Research Essentials

MAX Phases and Ultra-High Temperature Ceramics for Extreme Environments

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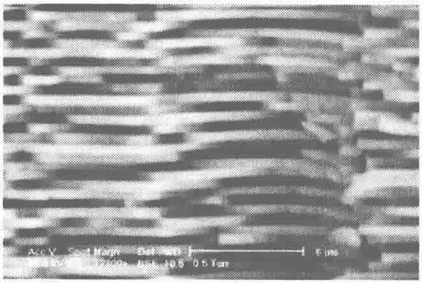
Preface

There is an impending need to develop structural ceramics that are not only stronger and tougher but also resistant to extreme environments during service. The combination of these attributes is essential for ceramics to meet the challenges and demanding needs in materials application for the 21st century in diverse strategic fields from building to transportation or energy. Ternary carbides and nitrides or MAX phases have emerged as potential candidates in view of their excellent physical and mechanical properties with the combination of merits of metals and ceramics. These ceramics have hexagonal structures with the general formula $M_{n+1}AX_n$ (where n = 1-3, M is an early transition metal, A is a group A element, and X is carbon or nitrogen). Unlike binary carbides or nitrides (e.g., TiC, TiN, and NbC) which are very hard and brittle, MAX phases possess a unique quasi-plasticity character that imparts excellent damage tolerance. They are also creep, fatigue, and corrosion resistant and have ultra-low friction. With proper alignment of the grains, they exhibit quasi-plasticity at room temperature. The mobility of dislocations and the multiplicity of shear-induced deformation modes are responsible for the observed plasticity. These ceramics can find applications in nuclear research, metallurgy, mining, and space-flight fields by virtue of their unique properties. For example, both Ti_3SiC_2 and Ti_3AlC_2 are candidate fuel cladding materials in future gas-cooled fast nuclear reactors due to their high radiation resistance. Ti_2AlC shows excellent oxidation resistance at intermediate and high temperatures in flowing dry or wet air. Ti_4AlN_3 exhibits plastic behaviour above 1000°C with a respectable "yield" of 450 MPa. Both Nb_4AlC_3 and Nb_2AlC have good high temperature stiffness up to 1400°C.

However, the mechanical properties of MAX phases have bending strengths of only 300-500 MPa and fracture toughness of just 5-7 MPa·m$^{1/2}$, which will undoubtedly inhibit their wider applications. One approach in this quest for the design of new and superior structural materials is by mimicking the architecture of biological materials. Through bio-inspired design, shell-like nanolaminar structures, similar to that of nacre (Figure 1), with greatly enhanced strength and toughness can be obtained. Hitherto, the notion of replicating the unique fracture resistance of biological shells in synthetic materials has generated much interest but has yielded

Figure 1. Microstructure of nacre (http://www.science.uts.edu.au/mau/virtual-tour.html)

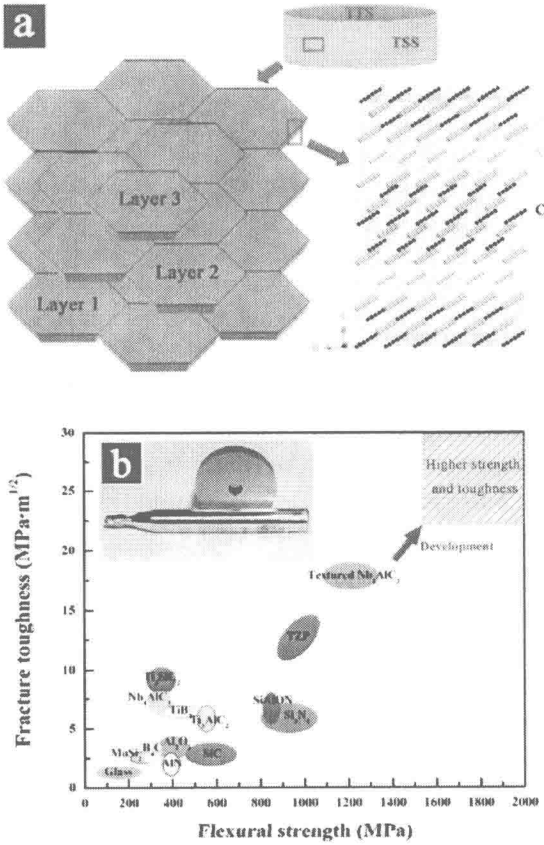


few real technological advances. Many material scientists in the world have tried to simulate the laminar configuration of nacre and expected to get the excellent mechanical properties of inorganic and hybrid ceramics.

