Structure Formation in Ti-C-Ni-Mo Composites during Reactive Sintering

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Reactive sintering is a novel process where synthesis reaction of the carbide phase is combined with solid and liquid phase sintering of the cermet during a single heating cycle. Ti-C-Ni-Mo composites were synthesized in situ from elemental powders of Ti, Ni, Mo and C by high energy milling, followed by reactive sintering. The milled powders with the grain size in nano-scale were pressed to compacts and sintered. During the sintering that was performed after pressing, the titanium carbide was formed first and then the TiC-NiMo cermet was sintered in the presence of liquid phase in one cycle. The interface between the binder phase and the carbide grains of the in situ composite has a good bonding strength because it is not contaminated with oxidation film or other detrimental surface reactions. The microstructure of such cermet is fine-grained and more homogeneous than that of cermets produced by conventional method. In the paper the phase evolution, microstructure formation and carbide grain growth during reactive sintering are explained.

Keywords: TiC-NiMo cermets, reactive sintering, structure formation.

INTRODUCTION

TiC-NiMo cermets combine high hardness with relatively low density – below 7 g/cm³, which makes them perspective materials to replace well-known WC-Co hardmetals in certain applications [1]. To produce TiC-NiMo cermets, TiC, Mo and Ni powders are used as starting powders. Carbide powder is mixed with binder metal powder, milled, pressed into green compacts, and sintered at high temperatures.

The main component of TiC-based cermets – TiC is extremely hard, being one of the hardest metal carbides known [2]. TiC exhibits excellent thermal stability and has a very high melting temperature of approximately 3100 °C. TiC is often used in application such as abrasives, cutting tools, grinding wheels and coated cutting tips.

However, one of the disadvantages of using TiC for commercial applications is its difficulty to produce. Currently, most of industrial TiC powder is produced through the reduction of TiO_2 with carbon at temperature from 1800 °C to 2000 °C for 10 hours (Fig. 1, a). The production of TiC by reduction is energy consuming and requires expensive high temperature equipment.

It was recently found that TiC powder can be fabricated by high-energy milling of titanium and carbon powders [3 – 5]. High-energy milling is performed at room temperature so there is no need for expensive high temperature reaction equipment, which could result in significant capital expenditure saving. High-energy reaction milling, a recent modification of mechanical alloying, has been studied extensively to synthesize nanostructure materials in-situ during milling. Thus, high-energy milling is an effective approach for production of nanostructure carbides as well as a cost-effective process in comparison with the current industrial carbothermic reduction for submicron-sized carbides. Synthesis of nanostructure TiC is possible because the reaction between Ti and C has a negative free energy of formation as shown in equation (1):

$$Ti + C = TiC \qquad \Delta G_{298} = -180.296 \text{ J/mol} \qquad (1)$$
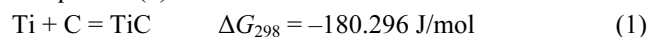
The main disadvantages of TiC-NiMo cermets are their relatively low strength and wear resistance, compared with WC-Co hardmetals mainly because of their coarse-grained structure (the carbide grain size is usually over 2 μm) [6].

TiC-NiMo cermets show a typical microstructure consisting of hard core, rim and binder phase (Fig. 1, a). The grains with "grey rim" are formed by dissolution and precipitation of (Ti, Mo)C around remaining TiC core (black). Active growth of the carbide grains during sintering is characteristic to TiC-NiMo cermets. The finer the powder is the higher is its interface energy and the faster the carbide grains tend to grow during sintering. Particle growth occurs in this case mainly by sintering together of adjacent grains and, as the roundness of the particles indicates, also by solution and precipitation.

Synthesis of the titanium carbide at room temperature by high-energy milling is feasible, but in the case of TiC-NiMo cermets it does not give much advantage, because for sintering the TiC powder must be heated up anyway.

