

NbC-BASED CERMETS: INFLUENCE OF SECONDARY CARBIDE ADDITION AND METAL BINDER

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Keywords: Niobium Carbide, Hardmetal, Cemented Carbide, Sintering, Grain Growth, Microstructure, Hardness, Fracture Toughness

Abstract

The influence of Al metal and WC, Cr₃C₂, VC, TiC and Mo₂C secondary carbide additions on the microstructure and mechanical properties of Fe, Co and Ni bonded NbC cermets was investigated. Powder mixtures were fully densified by pressureless liquid-phase sintering for one hour at 1420 °C in vacuum. Microstructural and compositional analysis, as well as the elemental distribution in the dense cermets, was performed by electron probe microanalysis (EPMA) to assess the effect of the additions on the NbC grain growth, NbC morphology and metal binder composition, allowing correlation of the microstructure with the fracture toughness and hardness of the cermets. The substitution of WC with 40 wt.%NbC in WC-12 wt.%Co cemented carbides resulted in a significant improvement of hardness when adding 0.9-3.6 wt.%VC or Cr₃C₂ as WC grain growth inhibitors. Compared to pure NbC-Ni, a limited NbC grain growth and homogeneous grain size distribution were obtained upon adding secondary phase carbides or Al metal. WC and Mo₂C significantly enhanced the hardness and toughness of NbC-Ni cermets. The Vickers hardness (HV 10) of 976 kg/mm² and indentation toughness of 9.2 MPa m^{1/2} of a NbC-15 vol.%Ni could be increased to 1357 kg/mm² and 10.1 MPa m^{1/2} respectively upon adding both 8.5 vol.%WC and 8.5 vol.%Mo₂C. The addition of 25-50 at.%Al in Fe binder also increased the hardness of NbC-Ni/Fe cermets, but with decreased toughness. The maximum hardness of the investigated cermets was obtained for a 40 wt.%NbC substituted WC-12 wt.%Co cemented carbide, exhibiting a Vickers hardness of 1697 kg/mm² and toughness of 7.8 MPa m^{1/2}, whereas the WC and Mo₂C added NbC-Ni cermets exhibited the optimum combination of hardness and fracture toughness.

Introduction

As a refractory carbide, niobium carbide (NbC) has a melting point of 3600 °C, density of 7.79 g/cm³, Vickers hardness of 19.6 GPa, Young's modulus of 338-580 GPa and electrical resistivity of 35 μΩ cm [1]. The density of NbC is much lower than that of the commonly used WC (15.68 g/cm³). Although WC-Co materials have been intensively investigated, NbC on the contrary has hardly been explored as the major carbide phase for cemented carbides and cermets. The solid solubility of NbC in Fe, Ni and Co at 1250 °C was reported to be only 1, 3 and 5 wt.% respectively, compared with 7 wt.% for WC in Fe [2]. Therefore, NbC matrix cutting tools and wear parts should be chemically more stable in contact with steel at elevated temperatures, than WC based materials. NbC-Co and NbC-Fe₃Al cemented carbides [3] were however very recently qualified as a competitive or even superior alternative in terms of wear resistance to WC- and Cr₃C₂-based cemented carbides and ceramics. Under dry oscillation, the wear resistance of binderless NbC was insensitive to relative humidity for both alumina and 100Cr6 bearing steel counterbodies, whereas the coefficient of friction of the cobalt- and Fe₃Al-bonded NbC grades was reduced with increasing relative humidity [4]. Although these tribological tests were conducted on KU Leuven based exploratory laboratory grades [4], they clearly illustrate the potential of these radically new NbC-based cermets for tribological applications. Earlier work revealed a remarkable NbC grain growth in NbC-Co based cermets when pressureless-sintered for one hour at 1360 °C [5]. NbC grain growth however can be largely suppressed when consolidating NbC-Co cermets in the solid state by hot pressing or spark plasma sintering (SPS) [5,6]. Huang et al. [7] investigated 0.45-60 wt.%NbC partially substituted WC-12 wt.%Co cemented carbides, processed by solid state SPS and conventional liquid-phase sintering (CS). A lower level of NbC addition (<0.9 wt.%) was found to limit WC grain growth during SPS and conventional sintering, whereas substantial (Nb,W)C grain growth was observed in the materials with higher NbC addition. To further improve the hardness of NbC-WC-Co cemented carbides, novel grade WC-Co cemented carbides containing a significant amount of NbC were developed by adding VC and Cr₃C₂ grain growth inhibitors [8]. Aluminides, a potential binder phase for NbC, are attractive for high-temperature structural material applications due to their good strength at intermediate temperatures and excellent corrosion resistance at elevated temperatures in oxidizing, carburizing and sulfurizing atmospheres [9,10].

In this study, the effect of Co, Ni, Fe, Ni-Al and Fe-Al metal binders on the microstructure and mechanical properties of pressureless liquid-phase sintered NbC-based cermets were investigated. An additional aim was to develop novel WC-Co cemented carbides containing 40 wt.% (54 vol.%) NbC. The influence of VC and Cr₃C₂ grain growth inhibitors on the microstructure and mechanical properties of WC-40 wt.% NbC-12 wt.%Co cemented carbides were investigated.

