Physical and mechanical properties of highly textured polycrystalline Nb$_4$AlC$_3$ ceramic

Chunfeng Hu$^{1,2}$, Yoshio Sakka$^{1,2,3}$, Toshiyuki Nishimura$^2$, Shuqi Guo$^4$, Salvatore Grasso$^{2,3}$ and Hidehiko Tanaka$^1$

$^1$ World Premier International Research Center (WPI) Initiative on Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
$^2$ Nano Ceramics Center, NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
$^3$ Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan
$^4$ Hybrid Materials Center, NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: SAKKA.Yoshio@nims.go.jp

Received 18 January 2011
Accepted for publication 3 April 2011
Published 7 July 2011
Online at stacks.iop.org/STAM/12/044603

Abstract
Highly textured polycrystalline Nb$_4$AlC$_3$ ceramic was fabricated by slip casting in a strong magnetic field followed by spark plasma sintering. Its Lotgering orientation factor was determined on the textured top and side surfaces as $f_{(00l)} \sim 1.0$ and $f_{(hk0)} = 0.36$, respectively. This ceramic showed layered microstructure at the scales ranging from nanometers to millimeters. The as-prepared ceramic had excellent anisotropic physical properties. Along the $c$-axis direction, it showed higher hardness, bending strength, and fracture toughness of 7.0 GPa, 881 MPa and 14.15 MPa m$^{1/2}$, respectively, whereas higher values of electrical conductivity ($0.81 \times 10^6$ $\Omega^{-1}$ m$^{-1}$), thermal conductivity (21.20 W m$^{-1}$ K$^{-1}$) and Young’s modulus (365 GPa) were obtained along the $a$- or $b$-axis direction.

Keywords: carbide, texture, nanolayered microstructure, physical properties, mechanical properties

1. Introduction

Ternary transition metal phases M$_{n+1}$AX$_n$ (MAX), where M is a transition metal, A is a IIIA–IVA group element, X is carbon or nitrogen, and $n = 1–3$, have been widely investigated for their ambient and high-temperature physical properties, such as high electrical and thermal conductivities, high Young’s modulus, excellent machinability, good thermal shock resistance and damage tolerance [1–5]. These MAX phases possess a laminar microstructure in the crystals of hexagonal symmetry [6]. More than 50 M$_2$AX phases, 6 M$_3$AX$_2$ phases and 8 M$_4$AX$_3$ phases have been discovered and investigated [7]. Their bending strength varies in the range of 300–500 MPa and the fracture toughness is just 5–7 MPa m$^{1/2}$ [8]. The limited mechanical properties of MAX phases undoubtedly inhibit their wider applications in engineering fields. Natural nacre possesses a soft–tough layer microstructure, which endows it with excellent compressive and tensile properties [9]. Therefore, many material scientists have tried to simulate the laminar configuration of nacre expecting to improve the mechanical properties of inorganic and hybrid ceramics. For example, Kovar et al [10] fabricated a multilayered ceramic that consisted of silicon nitride layers separated by boron nitride/silicon nitride interphases and measured its bending properties. They found that crack deflection and subsequent growth of delamination cracks were the source of energy dissipation during the fracture of layered ceramics, which contributed to the marked enhancement of the work of fracture. Munch et al [11] emulated the toughening mechanisms of nacre by combining aluminum...
oxide and polymethyl methacrylate to form ice-templated structures. The designed hybrid ceramic possessed a high yield strength of 200 MPa and a fracture toughness of 30 MPa m$^{1/2}$, which were comparable to those of aluminum alloys. It should be possible, by designing and optimizing the microstructure of ceramics, to obtain high strength and toughness simultaneously. Layered microstructural ceramics can be assembled using MAX phases, owing to their specific nanolayered crystal structure. In 2004, Murugaiah et al. attempted to fabricate textured Ti$_3$SiC$_2$ ceramic by tape casting followed by pressureless sintering. A dense polycrystalline microstructure with the basal planes parallel to the surface was obtained as a result of preferential grain growth. However, because the Ti$_3$SiC$_2$ grains could not be aligned to one direction, the ceramic texture was not homogeneous and the texture degree was low. Recently, tailored Al$_2$O$_3$, Si$_3$N$_4$, ZrO$_2$ and AlN ceramics have been successfully prepared using the strong magnetic field alignment (SMFA) method [13–19]. In this process, the ceramic crystals with asymmetric unit cell rotate to minimize the total energy in the magnetic field [20]. Ceramic particles are suspended in an aqueous solution of a dispersant, and a highly textured microstructure can be produced by aligning the grains and then drying and sintering them. The magnetic susceptibility of MAX phases is anisotropic owing to the anisotropic crystal structure. Using this property, Hu et al. [21, 22] fabricated highly textured Nb$_2$AlC$_3$ and Ti$_3$SiC$_2$ ceramics by the SMFA method. They found that these two phases behaved differently in the strong magnetic field. Whereas the c-axis of Nb$_2$AlC$_3$ was aligned parallel, that of Ti$_3$SiC$_2$ was oriented perpendicular to the magnetic field direction. A high flexural strength of 1219.2 MPa perpendicular to the c-axis direction and a high fracture toughness of 17.9 MPa m$^{1/2}$ parallel to the c-axis direction were measured [23]. However, during the powder preparation, oxide particles (~15 vol.%) were formed in the textured Nb$_2$AlC$_3$ matrix. Although such particles might improve the mechanical properties, their presence hinders understanding the intrinsic properties of textured Nb$_2$AlC$_3$ ceramic.