Using a novel method of tailoring the microstructure of MAX phases through strong magnetic field alignment (SMFA), Sakka and co-workers at the Japanese National Institute for Materials Science (NIMS) have recently succeeded in designing shell-like microstructure of textured Nb_4AlC_3 with the concomitant enhancement in strength and toughness (see Figure 2). In this process the ceramic crystals with asymmetric unit cell rotate to an angle to minimize the system energy in the magnetic field. Generally, the aqueous solution with dispersant was used as a medium to suspend the ceramic particles. The perfect textured microstructure could be designed by rotating the grains to the same direction in the suspension, followed by drying and sintering. The corresponding physical and mechanical properties, oxidation resistance and electrochemical stability of as-textured MAX phases can be optimized (see Figures 2b and 3). Key to this approach is the control of aligned grains in strong magnetic fields due to the magnetic susceptibility of the grains of MAX phases. The marked electrical and thermal conductivities, strength, toughness, modulus, hardness, oxidation resistance, as well as the high temperature properties can be achieved. For example, flexural strength of 1219 MPa perpendicular to the *c*-axis and fracture toughness of 18 $MPa{\cdot}m^{1/2}$ parallel to the *c*-axis were achieved in tailored Nb_4AlC_3 ceramic.

This shell-like methodology meets the quest for the design of new and superior structural materials by mimicking the architecture of biological structures. It should be noted that nacre and other shell-like structures generate their fracture resistance or toughness primarily by extrinsic mechanisms which "shield" an advancing crack from the applied load. These mechanisms, which are quite different to those of toughened synthetic materials, are simultaneously created at multiple dimensions, literally from nano- to macro-scales. From a fracture mechanics perspective, they

Figure 2. Shell-like design of nanolayered Nb_4AlC_3: (a) schematic, and (b) enhanced mechanical properties



generate a characteristic crack resistance curve (R-curve) behaviour where the fracture resistance actually increases with crack extension; in essence, these materials develop the majority of their toughening during crack growth.

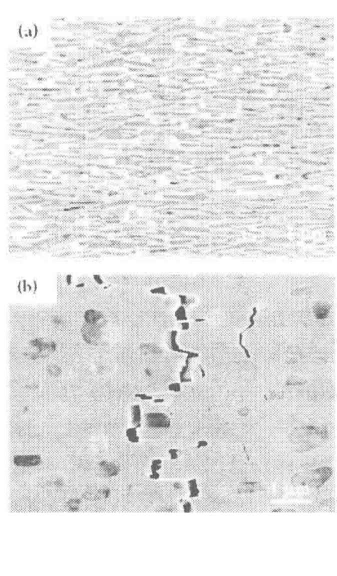
This approach is beginning to arouse serious attention worldwide in the ceramic field, because for the first time perfectly controlled microstructure of MAX phases with remarkable properties can be obtained. Not only single composition MAX phases can be textured, but also tailored composites can be fabricated through property and microstructure optimization. In the presence of strong magnetic fields, all non-cubic crystal structures show magnetic susceptibility. For instance, SiC, Al_2O_3, Si_3N_4, HfB_2 and ZrB_2 ceramics have been successfully textured in strong magnetic fields. These textured ceramics can find potential uses such as nuclear fuel cladding, aircraft nose and nozzle, aircraft brakes, electrical devices, automobile and aircraft engine components, and brake discs or pads for high speed trains.

Another class of materials that will also meet the challenges and demanding needs in adverse environments are the ultra-high temperature ceramics (UHTCs). These special ceramics can be used in environments of extreme service temperature (i.e., upwards of 1,500°C), chemical reactivity or erosive attack which are vital for specialty applications such as handling of molten metals, electrodes for electric arc furnaces, or aerospace materials in hypersonic aircraft, scramjet engines, rocket propulsion systems, atmospheric re-entry, and next-generation turbine engines.