Recently, a novel process for producing cermets – named as reactive sintering – was developed, involving high-energy milling of elemental powders, forming and following sintering [7 – 10].

In the paper the effect of the graphite content in the initial mixture on the phase evolution, microstructure formation and carbide grain growth during sintering of Ti-C-Ni-Mo composites are studied.

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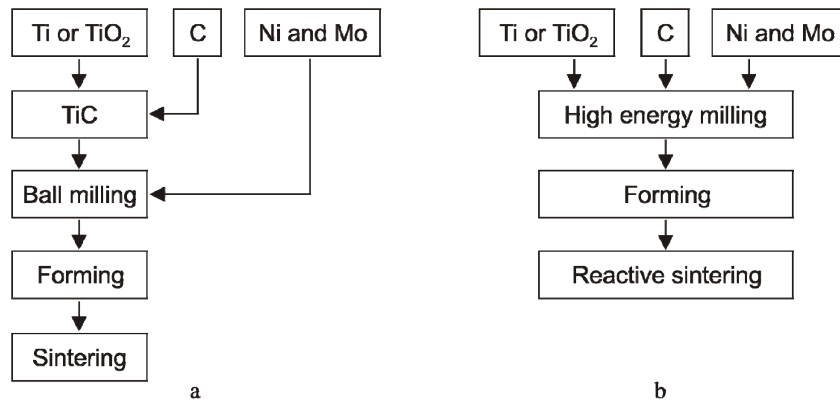E-mail address: *marty@staff.ttu.ee* (M. Viljus)

Fig. 1. Producing routes of cermets by conventional technology and reactive sintering: a – conventional technology; b – reactive sintering

MATERIALS AND EXPERIMENTAL METHODS

Commercially available pure titanium (Ti), carbon black (C), molybdenum (Mo) and nickel (Ni) powders were used as starting materials. The initial content of powder mixture was (in wt%): Ti – 30 and 35, C – 20 and 15, Ni – 40, Mo – 10. Milling was performed in an attritor mill equipped with WC-Co alloy reinforced vial. The charge ratio (WC-Co balls to powder mass ratio) was 5 : 1. Rotation speed of the impellers was 560 RPM for all the tests. Duration of the milling was 6 hours.

The as-milled powders were pressed to compacts and then heated in a vacuum furnace at temperature of 1400 °C during 30, 150 and 300 minutes. Phase identification of the compacts was carried out with X-ray diffraction (XRD) method with CuK$_\alpha$ radiation (Bruker AXS D5005). Morphology and grain sizes of the sintered samples were characterized using a scanning electron microscope JEOL-840A and Zeiss EVO MA-15.

The reference TiC-NiMo cermets were fabricated by conventional PM methods. Titanium carbide powder (50 wt%) was mixed with 50 wt% nickel-molybdenum powder and ball-milled during 72 hours with a ball-to-powder weight ratio of 10 : 1. Powder was compacted unaxially and sintered in vacuum at 1400 °C for 30, 150 and 300 min.

RESULTS AND DISCUSSION

The microstructure of TiC-based cermets produced by conventional technology exhibits a "core-rim" structure, bonded with a metallic phase (Fig. 2, a). The cermets have a core-rim type hard phase, where the cores (black) are pure cubic TiC and the rims are (Ti, Mo)C with variable composition from the core to the outer grain boundary. During the liquid phase sintering Mo continues to precipitate around the formed (Ti, Mo)C. The cermets have a peculiar structure as the metallic and the ceramic phase are present in form of two interpenetrating skeletons.

The microstructure of reactive-sintered Ti-C-50%NiMo cermets (Fig. 2, b) is without "core-rim" structure and has lower grain size. The composite consists only from (Ti, Mo)C and solid solution on the base of Ni. The carbide grains are rounded and separated by the nickel matrix. Compared with the industrial TiC-NiMo cermets, the microstructure of reactive-sintered (Ti, Mo)C-Ni cermets is more homogeneous and has finer structure - the average carbide grain size is below 1 μm. The microstructure of the cermets produced by conventional technology is less homogeneous and the mean carbide grain size is higher – about 2 μm (Fig. 2, a).

