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Nitride and carbide preforms for infiltration process

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ABSTRACT

Purpose: Infiltration of molten metals into porous ceramic preforms is the only technique suitable for the fabrication of high volume fraction of ceramic materials in MMCs. The most popular material for porous preforms is Al_2O_3 because of its low cost. Infiltration process generates thermal stresses in the Al_2O_3 preforms. The thermal shock resistance of Al_2O_3 is lower than for Si_3N_4 or Al_2O_3/TiC+TiN materials. The aim of this study is to obtain the nitride and carbide base preforms material for the infiltration process of molten aluminium alloys.

Design/methodology/approach: The method of obtaining the silicon nitride and oxide-carbonitride porous preform for the infiltration process is the free sintering process. Some of selected properties of this material are presented. The preforms were produced by the mixing of ceramic powders with organic binders, followed by forming, drying and firing. Ceramic preforms of 65% porosity were produced. Microscopic investigations revealed good joints between the ceramic particles.

Findings: The material consist of the base component (90 wt.% of α-Si_3N4, 5 wt.% of Al_2O_3, 5 wt.% of Y_2O_3), which were mixed with 40 wt.% of polyethylene glycol 6000 (mixed in Turbula) porosity is 25.7 %. The higher value of porosity 66.6% was obtained for material with 20 wt.% tylose. The grain size of Si_3N_4 and method of the mixtures preparing (mixing with or without milling) have the significant influence on compacts' porosity. For 68 wt.% Al_2O_3, 2 wt.% ZrO_2 and 30 wt.% Ti(C,N) with addition of glycol 6000, the value of porosity is 67%. α-Si_3N_4 material produced shows strong bonding with aluminium and AlSi11 aluminium alloy.

Practical implications: Pressureless infiltration of molten metals into ceramics is the most cost-effective approach to liquid-metal processing of MMCs. Metal matrix composites are applied widely in aircraft production technologies and defence technology.

Originality/value: Compared to widely used alumina performs, those made from non-oxide ceramics demonstrate better physicochemical compatibility with aluminium alloys. New kinds of porous materials were obtained.

Keywords: Porous ceramics; Non-oxide preforms; Si_3N_4; Alumina/carbonitrides; Wettability

MATERIALS

1. Introduction

Porous ceramics are used as a gas/liquid separators, catalyst supports and molecular sieves, for bone replacement and many other applications. There are several approaches for the fabrication of the micro/macro porous ceramics such as controlling of the size of ceramics particles to maintain constant pores size and its distribution among the particles, reducing of forming pressure or/and sintering time, mixing of ceramic powders either with bubble former or with additional organic particles, which vaporize and contribute to the formation of small homogeneously distributed pores [1].

Composite materials reinforced by ceramic phase are characterized by the very good mechanical properties over a wide range of temperatures, and they are applied widely in aircraft production technologies and defence technology [2]. Two basic methods are used in production of metal-matrix composites (MMCs): casting methods and powders metallurgical methods [3-6]. Pressureless infiltration of molten metals into ceramics is the most cost-effective approach to liquid-metal processing of MMCs. Infiltration of molten metals into porous ceramic preforms is the only technique suitable for the fabrication of high volume fraction of ceramic phase in MMCs structure. Molten metal infiltration can be classified into three categories, based on the source of driving force pressure assisting, such as vacuum driven and pressureless or capillarity driven [7-9]. The most common material used for the production of porous preforms is Al_2O_3 because of its low cost thus porous ceramic aluminium oxide is the relatively cheap reinforcement [10]. However, infiltration process generates thermal stresses in the Al_2O_3 preforms while the Al/Al_2O_3 interfaces formed at low processing temperatures are weak. Moreover, porous materials applied for the infiltration process should have good thermal shock resistance, the open pore structure inside preforms, good mechanical properties and good physico-chemical compatibility with infiltrated metal. In spite of excellent properties, the potential of porous ceramics has not been fully realized, because of their defects such as uncontrolled pore size and their inhomogeneous distribution, both contributing to decrease of mechanical properties of produced materials [1].