Experimental Procedure

Commercial carbide powders, NbC (Treibacher, FSSS: 1.18 μm , Austria), WC (Chongyi Zhangyuan Tungsten Co., 200 nm, China), Cr_3C_2 (Treibacher, FSSS: 1.95 μm , Austria), VC (Treibacher, FSSS: 1.15 μm , Austria) and Mo_2C (Chempur, 2 μm) and metal powders, Co (Umicore grade Co-HMP, FSSS; 0.55 μm , Belgium), Ni (Jingmen Gem Co. Ltd, FNiH-1b <1 μm , China) and Fe (Carbonyl, D_{50} : 3.4-4.5 μm , BASF, Germany) were used to prepare NbC-based cermets. The powders were mixed on a multi-directional mixer (Turbula, WAB, Switzerland) in ethanol for 24 hours using WC-6 wt.%Co milling balls (Ceratzit grade H20C, $\text{\O}10$ mm). The suspension was dried in a rotating evaporator at 65 $^\circ\text{C}$. The powder mixtures were then densified by conventional pressureless liquid-phase sintering of cold isostatically pressed (300 MPa) compacts ($\text{\O}20 \times 10$ mm) for one hour at 1420 $^\circ\text{C}$ in a dynamic vacuum (~ 7 Pa) at a heating/cooling rate of 20 $^\circ\text{C}/\text{minute}$.

The bulk density of the sintered cermets was measured in ethanol. The microstructure of polished surfaces was examined by electron probe microanalysis (EPMA, JXA-8530F, JEOL Ltd.), equipped with five wavelength dispersive X-ray spectroscopy (WDS) and one Energy Dispersive X-ray spectroscopy (EDS) type detector. The reported grain size values are the actually measured average intercept lengths measured on scanning electron micrographs. The Vickers hardness (HV 10) was measured (Model FV-700, Future-Tech Corp., Tokyo) with an indentation load of 98.1 N. The fracture toughness, K_{IC} , was measured from the length of the radial cracks originating from the corners of these indentations and calculated according to the formula of Shetty [11]. The reported values are the mean and standard deviation of five indentations.

Results and Discussion

Influence of Metal Binder of NbC Cermets

Backscattered electron micrographs (BSE) of the liquid phase sintered NbC cermets with 12 vol.% metal binders, ie Co, Co+0.9 vol.% Cr_3C_2 , Fe, Fe-25 at.%Al, Ni and Ni-25 at.%Al, are compared in Figure 1. For the Co, Fe and Ni bonded cermets, two backscattered electron contrasting phases could be differentiated in the micrographs. The bright and dark phases correspond to the NbC carbide and metal binder respectively.

As shown in Figure 1(a), the NbC grains in the NbC-12vol.%Co cermet exhibited an irregular shape and formed a highly interconnected carbide network. Some NbC grains merged, apparently excluding the Co binder from their grain boundary. The addition of 0.9 vol.% Cr_3C_2 , Figure 1(b) resulted in a reduced NbC grain contact (contiguity) and more spherical shaped NbC grains. During liquid phase sintering, grain growth occurs with the dissolution of smaller grains and the reprecipitation of dissolved material on larger grains. According to the WDS elemental mapping of the Cr_3C_2 -doped NbC-12vol.%Co cermet in Figure 2, the additional dark contrast phase located at some of the NbC grain boundaries is a Cr-rich phase, whereas Cr was hardly detected in any NbC grains. This Cr-rich phase could be M_7C_3 or M_{23}C_6 carbide, precipitated during cooling. In the Co binder, a very strong Cr peak was identified, which is in agreement with the Cr solution in the Co binder phase of WC-Co cemented carbides [12]. With the Cr_3C_2

addition, the morphology of the NbC grains changed from irregular to spherical shape. Due to the dissolution of Cr and C into the Co binder, the surface energy of the Co binder phase is altered and the wetting of the NbC grains is improved, which influences the grain growth and morphology of NbC grains.

In the case of an Fe binder, Figure 1(c), the shape of the large NbC grains is well-faceted with a slight rounding of the edges, while the small grains are almost spherical, whereas all NbC grains are angular with a Ni binder, Figure 1(e). The NbC grain size is in the 5-20 μm range. The most profound effect of the Al addition to the Fe, Figures 1(c) and (d) and Ni, Figures 1(e) and (f), binders is the NbC grain size reduction ($<10 \mu\text{m}$). Besides the NbC and metal binder grains, dark Al_2O_3 grains were found in the Al-doped cermets. In comparison to the Fe and Ni bonded cermets, the addition of 25 at.%Al resulted in a considerable NbC grain growth inhibition, a decreased NbC grain contact and an angular NbC grain morphology. During liquid phase sintering, the small NbC grains dissolved in the Fe or Ni binder and re-precipitated on larger NbC grains, Figure 1(c) and (e). The reduction of surface energy of the solid particles is the major driving force for small grains to dissolve and large grains to grow. When Al is dissolved in the binder, the interface energy of the liquid binder and the NbC grains, as well as the NbC solubility in the binder, are reduced, lowering the driving force for NbC dissolution-reprecipitation. This mechanism is also observed in TiC/TiN based cermets doped with WC, Mo_2C and VC [13,14]. The Fe-Al and Ni-Al binders are evenly distributed and the NbC grains have a narrow grain size distribution in the 5-10 μm range.

