using the InLens detector
d Image (c) analysed using the ImageJ software

4. Conclusion: Mechanical alloying of Al 6 wt% C is conducive to the formation of a metastable solid solution via the diffusion of carbon particles into aluminium. A homogenous mixture is reached after 1 h of milling, and particles with a size of 54 nm are formed after 20 h of milling. Whereas, after milling, no trace of carbide formation was observed.

By investigating the resulting powder after annealing, it was determined that the nanocomposite contained a homogeneously distributed carbide with an average size of 50 nm in a nanostructured matrix of 75 nm aluminium. Preforming a hardness of 320 HV for the nanocomposite.

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6 References

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