In these study, silicon nitride and aluminium oxide containing 30 wt.% of titanium carbonitride were chosen as reinforcing materials in order to produce porous preforms for infiltration process [11]. The strongly covalent bonds of Si_3N_4 produce a number of desirable engineering properties such as high strength, thermal stability up to approximately 2120 K, good resistance to oxidation and thermal shocks, high thermal conductivity and low thermal expansion coefficient, while its modulus of elasticity is greater then that of many metals. In order to achieve fully dense material by solid-state free sintering such additives as oxides (MgO, Y_2O_3, CeO_2, ZrO_2, Al_2O_3) or nitrides (AlN, TiN, ZrN, CrN, Mg_2N_3) are required. It makes possible to sinter silicon nitrides at 2150-2400K and at pressure up to 2 MPa with resulting density higher than 99.3% of the theoretical one [3] and corresponding high hardness at temperatures 870–1270 K and moderate thermal expansion coefficient. Sobczak et al. investigated the factors affecting interaction in the Al/Si_3N_4 system by comparing pure Si_3N_4 to Si_3N_4 containing 2wt.% of Y_2O_3 as sintering aid [12]. Introduction of Y_2O_3 improves the mechanical properties of Al/nitride couples but reactivity of this system decreases because a dense reaction-product region forms that contains interspersed fine AlN and Al_2O_3 precipitates [12].

Hard particles of titanium carbide and/or nitride in aluminium oxide increase the material's hardness at temperature up to 1073K, when compared to pure oxide ceramics. In the same time, the fracture toughness and bending strength is improved through crack impediment, crack deflection or crack branching caused by dispersed hard particles [13]. The higher hardness together with higher toughness of such composite material increases its resistance to abrasive and erosive wear considerably. And its influence on the lower thermal expansion and higher thermal conductivity contribute to better thermal shock resistance and thermal shock cycling capabilities when compared to nonreinforced oxide ceramics, Table 1 [13].

In [12] the sessile drop method was employed to study the wetting of silicon nitride with liquid aluminum or aluminum alloys. It was demonstrated that molten aluminum reacts with pure Si_3N_4 to form a mixture of AlN, Si, and Al-Si. This reaction is responsible for good wetting properties but also for the formation of an unfavorably thick reaction product region in the Al/Si_3N_4 couples. Introduction of 2 wt.% of Y_2O_3 to Si_3N_4 in order to improve mechanical properties of silicon nitride ceramics also improves the shear strength of Al/Si_3N_4 interfaces. On the other hand, the reactivity of yttria containing substrates with Al are much less due to the formation of dense reaction product region, composed of interspersed fine AlN and Al_2O_3 particles [12].

The main purpose of this study was to obtain Si_3N_4 porous preforms suitable for the infiltration by aluminum and aluminum alloys. The influence of various organic compounds on porosity of silicon nitrides and the possibility for the infiltration process by molten aluminum and aluminum AlSi11 alloy were investigated.

Table 1.
Comparison of the physical properties of oxide ceramics with aluminum oxide/titanium carbide composite [12]

Alumina materials	Oxide Ceramic $Al_2O_3+ZrO_2$	Al_2O_3/TiC composite
Hardness (Vickers)	2000	2200
Bending strength, N/mm^2	350	600
Fracture toughness, mN/mm^2	4.5	5.4
Thermal conductivity, $Wm^{-1}K^{-1}$	30	35

2. Experimental procedure

Mixture of powders were composed of 90 wt.% of α-Si_3N_4 (H.C.Starck, M11, 0.6 μm or B7, 1,1 μm), 5 wt.% of Al_2O_3 (Alcoa, A16SG, <0.5 μm) and 5 wt.% of Y_2O_3 (Fluka) and of 68 wt.% of Al_2O_3 (Alcoa, A16SG, <0.5 μm), 2 wt.% of ZrO_2 (Flucka, <0.5 μm) and 30 wt.% of Ti(C,N) (H.C.Starck). The powders were milled in the alumina rotary mill in the ethyl alcohol medium with porous forming additives:

- triethanolamine (waterless $C_6H_{15}N$, POCH),
- polyethylene glycol 3000 (Fluka),
- polyethylene glycol 6000 (PS PARK),
- polyethylene glycol 10000 (Fluka),
- methocel MC (Fluka),
- polyvinyl alkohol (Fluka),
- tylose MH 1000 (Fluka).

