

# Crystal growth kinetics of nanocrystalline aluminum prepared by mechanical attrition in nylon media

Claudio L. De Castro, Brian S. Mitchell\*

*Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118, USA*

Received 27 August 2004; received in revised form 4 January 2005; accepted 11 January 2005

## Abstract

Grain growth in nanocrystalline (nc) aluminum with an initial grain sizes of 22 and 40 nm produced by mechanical attrition using stainless steel and nylon media, respectively, was studied through X-ray diffraction, differential scanning calorimetry, and electron microscopy. Two-grain growth regimes are observed for aluminum milled in both nylon and stainless steel media. Grain growth occurred above  $T/T_M$  of 0.72 and 0.83 for samples milled in stainless steel and nylon, respectively. The enhanced stability of Al grain size milled in nylon is attributed to the nylon impurity (phase).

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Aluminum; Grain growth; Ball milling

## 1. Introduction

In recent years, the problem of crystal (grain) growth in nanocrystalline (nc) materials has received considerable attention, because nc materials may provide mechanical properties superior to those of their course-grained counterparts [1,2]. Grain growth occurs in polycrystalline materials in order to decrease the system energy by decreasing the total grain boundary energy, but this generally does not occur in most nc metals or alloys until temperatures exceed one-half of the absolute melting point,  $0.5 T_M$  [3]. Recent studies have investigated mechanisms through which thermal stability of nanocrystalline microstructures might be further enhanced [2]. A number of factors are known to affect the grain boundary mobility in nc materials including solute-impurity drag [2,4], second-phase drag (Zener) [5], and grain boundary segregation [6]. These factors, therefore, influence the grain growth kinetics of nc materials. Recent studies have shown that the time exponent of the parabolic relationships for grain growth seems to change during grain growth and approaches an “ideal” value of 0.5 found in high-purity materials or at high annealing temperatures. In this paper, we investigate

the effect of milling conditions, specifically milling media composition, on grain growth behavior of nc Al prepared by mechanical attrition.

## 2. Experimental details

Commercially available aluminum with a purity of 99.9% or better (Fisher Scientific, Hampton, NH) was milled in a grade 440-C stainless steel vial with the same grade of stainless steel milling media for 90 min in a SPEX model 8000D (Metuchen, NJ) high-energy ball mill. The temperature was maintained at 0 °C by placing the unit in a temperature-controlled laboratory refrigerator. Similarly, the aluminum powder was milled in a nylon vial (manufactured in house) with nylon-coated stainless steel spheres (Fisher Scientific) for 300 min. In all studies, a ball/powder ratio of 10:1 was used, and two drops of ethanol were employed as a dispersant.

The milled powders were annealed for times ranging from 5 to 200 min at nine temperatures (473, 573, 613, 673, 723, 748, 773, 813, and 873 K). The annealing was performed in a differential scanning calorimeter (DSC 29020 from TA Instruments, New Castle, DE) under a flowing argon atmosphere, which had been previously calibrated using pure indium samples. The Al powder samples were

\* Corresponding author. Tel.: +1 504 862 8257; fax: +1 504 865 6744.  
E-mail address: brian@tulane.edu (B.S. Mitchell).

hermatically sealed in an aluminum pan and heated at a rate of 80 K/min, then annealed for the specified times. All the powder-handling prior to annealing was done under inert argon atmosphere in a glove box.

Selected powder samples were compacted in a stainless steel mold with a hydraulic press into a 2.5 cm (1 in.) diameter preform at about 20 MPa. The preform was removed from the mold and wrapped within aluminum foil and then vacuum-sealed. The preform was then placed into a Hot Isostatic Press (HIP) (AIP Inc., Columbus, OH). The HIPing was performed by applying isostatic pressure at 310 MPa (45,000 psi, nitrogen atmosphere) on the sample, at temperatures ranging from 573 to 873 K for 30 min. The grain size of the consolidated samples was then determined via X-ray diffraction (XRD).