The X-ray elemental maps of Nb, Ni, Al, C and O of the liquid phase sintered 12 vol.% (Ni-25 at.%Al) cermet is shown in Figure 3. A similar elemental distribution was found in the (Fe-25 at.%Al) bonded cermet. The mapping clearly indicates that the Nb is confined to the carbide phase and both Al and Ni, as well as C were present in the binder phase. Due to the dissolution of C in the Ni binder, it is clear that the Nb/C ratio in the NbC phase has shifted to a lower carbon content. The dark sub-micron sized Al_2O_3 grains can be either due to Al_2O_3 impurities in the Al starting powder or the Al reduction of residual Nb_2O_5 at the surface of the NbC starting powder.

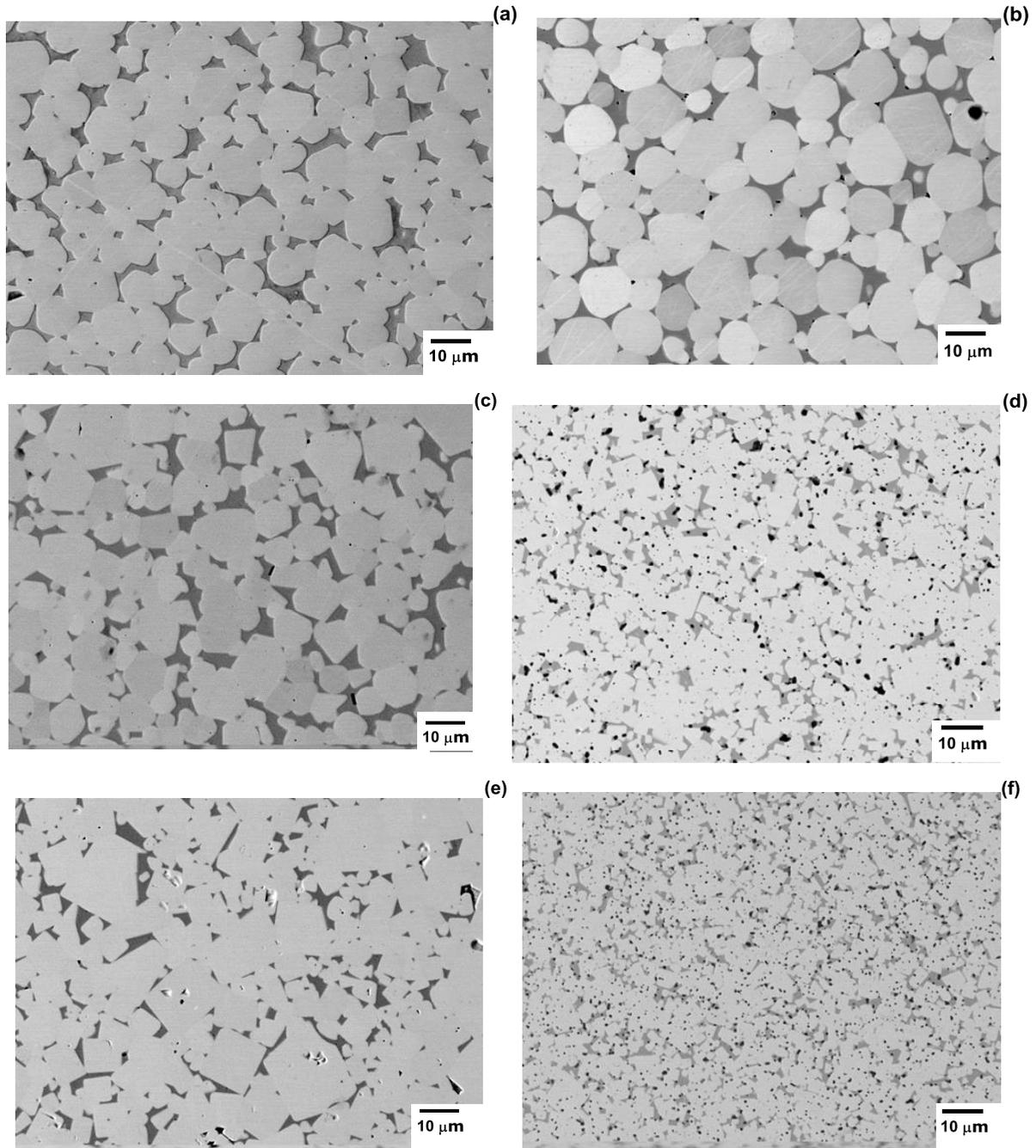


Figure 1. BSE micrographs of NbC cermets vacuum sintered at 1420 °C; NbC-12 vol.%Co (a), NbC-12 vol.%Co-0.9 vol.%Cr₃C₂ (b), NbC-12 vol.%Fe (c), NbC-12 vol.% (Fe-25 at.%Al) (d), NbC-12 vol.%Ni (e) and NbC-12 vol.% (Ni-25 at.%Al) (f).

