Effect of Ni Content on Microstructure and Mechanical Properties of NbC-WC-Ti(C0.7,N0.3)-Ni Cermets

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Abstract

In this study, Ni bonded NbC cermets, i.e., NbC-xNi-18WC-14Ti(C0.7,N0.3) (wt%) with a Ni from 6 to 20 wt%, were prepared by liquid phase sintering in vacuum for 90 min at 1390 or 1450 °C. Microstructural investigation was performed by SEM and XRD analysis. The phase composition in the cermets were simulated by thermodynamic modelling. All cermets were fully densified. Microstructure and phase analysis indicated that the NbC based cermets were composed of a core-rim structured cubic (Nb,W,Ti)(C,N) phase and a cubic Ni alloy binder. The variation in Ni content resulted in a significant effect on the hardness and toughness of the cermets. The hardness decreased whereas the fracture toughness increased nearly linearly with increasing Ni content. The NbC-9Ni-18WC-14Ti(C0.7,N0.3) (wt%) cermets, sintered at 1450 °C, exhibited a good combination of hardness (1500 kg/mm²) and indentation toughness (~8.8 MPa.m⁰⁵) as well as a three point flexural strength of 2000 MPa.

1. Introduction

The abrasion and chemical wear resistance of Ti(C,N)-based cermets are superior to that of WC-Co cemented carbides [1-3]. The performance of Ti(C,N) cermets is considerably influenced by secondary carbide additions like WC, Mo2C, NbC or TaC [2]. A small amount of NbC or TaC additions to Ti(C0.7,N0.3)-Ni systems was reported to allow improving the interrupted cutting performance by retaining hot hardness and increasing the thermal shock resistance at elevated temperatures [4]. As a refractory carbide, NbC offers the possibility to partially substitute WC in WC-Co cemented carbides [5, 6] or Ti(C,N) in Ti(C,N)-Ni based cermets [7, 8]. The addition of 5-40 wt% NbC to a Ti(C0.7,N0.3)-20 wt% Ni system showed a clear effect on the core-rim structure of the carbonitride grains [8]. Due to the refined carbonitride and solution carbide grain size, reduced wear rates were observed for the Ti(C,N)-Ni cermets with 10 wt% WC, NbC or TaC additions [7].

As a high hardness refractory carbide, NbC is hardly explored as a matrix carbide, although its physical and chemical properties show a high potential for wear and tribological applications [9]. Pure NbC as well as metal bonded NbC were reported to have a pronounced wear resistance under dry sliding conditions versus other monolithic ceramics and carbides and also had an increased tool life when compared to WC-Co inserts [10,11]. For successful turning operations, it was concluded that NbC based cermets should exceed a HV30 of 1400 kg/mm² and possess a high bending strength [9]. The additions of secondary carbides/nitrides also have a significant impact on the microstructure and mechanical properties of NbC based materials [10]. In ceramic-metal composites, the hardness and toughness can be tailored through the metallic binder content [13]. WC-Co cemented carbides can be used for different demanding wear conditions through a judicious variation of the Co content. There is however no information available on the influence of the Ni binder content on the microstructure and mechanical properties of NbC-based cermets. In this study, NbC-xNi-18WC-14Ti(C0.7,N0.3) cermets with Ni content ranging from 6 to 20 wt% were processed to obtain NbC-Ni based cermets with refined ceramic grains and tailored mechanical properties for wear resistant applications.

2. Experimental

2.1. Materials preparation

NbC (CBMM, FSSS=1.52 µm, Brazil), Ti(C0.7,N0.3) (H.C. Starck, FSSS=3.0 µm, Germany), WC (Umicore, CW5300, FSSS=2 µm, Belgium) and Ni (Vale, T123™, FSSS=3-7 µm, UK) powders were used to prepare the NbC cermets. The NbC powder has a total C and O content of 11.2 and 0.17 wt% respectively. The primary NbC grain size is in the submicrometer range, as shown in Fig. 1.a. The Ti(C0.7,N0.3) powder, as shown in Fig. 1.b, consists of both submicrometer and 5-10 µm sized particles.
The chemical composition of the investigated NbC cermets with different Ni content are summarized in Table 1. The theoretical density was calculated based on the mixture rule.

