Characterisation of an Al-BN nanocomposite prepared by ball milling and hot extrusion

U Arlic1*, Z Drozd2, Z Trojanová3, O Molnárová2 and A Kasakewitsch3

1Institute of Materials Science and Engineering, Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany
2Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague 2, Czech Republic
3Weber Maschinenbau GmbH, 26506 Norden, Germany

*E-mail: uwe.arlic@tu-clausthal.de

Abstract. Aluminium-matrix-nanocomposites were manufactured by ball milling of microscale aluminium powder with BN nanoparticles in air, followed by subsequent consolidation by hot extrusion. The microstructure of the samples was studied using scanning electron microscopy. Vickers microhardness measurements were used to probe the mechanical properties of the samples. The amplitude dependent damping of the nanocomposites was measured at room temperature after thermal treatment of samples, and the linear thermal expansion was measured over a wide temperature range from room temperature up to 670K in the as-extruded state. The experimental results give a comprehensive picture of the behaviour of this nanocomposite system over the range of thermomechanical treatment conditions examined in this study. Based on these experimental data some possible influences of BN nanoparticles on the anelastic, plastic and thermal properties of microcrystalline aluminium are discussed.

1. Introduction

Aluminium based nanocomposites are potential materials for structural applications in the aerospace and automotive industries [1]. A ductile aluminium matrix may be reinforced with nanoparticles of oxides, carbides, nanotubes, nitrides or borides. Nanoparticles can be used to significantly improve mechanical properties, including specific stiffness (ratio of stiffness to density), specific yield strength, and the ultimate tensile/compression strength [2-4]. High temperature properties and creep resistance may also be substantially improved [5]. The extent to which a certain property is present in a nanocomposite (NC) can be controlled by selecting the appropriate amounts of matrix and reinforcement materials. Hence, NCs provide flexibility in terms of the properties required.

A main problem for fabrication of nanocomposites is achieving a uniform distribution of nanoparticles, which in general exhibit a tendency to form clusters. Ball milling is a very effective method to prepare not only aluminium nanocomposites but also many others [5, 6]. The resulting properties of NCs depend on the type, size and distribution of the nanoparticles in the matrix. Bonding between nanoparticles and the matrix metal (alloy) is a very important factor influencing mechanical and physical properties of NCs [7]. The standard precipitation hardening of aluminium alloys is limited by thermodynamic restrictions. In contrast strengthening by addition of nanoscale ceramic particles
should show more stable behaviour especially at elevated temperatures. Hexagonal BN is a well-known ceramic material with a very high melting point of 3246K and a low density of 2.1x10^3 kgm^(-3). It has a layered structure similar to graphite. Within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the individual layers are held together by weak van der Waals forces. Hexagonal BN nanoparticles should act as sliding layers as well as diffusion barriers in metal matrix composites [8].

In this study nanoscale hexagonal boron nitride (hBN) was used as the reinforcement phase in a microscale aluminium matrix (Al-nc). The microstructure, and microhardness, as well as the damping and thermal properties were investigated with the aim better to understand behaviour of Al-BN nanocomposites.

2. Experimental procedure

The matrix, based on a mixtures of nanoscale aluminium powder and small amounts of aluminium oxide (Al_2O_3), was combined with hBN dispersoids by a powder metallurgical route. Additionally a reference sample of pure aluminium matrix powder (µAl) was prepared using the same experimental parameters. The basic matrix powder consists of ball milled water atomized Al (99.7wt.%) powder (45µm mean diameter). This matrix system was supplemented by an addition of BN powder (500nm mean diameter), with the combined powders mixed in by a planetary ball mill (Retsch, PM400) under an air atmosphere. The powders were both mixed in corundum-coated steel milling cups using 300 g of corundum balls (11mm mean diameter) and a 2:3 powder to ball mass ratio. The resulting mixtures exhibited non-agglomerated flake-like particles with an average diameter of 20µm and 5µm thickness. Due to the production process the powder mixture also contains a small amount of Al_2O_3 dispersoids. The powders were enclosed in commercial grade Al capsules and hot extruded (Collin 630t, non-ferrous metal extruder) to rods of 20mm diameter at 620K after preheating for 3 h at the same temperature [9].

