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The formation of reactive sintered (Ti, Mo)C-Ni cermet from nanocrystalline powders

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Abstract

Titanium carbide based cermets with molybdenum as alloying element and nickel as binding metal were produced using high energy powder milling of elemental powders of Ti, Ni, Mo and C (carbon black) followed by liquid state sintering. Reactive sintering process was applied where the synthesis of (Ti, Mo)C occurs in solid state and the final densification of the cermet is achieved during liquid state. Reactive sintering allows to obtain uniform fine-grained cermets and also to decrease the production costs of the cermets because it excludes the expensive very high temperature carbide synthesis. The phase and microstructure evolution is analysed by means of XRD, TGA and SEM equipment. Material properties are characterised by hardness and transverse rupture strength.

Keywords; TiC base cermets; reactive sintering; microstructure evolution, mechanical properties.

1. Introduction

Titanium carbide (TiC) based cermets have several attractive properties including high hardness, low density, wear and corrosion resistance [1]. The properties of these cermets depend on chemical composition, and production technology. Titanium carbide can be manufactured by different processes but the most commonly used industrial scale method uses titanium dioxide or titania (TiO₂). Together with carbon black titanium dioxide is carbothermically reduced at temperatures reaching up to 2000 °C [2, 3]. This is mainly due to the fact that TiO₂ is directly obtained from titanium ore refinement making titania powder one of the cheapest sources of titanium.

Some authors have reported that TiC can be synthesized from polymeric precursors prepared by titanium alkoxides and organic compounds at lower temperatures [4, 5] around 1100 –
1300 °C. However, titanium alkoxide is prone to hydrolysis which makes it difficult to handle. In addition, TiC can be synthesised by using pure Ti and carbon powders [2, 3, 6], gas phase reaction of TiCl₄ with hydrocarbons [7], autoclaving TiO₂ with magnesium and magnesium carbonate [8] etc.

Furthermore, according to some research works a reaction between metal and carbon powders can even occur during high energy milling [9] if sufficient kinetic energy is provided by the milling balls. This phenomenon is sometimes called mechanical activation of elementary powders and has been used to fabricate carbides in [10, 11]. With the aid of mechanical activation the formation of carbide occurs at much lower temperatures reducing the total energy consumption for cermet production. It is possible to acquire TiC only by high energy milling [12, 13] but after long milling times the titanium powder needs to be handled extremely carefully since the activated powder mixture can spontaneously react with oxygen in the air leading to an ignition of the powder even at near room temperatures.

The milling characteristics have a great impact to the homogeneity of the fabricated material. The key factors in milling are milling duration, ball to powder ratio and the kinetic energy of the milling balls that is determined by the mass of the ball and their speed from the milling apparatus. Researchers in [14] have observed that by milling of Ti and C powders for 8 hours with attritor fine grained TiC can be obtained at room temperature.

Choi in [15] used mechanical alloying method for fabricating ultrafine TiC-Ni cermet powders. In [16] mechanical activation is used for producing chromium carbide nickel cermets via reactive carburizing sintering where the synthesis of Cr₃C₂ takes place during the final sintering of the sample. Similar method is used for tungsten carbide cermets [17] where the elemental powders of tungsten (W), carbon (C) and cobalt (Co) are used. This method is based on integrated mechanical and thermal activation (IMTA) process where the carbide reactants and binder metal powders are mixed and activated in high-energy mills before the sintering process. With IMTA process carbides are synthesised, grains are formed and the binder metal is heated up to liquid phase for consolidation of the cermet compact [18]. The possibility of reactive sintering technology for titanium carbide based cermets has been proven in [19].
In reactive sintering the amount of carbon in the mixture has critical importance. Ideally, the stoichiometric titanium carbide with the Ti-C atomic ratio 1:1 would have 20.03% of carbon in weight [2]. Industrially produced TiC powder usually has about 19.6 wt% of carbon since the theoretical uniformity is nearly impossible to achieve and it is more beneficial not to have free carbon in TiC powder. The more carbon atoms are bonded within the compound, the better mechanical properties of the carbide [20] are achieved. According to Ti-C phase diagram at room temperatures, the homogeneity range of titanium carbide is about 15 to 19 wt% [21].

TiC-based cermets are typically produced by a liquid phase sintering process. During this process capillary forces from the wetting eutectic liquid promote densification. However, a major part of densification during sintering in nanocrystalline WC-Co hardmetals already takes place in the solid state before the liquid forms [22]. It has been reported that the solid state sintering contributes up to 90% of the total densification in hardmetals. Densification of high binder content Ti-Mo-Ni-C grades during pressureless reactive sintering is studied in [19].

