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PRESSURELESS REACTIVE SINTERING OF TiAl-TiC AND Ti_3Al-TiC COMPOSITES

REAKCIJSKO SINTRANJE KOMPOZITOV TiAl-TiC IN Ti_3Al-TiC PRI ATMOSFERSKEM TLAKU

Varužan Kevorkijan[1], **Srečo Davor Škapin**[2]
[1]Independent Researching plc, Betnavska cesta 6, 2000 Maribor, Slovenia
[2]Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
varuzan.kevorkijan@siol.si

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TiAl and Ti_3Al based composites reinforced with volume fractions 10–50 % of TiC particles were successfully prepared by pressureless reaction sintering of reaction mixtures consisting of commercial titanium aluminide powders (TiAl with traces of Ti_3Al and the single phased Ti_3Al) blended with the appropriate amount of ceramic reinforcement, 5–10 % of Al powder and, in some cases, also 5 % of Ti powder added as sintering agents. The green compacts made from the blended powder mixture were reaction sintered at 1300 °C for 2 h in an Ar + 4 % H_2-rich environment using a vacuum furnace. The morphology of the commercial powders and the microstructure of the as-sintered composites were studied by scanning electron microscopy and X-ray diffraction analysis.

The pressureless sintering of as-received TiAl and Ti_3Al powders resulted in samples with 10–15 % of the retained porosity. On the other side, the addition of 10 % of TiC particles to the sintering mixture improved pressureless densification enabling fabrication of composite samples with >95 % of theoretical density without addition of free aluminium. In these particular cases, densification was promoted by chemical reactions between TiAl or Ti_3Al and TiC leading to the formation of $Al_2Ti_4C_2$ and Ti_3AlC secondary bonding phases, respectively. However, as it was confirmed by sintering experiments, for successful (>95 % of theoretical density) ***pressureless*** densification of composite samples with more than 10 vol. of TiC, the addition of 5–10 % of free aluminium and 5 % of titanium, depending on the actual amount of TiC reinforcement, was necessary. The addition of Al and Ti promotes liquid reaction sintering and the formation of secondary Ti-Al-C bonding phases in an Al-Ti co-continuous network.

The tensile properties and Vickers hardness of composite samples were measured at room temperature. The improvement in tensile properties (except elongation) and Vickers hardness was found to correlate with the amount of TiC reinforcement in the matrix.

Key words: TiAl-TiC and Ti_3Al-TiC composites, pressureless reaction sintering, secondary bonding phases, microstructure, room temperature tensile properties, Vickers hardness

Z reakcijskim sintranjem smo pripravili goste kompozitne materiale (z gostoto večjo od 95 % teoretične gostote) na osnovi spojin TiAl in Ti_3Al, ojačanih z ustrezno količino keramične faze, z volumenskim deleže, Al-prahu 5–10 % in, v določenih primerih, tudi z dodatkom 5 % Ti-prahu. Uporabljen komercialni TiAl prah je vseboval sledove Ti_3Al, medtem ko je bil prah Ti_3Al enofazen. Dodatek prahov Al in Ti k izhodnim sestavam je omogočal boljše sintranje. Izhodne homogenizirane sestave smo enoosno stisnili v pelete in jih reakcijsko sintrali v vakuumski peči pri 1300 °C, 2 h v zaščitni atmosferi Ar + 4 % H_2. Morfologijo, sestavo in velikost delcev izhodnih prahov ter mikrostrukturo pripravljenih vzorcev smo analizirali z elektronskim vrstičnim mikroskopom in energijsko disperzijsko analizo ter z rentgensko praškovno difrakcijo.

Sintrani vzorci na osnovi spojin TiAl in Ti_3Al izkazujejo od 10 % do 15% poroznosti. Pri dodatku 10 % TiC k tem spojinam pa dobimo goste vzorce z gostoto več kot 95 % teoretične. V teh sistemih potečejo med segrevanjem reakcije med TiAl oziroma Ti_3Al in TiC, pri čemer nastajajo vezne sekundarne faze $Al_2Ti_4C_2$ in Ti_3AlC. Ugotovili smo, da za pripravo gostih kompozitnih materialov z reakcijskim sintranjem (>95 % teoretične gostote) pri vičjem dodatku kot 10 % TiC potrebujemo še 5–10 % Al in 5 % Ti, kar je odvisno od količine TiC. Dodana elementa Al in Ti omogočata reakcijsko sintranje v tekoči fazi in tvorbo sekundarnih veznih faz na osnovi Ti-Al-C, dispergiranih ko-kontinuirni matriki Al-Ti.