Samples for microstructural observations were prepared by the grinding, polishing and electrolytic etching in a Lectropol apparatus (using 33% HNO_3 + methanol electrolyte) at 248K and 15V for 5s (pure Al) or 2s (Al+BN). The grain size distribution and texture of samples were studied using a scanning electron microscope (FEI Quanta 200 FX) equipped with an EDAX EBSD (electron backscatter diffraction) camera. The EDAX OIM (orientation imaging microscopy) software was utilized for analysis of the EBSD observations. The microhardness of the samples was measured using an automatic microhardness tester (Qness Q10a) by Vickers indentation, using a load of 100gf (gramm force) and a dwell time of 10s.

The linear thermal expansion was measured over a wide temperature range from RT up to 670K for samples in the as-extruded state. The heating rate in the dilatometer (Netzsch 410) was 0.9K/min. The measurements were carried out in a protective atmosphere of purified Ar. Amplitude-dependent internal friction represented by the logarithmic decrement δ was measured as damping of the free vibrations in a bending mode (for details see [10]). The amplitude-dependent damping of the NCs was measured at RT after step by step thermal cycling between RT and an increasing upper temperature of the thermal cycle up to a maximum temperature of 773K. In the following the two sets of samples are referred to as µAl (Al 99.7wt.%) and Al+0.3BN (Al+0.3wt.% hBN).

3. Results and discussion

3.1. Microstructure of the Al-BN nanocomposite

Examples of the microstructure of both types of samples are shown in figures 1a (µAl) and 1b (Al+0.3BN). The micrographs, taken from the section perpendicular to the extrusion direction, show a very fine grain structure. The grain size distributions for these samples are shown in figure 2a,b, and confirm the presence of a very fine grain structure, as seen in figure 1. The mean grain size is about 2µm and it is approximately the same for both materials. For the case when materials are prepared by milling, refinement of the originally large grains into the microcrystalline regime is connected with a
large plastic deformation. This large plastic deformation is partially recovered during consolidation of the powder.

From the EBSD data the grain boundary misorientation angles were also measured and the resulting distributions are shown in figure 3a,b. Both of the distributions (for μAl and Al+0.3BN) have a similar character, each with two local maxima – one at a very small misorientation angle and one at a high misorientation angle. Note the relatively high fraction of low angle boundaries. Both samples exhibit a texture typically observed in extruded fcc (face-centered cubic) materials [11, 12] as it is obvious from the inverse pole figure insets in figures 2a and 2b.

![Figure 1](image1.png)

**Figure 1.** Microstructure of μAl (a) and Al+0.3BN (b) taken from the section perpendicular to the extrusion direction.

![Figure 2](image2.png)

**Figure 2.** Grain size distribution as determined from EBSD measurements for μAl (a) and Al+0.3BN (b). The inverse pole figure in the inserts document the existence of a texture in both materials.

3.2. Microhardness

The microhardness (HV0.1) was measured over the entire sample cross-section. The resulting microhardness maps are shown in figures 4a and 4b. A distinct difference between both materials is obvious from inspection of the microhardness maps. Note also the different scale in both pictures. The microhardness of the μAl sample exhibits relatively low values in the middle of cross-section while
higher values are observed at the edge. This variation most likely arises as a result of the additional friction deformation of rods in the extrusion tool. In contrast, the microhardness of the Al+0.3BN NC sample exhibits the highest values in the middle of the cross-section, and the lowest values in the edge area. These low microhardness values correspond to the mantle material used for the compacted powder. The real composite is inside of this mantle. The different values of microhardness determined for the μAl and Al+0.3BN samples indicate significant strengthening of the due to the hBN in the Al+0.3BN sample. The hBN particles are not visible in the electron microscope images collected in this study. According to our previous experience, nanoparticles in nanocomposites prepared by ball milling are not uniformly distributed in the matrix, but remain mainly in the vicinity of grain boundaries [13, 14].

