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Quantification of nitrogen impurity and estimated Orowan strengthening through secondary ion mass spectroscopy in aluminum cryomilled for extended durations

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ABSTRACT

The strength of aluminum alloys and composites processed through powder metallurgy can be improved through the addition of nano-scale dispersoids introduced during the cryomilling process. Quantification of Orowan strengthening from these dispersoids requires a reliable measurement of the impurity concentration. Secondary ion mass spectrometry (SIMS) was used to quantify the nitrogen impurity concentration using a ^{14}N ion implanted standard. An analytical approach is devised to determine the nitrogen concentration of an aluminum alloy and composite based on SIMS measurements. Results are compared to the measurements carried out by gas fusion analysis. An increase in nitrogen concentration was observed with an increase in cryomilling time up to 72 h. The nitrogen concentration varied from 1.64 ± 0.17 at% (0.80 ± 0.08 wt%) to 19.12 ± 1.10 at% (13.17 ± 0.71 wt%) for the 8 h and 72 h cryomilled nanocrystalline AA5083, respectively. Assuming that all nitrogen reacts to form dispersoids, the nitrogen concentration determined was used to calculate the volume and weight fractions of dispersoids, which in turn was used to estimate the strengthening contribution via Orowan strengthening. Orowan strengthening was calculated using dispersoids of 3, 9 and 15 nm. The range of Orowan strengthening contribution was estimated, in MPa, to be from 7.69 ± 0.78 to 3.03 ± 0.31 for the 8 h nanocrystalline AA5083 sample, and 154.97 ± 10.29 to 61.09 ± 4.06 for the 72 h nanocrystalline AA5083 sample.

1. Introduction

The low density of aluminum has long made it an attractive material in automotive and other applications especially where improved fuel efficiency and a high strength-to-weight ratio are desired. Recently, cryomilling in liquid nitrogen has been investigated as an additional processing step in powder metallurgy to enhance the strength-to-weight ratio. For example, cryomilled aluminum and boron carbide (B_4C) metal matrix composites have generated scientific and commercial interests after Ye et al. [1] reported exceptional compressive strength (~1 GPa). Since then, much work has focused on understanding the mechanisms that contribute to the high strength.

Several mechanisms have been proposed to explain the exceptional strength of these composites including Hall-Petch strengthening, strain-hardening, solution hardening, reinforcement strengthening and Orowan strengthening [1–6]. Among them, Orowan strengthening is of particular interest since the strength of the composite may be improved without loss of ductility. The Orowan–Ashby equation relates the increase in strength to the size and fraction of the nanoscale dispersoids and is given by [7]:

$$\Delta\sigma = \frac{0.13Gb}{\lambda} \ln \frac{d}{2b} \tag{1}$$

where G is the shear modulus, b is the Burgers vector, λ is the interparticle spacing and d is the diameter of the dispersoids. The shear modulus and Burgers vector for aluminum is 25.9 GPa and 0.286 nm, respectively [1]. The interparticle spacing, λ, may be determined utilizing the volume fraction, f^V, and the diameter, d, of the dispersoids [7]:

$$\lambda = \frac{2(1-y)d}{3f^V} \tag{2}$$

Orowan strengthening in these composites is believed to be derived from the presence of nanoscale dispersoids formed during

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cryomilling. Dispersoids observed via transmission electron microscopy and proposed via modeling are θ-Al_2O_3, χ-Al_2O_3, Al_4C_3 (hexagonal, hR7), AlN (hexagonal, hP4 or cubic, cF8), and nitrogen-rich amorphous regions [2,8–13]. Oxide dispersoids form by the breakup of the native oxide on the aluminum powder [10,14]. The carbides can form from mechanical alloying of the aluminum powder and the carbon-rich process control agent [10]. Nitrides form due to the interaction of the aluminum powder with the liquid nitrogen during milling.

According to the aluminum–nitrogen equilibrium phase diagram, there is negligible solubility of nitrogen in aluminum [15], therefore it is not unreasonable to assume that all of the nitrogen incorporated is in the form of either a crystalline aluminum nitride (AlN) or an amorphous domain rich in nitrogen. In previous studies it was found that nitrogen concentration increases with milling time up to 26 h [9,13]. If nitrogen resides in the aluminum powders as several nanometer-sized dispersoids of crystalline and/or amorphous phases, an increase in milling time would increase the volume fraction of nanoscale dispersoids, and consequently contribute to the Orowan strengthening. In this study, an analytical approach was devised, utilizing secondary ion mass spectrometry (SIMS), to determine the atomic and weight percent of nitrogen in cryomilled aluminum with an assumption that nitrogen resides in AlN or an amorphous domain of equivalent density. This approach was applied to determine nitrogen concentration from 8 to 72 h cryomilling time using data from previous work with the aluminum and boron carbide (B_4C) composites [13] and current work utilizing 100% cryomilled nanocrystalline aluminum. The Orowan strengthening contribution was then estimated as a function of cryomilling time.