For alumina with carbonitride material, l5 wt.% of glycol 400 to the initial mixture was added. After milling, the powder mixtures were dried and granulated. Material discs of 14 mm (samples for strength studies) and 23 mm diameter were formed by single action pressing at pressure of 30 MPa and dried for 48 hours at 498 K. Initial sintering was carried out using the electric furnace PSK–31 (for alumina base material) and at Baltzers MOV3 (for Si_3N_4 base material), at the heating rate of 100 K/h, in a two step process at 973 K and 1473 K. Next, Si_3N_4 base samples were free-sintered at nitride boride packing material in N_2 atmosphere at 1880 K for 60 min, using the GERO HTK 8/22G furnace. $Al_2O_3Ti(C,N)$ samples were free-sintered at 1970 K for 1h using the Baltzers MOV3 high vacuum furnace.

Densities and porosities of sintered samples were measured according to the Archimedes principles [14]. For Si_3N_4 samples characterized by the highest and the lowest value of porosity, the compressive strength were measured using INSTRON TT-DM apparatus with initial rate of strain 10^{-4} s^{-1}.

The sessile drop method was employed to study the wetting behaviour of Al (99,9999%) and its AlSi11 alloy (11 wt.% Si). For these studies, the dense substrates of the same composition as porous preforms were made using the same starting powder materials for compacting the substrates as well as the same conditions for their free sintering.

The wettability studies were done under vacuum at a temperature of 1123 K and 1173 K for 120 min. The solidified sessile drop samples were used for characterization of structure and mechanical strength of interfaces.

The samples were bisected perpendicularly to the substrate at the mid-plane of the contact circle. The first half of each sample was utilized for evaluation of mechanical properties of interfaces by improved push-off shear test. In the improved push-off shear test, the sample was placed in the holder of special design and loaded in INSTRON 1115 machine. A load was applied to the flat end of the bisected couple at the constant rate of 1 mm·min^{-1} and the load versus displacement data was digitally recorded until failure under shear occurred. Assuming uniform distribution of shear stress along the line during the push-off test, the shear strength was calculated by dividing the maximum load with lateral area estimated from geometry of the drop/substrate contact under 10x magnification [15].

3. Results and discussion

Because of decomposition of additives or very low porosity of produced Si_3N_4 and $Al_2O_3Ti(C,N)$ materials (below 20%), methocel, polyvinyl alcohol, triethanolamine and glycol 10000 and 3000 were not considered for further examination and only tylose and glycol 6000 were choose for sintering process.

Some selected properties of porous Si_3N_4 and $Al_2O_3Ti(C,N)$ samples containing various amount of porous forming additives are presented in Table 2 and Table 3. The most beneficial porous microstructure, characterized by open porosity was obtained for Si_3N_4 containing 20 wt.% of tylose in Turbula milling process, for Si_3N_4 containing glycol 6000 in Turbula milling process and for $Al_2O_3Ti(C,N)$ with addition of 25 wt.% of tylose. For all samples, the infiltration process in vacuum by fuchsine was carried out, showing complete infiltration in all bulk of each sample. Compressive strength of Si_3N_4 of 66.6% porosity was in the range of 1-2.5 MPa while for Si_3N_4 of 25.7% porosity, it was in the range of 6-13 MPa.

In Table 4, the contact angle measurements and the results of push-of shear strength tests are presented for Al (99,9999%) and AlSi11 and nonporous substrates of $\alpha-Si_3N_4$ (H.C.Starck, M11, 0.6 μm) containing 5 wt.% of Al_2O_3 (Alcoa, A16SG, <0.5 μm), 5 wt.% of Y_2O_3 (Fluka).

Wetting and mechanical strength of the metal/ceramic interfaces are a key factor for the fabrication of aluminum matrix composites by liquid phase processes. The results obtained for contact angle and shear strength of selected couples are very promising for application of the produced porous preforms in manufacture of composite materials of the Al-Si_3N_4 system since there is a strong metal/ceramic bonding, which depends on conditions of the experiment as shown in Table 4 and in Figures 1a and 1b.