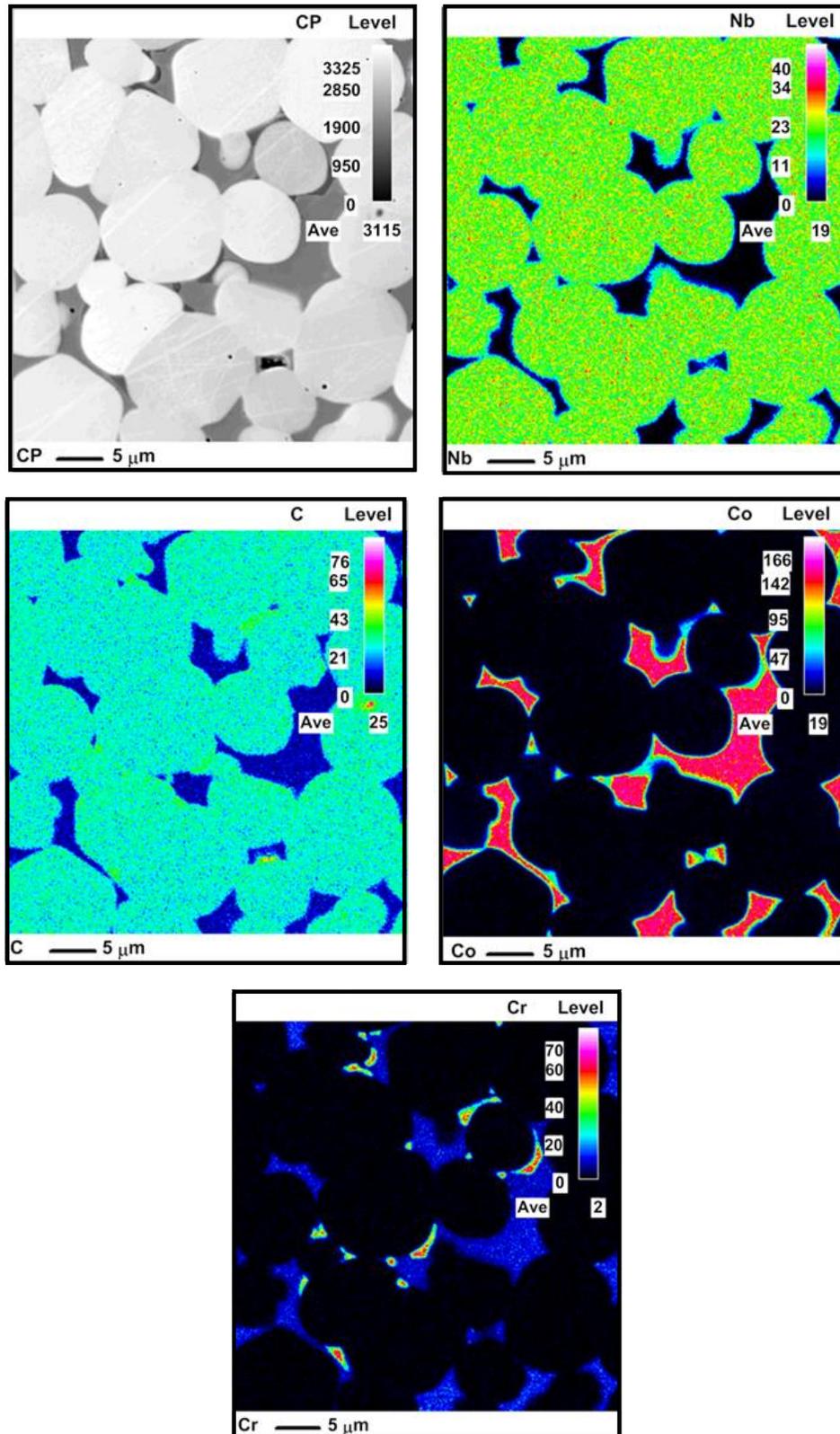
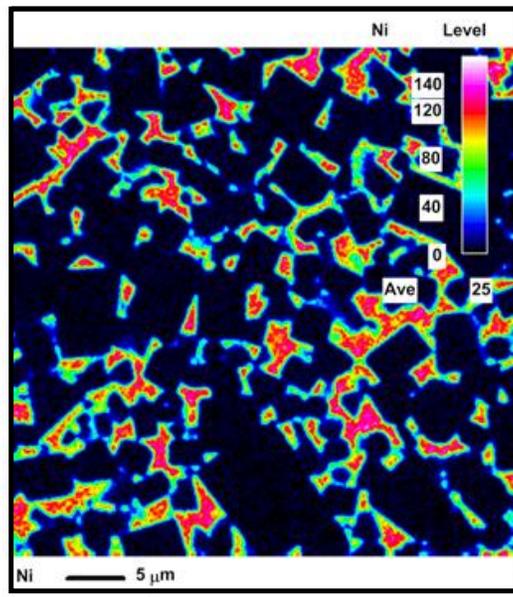
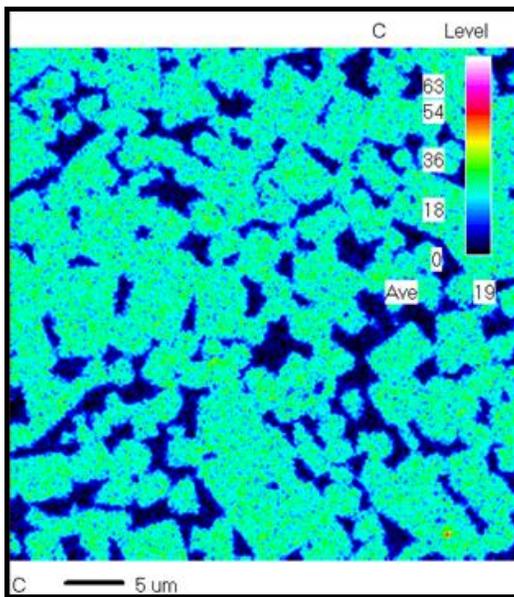
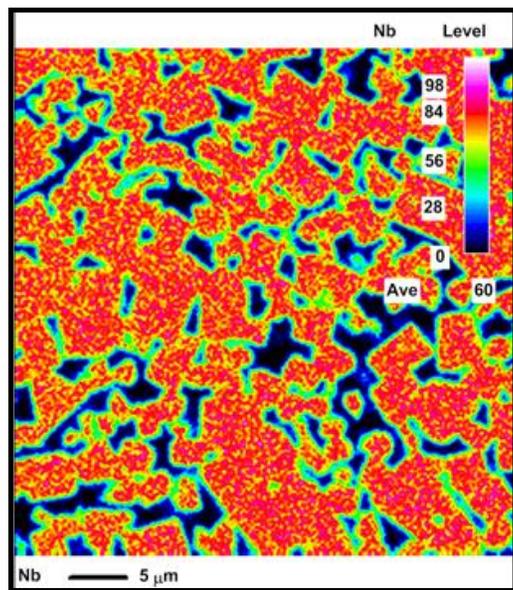
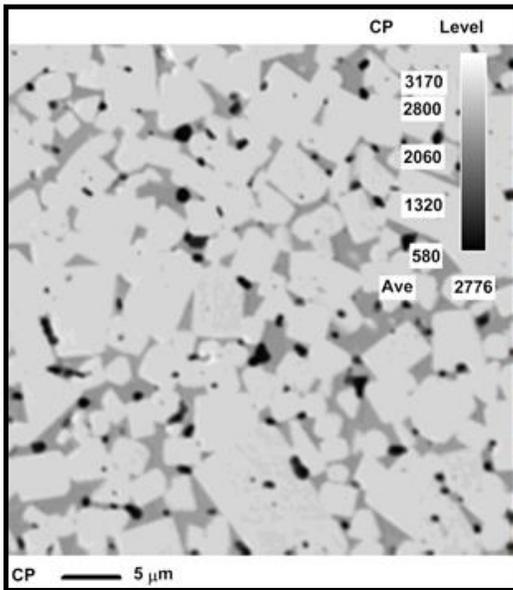