Grain growth during sintering is dependent on relatively small changes in the C content, evidently because it can markedly alter the characteristics of the liquid phase. High carbon content usually results with more rapid grain growth.

According to the Ti-C phase diagram, the composition of TiC$_x$ exists over a wide range of stoichiometry, from x = 0.47 to 0.98 (Fig. 3). Characteristics of TiC and its based alloys depend very much on the content of bonded carbon. TiC alloys produced with common technologies consist of 19% – 19.8% bonded carbon that is close to stoichiometric (20.30% C). It is not known yet what is the optimal content of C in the case of new technology.
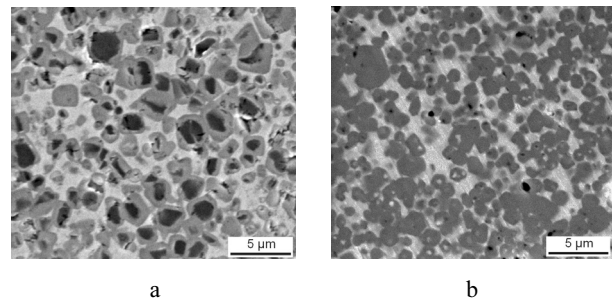

Fig. 2. Microstructure of TiC-NiMo cermets sintered at 1430 °C during 30 min by different technology: a – conventional technology; b – reactive sintering
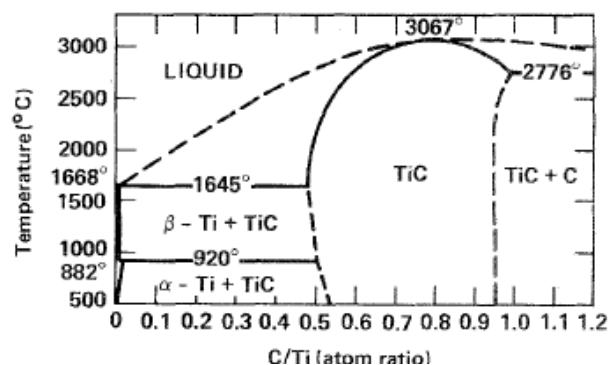

Fig. 3. Ti-C phase diagram [2]

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On Figures 4 and 5 the microstructures of 50 (Ti-20 % C) - 50 (NiMo) and 50 (Ti-15 % C) - 50 (NiMo) cermets, sintered at 1400 °C for 30 minutes, are presented. As seen in (Fig. 4), cermets with lower carbon content (15 wt %) are without free graphite in the structure. Cermets with higher carbon content (20 wt %) exhibit free graphite remaining in the microstructure (Fig.5).
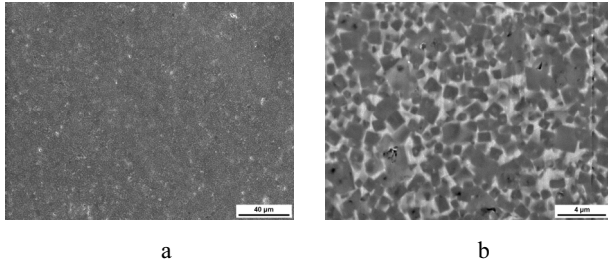

a   b

Fig. 4. Microstructure of 50 (Ti-15 % C) - 50 (NiMo) cermet
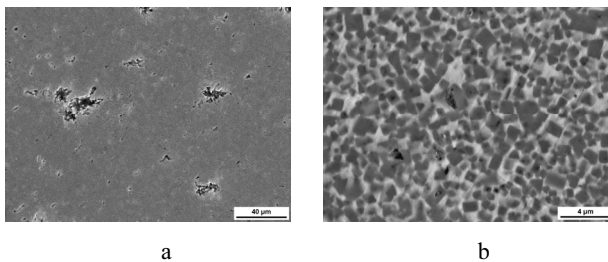