Mehanske lastnosti (natezno trdnost in trdoto) smo merili pri sobni temperaturi. Izboljšanje natezne trdnosti in Vickersova trdota sta sorazmerni, ratezek pa obratno sorazmeren večanju vsebnosti TiC v kompozitih.

Ključne besede: TiAl-TiC in Ti_3Al-TiC kompoziti, reakcijsko sintranje pri atmosferskem tlaku, sekundarne vezne faze, mikrostruktura, mehanske lastnosti pri sobni temperaturi, trdota po Vickersu

1 INTRODUCTION

TiAl- and Ti_3Al-based intermetallic-matrix composites (IMCs) reinforced with ceramic particles have several advantages over conventional titanium alloys, such as higher elastic modulus, lower density, better mechanical properties at elevated temperatures, and higher oxidation resistance [1,2]. However, bringing these attractive intermetallic composite matrices into commercial use largely depends upon the availability of practical and competitive processing routes. Due to difficulties in production of IMCs by foundry methods and the high cost of powder processing, the elemental powder metallurgy (EPM) route has been gaining more and more attention. According to the EPM processing route, near-net shape IMC products can be fabricated by the consolidation and forming of blended Ti and Al elemental powders and ceramic reinforcement, followed by a subsequent reactive synthesis and sintering process. However, due to the large difference between the partial diffusion coefficients of Ti and Al, the synthesis of TiAl/Ti_3Al alloys via reactive sintering follows a mechanism in which Al atoms move into the Ti lattice, thus leading to the formation of Kirkendall diffusion pores [5]. Although hot isostatic pressing (HIP) and other pressure-assisted methods have been reported to be effective in eliminating the porosity of reactively sintered TiAl- and Ti_3Al-based composite matrices [6–9], their high cost and low production efficiency make them unsuitable for commercial use.

In the present study the assumption was made that, if sufficient reactivity in the system is provided, ***pressureless*** sintered TiAl- and Ti_3Al-based IMCs with >95 % T. D. may be successfully obtained, starting from TiAl and Ti_3Al powders mixed with suitable ceramic reinforcement (such as TiC) and sintering additives (Al and Ti powders). During high temperature presureless sintering, TiC and Al react with the TiAl and Ti_3Al matrix forming different bonding phases. These promote further densification and elimination of porosity in the system.

Thus, the aim of this study was to investigate the potential of the pressureless sintering method in fabrication of fully dense, high quality TiAl- and Ti_3Al-based IMCs by applying reaction mixtures consisting of ***commercial*** titanium aluminide powders mixed with various amounts (volume fractions from 10 % to 50 %) of TiC ceramic particles, 5–10 % of Al and 5 % of Ti sintering agent.

2 EXPERIMENTAL

Composites were prepared with blending commercially available powders of either TiAl or Ti_3Al with TiC powder in appropriate amounts to create titanium aluminide-based matrices with volume fractions (10, 20, 30, 40 and 50) % of TiC discontinuous reinforcement.

The powder blends were thoroughly mixed and subsequently cold compacted. In all cases, the reaction synthesis was conducted at 1300 °C for 2 h in an Ar + 4 % H_2-rich environment using a vacuum furnace.

The as-synthesized composite samples were cut, machined and polished in accordance with standard procedures.

Microstructural characterization was performed by scanning electron microscopy (SEM), whereas X-ray diffraction (XRD) measurements were applied to the samples to identify the phases and their crystal structure.

The specimens for optical microscope (OM) observation were electrolytically polished in a solution of 95 % CH_3COOH and 5 % $HClO_4$, and then etched in a solution of 5 % HNO_3, 15 % HF, and 80 % H_2O. The main grain sizes were measured by the linear intercept method.

The specimens for XRD were abraded with SiC paper and were then subjected to diffraction using CuK_a radiation.

Quantitative determination of the volume percentage of the retained porosity was performed by analysing OM and SEM micrographs of infiltrated composites using the point counting method and image analysis and processing software.

The tensile properties (tensile strength, 0.2 % tensile yield strength and elongation) of the composite specimens were determined in accordance with the ASTM test method, E8M-96. The tensile tests were conducted on drum shaped tension-test specimens 3.5 mm in diameter and 16 mm gauge length using an automated servo-hydraulic tensile testing machine with a crosshead speed of 0.254 mm/60 s.