UHTCs such as ZrB_2, HfB_2, and ZrC and their composites have been extensively investigated in recent years because of their excellent high temperature stiffness, high hardness, high thermal shock resistance, as well as the good oxidation and ablation resistance. These properties are essential for use as cladding materials in re-entry and ultra-high speed aircrafts to provide thermal protection under extreme environments.

To date, material researchers have focused on UHTCs in terms of powders and bulk synthesis, microstructure characterization, physical and mechanical properties evaluation, oxidation and ablation testing, as well as the impact resistance. The powder synthesis is aimed at solving the problem of poor sinterability through modifying the particle morphology and reducing the grains to nano-sized. The use of precursor method has also enabled the ability to prepare rod-like and plate-like grains with relative ease. Additionally, in order to enhance the sintering ability, selective sintering additives are necessary to produce low temperature liquid phases in the samples or lowering the grain boundary Gibbs free energy. Generally, the intrinsic

Figure 3. (a) Shell-like microstructure of nano-layered Nb_4AlC_3, and (b) crack propagation with tortuous crack-path



strength and modulus of UHTCs are high enough for use in the aircrafts. However, the shortcomings of these ceramics are their brittleness and low damage tolerance, which will have an adverse effect on their wider applications.

Nevertheless, the introduction of graphite, carbon fiber, or silicon carbide fiber has contributed to the effectiveness and reliability of UHTCs. Recently, it has been considered that the microstructure design through texturing is very important to increase their physical and mechanical properties. For instance, Sakka and co-workers at NIMS have recently succeeded in using the SMFA method to design textured microstructures of UHTCs (e.g., ZrB_2, HfB_2 and B_4C) with improved mechanical properties. The oxidation resistance and ablation resistance have also been significantly enhanced through combining silicon carbide and transition metal silicides. All in all, UHTCs offer great promises as candidates for components on future hypersonic vehicles for outer space explorations.

This book deals with the recent advances in the science and technology of MAX phases and ultra-high temperature ceramics (UHTCs) and their performances in extreme environments. Hitherto, there is an enormous but fragmented amount of research papers on MAX phases and UHTCs published in various journals in recent years. A dedicated book on this topic is required to bring all the scattered research findings into a single volume which will provide an invaluable resource for both students and researchers in this field.

Eighteen peer-reviewed Chapters are presented in this book. Each chapter has been written by a leading researcher of international recognition on *MAX* phases or UHTCs. This book is concerned with the synthesis, characterisation, microstructure, properties, modelling and potential applications of these ceramics in extreme environments. The synopsis of each Chapter is as follows:

Chapter 1: This chapter describes the use of spark plasma sintering (SPS) to synthesize and consolidate MAX phases. It is shown that Ti/Si/TiC is the most appropriate powder mixture and Al is a good aid for the synthesis of high purity Ti_3SiC_2 by SPS. Various Ti_3SiC_2-based composites have also been consolidated by SPS and the related properties have been improved, such as hardness, strength, fracture toughness and conductivity. A few other MAX phases have also been synthesized and consolidated by SPS in one step using various powder mixtures.

Chapter 2: The susceptibility of MAX phases to thermal dissociation at 1300-1550 °C in high vacuum is explored in this chapter. Above 1400 °C, MAX phases decomposed to binary carbide (e.g., TiC_x) or binary nitride (e.g., TiN_x), primarily through the sublimation of A-elements such as Al or Si, which results in a porous surface layer of MX_x being formed. Positive activation energies were determined for decomposed MAX phases with coarse pores but a negative activation energy when the pore size was less than 1.0 μm. The kinetics of isothermal phase decomposition at 1550 °C was modelled using a modified Avrami equation. An Avrami exponent

(n) of < 1.0 was determined, indicative of the highly restricted diffusion of Al or Si between the channels of M_6X octahedra. The role of pore microstructures on the decomposition kinetics is discussed.

Chapter 3: This chapter reviews the various properties possessed by the UHTCs and critically analyses the issues concerned with such materials. Through such analysis an overview of the more recent research efforts that have been conducted to solve the various issues related to this material class is presented, which also highlights the difficulties associated with experimental assessments of the various properties of such materials. Last but notleast, the various present day applications and the potential applications for such materials are mentioned, with an outlook towards the issues that need to be addressed in the more recent future.

