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The Influence of Sintering Temperature of Reactive Sintered (Ti, Mo)C-Ni Cermets

Marek JÕELEHT [1]*, Jüri PIRSO [1], Kristjan JUHANI [1], Mart VILJUS [2]

[1] *Tallinn University of Technology, Department of Material Engineering, Ehitajate tee 5, 19086, Tallinn, Estonia*
[2] *Tallinn University of Technology, Centre of Materials Research, Ehitajate tee 5, 19086, Tallinn, Estonia*

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Titanium-molybdenum carbide nickel cermets ((Ti, Mo)C-Ni) were produced using high energy milling and reactive sintering process. Compared to conventional TiC-NiMo cermet sintering the parameters for reactive sintered cermets vary since additional processes are present such as carbide synthesis. Therefore, it is essential to acquire information about the suitable sintering regime for reactive sintered cermets. One of the key parameters is the final sintering temperature when the liquid binder Ni forms the final matrix and vacancies inside the material are removed. The influence of the final sintering temperature is analyzed by scanning electron microscopy. Mechanical properties of the material are characterized by transverse rupture strength, hardness and fracture toughness.
Keywords: titanium cermets, reactive sintering, mechanical properties.

1. INTRODUCTION

TiC based cermets offer an attractive combination of mechanical properties, such as strength/density, because of their relatively low density, high hardness, and excellent thermal and chemical stability [1]. TiC-NiMo cermets show a great potential as a substitute for the commonly used WC-Co based hardmetals.

TiC based cermets usually fabricated by conventional PM route: powder fabricating-forming-sintering [2]. Most industrial TiC powders are fabricated through the reduction of TiO_2 with carbon at the temperature of 1900 – 2300 °C for 10 – 20 hours in an inert atmosphere [3]. These then require crushing using jaw crushers, and fine-milling thereafter. However, such methods have serious disadvantages due to high cost of equipment and high power consumption because of very high reaction temperature. Self-propagating high-temperature synthesis (SHS) and mechanical alloying (MA) are also used to obtain TiC powder [3 – 6]. These processes do not need expensive high temperature reaction equipment which could result in significant capital expenditure savings.

Recently, a novel process for producing TiC based cermets – named as reactive sintering – was developed to produce cermet parts. When conventional powder metallurgical manufacturing uses ceramic powders of titanium carbide (TiC) and mixes it with elemental nickel (Ni) for binder and molybdenum (Mo) for alloying before final sintering then reactive sintering uses elemental titanium (Ti) and carbon black (C) instead of TiC. This means that the formation of the carbides occurs *in situ* in the sintering of the sample in one cycle [7 – 11]. Therefore an expensive titanium carburizing step is no longer required. Some researchers have synthesised TiC base cermets using SPS [12] and MA-PCS process [13].

In this paper the influence of reactive sintering temperature is investigated and the results are evaluated by microstructure and mechanical properties.

2. EXPERIMENTAL

Elemental powders of titanium, carbon black, nickel and molybdenum were mixed and milled in high energy attritor mill for 10 hours. The speed of attritor shaft was set at 540 rpm and WC-Co hardmetal balls were used with ball to powder ratio 10:1 respectively. Heptane was used as milling agent. The composition of the mixture is represented in Table 1.

Table 1. (Ti, Mo)C-Ni cermet's composition (wt.%)

Mixture	Ti	C	Ni	Mo
75(Ti+17C)-25NiMo	62.2	12.8	16.7	8.3
75TiC-25NiMo (Etalon)	75		16.7	8.3

Carbon to titanium ratio was chosen to be 17 wt%, which is in the midpoint of Ti-C phase diagram homogeneity range. Nickel, as the main binder element, content was kept low in order to acquire a relatively high hardness cermet. After milling the mixture was prepared for pressing where 60 MPa of pressure was used in uniaxial pressing. The green compacts were then sintered at different temperatures in graphite furnace under vacuum of around 20 Pa for 1 hour. The technological route of reactive sintering of TiC base cermets is shown in our prior work [10]. The microstructure and mechanical properties of the TiC base cermets may be improved by sintering in optimal temperature.

The sintering cycle is composed of two heating up steps and two dwellings followed by cooling. The first heating of 10 °/min was used until 1270 °C after which the temperature remained constant for 1 hour for the *in situ* synthesis of carbides to be competed. The second heating segment was 5 °/min until the final sintering temperature.

