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A new method to texture dense $M_{n+1}AX_n$ ceramics by spark plasma deformation

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ABSTRACT

This work explored a new method to texture $M_{n+1}AX_n$ phases by deforming discs of dense ceramics Maxthal 211® (nominally Ti_2AlC) and Maxthal 312® (nominally Ti_3SiC_2) in a spark plasma facility. The disc diameter increased by 40% without crack formation. After deformation, the MAX grains exhibited clear preferential crystallographic orientation, whereby the *c*-axis was aligned to the compression direction. The fracture toughness increased both parallel and perpendicular to the textured top surface compared with the as-sintered materials. The onset of plastic deformation was observed near the brittle-to-plastic transformation temperature, a fact that could be associated with the change in elastic response.

$M_{n+1}AX_n$ (MAX) phases are a family of ternary carbides and nitrides crystallizing in the hexagonal crystal system (space group *P*63/*mmc*). The MAX phase unit cells are characterised by near close-packed M layers interleaved with layers of a pure A element and the X atoms occupy octahedral sites between the two layers [1–4]. This graphite-like microstructure results in an exceptional combination of properties. High fracture toughness and impact resistance (properties characteristic for metals) are combined with properties usually associated with ceramics (high-temperature resistant, light weight, elastically stiff), making MAX phases potential candidate materials for high-temperature structural applications.

Fracture toughness can be further improved by aligning the nano-laminated MAX phase grains [5,6]. Texturing these ceramic materials results in an anisotropic mechanical response [5,7]. In contrast to other textured ceramics [7], the improvement in fracture toughness is observed both parallel and perpendicular to the texturing direction as compared to the randomly-oriented material [5].

The first successful attempt to texture bulk polycrystalline Ti_3SiC_2 involved hot pressing of pre-reacted MAX phase powders [8]. Another approach involved breaking up MAX ceramics into fine powder and subsequently densifying the powder compact by spark plasma sintering (SPS) [6,9]. An intermediate step of slip-casting a MAX powder suspension in a strong magnetic field can enhance the grain alignment, as reported for Nb_4AlC_3, Ti_3SiC_2 and Ti_3AlC_2 [5,10–12]. Recently, porous Ti_2AlN was preferentially oriented during well-controlled microwave-assisted sintering [13].

Considering high-temperature deformability, Ti_3SiC_2 is by far the most investigated MAX phase. Barsoum et al. [1,8] reported on the yielding behaviour of Ti_3SiC_2 under compression at 1300 °C. They further studied the influence of temperature on the material deformation behaviour and observed a ductile-to-brittle transition around 1100–1200 °C [14,15]. The same transition temperature range was indicated during tensile testing [16] and confirmed in several creep tests performed by Radovic et al. [17,18]. The 'yield point' of Ti_3SiC_2 in compression at 1300 °C, at relatively high strain rates (5×10^{-3} s^{-1}), was found to be around 300 MPa and 400 MPa for coarse- and fine-grained ceramics, respectively [14]. Above the transition temperature, the mechanical response of MAX phases depends on the strain rate for both compression [15] and tension [18]. In general, lower deformation rates result in larger strains to failure.

Radovic et al. [19] investigated the high-temperature elastic behaviour of select MAX ceramics by means of resonant ultrasound spectroscopy (RUS). These authors observed a linear decrease of the normalised *E*-modulus (E/E_{RT}), where $\frac{d(E/E_{RT})}{dT}$ varied between -0.75×10^{-4} and -1.44×10^{-4} K^{-1}. Also, the impulse excitation technique (IET) has been employed to characterise the temperature dependence of the dynamic Young's modulus of MAX phases according to ASTM C 1259 [20].

This work reports on the texturation of bulk, commercially-available materials Maxthal 312® (nominally Ti_3SiC_2) and Maxthal 211® (nominally Ti_2AlC) using a spark plasma sintering device.

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A schematic representation of the experimental procedure is given in Fig. 1. Primarily (99%) dense discs of 40 mm in diameter were prepared by spark plasma sintering of commercially-available Maxthal 312® and Maxthal 211® raw powders (Sandvik, Sweden). The powders were first cold pre-compacted and then spark plasma sintered at a heating rate of 100 °C/min with a dwell time of 5 min under 30 MPa at the sintering temperature, T_d, of 1350 °C and 1300 °C for Maxthal 312® and Maxthal 211®, respectively. The dense discs (40 mm ∅) were ground plane-parallel to a thickness of 8 mm. The discs were deformed in a second SPS run by placing the 40-mm diameter discs in a 56-mm graphite die, pre-loading them at 70 MPa and heating to the sintering temperature. Non-deformed, 56-mm diameter discs of each material were prepared according to the first SPS cycle described above for comparison. Spark plasma sintering (FCT-Systeme, HP D 25, Frankenblick, Germany) was performed in vacuum (~100 Pa) and temperature control was achieved by focusing an optical pyrometer at ~2–3 mm above the middle of the disc surface, as described in detail in [21].

The phase assembly in the ceramic discs was determined by X-ray diffraction (XRD; Seifert 3003), using a Cu K_α radiation source (operating conditions: 40 kV, 40 mA). The XRD pattern was measured with a step size of 0.02° 2θ and 2 s per step. Quantitative evaluation of the phase assembly was done based on the Rietveld refinement method with the TOPAS academic software. The Lotgering factor was used to express the degree of texture [22]:

$$f_L = \frac{P - P_0}{1 - P_0}$$

For the preferred orientation along the *c*-axis, P and P_0 correspond to the ratio $\Sigma I_{00l}/\Sigma I_{hkl}$, where ΣI_{00l} and ΣI_{hkl} are the sums of the peak intensities corresponding to the (001) and (hkl) planes, respectively. P refers to the peak intensities of the textured sample and P_0 to the peak intensities of the reference, isotropic powder sample. The JCPDS files used for phase identification were the following: 00-059-0189 for Ti_3SiC_2, 00-052-0875 for Ti_3AlC_2 and 00-029-0095 for Ti_2AlC.