Chapter 4: This chapter presents a detailed review of the processing of zirconium, hafnium, and tantalum based boride-carbide-nitride composites. The processing methodology and important steps involved in producing a pore-free microstructure are reported. The effect of adding secondary and ternary compounds on densification is highlighted, as is the reactive processing of ultra-high temperature ceramics (UHTCs) based on zirconium carbide through the formation of a transient non-stoichiometric carbide and transient liquid phase, which enable densification at much lower temperatures. This latter method is promising in that it readily leads to variation in the composition of secondary/ternary non-oxide phases in the composites as well as the incorporation of fibres which may otherwise degrade. Since the processing temperatures are lower, the grain size obtained after densification is finer and may lead to better mechanical properties (hardness, fracture toughness, and strength). Processing of fibre based composites with boride particulates and silicon carbide through the ceramic precursor route are also discussed.

Chapter 5: In this chapter, composites based on borides and carbides of Zr, Hf and Ta were produced with addition of $MoSi_2$ or $TaSi_2$. These silicides were selected as sintering aids owing to their high melting point (>2100°C), their ductility above 1000°C and their capability to increase the oxidation resistance. The microstructure of fully dense hot pressed UHTCs containing 15 vol% of $MoSi_2$ or $TaSi_2$, was characterized by x-ray diffraction, scanning and transmission electron microscopy. Based on microstructural features detected by TEM, thermodynamics calculations and the available phase diagrams, a densification mechanism for these composites is proposed. The mechanical properties, namely hardness, fracture toughness, Young's modulus and flexural strength at room and high temperature, were measured and compared to the properties of other ultra-high temperature ceramics produced with other sintering additives. Further, the microstructural findings were used to furnish possible explanations for the excellent high temperature performances of these composites.

Chapter 6: In this chapter, the processes available for powder synthesis, fabrication of dense bodies, and coating processes for ultra-high-temperature ceramics (UHTC) are highlighted. Amongst the borides, ZrB_2 and HfB_2 have received the most attention as potential candidates for leading edge materials because their oxidation resistance is superior to that of other borides due to the stability of the ZrO_2 and HfO_2 scales that form on these materials at elevated temperatures in oxidizing environments. However, the processing of these materials is very difficult as these materials are very refractory in nature.

Chapter 7: UHTCs based on polymer-derived ceramics (PDCs) are described in this chapter. The properties of PDCs are shown to be strongly related to their microstructure (network topology) and phase composition, which are determined by the chemistry and molecular structure of the polymeric precursor used and by the conditions of the polymer-to-ceramic transformation. Within this chapter, synthesis approaches, the nano/microstructure as well as the behaviour of PDCs at ultrahigh temperatures and in harsh environments are presented.

Chapter 8: In this chapter, Zr and Hf borides and carbides, have been produced with full density, fine microstructure and controlled mechanical and thermal properties, through different procedures: pressureless sintering and hot pressing, reactive synthesis/sintering, and spark plasma sintering. More recently, the use of near net shaping techniques and the development of UHTC porous components open the way for further and innovative applications. Structural lightweight parts, insulator panels, filters, radiant burners, solar absorbers are some of the possible applications.

Chapter 9: The use of the self-propagating high-temperature synthesis (SHS) technique in combination with the SPS technology is examined in this Chapter for fabricating fully dense MB_2-SiC and MB_2-MC-SiC (M=Zr, Hf, Ta) ceramics. The starting reactants are first processed by SHS to successfully form the desired composites. The resulting powders are subsequently consolidated by spark-plasma sintering (SPS). Bulk products with relative densities $\geq$ 96% can be obtained within 30 min, when the dwell temperature is 1800 °C at a pressure of 20 MPa. Hardness, fracture toughness, and oxidation resistance of the obtained dense bodies are comparable to, and in some cases superior than those reported for analogous products synthesized using alternative routes. Possible future developments of this approach with the final purpose of obtaining whiskers/fibers reinforced UHTCs are discussed.