* Corresponding author. Tel.: +372-620-3356; fax: +372-620-3196.
E-mail address: *marek.joeleht@gmail.com* (M. Jõeleht)

Three temperatures were chosen – 1470 °C, 1500 °C and 1530 °C. The cycles are illustrated by the following Fig. 1.

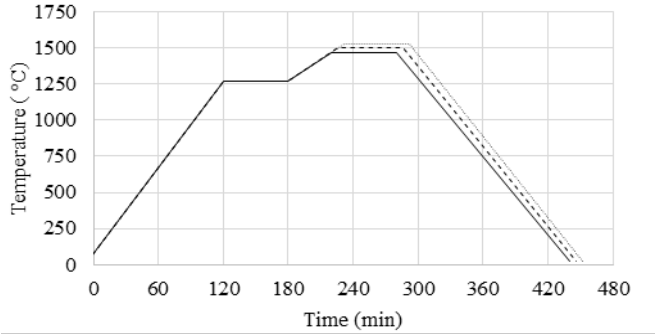


Fig. 1. Temperature – time graph of sintering cycles

In addition, a conventionally produced TiC-NiMo cermet with similar elemental composition was used as an etalon to compare the properties of reactive sintered cermet. The composition is also indicated in Table 2. Etalon cermet was sintered at 1500 °C but without additional step at 1270 °C as the step is not required.

The microstructure of the final samples was investigated with a scanning electron microscope ZEISS EVO MA-15. Vickers hardness was measured with Identec 5030SKV with 10 kg of force. Transverse rupture strength was tested via three-point bending test using Instron 8516. The fracture toughness (K_{1C}) was determined by measuring the crack length from the tip of the indentation made by Viker´s indention load of 300 N [14]. The indentation toughness is calculated by the following Eq. (1).

$$K_{1c} = 0.0726 \frac{P}{c^{3/2}} \quad (1)$$

where P is the indentation load in N and c is the average length from the crack tip to the hardness indent in mm. Density was measured by Archimedes method using Mettler-Toledo ME204.

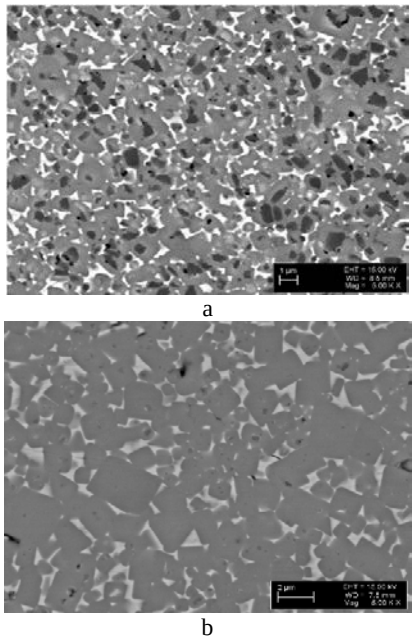
3. RESULTS AND DISCUSSION

3.1. Microstructure

The microstructure of TiC-NiMo cermets fabricated by conventional technology and reactive sintering is shown in Fig. 2. As seen in Fig. 2 a a typical microstructure of conventional TiC-NiMo cermets consists of pure TiC core (black phase), (Ti, Mo)C rim (gray phase) and Ni solid solution which contained some Ti, Mo elements (white phase). The microstructure of reactive sintered cermets consists of two phases – (Ti,Mo)C grains without "core-rim" phase within a Ni matrix (Fig. 2 b).

Such two phased microstructure of titanium carbide cermet was also obtained in [7 – 9] in contrast to conventional three phased microstructure where also pure TiC cores are present. Samples of reactive sintered (Ti, Mo)C-Ni cermets were sintered at different temperatures (Fig. 3) and grain size seems to be increased by the temperature but is in all cases around 1 µm (Fig. 4 and Table 2). The porosity is dependant on sintering temperature with an optimum at 1500 °C when considering SEM images (Fig. 3).