![Morphology of the NbC (a) and Ti(C0.7,N0.3) (b) starting powders.](image)

**Fig. 1.** Morphology of the NbC (a) and Ti(C0.7,N0.3) (b) starting powders.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Ni content (wt%)</th>
<th>Composition (wt%)</th>
<th>Theoretical density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Ni</td>
<td>6</td>
<td>NbC-6Ni-18WC-14Ti(C0.7,N0.3)</td>
<td>8.01</td>
</tr>
<tr>
<td>9Ni</td>
<td>9</td>
<td>NbC-9Ni-18WC-14Ti(C0.7,N0.3)</td>
<td>8.04</td>
</tr>
<tr>
<td>12Ni</td>
<td>12</td>
<td>NbC-12Ni-18WC-14Ti(C0.7,N0.3)</td>
<td>8.07</td>
</tr>
<tr>
<td>16Ni</td>
<td>16</td>
<td>NbC-16Ni-18WC-14Ti(C0.7,N0.3)</td>
<td>8.12</td>
</tr>
<tr>
<td>20Ni</td>
<td>20</td>
<td>NbC-20Ni-18WC-14Ti(C0.7,N0.3)</td>
<td>8.16</td>
</tr>
</tbody>
</table>

All powder mixtures were mixed on a multi-directional mixer (Turbula, WAB, Switzerland) in ethanol for 48 h using WC-6 wt% Co milling balls (Ceratizit grade H20C, Ø10 mm). The suspension was dried in a rotating evaporator at 65 °C. Cold isostatically pressed (200 MPa, EPSI) powder compacts were pressureless sintered for 90 min at 1390 and 1450 °C in vacuum (~20 Pa) at a heating rate of 3 °C/min in a graphite furnace.

### 2.2. Characterization

The bulk density of the sintered cermets was measured in ethanol. High resolution microstructural images were obtained by NanoSEM (Nova 450, FEI). Phase identification in the sintered cermets was conducted with a 0-0 X-ray diffractometer (XRD, Seifert 3000, Ahrensburg, Germany) in the 20-80° 2θ range using Cu Kα radiation (40 kV, 40 mA) on polished sample surfaces. Rietveld structural refinement analysis was performed to determine the lattice parameters of the carbide and binder phases [14]. The Vickers hardness, HV30, was measured (Model FV-700, Future-Tech Corp., Tokyo, Japan) with an indentation load of 294 N for 15 s at room temperature. The Palmqvist indentation fracture resistance, KIC, was calculated from the length of the radial cracks around the Vickers indentations, using the formula proposed by Shetty et al. [15]. The reported values are the mean and standard deviation of five indentations. The room temperature flexural strength was measured in a three-point bending test (Instron 4467, PA, USA) on rectangular samples (25.0 × 3.0 × 2.0 mm), with a span length of 20 mm and a cross-head displacement of 0.1 mm/min. Thermodynamic simulations were performed to estimate the phase constitution of the sintered cermets, using Thermo-Calc software [16] and a commercial Ni based database TCNi8.

### 3. Results and discussion

Fig. 2 shows the backscattered electron (BSE) contrast microstructures of the 6Ni grade cermet, sintered for 90 min at 1390 °C (Fig. 2.a) and the cermets sintered for 90 min at 1450 °C (Figs. 2.b-f).
Only two contrast phases, i.e. bright NbC based carbide grains and a darker Ni-based binder were detected in the cermets sintered at 1450 °C, whereas a few dark contrast Ti(C,N) rich grains were observed in the cermets sintered at 1390 °C. All sintered cermets were fully densified, regardless of the Ni content. These cermets exhibited clear core/rim structured carbonitride grains. Due to the lower atomic mass of Ti compared to Nb and W, the darker rim is richer in Ti, whereas the bright cores have a higher W and Nb concentration. Basically, a Ti-rich (Nb,W,Ti)(C,N) solid solution was formed around the Nb-rich (Nb,W,Ti)(C,N) grains. W was detected both in the rim and the core, as well as in the Ni binder. The formation of a Nb-rich core structure was attributed to the higher surface energy of NbC as compared to Ti(C,N) [8]. In the present study, the cores of the undissolved NbC grains acted as nucleation sites for the rim structure. With the interdiffusion of Ti and W, the core of the grains formed a Nb-rich (Nb,W,Ti)(C,N) mixed carbide, together with a Ti-rich rim. The overall surface energy of the cermets is therefore decreased when the Ti-rich (Nb,W,Ti)(C,N) rim is formed on the NbC core.