Chapter 10: The processing techniques, microstructures, and mechanical properties of directionally solidified eutectic UHTCs are reviewed in this chapter. It is considered the main methods for preparing of eutectic ceramics and the relationships between thermal gradient, growth rate and microstructure parameters. Principles of coupled eutectic growth, main types of eutectic microstructure and the relationship between the eutectic microstructure and the mechanical properties of directionally solidified eutectics at ambient and high temperatures are briefly described. The mechanical behavior and main toughening mechanisms of these materials in wide temperature range are also discussed. It is shown that the strength at high temperatures mainly depends on the plasticity of the phase components. By analyzing the dislocation structure, the occurrence of strain hardening in single crystalline phases during high-temperature deformation was revealed. The creep resistance of eutectic composites is superior to that of the sintered samples due to the absence of glassy phases at the interfaces, and the strain has to be accommodated by plastic deformation within the domains rather than by interfacial sliding. The microstructural and chemical stability of the directionally solidified eutectic ceramics at high temperatures are discussed. The aligned eutectic microstructures show limited phase coarsening up to the eutectic point and excellent chemical resistance. Directionally solidified eutectics, especially oxides revealed an excellent oxidation resistance at elevated temperatures. These materials display excellent potential for high-temperature applications.

Chapter 11: This chapter introduces the reactive melt infiltration (RMI) process and summarizes the progress in RMI process for the fabrication of carbon fiber reinforced ultra high temperature ceramic matrix composites (C/UHTC). Compared with chemical vapor infiltration (CVI) and polymer impregnation and pyrolysis (PIP), RMI does not suffer from the drawbacks of time-consuming and high cost. It is a promising means of achieving near-net shape manufacturing with quick processing time and at low cost. Recently, great efforts have been made on RMI process for C/UHTC composites. Carbon fiber reinforced ZrC, HfC and TiC composites have been successfully fabricated by RMI. In addition, future research directions for RMI have also been proposed.

Chapter 12: The crystal structure, synthesis and densification of zirconium diboride (ZrB_2) are summarized in this chapter. The ZrB_2-ZrC-SiC ceramic was synthesized by reactive hot pressing Zr, B_4C and Si powder-mixture. The thermal shock resistance of ZrB_2-SiC-ZrC ceramic was characterised using the water quenching method and it was shown to be significantly better than ZrB_2-15vol.% SiC ceramic. The isothermal oxidation of ZrB_2-SiC-ZrC ceramic was characterised at 1000-1400 °C and the mechanism of strength increase for the oxidized specimen indicated that the strength increased with the increasing reaction rate. The increase in strength was related to change rate in volume induced by reaction, the initial crack geometry, elastic modulus and the surface free energy. The formation of oxide layers resulted in (a) the healing of the surface flaws, (b) the increase in the flexural strength, (c) the appearance of the compressive stress zone beneath the surface oxide layers, (d) the decrease in the thermal stress, and (e) the consumption of thermal stresses. These five aspects were responsible for improving the thermal shock resistance of ZrB_2-SiC-ZrC ceramic. In the different oxidation stages, the quantitative models were proposed to predict oxidation kinetics.

Chapter 13: Two-dimensional C/C-ZrB_2-ZrC-SiC composites with three phases of ultra high temperature ceramics (UHTCs) are described in this chapter. The fabricated composite possesses a matrix of 20ZrB_2-30ZrC-50SiC synthesized from pre-ceramic precursors. Possible mechanisms of pyrolysis and formation of pure ZrB_2 from the precursors with various B/Zr molar ratios are suggested. It was found that a composite with a bulk density of 2.06 g/cm^3 and open porosity of 9.6% can be obtained after 16 cycles of polymer infiltration and pyrolysis (PIP). The formed matrix exhibits homogeneous dispersion of three matrix ceramics without any oxide impurities, i.e. the nano sized ZrB_2 and ZrC particles dispersed in a continuous SiC ceramic with clean crystalline boundaries. No erosion or interface reaction occurs upon the carbon fiber reinforcement, which therefore avoids a dramatic deterioration of mechanical strength of carbon fiber and the composite. It is shown that PIP offers two benefits; firstly the dense pyrolytic carbon interphase deposited on fiber surface by CVI serves as barrier coating. Secondly, pyrolysis of the novel organic polymeric precursors does not release corrosive by-products such as hydrogen chloride.