As can be seen in Fig. 3 a the sample sintered at the lowest temperature of 1470 °C has obtained a considerable amount of porosity within the material. The porosity of these samples can also be deduced from the fact that the density in this case was also the lowest – 5.26 ± 0.06 g/cm^3 (Table 2).



a

b

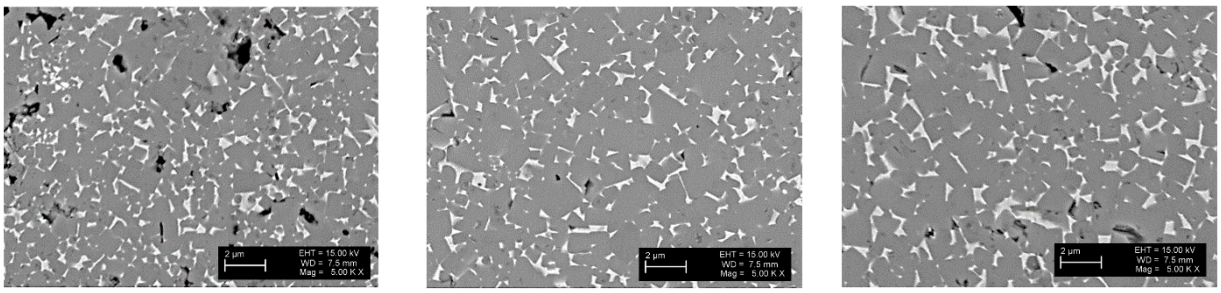
Fig. 2. SEM images of: a – conventionally produced TiC-NiMo cermet; b – reactive sintered (Ti, Mo)C-Ni cermet

Higher porosity is caused by too low sintering temperature. The viscosity of liquid phase is high and it cannot infiltrate between carbide grains. The porosity has also caused the decline of main mechanical properties.

3.2. Mechanical properties

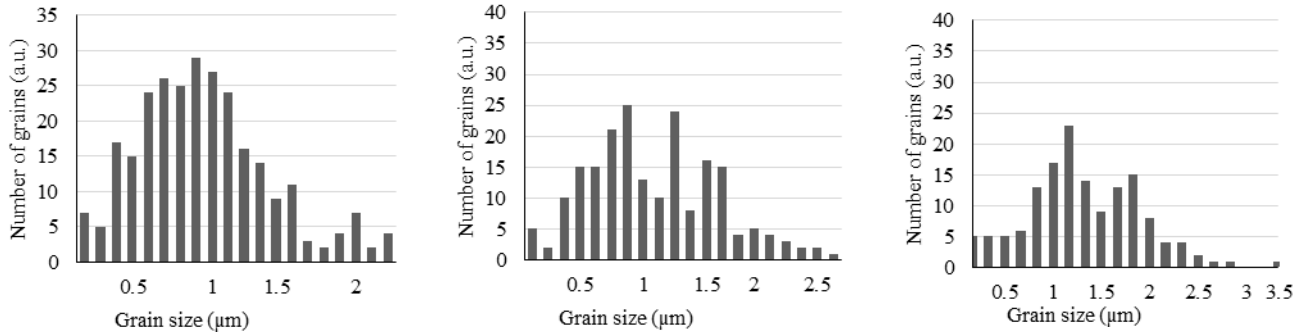
The mechanical properties depend on reactive sintering temperatures. The influence of final sintering temperature on hardness, strength and fracture toughness values are visualised in the following figures Fig. 5 – Fig. 7. The samples sintered at 1470 °C have lower mechanical properties via higher porosity. The highest density and least visual porosity are exhibited by samples sintered at 1500 °C (Fig. 3 b). This is also indicated by the higher density of the material 5.42 ± 0.06 g/cm^3 (Table 2). Samples sintered at this temperature also achieved the highest hardness and strength (Fig. 5 and Fig. 6).

The sample sintered at 1530 °C (Fig. 3 c) also has some porosity within the material but is considerably lower compared to the first sample in Fig. 3 a. Both hardness and strength of samples have lower values as samples sintered at 1500 °C. Only fracture toughness has the highest result (Fig. 7.) even when compared to the etalon. This phenomenon may be explain by bigger carbide grain size. During high temperature sintering the carbide grain growth is more rapid. It is well-known that cemented carbides with coarse structure have higher fracture toughness and lower hardness and strength than middle grain size one [1].



a b c

Fig. 3. Samples of reactive sintered (Ti, Mo)C-Ni cermets sintered to different temperatures: a – 1470 °C; b – 1500 °C; c – 1530 °C



a b c

Fig. 4. Grain size distribution of reactive sintered (Ti, Mo)C-Ni cermets sintered to different temperatures: a – 1470 °C; b – 1500 °C; c – 1530 °C

In Fig. 4 it can be seen that with increasing sintering temperature the grain size histogram widens considerably.