The main objective of the present work was to achieve full density fine-grain TiC phase cermets from Ti-Mo-Ni-C elemental powders using reactive sintering. The carbide synthesis in situ and the microstructure formation of (Ti, Mo)C-Ni cermets from nanocrystalline powders are investigated and mechanical properties of the materials are measured. The influence of different sintering parameters was also investigated for the completion of both carbide synthesis and cermet’s densification.

2. Experimental methods

The mixture of pure titanium (Ti), carbon black (C), molybdenum (Mo) and nickel (Ni) powders as starting materials were used. Carbon content of 17 wt% was aimed to the midpoint of the homogeneity range of the Ti-C phase diagram. The binder content of 25 wt% of with Ni-Mo ratio of 2:1 respectively was chosen to produce a material with relatively high hardness. The composition of the powder mixture is shown in Table 1.

The powder mixture was milled for 10 hours using attritor as the high energy milling device to achieve a homogeneous mixture that is mechanically activated for reactive sintering. The
milling speed of the attritor rotor was set to 540 RPM and 14 gram hardmetal balls (Ø 6 mm) were used with ball to powder ratio of 10:1. Green compacts were pressed uniaxially at 60 MPa and sintered in a graphite-heated furnace with vacuum around 20 Pa.

During sintering there are two essential processes occurring in the case of reactive sintering – carbide synthesis *in situ* and alloy formation. Therefore, the temperature-time graph has two steps or holding times at certain temperatures (Fig. 1) - T₁ and t₁ for carbide synthesis and T₂ and t₂ for cermet’s densification.

In order to estimate the required sintering temperatures of T₁ and T₂, TGA analyser SETARAM Setsys Evolution 1750 was applied with THERMO Scientific Nicolet 380 FTIR to analyse emitted gases. Phase identification was conducted with XRD analyser Bruker AXS D5005 using CuKa radiation. The microstructure was investigated with scanning electron microscope ZEISS EVO MA-15. The Vickers hardness of the samples was measured using Identec 5030SKV with 10 N loads. A three point bend test was conducted to evaluate the transverse rupture strength according to EVS-EN ISO 3327:2009.

3. Results and discussion

3.1. Sintering and microstructure formation

In the Fig. 2 it can be seen, that the samples of milled Ti-Mo-Ni-C powder start to shrink at about 540 °C and increased with temperature. A rapid densification occurs between 1200 and 1300 °C which is the range when Ti-Mo-Ni-C eutectic begins to melt. According to [23] the pseudobinary equilibrium phase diagram Ni-TiC, the eutectic temperature is 1270 °C. The rapid densification at these temperatures can be attributed to rearrangement of the carbide particles, causing small pores to disappear. Most of the densification took place in solid phase before melting Ti-Ni-Mo-C eutectic at 1295 °C. Shrinkage finished at temperature 1400 °C and linear shrinkage is 22 %.

Fig. 3 shows the X-ray diffraction (XRD) patterns for mixed and milled elemental powders of Ti, Ni, Mo, and C and after heating at different temperatures. As shown in Fig. 3 the intensity
of all peaks decrease during attritor milling. It may be explained by particles refining, amorphisation and accumulation of the strain energy by mechanical input energy. This causes the intensity of the peaks of Ti, Ni, Mo and C to shrink but also broaden. In addition, the XRD peaks show that (Ti, Mo)C has been partially synthesized already during the high energy milling process. In [12, 14, 24] found that nanocrystalline TiC particles can be produced during the high-energy milling of titanium and carbon powders. Contrary to [25] there are no peaks of pure TiC even after heating. It may be concluded that (Ti, Mo)C particles form preferably to TiC.

The formation of (Ti, Mo)C during milling is believed to be controlled by interdiffusion of C atoms. As seen in Fig.3 between temperatures up 540 to 720 °C remarkable exchanges in structure take place. In the sample, sintered at 720 °C all titanium peaks at 35.1, 38.4 and 40.2 degrees have disappeared. Instead Mo₂C peaks at 36.4, 42.3 and 61 degrees and titanium and nickel intermetallic compound peaks at 38.9, 41.4 and 45.3 have intensified. In addition, the WC peaks that are caused by residual from attritor milling at 31.6 and 48.5 degrees have disappeared which most is likely due to tungsten also dissolving in the binder and carbide phases.