In this study, we prepared Nb$_2$AlC$_3$ powders and slip cast them in a 12 T magnetic field in argon atmosphere. After spark plasma sintering [24, 25], dense textured Nb$_2$AlC$_3$ ceramics containing about 3 vol.% oxide particles were fabricated and characterized.

2. Experimental procedures

Nb$_2$AlC$_3$ powder was prepared in an argon atmosphere (99% purity) by crushing the dense Nb$_2$AlC$_3$ samples that were synthesized by in situ solid/liquid phase reaction [26]. The inert atmosphere prevented the oxidation of Nb$_2$AlC$_3$ powder during the crushing process. After sieving through a 125 mesh sieve, the powder was milled for 24 h in a Si$_3$N$_4$ jar with 3-mm-diameter Si$_3$N$_4$ balls in a planetary monomill machine (Pulversette 6, Fritsch GmbH, Germany). Ethanol was used as the dispersant and the milling was conducted at 300 rpm in argon. After drying in argon, the powder was used to prepare the suspension for slip casting. The solid loading was 20 vol.% and the polyethylenimine (molecular weight 10,000, Wako Pure Chemical Industries Ltd, Tokyo, Japan) dispersant content was 2 wt% of the powder [27, 28]. The suspensions were stirred for 2 h for ageing and then poured into glass pipes adhering onto a 0.2 µm filter fixed on the surface of a plaster plate. These operations were carried out in an argon-filled box, and the slip casting holder was wrapped with an argon-filled plastic bag. Then, the holder with the plastic bag was placed in a 12 T magnetic field system. After natural drying, samples of 22 mm diameter were obtained.