Metallographic cross-sections of the deformed ceramics were ground and polished using a 1-μm diamond suspension in the final step. The microstructure was studied by means of scanning electron microscopy (SEM; XL30-FEG, FEI, The Netherlands). Grain orientation maps were constructed by electron backscatter diffraction (EBSD; Nova 450 NanoSEM, FEI) equipped with an energy dispersive X-ray spectrometer (EDS; EDAX).

IET (IMCE HTVP 1750 IET) was employed to determine the temperature dependence of the dynamic Young's modulus up to 1400 °C, in vacuum, using a heating rate of 5 °C/min. The fracture toughness was determined by means of the single-edge V-notch beam technique (SEVNB). A pre-notch (0.4-mm thickness) was introduced with a diamond saw and the final notch (radius < 20 μm) was created by reciprocating a razor blade through the pre-notch in the presence of a 1-μm diamond abrasive. The reported fracture toughness values present the mean and standard deviation of 4 bars ($45 \times 4 \times 3$ mm^3).

Fig. 2 shows the XRD patterns of the raw powders (a and b), the textured side surface (TSS) (c and d) and the textured top surface (TTS) (e and f) of the deformed ceramics. The analysis of the phase purity of the commercial powders detected the presence of TiC in Maxthal 312® as minor (9 wt%) secondary phase. The TiC amount in the bulk ceramics remained constant during the different processing steps. The Maxthal 211® powder was found to be a mixture of three phases, two of which were MAX phases, i.e., 62 wt% of Ti_2AlC, 30 wt% Ti_3AlC_2 and 8 wt% of Ti_2Al_5. This ratio of $(Ti_2AlC)/(Ti_3AlC_2) \approx 2$ was maintained throughout the different processing steps.

Looking at the relative intensities of the different plane reflections, one may observe a shift towards a preferred crystallographic orientation from the starting powder to the spark plasma sintered disc and then to the deformed material, the shift being most explicit for Ti_3SiC_2. The relative intensities of the peaks in the XRD patterns of the raw powders correspond well to those of the reference JCPDS files. In the non-textured Ti_3SiC_2 (JCPDS 00-059-0189), the (104) peak has the highest intensity. However, in the deformed Ti_3SiC_2, the strongest reflection (008) corresponds to the (001)-direction, which is strongly aligned parallel to the compression axis, resulting in a Lotgering factor of 0.52.

In the case of Maxthal 211®, the change in relative peak intensity was less apparent, due to the close proximity of the (008) and (104) Ti_3AlC_2 peaks with the (103) and (006) Ti_2AlC peaks. Nevertheless, the increase in the intensity of the (002) peak of both Ti_3AlC_2 and Ti_2AlC phases in Fig. 2e is associated with the alignment of the MAX phase grains parallel to the (001)-direction. This texturing is supported by the results of the EBSD analysis of the deformed Maxthal 211® ceramics, as may be seen from the acquired phase mapping (Fig. 3a), phase orientation mapping (Fig. 3b), and the inverse pole figures for Ti_3AlC_2 and Ti_2AlC (Fig. 3c and d, respectively). The MAX phase grains clearly align with their *c*-axis, i.e., the (001)-direction, parallel to the compression axis. The calculated Lotgering factors are 0.51 for Ti_3AlC_2 and 0.49 for Ti_2AlC, respectively.

With the exception of some isolated pores, the materials remain dense after deformation. This fact, combined with the observed grain alignment, indicates that the deformation originates mainly from grain reorientation in the bulk ceramics. Fig. 4a and b show SEM images of deformed grains in the Maxthal 211® ceramic. For

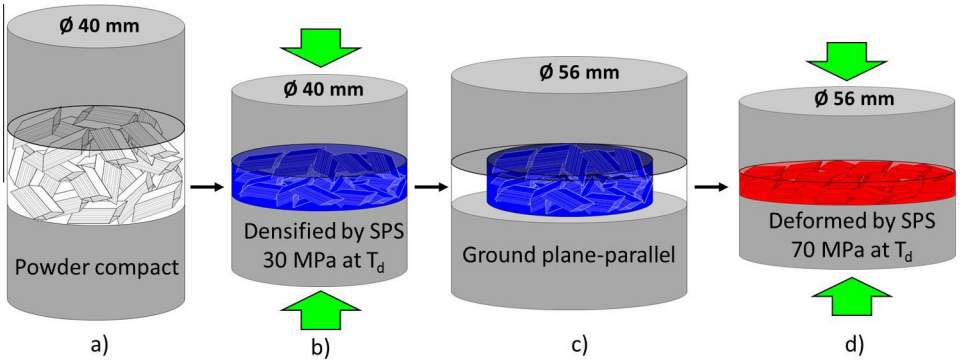

Fig. 1. The approach used in this work to texture MAX ceramics: (a) powder compaction, (b) densification of the powder compact by SPS, (c) the ground, plane-parallel disc loaded in a larger die in the SPS facility, and (d) deformation by hot compression in the SPS facility.