Laminated Object Manufacturing of *in-situ* synthesized MAX-phase composites

Maksim Krinitcyn[a,b,1], Zongwen Fu[c,*,1], Joseph Harris[c], Kirill Kostikov[a], Gennadii A. Pribytkov[a,b], Peter Greil[c], Nahum Travitzky[c,*]

[a] National Research Tomsk Polytechnic University, 30, Lenin ave., Tomsk 634050, Russia
[b] Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences, 2/4, pr. Akademicheskii, Tomsk 634055, Russia
[c] Friedrich-Alexander University Erlangen-Nürnberg, Department of Materials Science, Glass and Ceramics, Martensstrasse 5, D-91058 Erlangen, Germany

ABSTRACT

In this work green tapes comprised of TiC and SiC were further processed by lamination, pyrolysis and liquid silicon infiltration. The *in-situ* synthesis of MAX phase Ti_3SiC_2 by silicon infiltration was investigated and discussed. The synthesis was supported by thermodynamic calculations. The mechanical and microstructural properties of the siliconized composites were studied. The processing route, in combination with Laminated Object Manufacturing (LOM) resulted in the successful fabrication of a three-dimensional gear. The gear showed a defect-free structure with a linear shrinkage of less than 3% relative to the green state. Thus, this approach can be considered as a near-net-shaping process of ceramic components with complex geometries.

1. Introduction

MAX phases are a new group of advanced ceramic materials described by the formula $M_{n+1}AX_n$, where M is an early transition metal, A represents an A-group element, X denotes either nitrogen or carbon and n is an integer [1–3]. MAX phases are natural candidates for structural and high-temperature applications due to their very attractive properties [4–6]. One of the most well-known MAX phases is Ti_3SiC_2, which shows excellent physical and mechanical properties, *e.g.* outstanding toughness and hardness, high refractoriness and good machinability [7–10]. Ti_3SiC_2 can be synthesized from different starting powder blends by using a number of powder-based metallurgical methods, such as self-propagating high temperature synthesis and hot pressing [11–15]. In order to synthesize Ti_3SiC_2, the starting powder blend commonly includes Ti powder due to its high chemical activity [16]. Successful syntheses of MAX phases have been achieved using Ti/Si/C [17–19], Ti/C/SiC [20–22] and Ti/Si/TiC [23–25] as raw materials. Recent works have however, shown the possibility of synthesizing Ti_3SiC_2 using powder blends composed only of TiC and Si powder thereby omitting Ti powder in the initial powder mixture [26–29]. After the high temperature reaction, Ti_3SiC_2 in addition to some secondary phases such as silicon carbide and titanium silicide, due to the stoichiometry of the components in the initial powder mixture, are synthesized [21,28–31].

The aim of this work is to investigate the *in-situ* synthesis of MAX phase composite materials with complex macrostructures by using the forming process of tape casting, lamination and liquid silicon infiltration. Tape casting is widely used for the manufacturing of thin ceramic sheets of large area [32]. After tape casting and drying, green tapes can be further processed *via* punching, lamination and even additive manufacturing, *e.g.* Laminated Object Manufacturing (LOM). As one of the oldest and most established additive manufacturing processes, LOM offers the possibility to use tape cast ceramic green films and allows the manufacturing of bulk materials with complex geometries [33–36]. On the other hand, melt infiltration is one of the preferred techniques to fabricate dense ceramic-metal composites by non-reactive and reactive pressureless and pressure-assisted processing techniques [37–40]. The reactive infiltration of a metal melt into a porous ceramic preform may yield novel *in-situ* near net-shaped composites with tailored microstructures [41,42]. In this study tape-cast ceramic films, comprised of TiC and SiC with different ratios, were processed by LOM, pyrolysis and liquid silicon infiltration. The proposal of this study is the investigation of the *in-situ* synthesis of MAX phases during silicon infiltration.

2. Experimental

For tape casting slurries, ceramic powder blends composed of TiC

Table 1
Composition of the tape casting slurries.

Function	Component	Volume [vol%]			Mass [ma.%]			Density [g/cm³]
		#3	#5	#7	#3	#5	#7	
Powder	TiC	9.00	15.00	21.00	25.53	40.07	53.00	4.93
	SiC	21.00	15.00	9.00	38.79	26.09	14.79	3.21
Solvent	Ethanol-Toluene	54.15	52.67	51.21	25.39	23.26	21.36	0.82
Dispersant	Hypermer KD-1	2.01	2.20	2.38	1.28	1.32	1.36	1.11
Binder	PVB B98	7.11	7.77	8.43	4.50	4.63	4.75	1.10
Plasticizer	Santicizer 9280	6.73	7.36	7.98	4.50	4.63	4.75	1.16

(HC Stark, Goslar, Germany, d_{10}=0.9 μm, d_{50}=2.4 μm, d_{90}=5.4 μm) and SiC (α-SiC, ESK-SIC GmbH, Frechen, Germany, d_{10}=1.8 μm, d_{50}=3.9 μm, d_{90}=6.7 μm) powders with different ratios were used. Three different slurries with a TiC to SiC ratio of 30:70, 50:50 and 70:30 vol% further named #3, #5 and #7, respectively, were studied. The ceramic content was kept at 30 vol% in each slurry. Preparation of tape casting slurries was carried out in three steps. First, the TiC and SiC powder blends were dispersed in an azeotropic solvent mixture composed of 68 wt% ethanol and 32 wt% toluene by using a dispersing agent (Hypermer KD-1, Croda, London, UK). These dispersions were then deagglomerated in a tumbling mixer (Turbula, Willy A. Bachofen AG, Muttenz, Switzerland) with Al_2O_3 milling balls for 24 h. Second, binder (polyvinyl-butyral, B-98, Solutia Inc., St. Louis, USA) and plasticizer (Santicizer 9280, Ferro, USA) were added to the dispersions. Subsequently, the suspensions were homogenized for an additional 24 h in the tumbling mixer. Finally, the homogenized slurries were sieved through a 200 μm screen in order to remove milling balls and degassed under a pressure of 210 mbar for 30 min to yield bubble-free slurries. Table 1 shows the exact composition of the slurries used in this study.