X-ray diffraction measurements were carried out with a Scintag XDS2000 (Ecublins, Switzerland). Transmission electron microscopy (TEM) was performed using a JEOL JSM-2010 (Peabody, MA) microscope, and EDS was per-

formed using Oxford Instruments Series 500-XTF 5011 (Scotts Valley, CA). Hydrogen–carbon–nitrogen (HCN) analysis was performed on a Fisons EA 1108 (Waltham, MA) elemental analyser, and metal analysis was performed on a SRC 200 (Munich, Germany) X-ray fluorescence spectrometer (XRF).

### 3. Results

The (1 1 1), (2 0 0), and (2 2 0) XRD lines were chosen to determine the mean grain size of nanocrystalline aluminum particles according to full width at half maximum using the Scherrer equation. Peak widths were corrected for microstrain effects through Lorentzian peak fitting software. Representative TEM images of the as-milled powders embedded in epoxy resin and microtomed show grain sizes comparable with those determined by XRD (Fig. 1). The as-milled

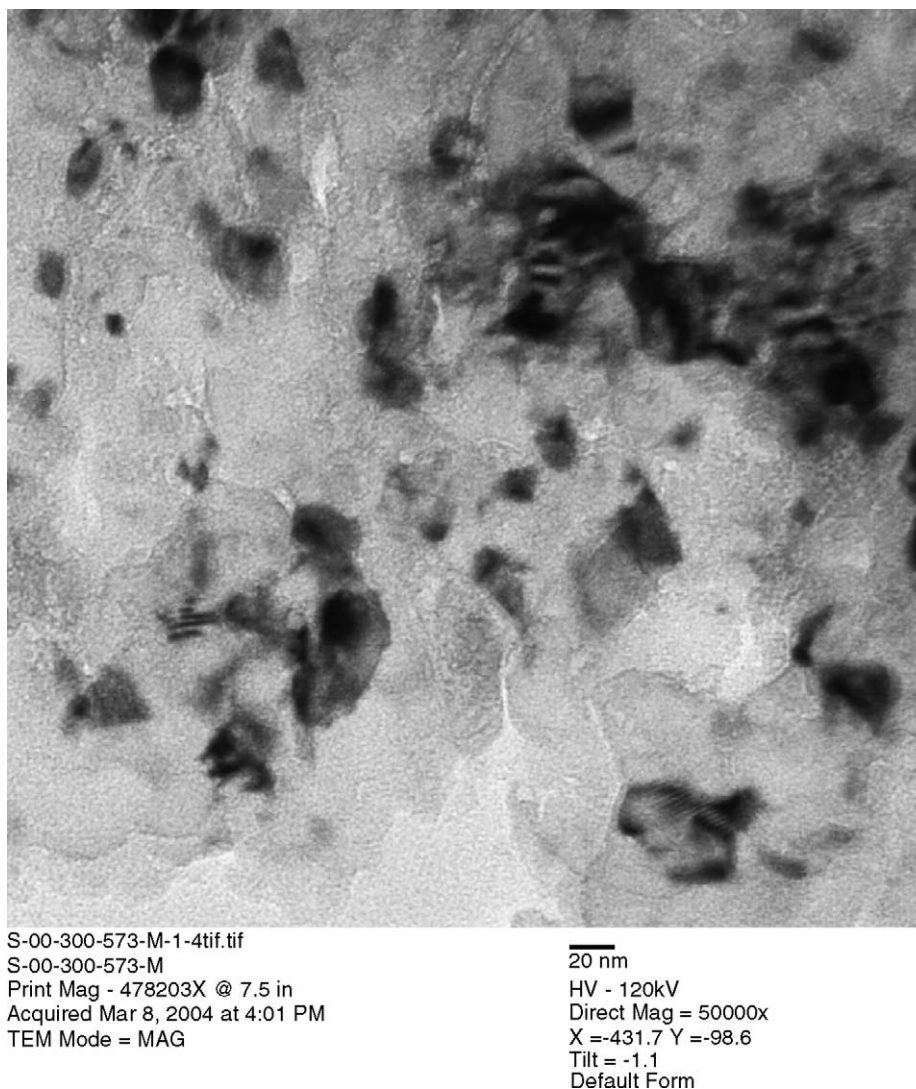


Fig. 1. TEM brightfield image of pure aluminum powder milled in stainless steel for 300 min and annealed at 573 K showing aluminum grains on the order of 20 nm.