The Vickers hardness (*HV*) measurements were performed at room temperature on polished composite samples as an average of 15 indentations. These measurements were made on an automatic digital tester using a pyramidal diamond indenter with a facing angle of 136° A 0.025 kg indenting load, 50 µm/s load applying speed, and a 15 s load holding time.

3 RESULTS AND DISCUSSION

3.1 Morphology of titanium aluminide powders applied

The as-received powders are non-agglomerated, with well shaped individual particles having similar particles

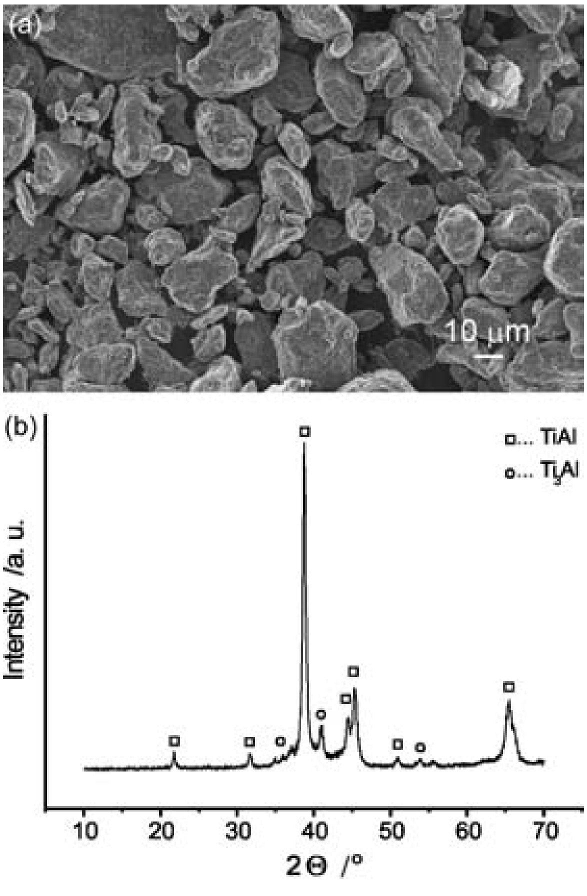

Figure 1: (a) SEM micrograph of as-received commercial TiAl powder and (b) XRD spectra of the TiAl powder showing traces of Ti_3Al compound

Slika 1: (a) SEM-posnetek komercialnega prahu TiAl in (b) XRD-spekter prahu TiAl s sledmi spojine Ti_3Al

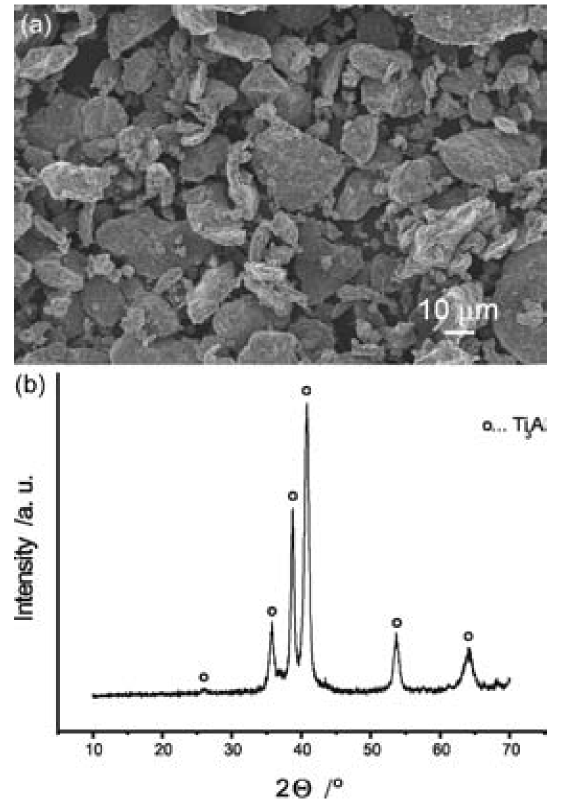

Figure 2: (a) SEM micrograph of as-received commercial Ti_3Al powder and (b) XRD spectra of the Ti_3Al powder

Slika 2: (a) SEM-posnetek komercialnega prahu Ti_3Al in (b) XRD-spekter prahu Ti_3Al

size (**Figure 1 and 2**). TiAl was with traces of Ti_3Al while Ti_3Al powder was single phase.

3.2 Microstructure development in IMCs reinforced with TiC

Generally, the microstructure of IMCs consists of an intermetallic matrix (based on an ordered intermetallic compound or a multiphase combination of intermetallic compounds), the ceramic particulate reinforcement and an interfacial region with the secondary phases formed during reactive sintering.

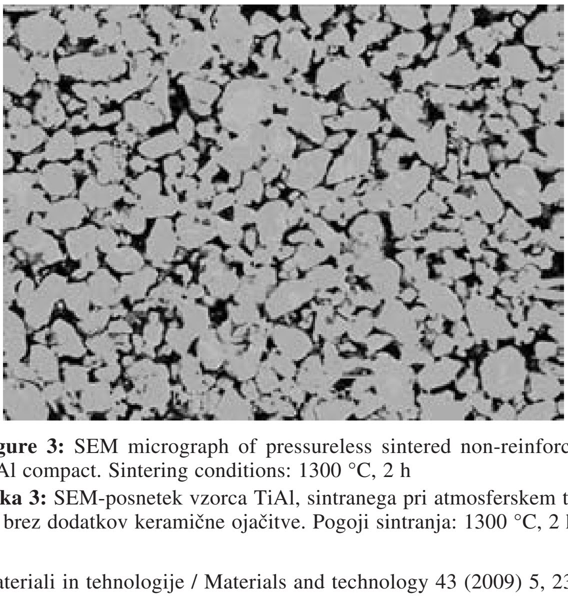

Figure 3: SEM micrograph of pressureless sintered non-reinforced TiAl compact. Sintering conditions: 1300 °C, 2 h

Slika 3: SEM-posnetek vzorca TiAl, sintranega pri atmosferskem tlaku brez dodatkov keramične ojačitve. Pogoji sintranja: 1300 °C, 2 h

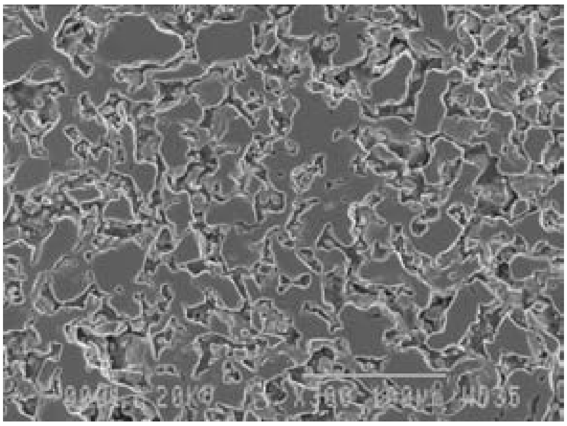

Figure 4: SEM micrograph of pressureless sintered non-reinforced Ti_3Al compact. Sintering conditions: 1300 °C, 2 h

Slika 4: SEM-posnetek vzorca Ti_3Al, sintranega pri atmosferskem tlaku brez dodatkov keramične ojačitve. Pogoji sintranja: 1300 °C, 2 h

Cost-effective, pressureless densification of TiAl and Ti_3Al powders, as well as of TiAl and Ti_3Al powders blended with ceramic particulates most often results in

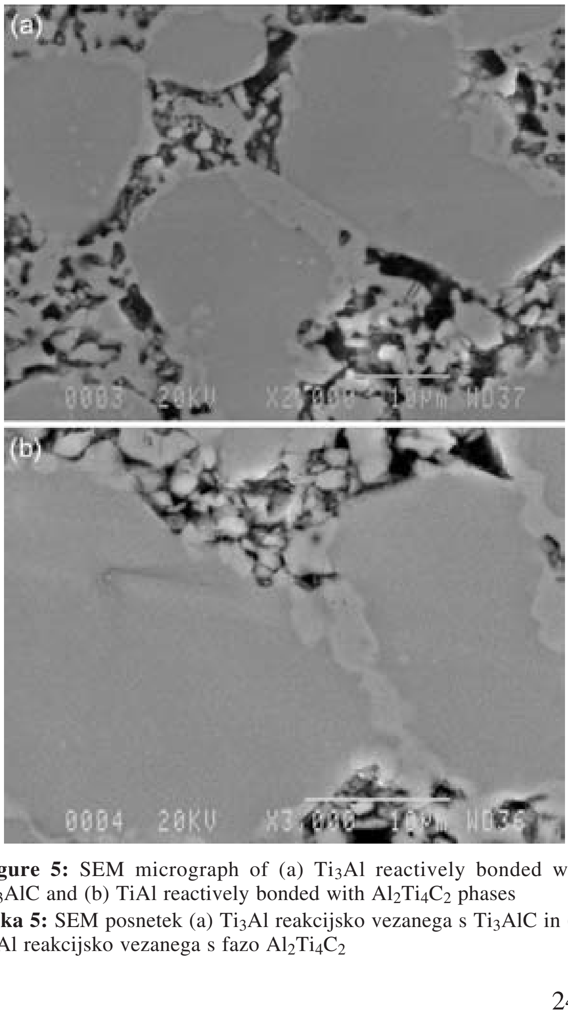

Figure 5: SEM micrograph of (a) Ti_3Al reactively bonded with Ti_3AlC and (b) TiAl reactively bonded with $Al_2Ti_4C_2$ phases

Slika 5: SEM posnetek (a) Ti_3Al reakcijsko vezanega s Ti_3AlC in (b) TiAl reakcijsko vezanega s fazo $Al_2Ti_4C_2$

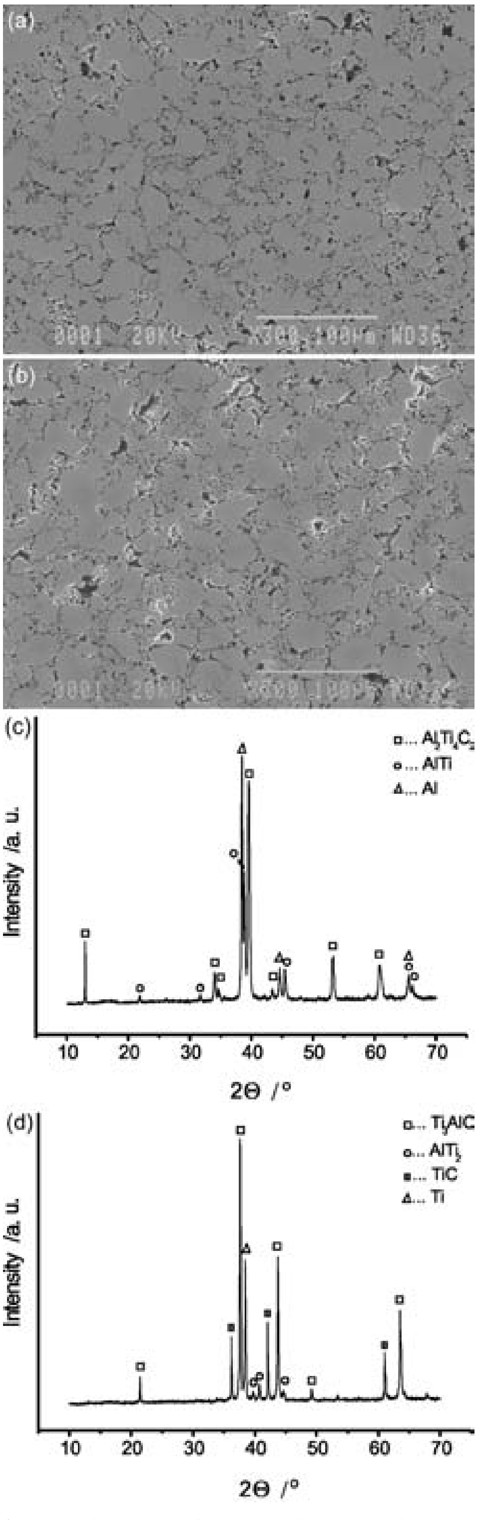

Figure 6: SEM micrograph of samples with the starting composition: (a) 90 % TiAl + 10 % TiC and (b) 90 % Ti_3Al-10 % TiC sintered up to 95 % T. D. Sintering conditions: 1300 °C, 2 h, (c) XRD spectra of the sample with the starting composition 90 % TiAl + 10 % TiC and (d) XRD spectra of the sample with the starting composition 90 % Ti_3Al + 10 % TiC

Slika 6: SEM-posnetek vzorcev z začetno sestavo: (a) 90 % TiAl + 10 % TiC in (b) 90 % Ti_3Al-10 % TiC sintranih nad 95 % T. G. Pogoji sintranja: 1300 °C, 2 h, (c) XRD-spekter vzorca začetne sestave 90 % TiAl + 10 % TiC in (d) XRD-spekter vzorca začetne sestave 90 % Ti_3Al + 10 % TiC

material that is not free of porosity. Typical microstructures of pressureless sintered non-reinforced TiAl and Ti_3Al samples made from the commercial powders used in this work are presented in **Figures 3 and 4**. The samples obtained are porous (85–90 % T. D.).