a   b

Fig. 5. Microstructure of 50 (Ti-20 % C) - 50 (NiMo) cermet

In Fig. 6 the XRD patterns of initial milled powder and compacts sintered at 1000, 1300 and 1430 °C during 30 min are shown. As seen on the patterns, at 1000 °C the titanium carbide compound is already formed, but besides TiC also Ni_3Ti and Mo_2C phases can be detected. The last phenomenon can be explained by higher enthalpy of formation of Ni_3Ti. At 1300 °C and 1430 °C only TiC and Ni phases are present in the alloy.
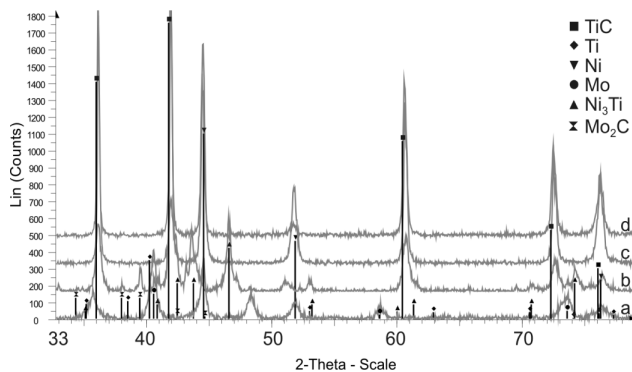

Fig. 6. XRD patterns of Ti-C-Ni-Mo mixture: a – after high energy milling (6 hours), b – after heating at 1000 °C, c – 1300 °C, d – 1400 °C

Powder particles after high-energy milling are in nanoscale (60 nm – 90 nm) size with internal crystallites of 10 nm – 15 nm size. During the high-energy milling, graphite is smeared onto powder particles. Meanwhile, C atoms first segregate in the crystal interfaces of Ti and Mo, then diffuse gradually, and finally, react with Ti and Mo during the heat-treatment to form titanium-molybdenum carbide completely. The powder mixture after mechanical activation has higher free energy and thus a higher chemical reactivity than the powder mixture without activation. According to XRD analysis, the synthesis reaction of (Ti, Mo)C took place at the temperatures about 1000 °C.

The thermal treatment causes at first the formation of (Ti, Mo)C at ca 1000 °C and then, at higher temperature (above 1300 °C), the formation of (Ti, Mo)C-Ni alloy by liquid phase sintering – all during one producing cycle. As seen in Fig. 7, the ultrafine carbide particles, formed by reactive sintering at 1000 °C, show a hierarchical structure in which the ultrafine carbide grains (ca 200 nm) are contained in larger strips.
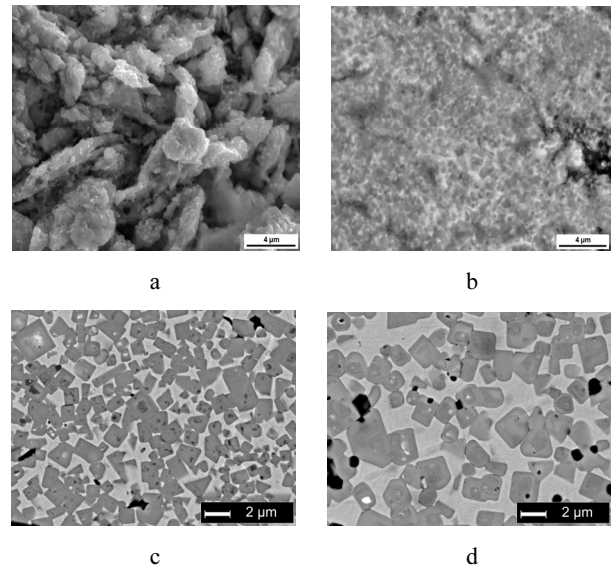