Figure 2. WDS elemental mapping of the NbC-12 wt.% Co-0.9 wt%Cr₃C₂ cermet, liquid phase sintered for one hour at 1420 °C in vacuum.



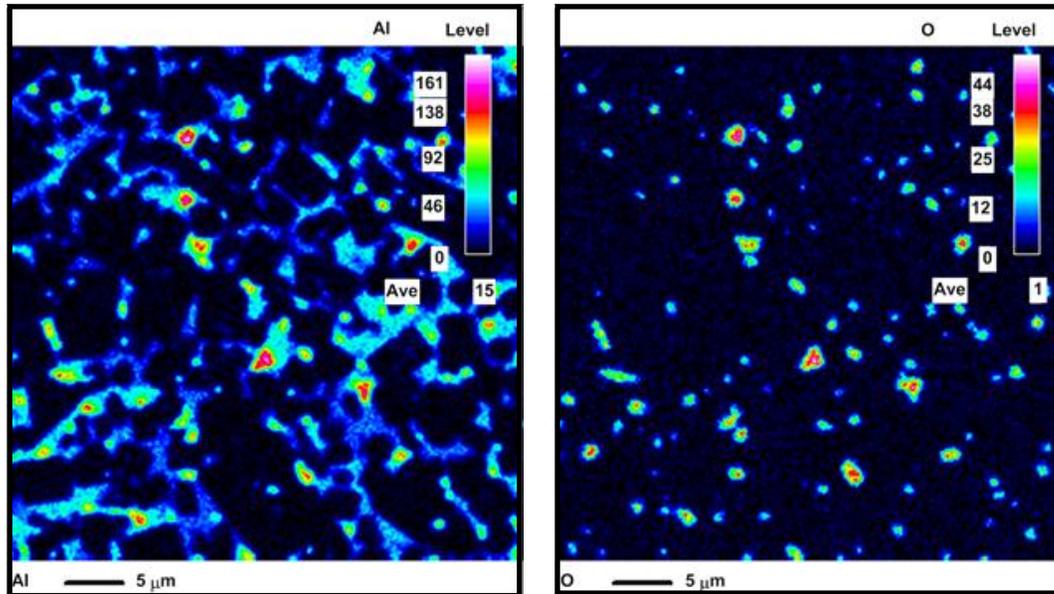


Figure 3. WDS elemental mapping of the NbC-12 vol.% Ni-25 at.%Al cermet, liquid phase sintered for one hour at 1420 °C in vacuum.

Influence of Secondary Carbide Additions

Cobalt Bonded WC-NbC Cemented Carbides. NbC substituted WC-Co cemented carbides with 40 wt.% (54 vol.%) NbC with and without VC or Cr₃C₂ addition were prepared by pressureless liquid-phase sintering for one hour at 1420 °C in vacuum.