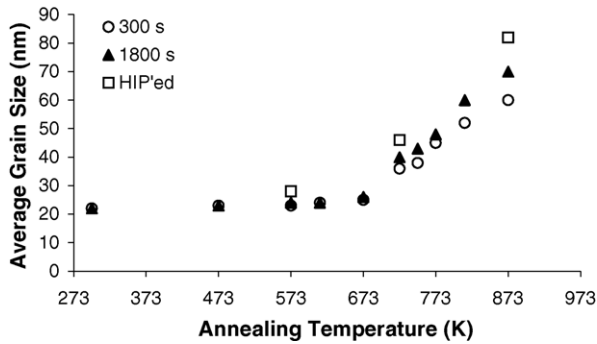


Fig. 2. Grain size as a function of annealing temperature for two annealing times (powders) and HIPed (disk)—Al powder milled in stainless steel media and vial.

Al sample was determined to have a limiting grain size of about 22 nm when milled in stainless steel media, and 40 nm when milled in nylon media at maximum milling times of 300 min.

Figs. 2 and 3 show the variation of grain size with annealing temperature for annealing times of 5 and 30 min, as well as HIPed (unannealed) samples, for powders milled in stainless steel and nylon, respectively. There are two well-defined growth stages with a transition at about 673 and 773 K for the stainless steel and nylon media, respectively. The average grain size remains stable for long anneals at temperatures as high as  $0.72 T/T_M$ , for samples milled in stainless steel, again in agreement with the results of Zhou et al. [8], but slightly higher at  $0.83 T/T_M$  for samples milled in nylon. The percentage average grain size for the samples milled in stainless steel is about 400% from the initial significant growth at 673 K, whereas for the samples milled in nylon this value is only about 200%.

Grain growth in conventional polycrystalline materials is controlled by atomic diffusion in the grain boundary and its kinetics described by:

$$D^{1/n} - D_0^{1/n} = kt \quad (1)$$

where  $D$  is the grain size at time  $t$ ,  $D_0$  the initial grain size,  $k$  the temperature-dependent rate constant, and  $n$  is the

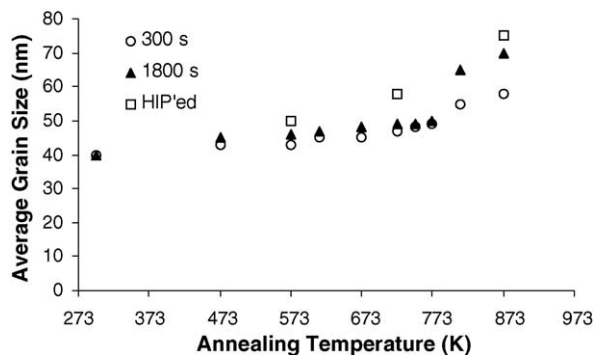


Fig. 3. Grain size as a function of annealing temperature for two annealing times (powders) and HIPed (disks)—Al powders milled in nylon media and vial.

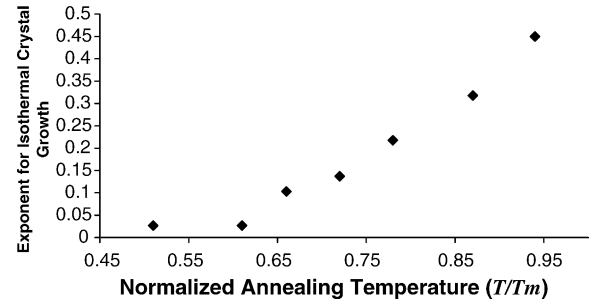


Fig. 4. Time exponent  $n$  for isothermal grain growth versus normalized temperature for nc aluminum milled in nylon.

grain growth exponent representing the grain growth behavior.