![Fig. 2. Backscattered electron micrographs of NbC-Ni based cermets, 6Ni cermet sintered at 1390 °C (a) and 6Ni (b), 9Ni (c), 12Ni (d), 16Ni (e) and 20Ni (f) cermets sintered 1450 °C.](image)

The XRD phase analysis indicated that all the cermets sintered at 1390 and 1450 °C contained a fcc solid solution Ni binder and cubic NbC solution phase. The content of the Ti(C,N) grains in the cermets sintered at 1390 °C was however too low to be detected by XRD analysis. The NbC-based solid solution (Nb,Ti,W)(C,N) phase has the same crystal structure as the cubic NbC phase. Due to the very close composition of the rim and core area, XRD analysis did not allow to differentiate their individual peak positions. Fig. 3.a shows the change in lattice parameters of the NbC solution and binder phases as a function of the Ni content. Both the lattice parameter of the NbC solution phase and Ni binder decrease with increasing Ni content. Since the atomic radius of W (139 pm) and Ti (144.2 pm) are smaller than for Nb (146 pm) [17], the cubic lattice parameter of the NbC phase decreases with increasing amount of solid solution alloying elements. The change of the NbC phase lattice parameter can be explained by the calculated phase composition, as presented in Figs. 3.b-d. At 1450 °C, mainly two phases, i.e. NbC solution and liquid Ni binder, are predicted in the cermets with 6 to 20 wt% Ni, as seen in Fig. 3.b. With increasing Ni content, more and more NbC is replaced by Ni, resulting in an increased concentration of WC and TiC in the NbC solution phase. The NbC solution phase has a very low TiN content, as shown in Fig. 3.c. The lattice parameter of the binder phase is mainly influenced by the dissolution of alloying elements [18]. With increasing Ni content, the concentration of WC in the Ni binder is decreased, whereas the TiC and NbC content remains low and constant, as shown in Fig. 3.d. Therefore, the lattice parameter of Ni binder is also decreased since the atomic radius of Ni (124.6 pm) is lower than for W (139 pm).
Fig. 3. Influence of the Ni content on the lattice parameter of the NbC solution and binder phase in the NbC-Ni based cermets (a) and thermodynamically estimated phase constitution (b) and chemical composition of the NbC solution phase (c) and Ni binder phase (d) at 1450 °C.

The Vickers hardness, indentation fracture toughness and three point flexural strength of the cermets are shown in Fig. 4. With increasing Ni content, the hardness decreased whereas the fracture toughness nearly increased linearly for the cermets sintered at 1390 or 1450°C. Sintering at 1450 °C reduced the hardness and increased the toughness compared to their equivalents sintered at 1390 °C. The 9Ni (NbC-9Ni-18WC-14Ti(C0.7,N0.3)) cermet, sintered at 1450 °C, exhibited a good combination of hardness 1500 kg/mm² and indentation toughness of ~ 8.8 MPa.m²/2, as well as a three point flexural strength of 2000 MPa. The crack propagation path originating from the corners of Vickers indentations of the 20Ni cermet, sintered at 1450 °C is shown in Fig. 4.d. Multiple crack paths are present, i.e., cracks propagate through NbC grains, along the NbC/NbC grain boundaries, along the NbC/Ni interface and through the binder. Intergranular fracture along the NbC/Ni and NbC/NbC grain boundaries are the major crack fracture mode at a high Ni content, indicating that crack deflection is a major toughening mechanism, besides crack bridging by the Ni binder. The crack deflection contribution and binder bridging effect are decreased at a 6 wt% Ni cermet, due to the lower amount of NbC/Ni interfaces.
Fig. 4. Influence of Ni binder content on the hardness (a), fracture toughness (b) and three-point flexural strength (c) of the NbC-Ni based cermets. Indentation crack propagation pattern of the NbC-20Ni-18WC-14Ti(C$_{0.7}$N$_{0.3}$) cermet sintered at 1450 °C.

4. Conclusions

Full densification of Ni bonded NbC-WC-Ti(C$_{0.7}$N$_{0.3}$) based cermets with 6 to 20 wt% Ni was achieved by pressureless liquid phase sintering in vacuum for 90 min at 1390 or 1450 °C. The WC and Ti(C$_{0.7}$N$_{0.3}$) starting powders completely dissolved in the NbC and binder phases during sintering. Core-rim structured NbC grains with a Nb- and W-rich core and a Ti-rich rim were formed in the cermets. The change in the lattice parameters confirmed the dissolution of WC and Ti(C$_{0.7}$N$_{0.3}$) in the binder and especially the NbC phase.

The variation in Ni content resulted in a clear effect on the hardness and toughness of the cermets. With increasing Ni content from 6 to 20 wt%, the hardness decreased from 1585 to 1128 kg/mm$^2$, whereas the fracture toughness increased from 7.97 to 13.06 MPa m$^{1/2}$ in the cermets sintered for 90 min at 1450 °C. The NbC-9Ni-18WC-14Ti(C$_{0.7}$N$_{0.3}$) cermet, sintered at 1450 °C, combined a good hardness of 1500 kg/mm$^2$, indentation toughness of ~ 8.8 MPa.m$^{1/2}$, and a three point flexural strength of 2000 MPa.

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