To produce dense samples, firstly, the green bodies were compacted by cold isotropic pressing (Nikkiso Co. Ltd, Tokyo, Japan) under a pressure of 392 MPa for 10 min. The as-prepared green bodies had sufficient strength to be machined for fitting into a graphite die of 20 mm inner diameter. The sintering was carried out with a spark plasma sintering facility (100 kN SPS-1050, Syntex Inc., Japan) in a vacuum of 10$^{-2}$ Pa. The sintering temperature was increased to 1450°C at a rate of 50°C/min and then maintained at 1450°C for 10 min. The applied pressure was 30 MPa and the loading direction was parallel to the slip casting direction. After sintering, the sample was naturally cooled in the furnace and its surface contamination was removed using a wheel with embedded diamond powder. The sample density was measured by the Archimedes method. The compositions at the textured top surface and textured side surface in a sintered sample were determined using an x-ray diffraction (XRD) analyzer (JDX-3500, JEOL Ltd, Japan) with Cu Kα radiation. The degree of texture was evaluated through the Lotgering orientation factor $f_L = (P - P_0)/(1 - P_0)$ [29]. The values of $P$ and $P_0$ were calculated from the ratio $\sum I(hk0)/\sum I(hkl)$ for the a- and b-axes orientations and from the ratio $\sum I(00l)/\sum I(hkl)$ for the c-axis orientation, where $\sum I(hk0)$, $\sum I(00l)$ and $\sum I(hkl)$ are the sums of peak intensities of the (hk0), (00l) and (hkl) planes, respectively. The data from the textured Nb$_2$AlC$_3$ sample were used to calculate $P$, and $P_0$ was evaluated using the previously reported results [30]. The values of $f(00l)$ and $f(hkl)$ were calculated for the top and side surfaces, respectively.

Electrical conductivity was measured using the four-wire probe at room temperature. A current of 50 mA was supplied by a dc precision current source (Model 6220, Keithley, Ohio). The current–voltage (I–V) characteristics of the samples were recorded using a digital nanovoltmeter (Model 2182, Keithley, Ohio). Thermal conductivity was measured with a xenon flash apparatus (LFA447 Nanoflash, NETZSCH, Germany) at room temperature, for a disk specimen of 10 mm diameter and 2 mm height. A layer of colloidal graphite spray was coated on the sample surface to enhance the absorption of xenon light and emission of infrared radiation to the temperature sensor. Vickers hardness was tested on the textured top and side surfaces under loads of 0.245, 0.98, 4.9, 9.8 and 49 N with a dwell time of 15 s in a microhardness tester (MVK-E, Akashi Co., Japan). The indents and their cross sections were observed using a scanning electron microscope (SEM, JSM-7100F, JEOL Ltd, Japan) equipped with an energy dispersive spectroscopy (EDS) system. The load versus depth indentation characteristics were measured.
with a dynamic ultra-microhardness tester (SHIMADZU DUH-W201S, Shimadzu Co, Japan) using a Berkovich indenter with a ridge angle of 115°. The maximum load was 1.96 N. Twenty loading/unloading cycles were applied to the sample at a speed of 70.6 mN s\(^{-1}\). The indents were observed with a VHX-600 digital microscope (KEYENCE Corp., Osaka, Japan). The elasticity was evaluated with an ultrasonic setup (TDS 3034B, Tektronix Inc., USA) and the flexural strength and fracture toughness of as-prepared Nb\(_4\)AlC\(_3\) were measured with a mechanical strength testing system (Model 4505, Instron Corp., MA). The sample dimensions for three-point bending strength and fracture toughness tests were 1.5 × 2 × 18 mm and 2 × 4 × 18 mm, respectively. For single-edge notch beam samples, the notch was about 2 mm deep and 0.14 mm wide. The testing span was 16 mm. The cross-head speeds were 0.5 and 0.05 mm min\(^{-1}\) for the bending strength and fracture toughness measurements, respectively. The fracture surface was observed with SEM.

3. Results and discussion

Figure 1 shows XRD patterns and microstructures of the texture top and side surfaces of tailored Nb\(_4\)AlC\(_3\) ceramics. All strong diffraction peaks belong to (00\(l\)) planes for the top surface (figure 1(a)), revealing that the c-axis of the grains is perpendicular to the top surface. On the top surface, all diffraction peaks originate from the (1\(kl\)) planes (figure 1(b)), indicating that not all the a- and b-axes of the Nb\(_4\)AlC\(_3\) grains are parallel or perpendicular to the examined surface. This result shows that whereas the SMFA method allows aligning the c-axis of the grains, control over the orientation of the a- and b-axes is limited by the same magnetic susceptibility along these two directions. The calculated Lotgering orientation factors confirm the highly textured degree of the as-prepared ceramic: on the textured top surface, \(f_{(00l)}\) was close to 1.0, and \(f_{(hk0)}\) was 0.36 on the textured side surface.