At 1000 °C the intermediate phases (Mo₂C, Ti₂Ni) have disappeared. Some graphite still exists until 1100 °C but from 1270 °C only the final two phases of (Ti, Mo)C and Ni are present (Fig. 3). The reactive sintering of Ti-Ni-Mo-C system can be summarized as follows:

\[
2\text{Ti} + 2\text{Mo} + \text{Ni} + 2\text{C} \rightarrow \text{Ti}_2\text{Ni} + \text{Mo}_2\text{C} + \text{C} \rightarrow 2(\text{Ti}, \text{Mo})\text{C} + \text{Ni}.
\]

The thermogravimetric analysis (TGA) graph (Fig. 4) illustrates the weight change of the sample and also the first derivative over time i.e. the speed of weight change. The results exhibit two temperatures where some of the material is separated with peaks at 288 °C and 1290 °C. First weight loss of approximately 3 % is mostly due to the evaporation of paraffin wax that is added into the mixture to enhance the pressing properties of green compacts. Second weight loss is approximately 1.5 % and is most likely the reduction of metal oxide impurities since some release of carbon oxide was registered by the gas analysis and the value of weight loss is minimal.
The second TGA graph (Fig. 5) demonstrates the thermal changes in the sintering chamber. The difference is calculated from the equipment’s baseline, acquired with the same sintering parameters that were used with the samples. Peaks with a negative number indicate an endothermic reaction, while positive peaks refer to an exothermic reaction.

First heat flow change is registered at 56 °C that is close to the melting point of paraffin wax. Second fluctuation occurs with a peak at 507 °C followed closely by a peak at 647 °C. Those are most probably occurring due to the phase changes (Mo₂C and Ti₂Ni) as seen in XRD diagram taking place (see Fig.3). The final changes in the TGA heat flow graph indicate peaks at 1295 and 1353 °C. The first of these can be explained with the melting of (Ti, Mo)C-Ni eutectic and the second with the previously mentioned carbon oxide reaction that resulted in a minor weight loss.

SEM images of milled powder and green compacts sintered at different temperature are shown in Fig.6. The SEM micrograph of the milled starting mixtures milled in attritor for 10 hours is shown in Fig. 6a. As seen in Fig. 6b some diffusion processes have taken place at temperatures before 720 °C. There are white-colored aggregates in the structure which is composed of two kinds of grains - Ni and Mo. The black and dark-grey particles are graphite and Ti respectively. Fig.6c shows SEM image of in situ (Ti, Mo)C–Ni composite sintered at 1200 °C with conglomerates that have formed in structure at this temperature. They are composed of two kinds of grains - (Ti, Mo)C and solid solution on the Ni phase. As shown on Fig. 6d, at 1270 °C (Ti, Mo)C-Ni eutectic has melted regions and the formation of the final microstructure of the cermet has begun. At this stage the liquid phase has not yet infiltrated fully between all as formed carbide grains, resulting in a heterogeneous structure.

In Fig. 6e the microstructure of the (Ti, Mo)C–Ni composite sintered at 1330 °C is illustrated. The microstructure is composed from ultrafine carbide grains surrounded by fully melted binder but the binder is still distributed somewhat heterogeneously with binder „lakes“ in the structure.
In Fig. 6f the final structure of (Ti, Mo)C-Ni cermets sintered at 1500 °C for 30 minutes is shown. During liquid phase sintering carbide grain growth is seen due to Ostwald ripening. Smaller grains have higher solubility in the binder than larger ones and therefore the larger grains grow at the expense of the smaller ones. Their surfaces are free from gas absorption, oxidation or other detrimental surface reaction contamination. The microstructure of reactively sintered cermet (see Fig. 6f) is without “core-rim” structure as in common TiC-NiMo sintering. The binder phase is distributed homogeneously between the carbide grains. With direct heating to 1500 °C the porosity of the final sample is clearly visible in Fig.7a. Therefore an additional dwelling at temperature T\textsubscript{1} (see Fig. 1.) was introduced to make sure the synthesis of carbides is finished before the final densification of the cermet. Most of the porosity in Fig.7b is eliminated compared to Fig.7a, but some small pores still exist in the structure. Sample in Fig.7b has additional dwelling at 1270 °C (T\textsubscript{1}) for 60 minutes (t\textsubscript{1}). The grain size of the sample is 1.10±0.49 µm (Fig. 7b) which is very similar to the previous sample with average grain size 0.98±0.43 µm (Fig.7a) meaning that the dwelling at this temperature T\textsubscript{1} does not encourage later grain growth. Properties of the two samples are given in Table 2.