BSE images of the WC-40 wt.% NbC-12 wt.%Co cemented carbides without and with 1.8 wt.% VC, 3.6 wt.% VC or 3.6 wt.% Cr₃C₂ are compared in Figure 4. Bright WC, grey NbC and dark Co binder phases could be differentiated based on their backscattered electron contrast. The grey NbC grains form a skeleton due to their 54 vol.% content and are actually (Nb,W)C solid solution grains. The Co binder is mainly present in-between the WC grains and not at the NbC grain boundaries, due to a different wetting between Co and WC/NbC [7]. In the 1.8 and 3.6 wt.% VC-doped grades, free VC grains could not be distinguished from NbC grains due to their similar atomic number. Compared to the NbC substituted WC-Co cemented carbide in Figure 4(a), it is apparent that the addition of 3.6 wt.% VC has a grain growth inhibiting effect on the WC grains. Similar to the VC-doped cemented carbide, the Cr₃C₂-doped grade, Figure 4(d) is composed of bright WC, grey (Nb,W,V/Cr)C and dark Co binder phases. The average WC grain size was only 0.16 and 0.21 μm when the cemented carbides were doped with 3.6 wt.% VC and Cr₃C₂, respectively.

The experimental results show that the NbC addition limits WC grain growth and a significant amount of WC grains dissolved into the NbC grains. The growth of the remaining WC grains was further inhibited with the VC or Cr₃C₂ addition. The WC grain growth inhibiting efficiency of VC in the WC-NbC-Co cemented carbide is higher than that of Cr₃C₂. When compared to plain WC-Co grades, a higher grain growth inhibitor content is needed in the NbC-substituted

WC-Co cemented carbide since the V and Cr not only dissolve in the Co binder and segregate at the WC interfaces, but also form (Nb,W,V/Cr) solid solution grains. However, the addition of VC and Cr_3C_2 has no clear influence on the (Nb,W)C grain size.

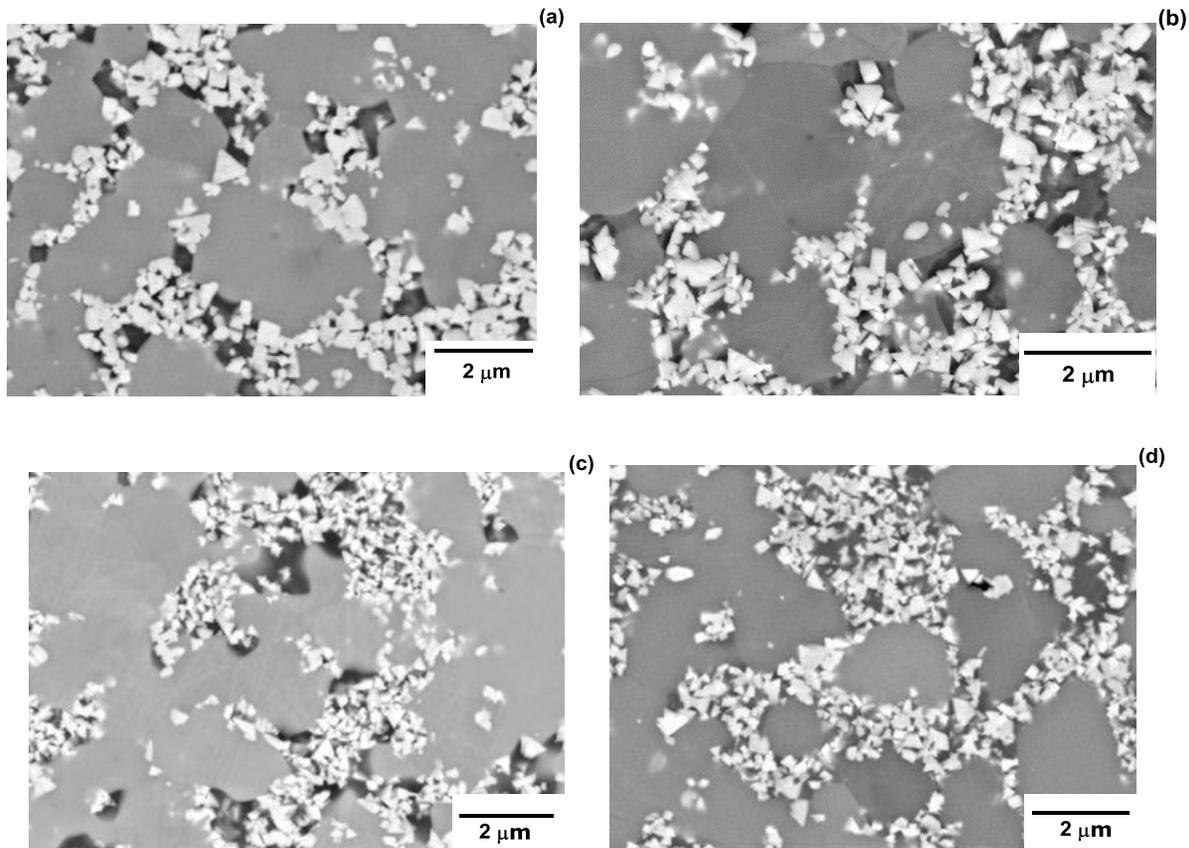


Figure 4. BSE micrographs of vacuum sintered (one hour at 1420 °C) WC-40 wt.% NbC-12 wt.%Co; without additives (a) and with 1.8 wt.% VC (b), 3.6 wt.% VC (c) and 3.6 wt.% Cr_3C_2 (d).