![Figure 3. Distribution of grain boundary misorientation angles for (a) μAl, and (b) Al+0.3BN.](image)

![Figure 4. Maps showing the microhardness (HV0.1) measured in the cross-section of samples: (a) μAl, and (b) Al+0.3BN.](image)

Several strengthening mechanisms in NCs can be considered, including Orowan strengthening [15] grain boundary strengthening [16], and increased dislocation density due to large differences in the thermal expansion coefficient between the matrix and ceramic dispersoids (e.g., BN and Al₂O₃) [17]. As mentioned above, bonding between both phases is very important factor. In the case of Al-BN NCs, high strength can be also achieved due to formation of a strong chemical bonding at the Al/BN interface. This chemical bonding provides effective load transfer from the matrix to particles [18].
3.3. Internal friction

The amplitude dependency of the logarithmic decrement are shown in figures 5a,b for lower and higher maximum strain amplitudes respectively. Note that the temperatures depicted in the figures are not measurement temperatures, but rather indicate the upper temperatures of the thermal cycles. The strain dependence of the decrement can be divided into a strain independent and a strain dependent component. For such experimental measurements the decrement can be expressed as

\[ \delta = \delta_0 + \delta_H(\varepsilon) \]

where \( \delta_0 \) is the amplitude independent component, found at low amplitudes. While several mechanisms may contribute to the amplitude independent component (dislocations, grain boundaries, thermoelastic effect, etc.) the strain amplitude dependent component \( \delta_H \) is usually caused by the presence of dislocations in the material. The strain amplitude dependence of the logarithmic decrement suggests dislocation unpinning processes from pinning points (solute atoms, vacancies, small clusters of point defects). Interactions between dislocations and pinning points may be explained using the Granato-Lücke theory of dislocation damping [19, 20]. In this theory, vibration of shorter and longer dislocation segments is the main source of internal friction. The critical strain \( \varepsilon_{cr} \) at which the internal friction becomes amplitude dependent may be used to calculate the effective critical stress amplitude corresponding to the micro yield stress according to the following equation

\[ \sigma_c = E \varepsilon_{cr} \]

where \( E \) is the Young’s modulus. The stress necessary for a thermal break-away of dislocation loops \( \sigma_T \) at a finite temperature is given by [21]

\[ \sigma_T = \sigma_M \left[ 1 - \left( \frac{kT}{U_1} \ln A \right)^{2/3} \right] \]

where \( U_1 \) is an effective activation energy, \( A \) is model parameter and \( kT \) has its usual meaning. The stress necessary for break-away of shorter dislocation segments from their pinning points in the pure mechanical process is described by

\[ \sigma_M = \frac{2F_m}{b(\ell_1 + \ell_2)} \]

Here \( F_m \) is the maximum force between the dislocation and the pinning point, and \( \ell_1 \) and \( \ell_2 \) are the lengths of neighbouring dislocation segments.

The amplitude dependency of the decrement seen in figure 5 shows that the amplitude-dependent component of decrement \( \delta_H \) increases with increasing upper temperature of the thermal cycle (see figure 5a). This tendency was reversed after cycling with the upper temperature higher than 633K (figure 5b). A similar tendency was observed also for the critical strain \( \varepsilon_{cr} \), which decreases with increasing upper temperature of the thermal cycle up to 633K. Thermal cycling with an upper temperature higher than 633K results in an increase in the critical strain.

As a rule the coefficient of thermal expansion (CTE) of the ceramic reinforcement phase is lower than that of most the metallic matrix in most composites. This means that when the composite is subjected to a temperature change, thermal stresses will be generated. Even small temperature changes may generate thermal stresses. These internal stresses generated by thermal cycling of composites can be reduced by various relaxation mechanisms including dislocations generation and glide, decohesion or sliding of the matrix-reinforcement interface, and diffusion of solute atoms in the matrix.
In the present samples thermal cycling of the Al-BN nanocomposite generated thermal stresses in the Al matrix in the vicinity of the BN and Al₂O₃ dispersoids. When the difference between room temperature and the upper temperature reached 200K new dislocations were induced into the Al matrix. Because the number of pinning points remained constant and dislocation density increased the effective length of dislocation segments \( \ell \) and thus the critical strain decreased. The Al matrix was step by step plastified. When the radius plastic zones increases above a certain value, the plastic zones may overlap. In such overlapped zones dislocation loops formed near interfaces have the opposite sign on the both sides of the particle. Under internal stresses dislocations move and annihilate in the matrix. This means that the dislocation density after cycling at temperatures higher than 633K again decreases. Accordingly both logarithmic decrement and the critical strain strongly depend on the dislocation density.