As shown in figure 1(c), only transgranular fracture can be observed and no laminar character exists on the textured top surface, which is due to the weak bonding between the basal planes of Al atoms and Nb atoms [31]. The cracks are prone to propagate along the weak basal planes. Only a layered pattern is observed on the textured side surface (figure 1(d))—the Nb\(_4\)AlC\(_3\) grains are stacked forming a texture with a characteristic size ranging from nanometers to millimeters. Such tailored ceramic should have anisotropic properties along the directions of the textured top surface and side surface, and indeed, calculations of the Nb\(_4\)AlC\(_3\) crystal structure predict different physical properties along the c-axis and a, b-axes [31]. Figures 1(c) and (d) also reveal the presence of about 3 vol.% oxide particles (light gray particles), which were probably introduced during the powder preparation and sintering [32, 33].

Electrical conductivity measurements revealed higher values perpendicular (0.81 × 10\(^6\) Ω\(^{-1}\) m\(^{-1}\)) than parallel to the c-axis direction (0.49 × 10\(^6\) Ω\(^{-1}\) m\(^{-1}\)). It is known that the main contribution to the density of state at the Fermi level in Nb\(_4\)AlC\(_3\) originates from the Nb d electrons and not from Al electrons, owing to a scooping effect resulting from the presence of the Nb d states [34]. Therefore, Al electrons should not significantly contribute to the conduction. Because Nb and Al planes are stacked along the c-axis, the electrical conductivity along that axis should be lower than perpendicular to it. Moreover, the thermal conductivity value is higher for the direction perpendicular (21.2 W m\(^{-1}\) K\(^{-1}\)) than parallel to the c-axis (14.1 W m\(^{-1}\) K\(^{-1}\)). According to

![Figure 1](image-url)
Figure 2. Vickers hardness measured on the textured top surface (TTS) and textured side surface (TSS) as a function of indentation load. Inset shows SEM images of (a) the indent induced by a load of 49 N on the TSS, (b) a fracture surface crossing the indent, with the boxed area magnified in (c).

Figure 3. Displacement as a function of indentation load on the textured top surface (TTS) and textured side surface (TSS) during the ultra-microhardness test. Inset shows optical images of the indents induced by the Berkovich indenter under a cyclic load of 1961 mN.

The Nb$_2$AlC$_3$ matrix is undamaged below the shear band. This result indicates that mechanical energy can be completely dissipated in a small region through several damage mechanisms.

The indentation response of textured Nb$_2$AlC$_3$ ceramic was further characterized by the cyclic load-displacement curves shown in figure 3. It reveals open-loop, irreversible indentation cycles with a progressively decreasing loop area. This behavior can be explained by the formation of incipient kink bands that produce regular kink bands. The loop area of the indentation curve is larger for the textured top surface than for the textured side surface because the kink bands are formed easier on the top surface [38]. The smaller indentation depth converts to the higher hardness on the side surface (710.0 GPa) than on the top surface (466 GPa). The inset figures show the indents induced by 20 cycles of 1.96 N load on the side and top surfaces. The indent is anisotropic and is not regularly trigonal on the side surface. Along the c-axis direction, plastic deformation of Nb$_2$AlC$_3$ grains is the main damage mode, resulting in the grain pushing-out, crushing, delaminations and kink bands. In contrast, there is no obvious damage along the a- and b-axes directions, indicating elastic recovery. The regular triangular indent on the textured top surface indicates an isotropic mechanical response, and the crushed grains are distributed homogeneously around the indent.