Nickel Bonded NbC-MeC Cermets. The microstructures of the NbC-15 vol.%Ni without and with 5 vol.% Mo_2C , 8.5 vol.% WC + 8.5 vol.% Mo_2C or 8.5 vol.% WC + 8.5 vol.% Mo_2C + 8.5 vol.% TiC addition, prepared via vacuum liquid-phase sintering for one hour at 1420 °C, are compared in Figure 5. Although some of these cermets have a high secondary carbide content phase addition, they all exhibited only a bright-grey NbC phase and a dark-grey Ni based metal binder. The NbC-15 vol.%Ni cermet, Figure 5(a) has relatively large (<15 μm) facet shape NbC grains with a slight rounding of the edges and mostly separated by the Ni binder. The addition of 5 vol.% Mo_2C significantly decreased the NbC grain size (<3 μm), as shown in Figure 5(b).

The NbC grain size is further reduced to 1-2 μm upon extra addition of WC and WC + TiC, as shown in Figures 5(c) and (d). These carbides are known to have a very high solubility ($\text{WC} > \text{Mo}_2\text{C} > \text{TiC}$) in Ni at the sintering temperature [15]. The surface energy of the liquid Ni binder was changed during sintering and dissolution of the secondary phase carbides, thereby influencing the NbC grain growth. The combined addition of WC + Mo_2C + TiC is a more efficient NbC grain growth inhibitor than the combination of WC + Mo_2C .

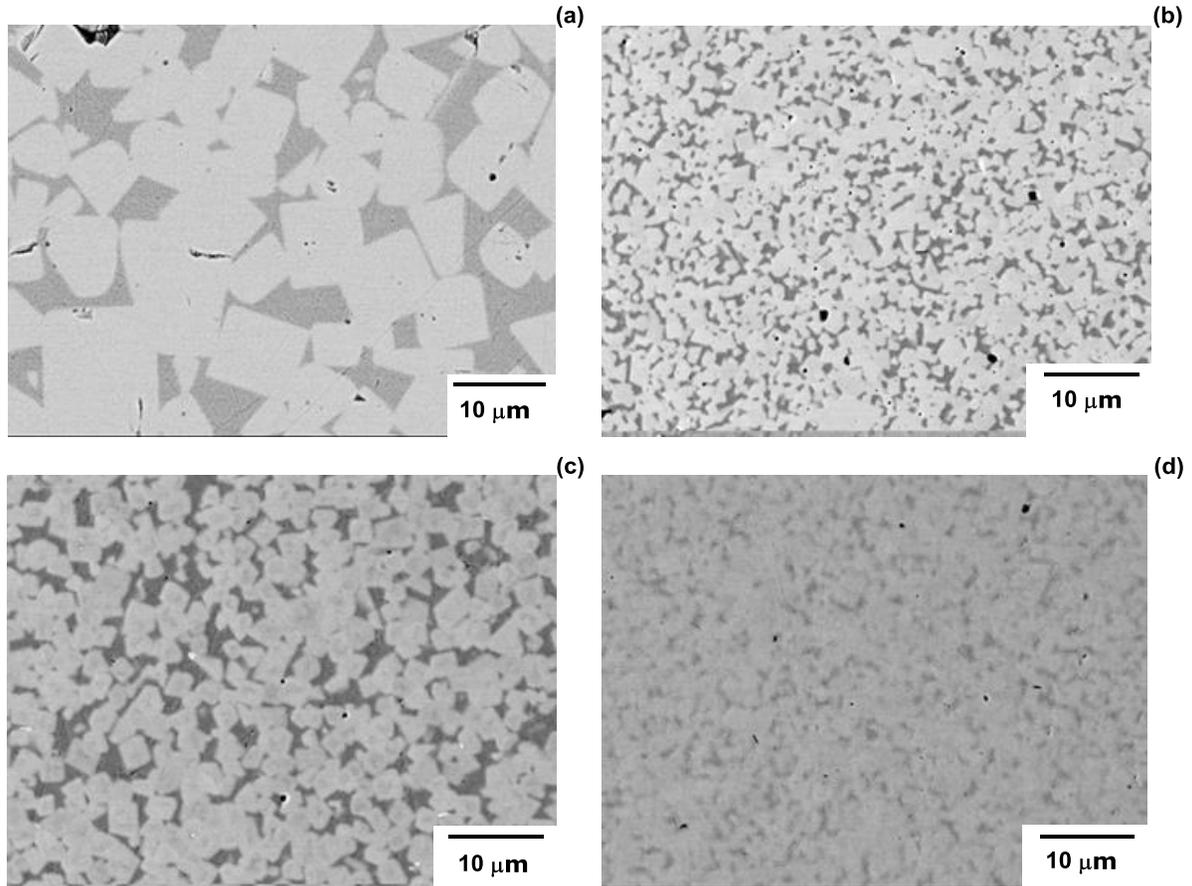


Figure 5. BSE micrographs of NbC-15 vol.%Ni cermets, vacuum sintered for one hour at 1420 °C; without additives (a) and with 5 vol.%Mo₂C (b), 8.5 vol.%WC + 8.5 vol.%Mo₂C (c) and 8.5 vol.%WC + 8.5 vol.%Mo₂C + 8.5 vol.%TiC (d).