Tape casting was carried out on a tape-casting machine equipped with a dual doctor blade casting head. A silicon-coated PET foil (Mitsubishi Plastics, Inc., Japan) with a thickness of ~100 μm was used as a tape carrier. The front and rear doctor blades were adjusted to a gap height of 1.0 mm and 1.2 mm, respectively. The casting speed was set to 700 mm/min in all cases. After drying, tapes #3, #5 and #7 showed a thickness of ~0.55 mm, ~0.40 mm and ~0.35 mm, respectively. The dried tapes were cut to a square shape of 40×40 mm² for mechanical testing. These green tapes were then laminated by thermal compression (Polystat 200 t; Servitec GmbH, Wustermark, Germany) at 353 K under a pressure of 3.5 MPa for 10 min to yield stacks with a thickness of ~5 mm. Moreover, green tapes of blend #3 were processed *via* laser equipped Laminated Object Manufacturing machine (1015, Helysis Inc., MI, USA) [43,44] in order to fabricate a 3D gear structure. Based on former works [36,45,46], the laser power was set to 20.2 W during LOM. The cutting and roller speeds were 30 mm/s and 60 mm/s, respectively. The roller temperature was kept at 333 K. For cold low pressure lamination double sided adhesive tapes (TESA, Norderstedt, Germany) were used between each single green tape to promote interconnection [47]. Subsequently, the multilayer green laminates were pyrolyzed in an argon atmosphere up to 1173 K for 1 h with a heating rate of 3 K/min followed by sintering in argon at 1873 K with a holding time of 2 h and a heating rate of 4 K/min. After sintering at 1873 K, the samples still showed a porous microstructure due to a small linear shrinkage of less than 3%. In order to achieve the *in-situ* synthesis of MAX phases and to reduce the porosity of the final products, the sintered samples were then infiltrated by liquid silicon under vacuum (< 100 Pa) at 1723 K for 2 h. In samples #3, #5 and #7 the theoretical density, which could be calculated by the density values shown in Table 1, was also measured and verified using a helium pycnometer (AccuPyc II 1340, Micrometrics, USA) before and after sintering. The bulk density of the laminates was determined by measuring the weight and geometry of the samples using calipers.

The porosity was calculated from the measured bulk and theoretical densities by using the following formula

$$P = 1 - \frac{\rho_{bulk}}{\rho_{theo}}$$

where P denotes the porosity, ρ_{theo} the theoretical density and ρ_{bulk} the bulk density. The microstructure and phase composition of the composites after sintering and silicon infiltration were analyzed by scanning electron microscope (SEM, Quanta 200, FEI, Czech Republic equipped with energy dispersive analysis (EDS)) and by using the Bragg-Brentano X-ray diffractometer (D500, Siemens, Germany) at a scanning rate of 1°/min over a 2θ range of 20–70°. The mechanical properties of the siliconized multilayer laminates were measured. Bars with dimensions of 2×2.5×27 mm³ were cut out of the fabricated composites and ground to a 15 μm diamond finish. The tensile surfaces of the samples were then polished to a 3 μm diamond finish prior to bending. Average values of bending strength, Young's modulus and hardness were calculated from at least seven measurements according to DIN 843-1 (four-point bending test), DIN 843-2 (ultrasonic test) and DIN 843-4 (Vickers hardness test).

3. Results

Multilayer laminate MAX-phase structures were fabricated using tape casting, thermal compression and heat treatments, with different initial powder ratios. After tape casting and drying, samples formed from powder mixtures #3, #5 and #7 showed a porosity of ~24%, ~22% and ~21%, respectively. After pyrolysis and sintering in argon, the porosity in samples #3, #5 and #7 increased to ~43%, ~39% and ~40%, respectively, owing to the thermal degradation of organic additives in green tapes during thermal treatments. Post silicon melt infiltration of the multilayer laminates with the composition #3 resulted in the defect-free and nearly dense composites. The siliconized samples #5 and #7 showed structural deformation such as cracks and delamination, thought to be caused by volume changes due to the *in-situ* reaction between TiC and molten Si at high temperatures (see Eqs. (1) and (2) [26,31]).

$$3\,TiC + 2\,Si\,(liquid) = Ti_3SiC_2 + SiC \tag{1}$$

$$TiC + 3\,Si\,(liquid) = TiSi_2 + SiC \tag{2}$$

The occurrence of this *in-situ* reaction during liquid silicon infiltration was verified by XRD analysis (Fig. 1). Before silicon infiltration, all samples regardless of composition showed similar XRD patterns, in which only SiC and TiC phases were found. In all three siliconized samples the TiC phase disappeared, indicating a complete reaction of TiC with molten Si. After silicon infiltration SiC, Si and TiSi₂ phases were detected in all three samples. Siliconized samples #5 and #7 clearly showed the presence of Ti₃SiC₂, which was not detected in sample #3 after infiltration.

The observations from XRD analyses were corroborated by SEM and EDS analysis. Fig. 2 shows the microstructure of the multilayer TiC/SiC laminates with different compositions before and after silicon