Chmelík and co-workers [22], measuring the acoustic emission from a thermally treated composite (without any applied stress), have shown that new dislocations are formed in the cooling part of the thermal cycle.

3.4. Thermal expansion

Temperature dependences of the thermal expansion coefficient for \( \mu \)Al and nc Al+0.3 BN are shown in figure 6. The measured CTE values for the NC sample are significantly lower than those for the \( \mu \)Al sample. The extrapolated CTE at 300K for Al+0.3BN is \( 23 \times 10^{-6} \text{K}^{-1} \) and for \( \mu \)Al is \( 23.8 \times 10^{-6} \text{K}^{-1} \) for. Using the rule of mixtures the CTE of a composite can be calculated as:

\[
\alpha_c = (1 - V_p) \alpha_m + V_p \alpha_p
\]  

(5)

where \( \alpha_c, \alpha_m \) and \( \alpha_p \) represent the CTEs of the composite, matrix, and particle, respectively, and \( V_p \) is the volume fraction of the reinforcing phase particles. Taking a value for polycrystalline BN CTE(hBN) of \( 4.563 \times 10^{-6} \text{K}^{-1} \) [23] the value calculated using the rule of mixture CTE is practically the same as for \( \mu \)Al owing to the very small nanoparticle content. In the quasi-harmonic Debye model, the thermal expansion coefficient, \( \alpha \), is described by

\[
\alpha = \frac{\gamma C_v}{K_T V} = \frac{\gamma C_p}{K_S V}
\]  

(6)

where \( \gamma \) is the Grüneisen parameter, \( V \) the volume, \( K_T \) the isothermal bulk modulus, \( K_S \) the adiabatic bulk modulus, and \( C_v \) and \( C_p \) are the heat capacities at constant volume and pressure, respectively [24]. The lower values of CTE than expected are very probably a consequence of the lower material density.
Material prepared by ball milling and hot extrusion may contain a certain fraction of pores [25]. Consolidation defects like pores and cracks could not fully be avoided by hot extrusion at different temperatures. Annealing experiments show that additional consolidation of the hot extruded materials occurs at higher temperatures above 673K but micro cracks could not completely be removed. Additionally, thermal cracks could be nucleated in powder metallurgical materials by quenching from high temperatures.

4. Conclusions
An aluminium-based nanocomposite containing 0.3wt.% of BN nanoparticles was successfully prepared by ball milling of Al and BN powders followed by hot extrusion. The nanocomposite also contained a small fraction of Al₂O₃ dispersoids introduced by surface oxidation of the Al powder. For comparison pure Al samples were also prepared from milled and consolidated powder. The mechanical and physical properties of the as-extruded samples were investigated leading to the following main conclusions:

- Both NC materials exhibit a very fine grain structure, with mean grain size of approximately 2 μm;
- Microhardness measurements reveal significant strengthening of the nanocomposite as compared with the sample prepared from only Al powder;
- Internal friction measurements suggest that new dislocations are produced after thermal cycling of the nanocomposite;
- The nanocomposite exhibits a distinct reduction in thermal expansion coefficient compared with the value expected based on a rule of mixtures analysis. This lower value is attributed to porosity of the material prepared using a powder metallurgical route.

Acknowledgements
We are sorry that our acknowledgments came too late to Professor Werner Riehemann from the Clausthal University of Technology, who gave the impetus to this work.