As seen in Fig. 5 – Fig. 7 the hardness, strength and fracture toughness of the reactive sintered cermets are similar compared with conventional cermets with the same composition.

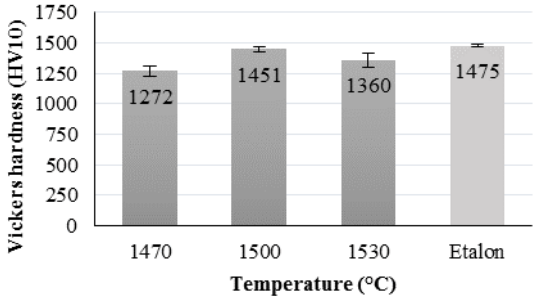


Fig. 5. The influence of final sintering temperature to (Ti, Mo)C-Ni cermet's hardness

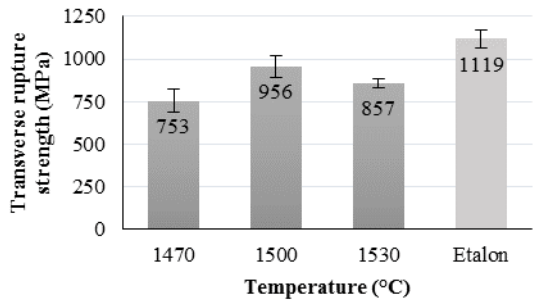


Fig. 6. The influence of final sintering temperature to (Ti, Mo)C-Ni cermet's transverse rupture strength

The hardness of the reactive sintered cermets form a curve with the peak at 1451 HV10 which is very close to the etalon material. On the other hand, the strength of the reactive sintered samples is significantly lower compared to etalon. This can be explained with the porosity of the materials. The sample at 1500 °C has the highest density of the reactive sintered materials and lowest visual porosity when considering the SEM images. The hardness of the sample is not as dependant on the porosity of the sample compared to the strength properties of the material.

The fracture toughness of the samples seems to follow a linear growth with increasing sintering temperature. The low value of 8.70 MPa√m for the 1470 °C sample again most likely caused by the high porosity, but the reason for the sample sintered at 1530 °C having the highest fracture toughness value of 12.11 MPa√m. This result is comparable to the fracture toughness of the etalon material (Fig. 7).

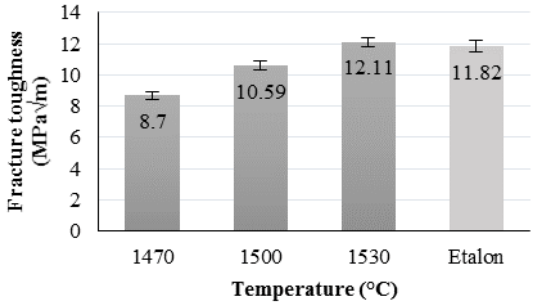


Fig. 7. The influence of final sintering temperature to (Ti, Mo)C-Ni cermet's Fracture toughness

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Table 2. Structural characteristics and mechanical properties of reactive sintered (Ti, Mo)C-Ni cermets

Sintering temperature, °C	Grain size, µm	Hardness, HV10	Transverse rupture strength, MPa	Fracture toughness, MPa√m	Density, g/cm^3
1470	1.04	1272 ±44	753 ±69	8.70 ±0.23	5.26 ±0.06
1500	1.25	1451 ±22	956 ±64	10.59 ±0.30	5.42 ±0.06
1530	1.43	1360 ±59	857 ±28	12.11 ±0.27	5.40 ±0.06
1500*	1.26	1475 ±31	1119 ±60	11.82 ±0.37	5.70 ±0.03
*Etalon cermet 75TiC-25NiMo					

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4. CONCLUSIONS

Temperature of reactive sintered of (Ti, Mo)C-Ni cermet with of 16.7 wt% Ni as the matrix and 8.3 wt% Mo was investigated. It was found that optimum reactive temperature for such composition is 1500 °C. At this temperature the microstructure had the smallest number of pores and achieved highest density. Mechanical properties showed a peak at this temperature reaching hardness of 1451 ± 22 HV10, transverse rupture strength of 956 ± 64 MPa and fracture toughness of 10.59 ± 0.30 MPa√m. These results are comparable to conventionally produced alloys with similar compositions. Deviations from the optimal temperature as little as 30 °C results in a significant decrease in material properties. This indicates that a precise temperature control is needed for maintaining optimal material properties.

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