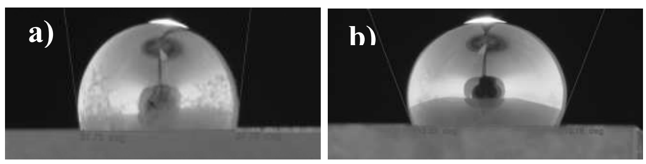

Fig. 1. Aluminium drop on dense silicon nitride substrate containing 90 wt.% α-Si_3N_4, 5 wt.% Al_2O_3, 5 wt.% Y_2O_3 recorded in contact angle measurements by sessile drop method:
a) 1173K, 120 min, θ=97°, b) 1123 K, 120 min, θ=110°

Table 2.
Apparent density, open porosity, percent of theoretical density for compacts with 90 wt.% $\alpha-Si_3N_4$ (H.C. Starck, M11i B7) submicropowders, 5 wt.% Al_2O_3 (Alcoa, A16SG, particles size <0,5 μm), 5 wt.% Y_2O_3 (Fluka)

Type of the porous forming additives	Additives, wt. %	Apparent density, g/cm^3	Open porosity, %	% of theoretical density, %	Density, %
Tylose **m***	20	1.685	46.5	51.20	48.8
Tylose **t****	20	1.100	66.6	33.4	66.6
Glycol 6000 **t****	40	2.444	22.2	74.3	25.7
Tylose **m***	20	1.632	47.7	49.6	50.4
Tylose **t****	20	1.213	62.8	36.9	63.1

m* - the ball mill, mixing and milling process,
t* - Turbula, only mixing process.

Table 3.
Apparent density, open porosity, percent of theoretical density for compacts with 68 wt.% Al_2O_3 (Alcoa, A16SG, particles size <0,5 μm), 2wt.% of ZrO_2 (Flucka, <0.5 μm) and 30 wt.% of Ti(C,N) (H.C.Starck)

Type of the porous forming additives	Additives, wt. %	Apparent density, g/cm^3	Open porosity, %	% of theoretical density
Tylose	25	1.55	36.0	64.0
Tylose	20	1.82	42.1	57.9
Glycol 6000	20	2.92	67.4	36.6
Tylose +Glycol 6000	5+25	1.97	45.5	54.5

Table 4.
Contact angle measurements and results of push-off shear strength tests for selected Al/ceramic and AlSi11/ceramic couples

Metal/substrate couple	Experimental conditions			Contact angle θ, deg.	Shear strength, MPa
	Temperature, K	Duration, min	Vacuum, hPa		
Al/Si_3N_4+5wt%Y_2O_3+5wt%Al_2O_3	1173	120	$3{,}22x10^{-6}$-$7{,}72x10^{-7}$	97	45.86
Al/Si_3N_4+5wt%Y_2O_3+5wt%Al_2O_3	1123	120	$4.28x10^{-6}$–$8.37x10^{-7}$	110	48.21
$AlSi11/Si_3N_4$+5wt%Y_2O_3+5wt%Al_2O_3	1123	120	$5.17x10^{-6}$–$1.01x10^{-6}$	128	81.77
$AlSi11/Si_3N_4$+5wt%Y_2O_3+5wt%Al_2O_3	1173	120	$1.79x10^{-6}$–$7.00x10^{-7}$	81	189.77
$Al/Al_2O_3Ti(C,N)$	1173	120	$9.28x10^{-6}$–$5.09x10^{-6}$	120	
$Al/Al_2O_3Ti(C,N)$	1123	120	$9.19x10^{-6}$–$5.58x10^{-6}$	150	

4. Conclusions

All silicon nitride and alumina-carbonitride materials are characterized by the open porosity. The highest value of porosity 66.6% was obtained for Si_3N_4 base material with 20 wt.% tylose. Both the grain size of Si_3N_4 and method of the mixtures preparing (mixing with or without milling) have a significant influence on porosity of compacts. The wettability studies shown the influence of the experiment conditions on the contact angle and shear strength values for aluminum or aluminum alloys/Si_3N_4 couples. Results of push-of shear strength studies for Si_3N_4 /AlSi11 indicates a strong bonding between aluminum alloys and silicon nitride substrates.

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