References
[1] Koli D K, Agnihotri G and Purohit R 2015 Advanced Aluminium Matrix Composites: The Critical Need of Automotive and Aerospace Engineering Fields Materials Today: Proceedings 2 3032–41
[2] Yamaguchi M, Bernhardt J, Faerstein K, Tsuchia K, Shtansky D, Bando Y, Golovin I, Sinning H and Goldberg D 2013 Fabrication and characteristics of melt-spun Al ribbons reinforced with nano/micro-BN phases Acta Mater. 61 7604–15
[3] Saravanan L and Senthilvelan T 2015 Investigations on the hot workability characteristics and deformation mechanisms of aluminium alloy-Al₂O₃ nanocomposite, Materials and Design 79
6–14

[4] Mokdad F, Chen D L, Liu Z Y, Ni D R, Xiao B L and Ma Z Y 2017 Hot deformation and activation energy of a CNT-reinforced aluminum matrix nanocomposite, Mater. Sci. Eng. 695 322–31

[5] Hosseini Monazzah A, Simchi A and Seyed Reihani S M 2010 Creep behavior of hot extruded Al-1203 nanocomposite powder Mater. Sci. Eng. 527 2567–71

[6] Casati R, Fiocchi J, Fabrizi A, Lesic N, Bonollo F and Vedani M 2017 Effect of ball milling on the ageing response of Al2618 composites reinforced with SiC and oxide nanoparticles J. Alloys Compd 693 909–12

[7] Trojanová Z, Ferkel H, Lukáč P and Riehemann W 2002 Two new high-damping magnesium composites Phys. Stat. Sol. (a) 193 205–10

[8] Reischer F, Pippel E, Woltersdorf J, Stockel S and Marx G 2007 Carbon fibre-reinforced magnesium: Improvement of bending strength by nanodesign of boron nitride interlayers. Materials Chemistry and Physics 104 83–7

[9] Kazakewitsch A and Riehemann W 2012 Amplitude Dependent Damping of Aluminum-Matrix-Nanoparticle-Composites Solid State Phenomena 184 307–12

[10] Göken J and Riehemann W 2002 Thermoelastic damping of the low density metals AZ91 and DISPAL Mater. Sci. Eng. 324 134–40

[11] Böhm H 1992 Einführung in die Metallkunde Bibliographisches Institut GmbH

[12] Gottstein G 2014 Materialwissenschaft und Werkstofftechnik, Physikalische Grundlagen Springer-Verlag Berlin Heidelberg

[13] Ferkel H and Mordike B L 2001 Magnesium strengthened by SiC nanoparticles Mater. Sci. Eng. A 298 193–9

[14] Drozd Z, Trojanová Z, Artic U, Kasakewitsch A and Dash K Effect of BN and graphite nanoparticles on mechanical and physical properties of magnesium In this volume

[15] Yeh Y H, Nakashima H, Kurishita H, Goto S, Yoshinaga H 1990 Threshold Stress for High-Temperature Creep in Particle Strengthened Al-1.5 vol%Be Alloys Mater. Trans. JIM 31 284-292

[16] Hansen N 1977 The effect of grain size and strain on the tensile flow stress of aluminium at room temperature Acta Metall. 25 863–79

[17] Arsenault J R and Shi N 1986 Dislocation generation due to differences between the coefficients of thermal expansion Mater. Sci. Eng. 81 175–187

[18] Krasheninnikov A V, Berseneva N, Kvashnin D G, Enkovaara J, Björkman T, Sorokin P and Goldberg D 2014 J. Phys. Chem. C118 26894–901

[19] Granato A V and Lücke K 1956 Theory of mechanical damping due to dislocations J. Appl. Phys. 27 583–93

[20] Granato A V and Lücke K 1956 J. Application of dislocation theory to internal friction phenomena at high frequencies Appl. Phys. 27 789–805

[21] Granato A V and Lücke K 1981 Temperature dependence of amplitude dependent dislocation damping J. Appl. Phys. 52 7136–42

[22] Chmelik F, Trojanová Z, Kiehn J, Lukáč P and Kainer K U 1997 Non-destructive characterization of microstructure evolution in Mg based metal matrix composites submitted to thermal cycling Mater. Sci. Eng. 234-236 774–7

[23] Brožek V, Dufek V, Harok V and Rohan P [http://konsys-t.tanger.cz/files/proceedings/metal_00/papers/135.pdf]

[24] Grüneisen E 1912 Theorie des festen Zustandes einatomiger Elemente Ann. Physik 39 257–306

[25] Vijay A 2011 Analysis of Grüneisen parameter and its volume derivatives for NaCl and hcp iron Indian J Pure & Appl. Phys. 49 825–8