Chapter 14: The mechanical and ablation properties of the 2D C/C-ZrB_2-ZrC-SiC composites fabricated by infiltration and co-pyrolysis of blended polymeric precursors, are described in this chapter. Flexural strength and fracture toughness of these composites were found to be influenced strongly by the thickness of the deposited pyrolytic carbon interphase. The pseudo-plastic strain to failure phenomena of the composite is ascribed to sliding of the interphase and pulling out of carbon fibers from the brittle ceramics matrix. Ablation properties of the composite was investigated with a plasma torch and arc-heated wind tunnel tests at temperatures above 1800~2200°C. It is shown that the composite exhibits very low ablation rates of 0.18×10^{-3} mm/s at 1800°C and 0.37×10^{-3} mm/s at 2000°C in the plasma torch after 1000s testing, as compared to a similar rate of 0.30×10^{-3} mm/s in the wind tunnel at 1900°C after 600s testing. However, the ablation rates increase with increasing of temperatures from 1800 to 2200°C. The maximum ablation rates is only 1.67×10^{-3} mm/s in a plasma torch at 2200°C for 1000s, as compared with the C/C-SiC composite with the same fiber and interphase contents. Excellent ablation and thermal shock resistances of the composite can be attributed to its architecture of carbon fiber and interphase, as well as its matrix microstructures characterized by nano sized dispersions of ZrB_2-Zr-SiC phases inherent formed by co-pyrolysis of three polymeric precursors. These meso- and microstructures make the composites possess very small and steady coefficients of thermal expansion of 1.5~2.5×10^{-6}/K and high thermal conductivities of 10~14W/mK.

Chapter 15: This chapter summarises the recent studies on the wetting behaviors of ceramics which include carbides, oxides, nitrides and borides at a wide temperature range and under various atmospheres. Also their joining experiments, mainly by brazing and reaction joining methods, are reviewed. The typical and fundamental physical, mechanical and microstructural examinations, such as contact angle, joint strength and interlayer structure, are also presented.

Chapter 16: This chapter presents the synthesis of non-stoichiometric zirconium carbide (ZrC_x) using spark plasma sintering. The microstructural features of a sintered $ZrC_{0.6}$ sample were investigated via the measurements of XRD, TEM, and HRTEM. It was found that the carbon vacancies have an ordered arrangement in C sublattice, forming a Zr_2C-type cubic superstructural phase with space group of $Fd\bar{3}m$. Moreover, it was observed that the superstructural phase exists in nanodomains with an average size of ~30 nm owing to the ordering length in nanoscale. During the heating treatment in air, it was observed that the diffusion of oxygen atoms is significantly facilitated through the ordered carbon vacancies. For the heating treatment at low temperature (<300°C), the oxygen atoms diffuse easily into and occupy the ordered carbon vacancies, forming the oxy-carbide of $ZrC_{0.6}O_{0.4}$ with ordered oxygen atoms. At the heating temperature higher than 350°C, an amorphous layer of $ZrC_{0.6}O_{y>0.4}$ was identified form as a result of diffusion of superfluous oxygen atoms into Zr-tetrahedral centers. Within the amorphous layer, metastable tetragonal zirconia nanocrystals are recognized to be gradually developed.

Chapter 17: This chapter investigates the ablation as well as the associated thermal shock resistance of tungsten composites reinforced with TiC and ZrC particles. Samples with compositions 30TiC/W and 40TiC/W failed to withstand the thermal shock of 2000 °C/s during heating. In contrast, 30ZrC/W and 40ZrC/W withstood the thermal shock. Additionally, ZrC/W composites exhibited better ablation resistance than TiC/W composites. The thermal stress fields of the composite at both macro-/micro-scales induced by thermal shock at the early stage of the ablation were analyzed using finite element method. The calculated results of the damage mode of the composites show that crack initiates at the disk sample peripheral zone and then propagates to the sample center, which is consistent with the experimental observation.

Chapter 18: This chapter reviews the novel fabrication process of continuous SiC_f/SiC composites based on electrophoretic deposition (EPD). It is shown that the EPD process is very effective for achieving relatively homogeneous carbon coating with the thickness of several tens to hundreds nanometers on SiC fibers. Carbon interface with the thickness of at least 100 nm formed by EPD acted effectively for inducing interfacial debonding and fiber pullout during fracture, and the SiC_f/SiC composites showed excellent mechanical properties. From these results, it was demonstrated that the fabrication process based on EPD method is an effective way to control the interfaces of SiC_f/SiC composites and to obtain high-performance SiC_f/SiC composites.