2. Analytical approach

2.1. *Secondary ion mass spectroscopy and the relative sensitivity factor*

Previously, impurity concentrations of oxygen, hydrogen, carbon and nitrogen were determined through either a gas fusion (GF) or combustion-type techniques [9,16–18]. The disadvantage of these techniques is that it is not possible to differentiate surface contamination from the bulk impurity concentrations and the sample is consumed during the process. An alternative method of impurity concentration measurement is SIMS which can quantify any element and perform separate analyses of both the surface and the bulk via depth-profiling. In addition, SIMS quantification is more statistically confident than GF chemical analysis.

SIMS measures the quantity of secondary ions produced during sample erosion by the primary ion beam. These counts are dependent on operating parameters such as current, type of primary beam, and material [19]. A relative sensitivity factor (RSF) is calculated in order to convert secondary ion intensity (counts s^{-1}) from SIMS to atomic density (atoms cm^{-3}) utilizing an ion-implanted calibration sample with a known fluence. An RSF is defined by [20]:

$$N_i = \frac{I_i}{I_m} RSF \tag{3}$$

where N_i is the impurity atomic density (atoms cm^{-3}), I_i is the impurity isotope secondary ion intensity (counts s^{-1}), and I_m is the matrix isotope secondary ion intensity (counts s^{-1}). An RSF can be determined from an ion-implanted calibration sample (assuming constant impurity background) utilizing the relation [20]:

$$RSF = \frac{\phi I_m}{\left[\sum I_i\right] - I_b d} \tag{4}$$

where φ is the ion implant fluence (atoms cm^{-2}), d is the implantation depth (cm), ΣI_i is sum of the impurity isotope secondary ion counts over the depth profile (counts cm s^{-1}) and I_b is background ion intensity of the impurity isotope (counts s^{-1}). Utilizing a SIMS depth profile of an ion implanted sample and Eq. (4), the RSF may be determined. Once the RSF is known, Eq. (3) may be applied to determine the nitrogen concentration in terms of atomic density (number of atoms per unit of volume) for samples with a similar matrix.

In order to convert nitrogen atomic density into atomic and weight percent, it is important to understand in which phase the nitrogen resides. For the composites, it has been shown that B_4C and nitrogen do not interact during or after the cryomilling process and that nitrogen is found in nitrogen-rich dispersoids within the aluminum grain or in the aluminum grain boundaries [13]. In order to simplify the derivation, it is assumed that all of the atoms of nitrogen are in the crystal structure or in an amorphous structure of similar density. The atomic density of nitrogen, N_N, was measured using SIMS. In order to calculate the atomic percent of nitrogen, it is necessary to calculate the atomic density of the various phases present in the composite. The atomic density, N_i, of element or compound i may be calculated by:

$$N_i = \frac{\rho_i N_A}{M_i} = \frac{n_i}{V_{cell,i}} \tag{5}$$

where ρ_m is the density of element or compound i, N_A is Avogadro's number, and M_i is the atomic mass of element or compound i. Alternatively, the atomic density may also be expressed in terms of the number of atoms in its unit cell, n_i, and the volume of the unit cell, $V_{cell,i}$. Calculating the atomic densities of all phases present will be necessary in order to calculate the atomic and weight percent of nitrogen in the composite.

2.2. *Determination of nitrogen concentrations*

The atomic percent of nitrogen is simply the ratio of the nitrogen atomic density, N_N, to the atomic density of the whole, N_T, multiplied by 100. N_T may be calculated as the atomic density multiplied by the volume fraction of each phase present. The atomic densities of aluminum, B_4C and AlN may be calculated from Eq. (5) or found in tables such as in Burenkov et al. [21]. If, N_{Al} is the atomic density of aluminum, N_{B_4C} is the atomic density of B_4C, $f^V_{B_4C}$, and f^V_{AlN}, are the volume fractions of B_4C and AlN in the composite, respectively. The atomic percent of nitrogen is expressed as:

$$at\%N = \frac{N_N}{N_{Al}\left(1 - f^V_{B_4C} - f^V_{AlN}\right) + N_{B_4C} \cdot f^V_{B_4C} + N_{AlN} \cdot f^V_{AlN}} \cdot 100\% \tag{6}$$

A similar derivation may be performed to determine the weight percent of nitrogen in the composite. To determine the weight fraction of nitrogen, it is necessary to calculate the mass density of nitrogen atoms, W_N, in the volume, V. W_N can be described as the product of the nitrogen atomic density, N_N, by the molecular weight of nitrogen, M_N, divided by Avogadro's number. The mass density of the composite after cryomilling can be described as the summation of the densities of each component, multiplied by their respective volume fraction. If ρ_{B_4C}, ρ_{AlN}, and ρ_{Al} are the densities of the B_4C, the AlN and the Al phases, respectively, the weight percent of nitrogen may be found by dividing mass density of nitrogen atoms by the composite mass density: