PRESSURELESS REACTIVE SINTERING OF TiAl-TiC AND Ti₃Al-TiC COMPOSITES

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TiAl and Ti₃Al 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 aluminate powders (TiAl) with traces of Ti₃Al and the single phased TiAl 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 % H₂ 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 Ti₃Al 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 Ti₃Al and TiC leading to the formation of Al₃Ti₇C, Ti₃AlC and Ti₃Al 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 Ti₃Al-TiC composites, pressureless reaction sintering, secondary bonding phases, microstructure, room temperature tensile properties, Vickers hardness

1 INTRODUCTION

TiAl- and Ti₃Al-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 (EP) route has been gaining more and more attention. According to the EP 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/Ti₃Al 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. 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 Ti3Al-based composite matrices, 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 Ti3Al-based IMCs with >95% T. D. may be successfully obtained, starting from TiAl and Ti3Al powders mixed with suitable ceramic reinforcement (such as TiC) and sintering additives (Al and Ti powders). During high temperature pressureless sintering, TiC and Al react with the TiAl and Ti3Al 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 Ti3Al-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 Ti3Al 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 % H2-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% CH3COOH and 5% HClO4, and then etched in a solution of 5% HNO3, 15% HF, and 80% H2O. 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 CuKα 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 and 2. TiAl was with traces of Ti₃Al while Ti₃Al 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.

Cost-effective, pressureless densification of TiAl and Ti₃Al powders, as well as of TiAl and Ti₃Al powders blended with ceramic particulates most often results in

Figure 2: (a) SEM micrograph of as-received commercial Ti₃Al powder and (b) XRD spectra of the Ti₃Al powder
Slika 2: (a) SEM-posnetek komercialnega prahu Ti₃Al in (b) XRD-spekter prahu Ti₃Al

size (Figure 1 and 2). TiAl was with traces of Ti₃Al while Ti₃Al powder was single phase.

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Figure 4: SEM micrograph of pressureless sintered non-reinforced Ti₃Al compact. Sintering conditions: 1300 °C, 2 h
Slika 4: SEM-posnetek vzorca Ti₃Al, sintranega pri atmosferskem tlaku brez dodatkov keramične ojačitve. Pogoji sintranja: 1300 °C, 2 h

Figure 5: SEM micrograph of (a) Ti₃Al reactively bonded with Ti₃AlC and (b) TiAl reactively bonded with Al₂Ti₄C₂ phases
Slika 5: SEM posnetek (a) Ti₃Al reakcijsko vezanega s Ti₃AlC in (b) TiAl reakcijsko vezanega s fazo Al₂Ti₄C₂

Figure 3: SEM micrograph of pressureless sintered non-reinforced TiAl compact. Sintering conditions: 1300 °C, 2 h
material that is not free of porosity. Typical micro-
structures of pressureless sintered non-reinforced TiAl
and Ti₃Al 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 Ti₃Al-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 Ti₃Al based composites not overcome 10 %, pressu-
reless sintering was completed without addition of any
sintering agents. Densification was promoted by chemi-
ical reactions between TiAl or Ti₃Al and the formation
of Al₂Ti₄C₂ and Ti₃AlC secondary phases:

\[ 2\text{TiAl} + 2\text{TiC} = \text{Al}_2\text{Ti}_4\text{C}_2 \] (1)
\[ 2\text{Ti}_3\text{Al} + \text{TiC} = \text{Ti}_3\text{AlC} + \text{AlTi}_2 + 2\text{Ti} \] (2)

As evident in Figures 5 a,b, the in situ formed
Al₂Ti₄C₂ and Ti₃AlC 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 inter-
face region, while high magnification observation
revealed the presence of numerous fine pores uniformly
distributed through the secondary phase, Figure 7.
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 Ti3Al

![Figure 8: SEM micrograph and XRD spectra of the sample with the starting composition of TiAl-50 % TiC-5 % Al. The secondary formed Al2Ti4C2 and AlTi2 phases are porous.](image)

![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).](image)
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 aluminum 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 Ti₃Al secondary intermetallics inside the pores leading to its closing.

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 Ti₃Al-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 Ti₃Al-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 Ti₃Al 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 Ti.

The best tensile properties (except elongation) were obtained in TiAl-TiC and Ti₃Al-TiC samples with the highest amount (50 %) of ceramic reinforcement.

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