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REFERENCES

Bale, H. A., Haboub, A., MacDowell, A. A., Nasiatka, J. R., Parkinson, D. Y., & Cox, B. N. et al. (2013). Real-time quantitative imaging of failure events in materials under load at temperatures above 1,600°C. *Nature Materials*, *12*, 40–46. doi:10.1038/nmat3497 PMID:23223124.

Barsoum, M. W. (2000). The $M_{n+1}AX_n$ phases: A new class of solids: Thermodynamically stable nanolaminates. *Progress in Solid State Chemistry*, *28*, 201. doi:10.1016/S0079-6786(00)00006-6.

Barsoum, M. W., & El-Raghy, T. (2001). The MAX phases: Unique new carbide and nitride materials. *American Scientist*, *89*, 334–343.

Fahrenholtz, W. G., & Hilmas, G. E. (2012). Oxidation of ultra-high temperature transition metal diboride ceramics. *International Materials Reviews*, *57*, 61–72. do i:10.1179/1743280411Y.0000000012.

Grasso, S., Hu, C., Vasylkiv, O., Suzuki, T., Guo, S., Nishimura, T., & Sakka, Y. (2011). High hardness B_4C textured by a strong magnetic field technique. *Scripta Materialia*, *64*, 256–259. doi:10.1016/j.scriptamat.2010.10.010.

Hu, C. F., Sakka, Y., Grasso, S., Nishimura, T., Guo, S. Q., & Tanaka, H. (2011). Shell-like nanolayered Nb_4AlC_3 ceramic with high strength and toughness. *Scripta Materialia*, *64*, 765–768. doi:10.1016/j.scriptamat.2010.12.045.

Hu, C. F., Sakka, Y., Tanaka, H., Nishimura, T., & Grasso, S. (2011). Fabrication of textured Nb_4AlC_3 ceramic by slip casting in a strong magnetic field and spark plasma sintering. *Journal of the American Ceramic Society*, *94*, 410–415. doi:10.1111/j.1551-2916.2010.04096.x.

Low, I. M. (2012). *Advances in Science & Technology of MAX Phases*. Cambridge, UK: Woodhead Publishing.

Low, I. M. (2012). *MAX Phases: Microstructure, Properties and Applications*. New York: Nova Science Publishers.

Low, I. M., Pang, W. K., Kennedy, S. J., & Smith, R. I. (2011). High-temperature thermal stability of Ti_2AlN and Ti_4AlN_3: A comparative diffraction study. *Journal of the European Ceramic Society*, *31*, 159–166. doi:10.1016/j.jeurceramsoc.2010.09.014.

Ni, D. W., Zhang, G. J., Kan, Y. M., & Sakka, Y. (2009). Highly textured ZrB_2-based ultra-high temperature ceramics via strong magnetic field alignment. *Scripta Materialia*, *60*, 615–618. doi:10.1016/j.scriptamat.2008.12.027.

Ni, D. W., Zhang, G. J., Kan, Y. M., & Sakka, Y. (2009). Textured HfB_2-based ultra-high temperature ceramics with anisotropic oxidation behaviour. *Scripta Materialia*, *60*, 913–916. doi:10.1016/j.scriptamat.2009.02.013.

Pang, W. K., Low, I. M., O'Connor, B. H., Studer, A. J., Peterson, V. K., & Palmquist, J. P. (2010). Diffraction study of high-temperature thermal dissociation of Maxthal Ti_2AlC in vacuum. *Journal of Alloys and Compounds*, *509*, 172–176. doi:10.1016/j.jallcom.2010.09.019.

Sun, Z. M. (2011). Progress in research and development on MAX phases. *International Materials Reviews*, *56*, 143. doi:10.1179/1743280410Y.0000000001.

Wuchina, E., Opila, E., Opeka, M., Fahrenholtz, W., & Talmy, I. (2007). UHTCs: Ultra-high temperature ceramic materials for extreme environment applications. *Interface*, *16*, 30–36.

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