However, based on the experimental results of pressureless sintering of TiAl-TiC and Ti_3Al-TiC samples, it was recognized that addition of TiC improves the densification of the system, enabling pressureless fabrication of composites with more than 95 % of T. D., **Table 1**. Until the amount of TiC reinforcement in TiAl and Ti_3Al based composites not overcome 10 %, pressureless sintering was completed without addition of any sintering agents. Densification was promoted by chemical reactions between TiAl or Ti_3Al and the formation of $Al_2Ti_4C_2$ and Ti_3AlC secondary phases:

$$2TiAl + 2TiC = Al_2Ti_4C_2 \tag{1}$$

$$2Ti_3Al + TiC = Ti_3AlC + AlTi_2 + 2Ti \tag{2}$$

As evident in **Figures 5 a,b**, the *in situ* formed $Al_2Ti_4C_2$ and Ti_3AlC phases are involved in bonding of intermetallic grains and elimination of Kirkendall diffusion pores resulting in samples with density about 98 % T. D., **Table 1**.

The resulting microstructures of the sintered composite samples with 10 % of TiC particulate are presented in **Figure 6 a, b**.

As evident in **Figure 6 a,b**, the sintered samples possessed a near uniform distribution of equiaxial intermetallic grains, secondary phases and retained porosity. Larger pores were located mostly at the interface region, while high magnification observation revealed the presence of numerous fine pores uniformly distributed through the secondary phase, **Figure 7**.

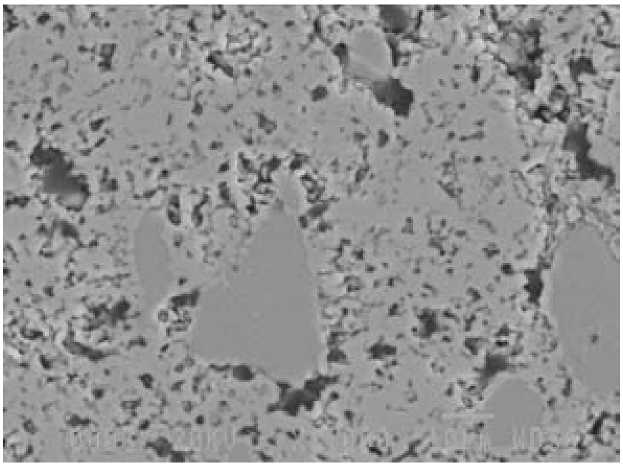

Figure 7: SEM micrograph of porous secondary phase between TiAl grains. Numerous fine pores are nearly uniformly distributed, including some larger ones at the interface. The grey inclusions are solidified aluminium.

Slika 7: SEM-posnetek porozne sekundarne faze med zrni TiAl. Številne fine pore so skoraj enakomerno razporejene, vključno z nekaterimi večjimi na fazni meji. Vključki sive barve so iz strjenega aluminija.

Table 1: Average room temperature tensile properties and Vickers hardness of various laboratory prepared composite samples
Tabela 1: Povprečne vrednosti mehanskih lastnosti, izmerjene pri sobni temperaturi in vrednosti trdote po Vickersu vzorcev kompozitov

Initial chemical composition in volume fractions (%)	Retained porosity (%)	*E* (GPa)	Tensile strength (MPa)	0.2 % tensile yield strength (MPa)	Vickers hardness (GPa)	Elongation in 50 mm (%)
$90Ti_3Al + 10TiC$	4.1 ± 0.4	118 ± 12	474 ± 47	323 ± 32	2.9 ± 0.3	0.5 ± 0.05
$75Ti_3Al + 20TiC+5Al$	3.9 ± 0.4	158 ± 16	518 ± 52	389 ± 39	3.6 ± 0.4	0.3 ± 0.03
$60Ti_3Al + 30TiC+10Al$	3.6 ± 0.4	194 ± 20	547 ± 55	419 ± 42	5.8 ± 0.6	0.2 ± 0.02
$50Ti_3Al + 40TiC+10Al$	3.3 ± 0.3	222 ± 22	596 ± 60	448 ± 45	6.2 ± 0.6	0.1 ± 0.01
$40Ti_3Al + 50TiC+10Al$	4.4 ± 0.4	253 ± 25	619 ± 62	490 ± 49	6.5 ± 0.7	0.1 ± 0.01
90TiAl + 10TiC	4.0 ± 0.4	196 ± 20	339 ± 34	273 ± 27	2.7 ± 0.3	0.5 ± 0.05
75TiAl + 20TiC+5Al	3.8 ± 0.4	215 ± 22	368 ± 37	289 ± 29	3.2 ± 0.3	0.3 ± 0.03
70TiAl + 20TiC+10Al	3.4 ± 0.3	226 ± 23	419 ± 42	322 ± 32	5.1 ± 0.5	0.2 ± 0.02
60TiAl + 30TiC+10Al	3.9 ± 0.4	244 ± 24	453 ± 45	346 ±35	5.6 ± 0.6	0.2 ± 0.02
50TiAl + 40TiC+10Al	4.0 ± 0.4	272 ± 27	493 ± 49	380 ± 38	6.0 ± 0.6	0.1 ± 0.01
40TiAl + 50TiC+10Al	4.2 ± 0.4	299 ± 30	516 ± 52	412 ± 41	6.4 ± 0.6	0.1 ± 0.01