To obtain isothermal grain growth kinetics, the grain size versus time data of the nc Al milled in nylon were fitted mathematically to Eq. (1), by a non-linear general curve fitting routine to determine the best fit values for the three parameters,  $D_0$ ,  $k$ , and  $n$ . The  $n$ -values determined by this procedure are plotted in Fig. 4 as a function of normalized annealing temperature. The value of  $n$  approaches 0.5 as  $T/T_M$  increases, the same trend that is observed for a polycrystalline high-purity aluminum [9]. The fact that the time exponent is different than 0.5 suggests that grain boundary (GB)-pinning forces are operative [9].

#### 4. Discussion

As the annealing temperature is increased above 773 K, modest grain growth occurs for the nylon-milled samples. At lower temperatures, the grain size difference between the different annealing times and HIPed samples is negligible; while at higher temperatures, these differences become distinct. It is postulated that this grain-growth transition temperature coincides with the decomposition of nylon during heat treatment. Previous results [7] have shown that nylon contamination can be mitigated from as-milled aluminum samples by proper heat treatment, with nylon degradation occurring between 713 and 733 K. The aluminum samples, milled in stainless steel media, also experience negligible grain growth at lower temperatures, followed by more pronounced grain growth above 673 K, in agreement with previous work by Zhou et al. [8]. Fig. 5 confirms this two-regime grain growth behavior showing the average grain size as a function of annealing times at various temperatures.

The most striking observation in the present investigation is the increased temperature of grain size stability; the Al crystals remain nanoscale for long anneals at homologous temperatures ( $T/T_M$ ) as high as 0.83 in the samples milled in nylon. Mechanisms that reportedly impart thermal stability to nc microstructure prepared by MA include grain boundary-pinning by impurities (solute drag), pores (pore drag), second-phase particles, and effects of specimen thickness.

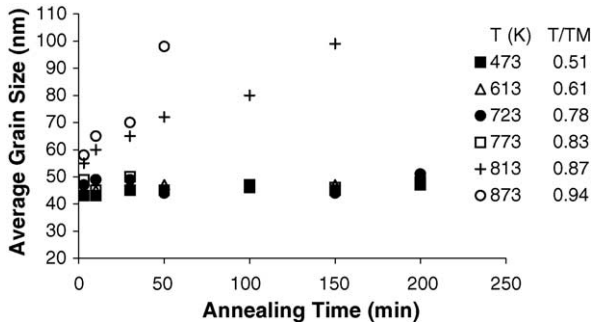


Fig. 5. Grain size as a function of annealing time at various temperatures for the as-milled nc Al sample milled in nylon.

The pinning force arising from impurities (which are practically unavoidable in the ball-milled Al sample) may play an important role in limiting grain boundary movement. Concentrations of the primary impurities in the as-milled powders are listed in Table 1. These data show that there

