Sintering kinetics of Mo-free cermets

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Abstract

Titanium carbonitride-based cermets are important materials for contemporary cutting tools. Ceramic powders of Ti(CN), TaC, WC were mixed, compacted and heat-treated at high temperatures to form (Ti,W,Ta)(C,N) solid solution, which was then ball-milled to fine powders before being mixed with metallic binder and compacted. Liquid-phase sintering of the samples was carried out in a nitrogen atmosphere at different sintering temperatures and holding times. The microhardness and porosity of the sintered cermets were studied. It is demonstrated that the microhardness increases with sintering temperature, but at the same time, the porosity level also goes up with temperature and time. At the beginning of sintering (zero holding time), the majority of the pores are small (0.1–1 μm); during sintering, the larger pores grow at the expense of smaller pores and the resulting pores are all concentrated in the 10–100 μm range. The number of larger pores increases with temperature and prolonged holding time, which results in deteriorated properties. © 1997 Elsevier Science S.A.

Keywords: Sintering kinetics; Titanium carbonitride; Cermet; Sintering; Microhardness

1. Introduction

Cermet tools have many advantages. They are light in weight and high in mechanical strength, toughness and heat conductivity. Their high heat conductivity leads to a low temperature gradient, resulting in less thermal stresses and cracks and are thus preferred for high-speed cutting tool materials. In cutting performance, cermet cutting tools result in better control of the geometrical accuracy of the work-pieces, in better chip and tolerance control, in longer tool life, in improved surface finish, in increased feeding rate and in consistent maintenance of critical dimensions [1,2].

In traditional titanium carbonitride-based cermets, molybdenum is regarded as an indispensable ingredient in order to maintain the sinterability and wettability. With the invention of the pre-sintering solid-solution treatment of hard-phase powder mixtures [3], the processing of cermets has come to a new stage where molybdenum is no longer indispensable. In essence, ceramic powders Ti(CN), TaC, WC, etc., were mixed, compacted and heat-treated at high temperature to form solid solution. The solid solution effect can be examined by lattice parameter measurement using high angle X-ray diffraction when the participating atoms are of different ionic diameters. Fig. 1 is such a measurement [4] in the study of a pre-sintering solid solu-

![Graph showing lattice constants](image-url)

Fig. 1. Extrapolation in measuring the lattice constant of the titanium carbonitride solid solution. Shown in the plot as open circles are the results for samples treated at 1800°C for 12 h in nitrogen partial pressure (10⁻³ Torr). Also shown are the results after 1.5 h at 1700°C. The lattice constant increased from 4.2678 to 4.2726 Å [4].
tion of Ti(C,N) + TaC + WC mixture. The increase in lattice parameter indicated dissolution of Ta and W into Ti(C,N) to form (Ti, Ta, W)(C, N) solid solution. Zhang and Jana [5] ball-milled the treated samples to fine powders and sintered them again with Ni/Co binder at 1450°C through 1530°C. Later, the authors sintered the same materials at higher temperatures (1550 through 1650°C for 0 to 4 h) and found that the cermet sintered at 1550°C for 2 h had the greatest high-temperature (800 to 1000°C) modulus of rupture (MOR) in comparison with other temperatures and timing conditions [6]. The present paper studies the same cermets from a kinetic point of view by examining the microhardness and evolution of pore size and porosity.

2. Experimental procedure

Commercially obtained ceramic powders of Ti(Co.3N0.7) (1.3 ~ 2 µm), TaC (1.5 ~ 2.5 µm) and WC (2 µm) were mixed thoroughly in the weight proportions of 70:10:20. The mixing was done in a planetary ball mill (Fritsch P/M 5), at a ball-to-powder weight ratio of 10:1 for 30 min. 5% (by weight) polyethylene glycol was dissolved in 2-propanol alcohol on a hot plate and added in the powder-mix before making the green compacts. The green compacts were made in a steel cold die at a uniaxial pressure of 150 MPa. The compacts were put into latex rubber gloves which were in turn degassed and CIP (cold isostatic pressing)-treated at 350 MPa for 10 min. The compacts were treated for binder-burn-out at 400°C for 2 h in vacuum. The solid-solution treatment was performed under 10⁻³ Torr nitrogen pressure at 1800°C for 12 h. The treated compacts were pulverized and milled to less than 2 µm in a Fritsch planetary ball mill. These hard-phase powders were then thoroughly mixed with 8 weight percent of Ni powders (2.2 to 3.0 µm) and 7 wt.% of Co powders (1.6 µm). The powder mix was dampened with 2-propanol alcohol and pressed into 51 mm x 7 mm x 5 mm rectangular beam-shaped samples with a uniaxial hydraulic pressure of 180 MPa. The cermet compacts then underwent the same CIP and binder-burn-out procedures and were finally sintered at

Fig. 2. Microhardness versus sintering time for different sintering temperatures. The maximum microhardness was obtained for 1 h sintering.