The elastic moduli parallel and perpendicular to the c-axis direction were determined as 353 and 365 GPa, respectively. It is known that the elastic constants describe the material response to applied stress and provide useful information about the bonding character. For Nb$_2$AlC$_3$, the Nb–Al bonds are softer than all the Nb–C bonds [31]. Therefore, the Young’s modulus along the c-axis should be lower, according to theoretical calculations, resulting in the weaker resistance against uniaxial tension. The shear moduli parallel and perpendicular to the c-axis direction were deduced as 153 and
higher along the c-axis direction, whereas higher electrical conductivity (0.81 × 10^6 Ω^{-1} m^{-1}), thermal conductivity (21.2 W m^{-1} K^{-1}) and Young’s modulus (365 GPa) were measured along the a- or b-axis direction.

Acknowledgments

This work was partially supported by Grant-in-Aid for Scientific Research B No. 20350099 from Japan Society for the Promotion of Science (JSPS) and by the World Premier International Research Center (WPI) Initiative, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

[1] Barsoum M W and El-Raghy T 1996 J. Am. Ceram. Soc. 79 1953
[2] Barsoum M W, Yoo H-I, Polushina I K, Rud’ V Yu, Rud’ Yu V and El-Raghy T 2000 Phys. Rev. B 62 10194
[3] El-Raghy T, Zavaliangos A, Barsoum M W and Kalindidi S R 1997 J. Am. Ceram. Soc. 80 513
[4] Zhou Y C and Sun Z M 1999 Mater. Res. Innovat. 2 360
[5] Hu C F, Zhou Y C and Bao Y W 2008 Ceram. Int. 34 537
[6] Jeitschko W; Nowotny H and Benesovsky F 1963 Monatsh. Chem. 94 672
[7] Hu C F, Li F Z, He L F, Liu M Y, Zhang J, Wang J M, Bao Y W, Wang J Y and Zhou Y C 2008 J. Am. Ceram. Soc. 91 2258
[8] Barsoum M W 2000 Prog. Solid State Chem. 28 201
[9] Lin A Y M, Meyers M A and Vecchio K S 2006 Mater. Sci. Eng. C 26 1380
[10] Kovar D, Thouless M D and Halloran J W 1998 J. Am. Ceram. Soc. 81 1004
[11] Munch E, Launey M E, Alsem D H, Saiz E, Tombs A P and Ritchie R O 2008 Science 322 1516
[12] Murugaiah A, Souchet A, El-Raghy T, Radovic M, Sundberg M and Barsoum M W 2004 J. Am. Ceram. Soc. 87 550
[13] Sakka Y, Suzuki T S and Uchikoshi T 2008 J. Eur. Ceram. Soc. 28 935
[14] Tsuda K and Sakka Y 2009 Sci. Technol. Adv. Mater. 10 014603
[15] Zhu X W, Sakka Y, Suzuki T S and Uchikoshi T 2010 Acta Mater. 58 146
[16] Sakka Y and Uchikoshi T 2010 KONA Powder Particle J. 28 74
[17] Zhu X W, Suzuki T S, Uchikoshi T and Sakka Y 2008 J. Eur. Ceram. Soc. 28 929
[18] Suárez G, Sakka Y, Suzuki T S, Uchikoshi T and Aglietti E F 2009 Mater. Res. Bull. 44 1802
[19] Suzuki T S, Uchikoshi T and Sakka Y 2009 J. Eur. Ceram. Soc. 29 2627
[20] Sakka Y and Suzuki T S 2005 J. Ceram. Soc. Japan 113 26
[21] Hu C F, Sakka Y, Tanaka H, Nishimura T and Grasso S 2011 J. Am. Ceram. Soc. 94 410
[22] Hu C F, Sakka Y, Grasso S, Suzuki T and Tanaka H 2011 J. Am. Ceram. Soc. 94 742
[23] Hu C F, Sakka Y, Grasso S, Nishimura T, Guo S Q and Tanaka H 2011 Scr. Mater. 64 765
[24] Grasso S, Sakka Y and Maizza G 2009 Sci. Technol. Adv. Mater. 10 053001
[25] Grasso S, Sakka Y, Maizza G and Hu C F 2009 J. Am. Ceram. Soc. 92 2418
[26] Hu C F, Sakka Y, Tanaka H, Nishimura T and Grasso S 2009 J. Alloys Compd. 487 675