In samples with 20–50 % of TiC reinforcement, successful pressureless densification was achieved only by addition of 5–10 % of free aluminium as sintering agent. The role of free aluminium was twofold: (i) it reacted with TiC forming Al-Ti-C bonding phase and (2) provided liquid Al-Ti phase necessary for liquid reaction sintering and impregnation of pores.

The microstructure of the composites obtained, **Figure 8**, is characterized by isolated TiAl and Ti_3Al

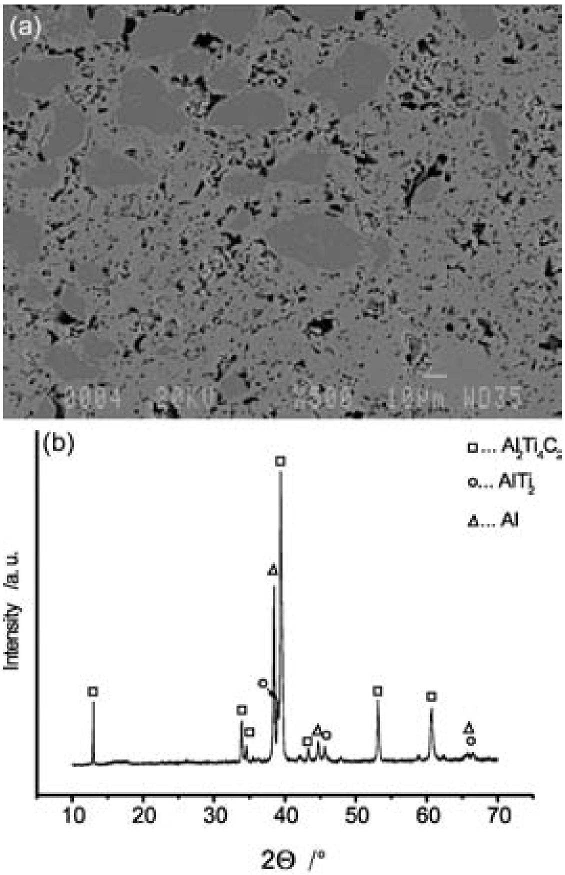

Figure 8: SEM micrograph and XRD spectra of the sample with the starting composition of TiAl-50 % TiC-5 % Al. The secondary formed $Al_2Ti_4C_2$ and $AlTi_2$ phases are porous.

Slika 8: SEM-posnetek in XRD-spekter vzorca začetne sestave TiAl-50 % TiC-5 %Al. Sekundarno ustvarjene faze $Al_2Ti_4C_2$ in $AlTi_2$ so porozne.