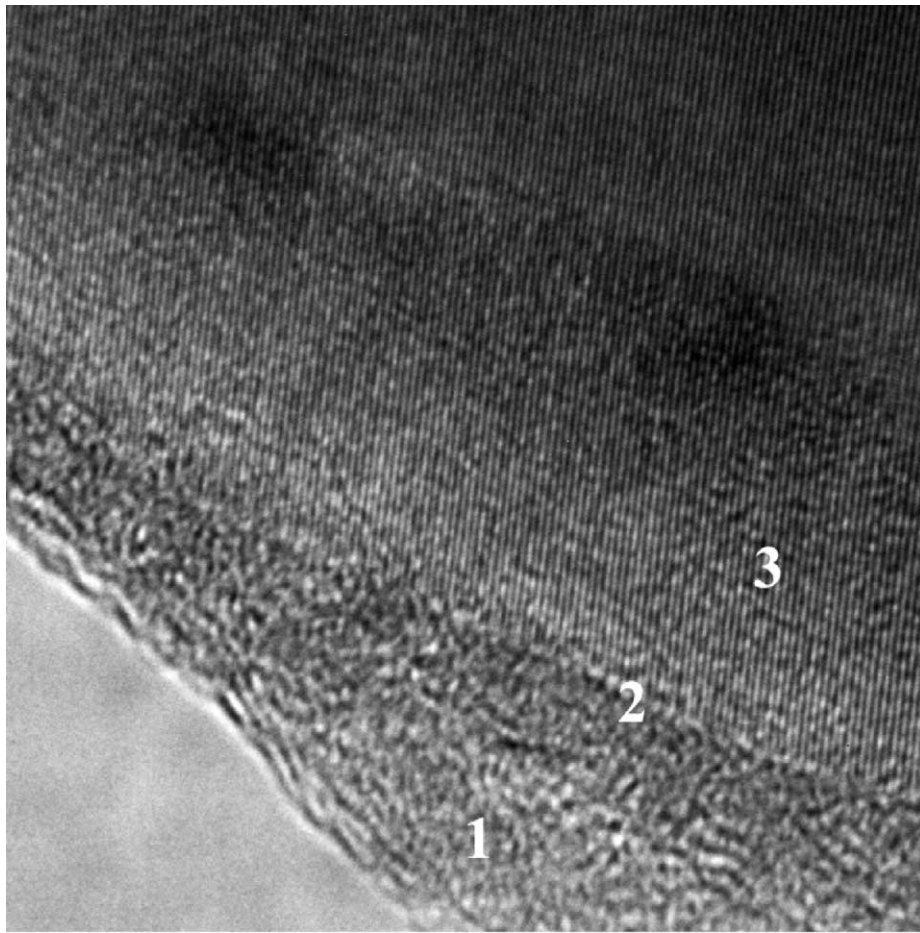
Table 1

Impurity concentrations (in wt.%) in as-milled nc Al

	Sample					
	C	N	H	Fe	Cr	Mn
Al (as-milled, 90 min, stainless steel)	–	–	–	0.1916	0.0032	0.0004
Al (as-milled, 300 min, nylon)	4.56	1.03	1.78	–	–	–

is the presence of both interstitial and substitutional solute atoms. It was previously reported by Malow and Koch [3] that substitutional solute atoms are responsible for inhibiting grain boundary migration in nc Fe.

Carbon, nitrogen, and oxygen, which are constituents of nylon and may be viewed as impurities or second phases, present in the samples, are expected to cause Zener-pinning. According to the Zener-pinning theory [10], to stabilize a grain size ( $D$ ) by pinning particles with a diameter ( $R$ ), the required volume fraction ( $f$ ) of pinning particles should be



1 nm  
HV = 200 kV  
Direct Mag = 800000x

Fig. 6. TEM image of aluminum milled with nylon media for 300 min and then heat treated at 773 K for 30 min: (1) carbon-containing phase; (2) interface containing carbon and aluminum; (3) crystalline aluminum phase.

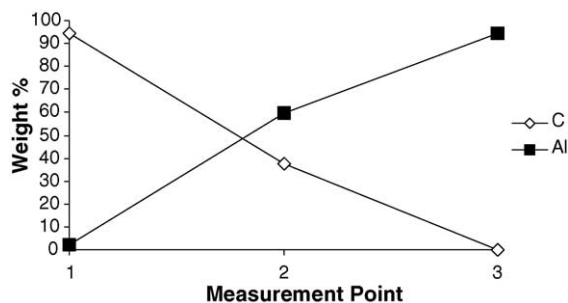


Fig. 7. Elemental concentration over the measurement range in Fig. 6.