4. Conclusions

A tailored Nb$_4$AlC$_3$ ceramic was successfully prepared by slip casting in a strong magnetic field followed by spark plasma sintering. Its Lotgering orientation factor was determined on the textured top and side surfaces as $f_{\langle 001 \rangle} \sim 1.0$ and $f_{\langle b01 \rangle} = 0.36$, respectively. The as-obtained ceramic has a laminar structure with a characteristic length ranging from nanometers to millimeters and excellent, anisotropic physical properties. Its Vickers hardness (7.0 GPa), flexural strength (881 MPa) and fracture toughness (14.1 MPa m$^{1/2}$) were

Figure 4. Crack propagation along the c-axis direction on the textured side surface.

149 GPa, respectively. Shear modulus describes the resistance of a material to shape change, and thus it should be lower along the a- and b-axes than along the c-axis owing to the existence of weak basal planes. Poisson ratios were calculated as 0.15 and 0.22 parallel and perpendicular to the c-axis direction, respectively, and the corresponding flexural strength values were measured as 881 and 789 MPa. Compared with the strength of 455 MPa, obtained for the untextured Nb$_4$AlC$_3$ ceramic synthesized by spark plasma sintering [26], the marked enhancement achieved in this study can be attributed to the coordinated effect of aligned grains. Similar to the natural nacre that possesses excellent compressive and tensile properties, the textured Nb$_4$AlC$_3$ ceramic effectively inhibits the stress concentration and prevents the rapid crack propagation and catastrophic fracture. Additionally, the enhanced fracture toughness parallel and perpendicular to the c-axis direction was determined as 14.1 and 9.3 MPa m$^{1/2}$, respectively. This result indicates the prominent toughening effect of regularly aligned Nb$_4$AlC$_3$ grains. By investigating the crack propagation, we deduced that grain pulling-out and bridging are the main damage mechanisms, as shown in figure 4. The zigzag shape of the crack results in a large surface area that enhances the dissipation of mechanical energy [39]. We conclude that the texture method allows obtaining tailored Nb$_4$AlC$_3$ ceramics with high strength and toughness.

95 (881 MPa) and fracture toughness (14 GPa) were measured along the a- or b-axis direction.

Acknowledgments

This work was partially supported by Grant-in-Aid for Scientific Research B No. 20350099 from Japan Society for the Promotion of Science (JSPS) and by the World Premier International Research Center (WPI) Initiative, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.
[27] Zhu X W, Uchikoshi T, Suzuki T S and Sakka Y 2007 J. Am. Ceram. Soc. 90 797
[28] Tang F Q, Uchikoshi T, Ozawa K and Sakka Y 2006 J. Eur. Ceram. Soc. 26 1555
[29] Zhu X W and Sakka Y 2008 Sci. Technol. Adv. Mater. 9 033001
[30] Hu C F, Li F Z, Zhang J, Wang J M, Wang J Y and Zhou Y C 2007 Scr. Mater. 57 893
[31] Wang J M, Wang J Y, Zhou Y C and Hu C F 2008 Acta Mater. 56 1511
[32] Sakka Y, Ohno S and Uda M 1992 J. Am. Ceram. Soc. 75 244
[33] Sakka Y, Okuyama H, Uchikoshi T and Ohno S 2002 J. Alloys Compd. 346 285
[34] Bouhemadou A 2010 Braz. J. Phys. 40 52
[35] Clinton D J and Morrell R 1987 Mater. Chem. Phys. 17 461
[36] Sun Z M, Murugaiah A, Zhen T, Zhou A and Barsoum M W 2005 Acta Mater. 53 4359
[37] Barsoum M W, Zhen T, Kalidindi S R, Radovic M and Murugaiah A 2003 Nat. Mater. 2 107
[38] Kooi B J, Poppen R J, Carvalho N J M, Hosson J Th M and Barsoum M W 2003 Acta Mater. 51 2859
[39] Becher P F 1991 J. Am. Ceram. Soc. 74 255