3.2. Mechanical properties

The mechanical properties of reactive sintered (Ti, Mo)C-Ni cermets were measured in two test series. The samples are compared by the hardness and transverse rupture strength (TRS) values of the materials. In the first test series the holding times t\textsubscript{1} and t\textsubscript{2} were altered (see Fig. 1). In the second test series the influence of temperature T\textsubscript{1} was investigated.

The first test series had fixed temperatures T\textsubscript{1} and T\textsubscript{2} at 1270 °C and 1500 °C respectively. Three holding times of t\textsubscript{1} at 1270 °C were used – 0, 10 and 30 minutes. The holding times t\textsubscript{2} at 1500 °C were 10, 30 and 60 minutes. The hardness and strength values of cermets are represented by following figures (Fig.8 and Fig.9).
The hardness values range from 1300 to 1500 HV\textsubscript{10} and in all cases the longer dwelling time of 30 minutes at 1270 °C has shown better hardness values compared to shorter dwelling times (Fig.8). These results indicate that the current additional dwelling step is required to finish the carbide synthesis and to evaporate gas from middle of grade. Similar trends are present in the strength values of the samples in Fig. 9. In this graph it can be seen that without a two-step sintering (t\textsubscript{1} = 0 min) the overall strength of the material increases with the final holding time, but are evidently still lower than samples with 30 minutes of holding time at 1270 °C (T\textsubscript{1}). Sample with t\textsubscript{1} of 30 minutes and t\textsubscript{2} of 60 minutes presented TRS of 712 MPa.

To further investigate the two-step sintering process a second test series was carried out. In this case the holding times at both t\textsubscript{1} and t\textsubscript{2} were chosen to be 60 minutes. The influence of the first dwelling step’s temperature T\textsubscript{1} was altered. Temperatures of 1200, 1270 and 1340 °C were implemented. The second dwelling step temperature T\textsubscript{2} and holding time t\textsubscript{2} remained constant being 1500 °C and 60 minutes respectively. The hardness and strength results are represented in the following figures (Fig. 10 and Fig. 11).

In Fig. 10 the highest hardness of 1712±39 HV\textsubscript{10} was obtained by sample with dwelling at 1270 °C. Deviations from this temperature resulted in lower values. On the other hand, the strength of the samples does not seem to be affected by the temperature T\textsubscript{1} when considering the error margins (Fig.11). All the samples exhibited TRS near 800 MPa (797 MPa for the highest sample at 1200 °C).

Considering the results of both test series it can be deduced that a two-step sintering process is required for reactive sintering technology in the case of (Ti, Mo)C-Ni cermets. In order to finalize the carbide synthesis process and gas to evaporate an additional dwelling at 1270 °C is required before final liquid state sintering. From material properties perspective this step is mostly important for the hardness of the material. This means that the conditions for (Ti, Mo)C synthesis need to be in certain limits for the carbide to form. Even with longer holding time temperatures of 1200 °C and 1340 °C for T\textsubscript{1} resulted in a 15 % and 30 % lower hardness respectively. Within the framework of the current research parameters it would seem that the strength of reactive sintered (Ti, Mo)C-Ni cermets mainly depend on the sintering duration of
the two steps rather than the temperature of the first dwelling step. An optimal regime of the two steps include 60 minute dwelling at both 1270 °C and 1500 °C with heating rate of 10 °/min. Resulting (Ti, Mo)C-Ni cermet presented with hardness of 1712 HV$_{10}$ and transverse rupture strength of 797 MPa.

4. Conclusions

In this paper the formation of reactive sintered (Ti, Mo)C-Ni cermet’s microstructure and mechanical properties with low binder content were investigated. The synthesis of Mo$_2$C and also (Ti, Mo)C occurs at three different stages. First of all, some of the carbides are formed during high energy milling. Secondly, after 720 °C all the titanium in the mixture has been used to form Ti$_2$Ni and (Ti, Mo)C with still some residual molybdenum present. Thirdly, at 1270 °C the synthesis of the carbides has finished with only two phases in the sintered microstructures – (Ti, Mo)C and Ni. During reactive sintering a very fine and thermodynamically stable carbide grains within a metal matrix were formed. According to the current research it can be concluded that reactive sintering is able to assure a uniform microstructure in the case of titanium based cermets. A two-step sintering regime is needed for the cermets structure to be fully formed. The final microstructure of reactive sintered (Ti, Mo)C-Ni is a two phased system. The sintering parameters for two-step sintering such as dwelling temperatures and holding times have significant influence to the final mechanical properties of the material. An optimal regime of the two steps include a 60 minute dwelling at both 1270 °C and 1500 °C with heating rate of 10 °/min. Resulting (Ti, Mo)C-Ni cermet presented with hardness of 1712 HV$_{10}$ and transverse rupture strength of 792 MPa.