1.33  $R/D$ . Considering the  $D$ - and  $R$ -values in the present case, Zener-pinning forces may be the primary source of stabilization due to a significant volume fraction of the nylon phase (impurity), which was estimated to be about 7.4% up to about 723 K, the temperature at which nylon decomposes in the sample. In this study, the grain growth was negligible up to 773 K, so that the nylon can be decomposed in the sample and grain growth can be prevented at annealing temperature as high as 773 K, which becomes a good design parameter for consolidating these samples via HIP. Fig. 6 shows a TEM image of an aluminum sample milled with nylon for 300 min and then heat treated at 773 K for 30 min. There are two distinctive phases—a carbon-containing and crystalline phases that contain crystalline aluminum. The carbon impurities, which appear to be amorphous, prevent grain growth of the aluminum sample due to Zener-pinning forces. Fig. 7 shows interface chemistry determination at three different points of Fig. 6. This determination further enhances the fact that the carbon phase prevents the aluminum grain growth due to Zener-pinning.

Finally, one would expect the presence of grain boundary impurities to significantly impact mechanical properties; specifically, to cause embrittlement in the HIPed samples. However, preliminary mechanical property tests on these samples indicate that the elastic modulus, yield point (0.2% proof stress), and ultimate tensile strength of the HIPed samples are comparable to those of cast, pure aluminum (69, 0.3, and 0.8 GPa, respectively [11]) at room temperature. The mechanical and corrosion properties of the aluminum samples milled in various milling media are the subject of separate publications [12,13].

## 5. Conclusions

Grain growth in nc Al produced via high-energy ball milling was studied. Two grain-growth regimes were observed for aluminum milled in both nylon and stainless steel media. For the samples milled in nylon, below  $0.83 T_M$  nc Al grain sizes were stable at approximately 40 nm, even after long annealing times (e.g., 200 min). At high temperatures, grains grew steadily to about 80 nm. For the samples milled in stainless steel grain sizes were stable at approximately 22 nm below  $0.72 T_M$ . At high temperatures, grains grew to about 80 nm. The grain growth of Al samples milled in stainless steel was much more facile than the ones milled in nylon. Finally, the stability of Al grain size milled in nylon is due to the nylon impurity (phase) that is present until nylon decomposes in the sample by heating treatment (about 723 K). The stability of Al grain size milled in stainless steel is due to the small wt.% presence of interstitial and substitutional impurities.

## Acknowledgments

The authors wish to acknowledge support for this project from the National Science Foundation (DMI-0099771) and NASA (NCC3-946).

## References

- [1] H. Gleiter, *Acta Mater.* 45 (2000) 2177.
- [2] T.R. Malow, C.C. Koch, *Acta Mater.* 45 (1997) 2177.
- [3] T.R. Malow, C.C. Koch, *Synthesis and Processing of Nanocrystalline Materials*, TMS, Warrendale, PA, 1996, p. 33.
- [4] P. Knauth, A. Charai, P. Gas, *Scr. Mater.* 28. (1993) 325.
- [5] K. Boylan, D. Ostrander, U. Erb, *Scr. Metall. Mater.* 25 (1991) 2711.
- [6] C. Bansal, Z. Gao, B. Fultz, *Nanostruct. Mater.* 5 (1995) 327.
- [7] C. De Castro, B.S. Mitchell, *J. Mater. Res.* 17 (12) (2002) 2997.
- [8] F. Zhou, et al., *J. Mater. Res.* 16 (12) (2001) 3451.
- [9] P.A. Beck, J.C. Kremer, L.J. Demer, *Trans. Am. Inst. Min. Eng.* 175 (1948) 372.
- [10] C.S. Smith, *Trans. AIME* 9 (1949) 15.
- [11] F. King, *Aluminum and Its Alloys*, Ellis Horwood, Ltd., Chichester, England, 1987, p. 139.
- [12] C.L. De Castro, B.S. Mitchell, *Acta Mater.*, submitted for publication.
- [13] C.L. De Castro, B.S. Mitchell, *Corrosion*, submitted for publication.