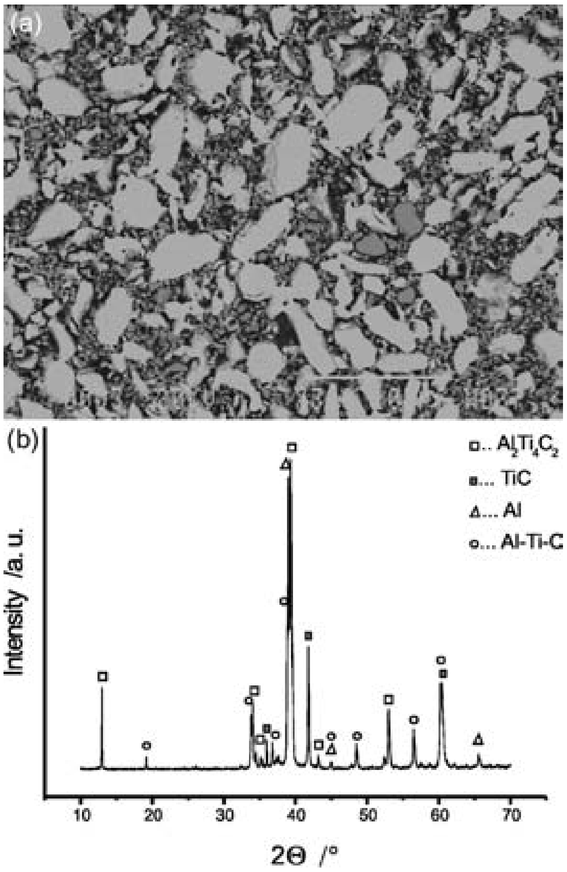

Figure 9: SEM micrograph and XRD spectra of TiAl-50 % TiC-10 % Al-5 % Ti composite sample with a secondary phases well infiltrated with solidified Al-Ti alloy (dark continuous phase)

Figure 9: SEM posnetek in XRD-spekter vzorca začetne sestave TiAl-50 % TiC-10 % Al-5 % Ti s sekundarnimi fazami popolnoma infiltriranimi z zlitino Al-Ti (temna zvezna faza)

grains well surrounded by a secondary bonding phases and finely dispersed TiC particulates.

However, as evident in **Figure 8**, the secondary phases formed during reactive sintering of specimens with a high amount of TiC and 5 % of Al remain porous. For a more complete densification of secondary phases, the free aluminium content in the green compacts was increased to 10 % and 5 % of Ti powder was also added. The role of Ti was to promote the infiltration of an Al-Ti alloy into the porous regions of the secondary phases and the formation of TiAl and/or Ti_3Al secondary intermetallics inside the pores leading to its closuring.

The microstructure of samples sintered with addition of Al and Ti is shown in **Figure 9**.

3.3 Mechanical properties

The results of room temperature tensile tests on composite samples are listed in **Table 1**. As a result of matrix reinforcement, significant improvements in Young's modulus, tensile strength and ultimate tensile strength as well as Vickers hardness of the fabricated composites were observed, resulting in IMCs with excellent mechanical properties. These mechanical properties were found to be slightly better in composites with Ti_3Al-based matrix compared to the TiAl-based matrix counterparts. Comparing the mechanical properties of composite samples with various volume fractions of ceramic particles in the matrix, it was found that Young's modulus, tensile strength, ultimate tensile strength and Vickers hardness increased while elongation decreased with an increasing fraction of ceramic reinforcement.

4 CONCLUSION

A study of the fabrication of TiAl- and Ti_3Al-based intermetallic matrix composites (IMCs) discontinuously reinforced with 10 % to 50 % of TiC was conducted by applying conventional pressureless reactive sintering of single phase TiAl or Ti_3Al powders and ceramic reinforcement. Following this cost-effective procedure, composites till 10 % of TiC reinforcement were routinely pressureless sintered to densities higher than 95 % of T. D. by solid state sintering with no sintering agents. On the contrary, in samples with more than 10 % of TiC reinforcement, the prerequisite for complete densification was the addition of small amount of Al powder or the mixture of Al and Ti powders with slight excess of Al over Ti-Al or 3Ti-Al stoichiometric composition. The elemental aluminium and titanium were involved in the formation of secondary bonding phases and liquid reaction sintering while the excess of aluminium is necessary for complete infiltration of pores in the secondary phases formed during reactive sintering. In this way, dense composite samples with 10 % to 50 % of TiC reinforcement and a retained porosity less than 5 % were successfully obtained, revealing the significant industrial potential of this fabrication method.

Metallographic analysis of the as-densified microstructures confirmed that during densification TiAl and Ti_3Al react with TiC and Al forming various secondary phases ($Al_2Ti_4C_2$, Ti_3AlC, $AlTi_2$) responsible for simultaneous bonding of intermetallic grains and elimination of pores. An un-identified, continuous Ti-Al-C phase was also detected in samples sintered with addition of Al and Ti.

Regarding the room temperature tensile properties, the improvement of tensile strength, tensile yield strength and modulus was found to correlate with the amount of ceramic reinforcement in the matrix. However, quite the opposite behaviour was found regarding elongation, where the introduction of ceramic particles into the intermetallic matrix in all specimens led to a significant reduction of elasticity.

The best tensile properties (except elongation) were obtained in TiAl-TiC and Ti_3Al-TiC samples with the highest amount (50 %) of ceramic reinforcement.

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