Fig. 3. Porosity profile for zero holding time at different temperatures. At the beginning of sintering, most pores were of small scale (0.1 ~ 1 µm).
1550, 1600 and 1650°C for 0, 0.5, 1, 2 and 4 h in a nitrogen atmosphere (10⁻³ Torr). The heating rate was maintained at 1000°C h⁻¹ for the first hour of heating, then reduced to 500°C h⁻¹ until the desired sintering temperature was reached. After the desired holding time, the furnace was turned off to allow cooling. The ‘zero’ holding time was realized by heating the samples to the respective sintering temperature and immediately cooled down without any holding. Vickers hardness was measured using 1000 g force for 15 s. The pore size distribution was characterized using a mercury porosimeter (Micromeritics PoreSizer 9320), the pressure used enabling the penetration of pores ranging from about 0.06 to 360 μm. The PoreSizer measures the volume distribution of pores in the material by mercury intrusion/extrusion. In mercury porosimetry, mercury is forced to penetrate into the interconnected micropores and voids in a compact. The amount of mercury used is then related to the porosity or the bulk density of the material under study [8].

3. Results and discussion

3.1. Effect of sintering temperature and time on microhardness

The hardness data are plotted against sintering time in Fig. 2. Two points are worth noting: first, there is a maximum in hardness for all of the temperatures at one hour sintering; after that, prolonged sintering causes the hardness to drop, which is attributed to pore growth (see the discussion in the next section) and grain coarsening. Second, at the same sintering time, the higher the temperature, the harder the sintered body. This is a result of higher diffusion rates, better wetting and solubility of the solid in liquid at higher sintering temperatures. However, a greater microhardness does not necessarily bring about good strength, as mentioned earlier, the reason lying in the porosity level and pore size, which play a more important role in the strength of a material than does the microhardness.

3.2. Effect of sintering time on porosity

At the beginning of sintering, as seen in Fig. 3 where the samples were sintered for ‘zero’ hours, the majority of the pores were small (0.1 ~ 1 μm) for all of the temperatures. In this ‘zero time sintering’, the porosity level decreased with increasing temperature. Careful study of this sintering reveals two important points: (1) during heating, sintering has already taken place and the higher the temperature the denser the sample; (2) pore coarsening has not taken place yet because of the short time. During sintering, however, the pore structure evolves gradually, as seen in Fig. 4: after holding for 1.5 h, small pores were almost eliminated completely, whilst the larger pores were observed to grow, the majority of the pores being found to be concentrated within a pore-size range of 10 ~ 100 μm. Similar observations were reported by Zheng and Reed [7]. It is also evident that the porosity level increased with in-
increasing temperature: for the same time of sintering, the porosity level at 1650°C was the greatest whilst that at 1550°C was the lowest. This was probably part of the reason why the high-temperature strength was better when sintered at 1550°C in comparison with those sintered at 1600 and 1650°C; c.f. [6].

Prolonged sintering also aggravates the porosity. This can be seen clearly in Fig. 5 where the samples were sintered at 1550°C for different durations. At no holding time, again the pores were small and concentrated in the 0.1 ~ 1 μm range. After holding for 0.5 ~ 4 h, almost all the pores shifted to 10 ~ 100 μm. The porosity level went up with increasing sintering time, the level being the highest at 4 h.

![Graph](image)

Fig. 5. Porosity profile at 1550°C for different sintering times. Prolonged sintering resulted in an elevated porosity level.

**4. Conclusions**

In this work, the pre-sintering solid solution treatment was applied to form carbonitride solid solution of Ti, W and Ta. This solid solution was then pulverized and sintered with metallic binder phase Ni/Co at 1550 ~ 1650°C up to 4 h under 10⁻³ Torr nitrogen pressure. Vickers hardness testing showed that, for this cermet, sintering at 1650°C for 1 h resulted in the greatest hardness at room temperature. However, mercury porosimeter measurements indicated that both elevated temperatures and prolonged sintering time resulted in increase in pore size and porosity level. At the beginning of sintering, most of the pores were small (0.1 ~ 1 μm in diameter) but large in quantity; after sintering for a short period of time, the total amount of porosity dropped dramatically, but the bigger pores grew to a range of 10 ~ 100 μm in diameter. For prolonged sintering, a higher sintering temperature was seen to aggravate the porosity level, whereas for very short-time sintering, or 'zero holding', higher temperature resulted in faster densification without causing pore coarsening. As such, short-time sintering is preferred for a denser Mo-free cermet.

**Acknowledgements**

The Funding of this work came from Nanyang Technological University’s Applied Research Fund # ARP 66/91. The authors are grateful to Mr. K.P. Phua for data collection.

**References**