Acknowledgements

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References


Tables

**Table 1.** The powder composition of Ti+17C-25NiMo cermet (wt%).

<table>
<thead>
<tr>
<th>Powder mixture</th>
<th>Titanium</th>
<th>Carbon</th>
<th>Nickel</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>75(Ti+17C)-25NiMo (2:1)</td>
<td>62.2</td>
<td>12.8</td>
<td>16.7</td>
<td>8.3</td>
</tr>
</tbody>
</table>

**Table 2.** Material properties for samples sintered at 1500 °C for 60 minutes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering</th>
<th>Grain size (µm)</th>
<th>Density (g/cm³)</th>
<th>Hardness (HV₁₀)</th>
<th>TRS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500 °C for 60 min</td>
<td>0.98±0.43</td>
<td>5.17</td>
<td>1458±20</td>
<td>385</td>
</tr>
<tr>
<td>2</td>
<td>1500 °C for 60 min</td>
<td>1.10±0.49</td>
<td>5.35</td>
<td>1712±39</td>
<td>792</td>
</tr>
<tr>
<td></td>
<td>(1270 °C for 60 min)</td>
<td></td>
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Figures

Figure captions:

Figure 1. Temperature-time graph of reactive sintering process.

Figure 2. Dimensional change during reactive sintering of Ti+17C-25NiMo (2:1) grades.

Figure 3. X-ray diffraction patterns of Ti+17C-25NiMo unmilled, milled for 10 h and the green grades sintered at different temperatures.

Figure 4. Weight change and the rate of weight change of Ti+17C-25NiMo powder by thermogravimetric analysis.

Figure 5. Heat flow change of Ti+17C-25NiMo by thermogravimetric analysis.

Figure 6. SEM images of Ti+17C-25NiMo composites reactive sintered at different temperatures for 30 minutes.

Figure 7. SEM images of reactive sintered Ti+17C-25NiMo cermets at 1500 °C for 60 minutes.

Figure 8. Hardness of Ti+17C-25NiMo samples depending on t₁ at 1270 °C and t₂ at 1500 °C.

Figure 9. TRS of Ti+17C-25NiMo samples depending on t₁ at 1270 °C and t₂ at 1500 °C.

Figure 10. Hardness of Ti+17C-25NiMo depending on T₁ with both t₁ and t₂ of 60 minutes and T₁ at 1500 °C.

Figure 11. Transverse rupture strength of Ti+17C-25NiMo depending on T₁ with both t₁ and t₂ of 60 minutes and T₂ at 1500 °C.
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Figure 6. SEM images of Ti+17C-25NiMo composites reactive sintered at different temperatures for 30 minutes.

a) green compact of milled powder
b) sample sintered at 720 °C
c) sample sintered at 1200 °C
d) sample sintered at 1270 °C
e) sample sintered at 1330 °C
f) sample sintered at 1500 °C
a) directly heated to 1500 °C
b) additional dwell at 1270 °C

Figure 7. SEM images of reactive sintered Ti+17C-25NiMo cermets at 1500 °C for 60 minutes.

Figure 8. Hardness of Ti+17C-25NiMo samples depending on $t_1$ at 1270 °C and $t_2$ at 1500 °C.

Figure 9. TRS of Ti+17C-25NiMo samples depending on $t_1$ at 1270 °C and $t_2$ at 1500 °C.
Figure 10. Hardness of Ti+17C-25NiMo depending on $T_1$ with both $t_1$ and $t_2$ of 60 minutes and $T_1$ at 1500 °C.

Figure 11. Transverse rupture strength of Ti+17C-25NiMo depending on $T_1$ with both $t_1$ and $t_2$ of 60 minutes and $T_2$ at 1500 °C.
Highlights

- Reactive sintered (Ti, Mo)C-Ni cermets were produced.
- Carbide formation occurs in three steps.
- The final microstructure of the cermet has two phases.
- A two step sintering is required for reactive sintering.