a   b

c   d

Fig. 7. Microstructure of Ti-20 wt % C - 50 wt % NiMo cermet sintered at different temperature and different time: a – 1000 °C, 30 min; b – 1300 °C, 30 min; c – 1400 °C, 30 min; d – 1400 °C, 300 min
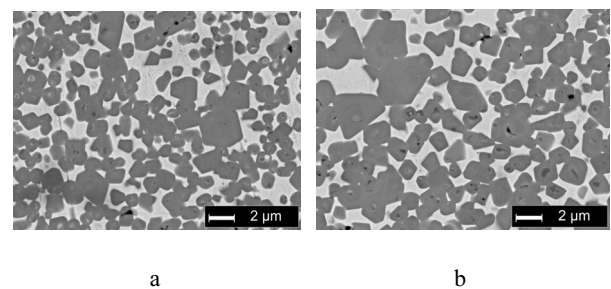

a   b

Fig. 8. Microstructure of Ti-15 wt % C - 50 wt % NiMo cermet sintered at 1400 °C during different time: a – 150 min, b – 300 min
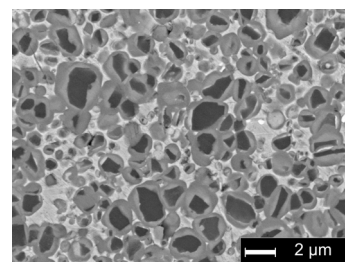

Fig. 9. Microstructure of TiC-50 wt % NiMo cermet sintered at 1400 °C during 300 min

The particles size in the composite after milling is 30 nm – 50 nm and the carbide grain size in the sintered TiC-NiMo cermet is about 900 nm, meaning that the carbide grains grow up to 30 times during sintering. The main target is to keep the grain growth as low as possible.

Three mechanisms have been proposed as an explanation for grain growth in the TiC-NiMo cermets [11]. They are: 1 – coalescence of adjacent grains, 2 – solution in the binder phase during heating and precipitation during cooling, and 3 – transfer of carbide from smaller to larger grains by diffusion through the liquid binder. Most probably all three take part at the same time to various degrees.

However, recent studies have revealed that a major part of densification in the sintering in such composites already takes place in the solid state before the liquid forms [12 – 14]. It has been reported that the solid-state sintering contributes up to 90 % of the total densification in cermets. Sintering temperature and time are among the most important factors determining the structure and properties of TiC-NiMo cermets. During the later stage of liquid phase sintering, carbide grain growth occurs due to Ostwald ripening mechanism. Smaller grains have higher solubility in the binder and therefore the larger grains grow at the expense of the smaller ones. On cooling, some Mo and Ti are retained in the Ni phase. Conventionally the binder phase content up to 6 wt % Ti. The Mo content in the binder depends on Mo powder content in the initial powder mixture.

As seen from Figs. 7 and 8, the grain size of the in situ synthesized carbides is lower and they also grow slower during sintering than in cermets fabricated due conventional technology (Fig. 9).

CONCLUSIONS

Reactive sintering is a powerful technique to obtain titanium carbide based cermets from the mixtures of elemental powders in one step. The carbide particles are synthesized in powder mixture during low temperature heating (~1000 °C) in situ, which eliminates expensive long-time, high-temperature (1800 °C – 2000 °C) synthesis of TiC. The surface of as-formed nanosize carbide particles is free from oxide film, absorbed gas or other detrimental surface contamination. Thermodynamically stable carbide grains within the metal matrix are formed. The carbide grain growth during reactive sintering is somewhat retarded as compared with the traditional process. The carbon content doesn't have critical impact on the microstructure of the sintered cermets. The microstructure of the reactive sintered cermets is fine-grained and more homogeneous than that of the cermets produced by the conventional method. To sum up, the reactive sintering technique enables to produce the cermets with better microstructure as well to decrease the production costs of the alloys.

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