Mechanical Properties

The Vickers hardness (HV 10) and fracture toughness (K_{IC}) of all investigated NbC cermets, prepared under exactly the same sintering conditions, are compared in Figure 6 and summarized in Table I. The theoretical density was calculated based on the mixture rule. Generally, the hardness of the cermets can be divided into four categories. The Co bonded WC-NbC-VC/Cr₃C₂ cemented carbides have the highest hardness, followed by the Ni bonded NbC-MeC cermets and the NbC-Ni and -Fe cermets which have a lower hardness. The CS prepared NbC-Co cermets exhibited the lowest hardness level. Since all grades have a comparable binder content, the difference in hardness of the NbC matrix cermets can be directly attributed to the nature of the binder and the constituent components, ie the binder composition and the NbC grain size. Based on the microstructural analysis, the refinement of the NbC grain size in the Al-doped Fe/Ni binder NbC cermets improved the hardness. The hardness of the Fe-Al, Ni-Al, Co and Ni binders are difficult to compare since they exhibit a different grain size. Considering the pure metal binder, the Fe bonded NbC cermets had the highest hardness of 1293 kg/mm², followed by the Ni and Co bonded cermets.

For the Co bonded WC-NbC-VC/Cr₃C₂ cemented carbides, the hardness increases with increasing grain growth inhibitor content. The highest hardness was obtained when adding 3.6 wt.%VC, followed by 3.6 wt.%Cr₃C₂ and 1.8 wt.%VC. For straight WC-Co cemented carbides, the hardness is mainly dependent on the WC grain size (Hall-Petch relationship) and the Co content. The finer the WC grain size, the higher the hardness for a given Co volume fraction.

In the NbC substituted cemented carbides, the fine WC grains are evenly dispersed in the (Nb,W,V/Cr)C-Co matrix. The critical factors affecting the mechanical properties of these cemented carbides are the properties of the (Nb,W,V/Cr)C and WC phases. Since the WC grain size refinement is accompanied by a reduction of the residual WC volume fraction, the increased hardness of the VC and Cr₃C₂-doped grades might also be partially due to solid solution hardening of the NbC phase. The higher hardness of the (Nb,W,V/Cr)C phase, however, remains to be proven.

Regarding the fracture toughness, there is a negative correlation between the hardness and fracture toughness of NbC matrix materials, ie the hardness increases and fracture toughness decreases with decreasing NbC grain size for a given binder type and binder content. The binder plays a crucial role in shielding the stress field in front of a crack tip to improve the toughness [16]. Ductile failure of the Co, Ni and Fe binder is usually found on fractured NbC-Co/Ni/Fe surfaces. Since the Fe-Al and Ni-Al have an intrinsically low room temperature ductility, the Al-doped cermets have a lower fracture toughness. For a given low hardness value of around 1250 kg/mm², the Ni bonded NbC cermets had the highest toughness of 12 MPa m^{1/2}, whereas the Fe and Co bonded cermets exhibited a toughness of only 6-7 MPa m^{1/2}. With increased hardness to 1500 kg/mm², the MeC-added NbC-Ni cermets still had the highest toughness of 8.5 MPa m^{1/2}, whereas the corresponding NbC-12 vol.% (Fe-25 at.% Al) cermet had a toughness of 5.9 MPa m^{1/2}. Analysis of the microstructures and mechanical properties in Figures 2-6 reveals that the addition of Al and secondary carbides have a great impact on the final NbC grain size and microstructure as well as the concomitant increased hardness and reduced toughness.

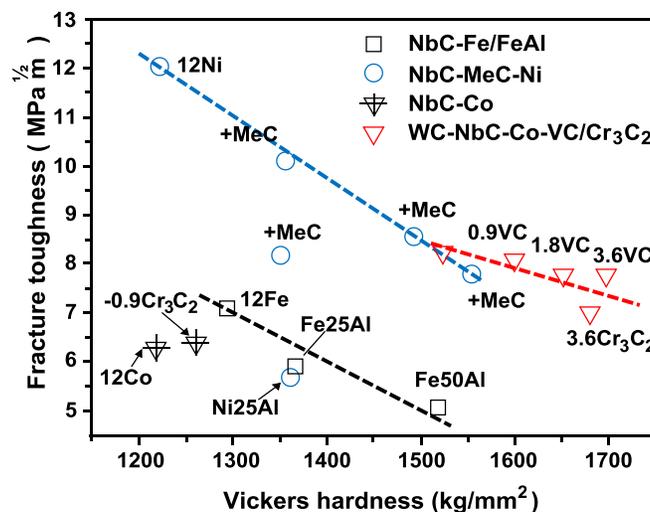


Figure 6. Vickers hardness and fracture toughness of all investigated NbC cermets and WC-NbC-Co cemented carbides.

Table I. Hardness and Fracture Toughness of the Investigated Cermets and Cemented Carbides

Materials	Density (g/cm³)	R.D. (%)	HV 10 (kg/mm²)	K_{IC} (MPa m^{1/2})
Cobalt bonded NbC cermets				
NbC-12 vol.% Co	7.83	98.8	1218 ± 32	6.30 ± 0.41
NbC-12 vol.% Co-0.9 vol.%Cr ₃ C ₂	7.78	98.5	1260 ± 13	6.40 ± 0.20
Iron bonded NbC cermets				
NbC-12 vol.%Fe	7.75	99.3	1293 ± 27	7.09 ± 0.50
NbC-12 vol.% (Fe-25 at.%Al)	7.68	100	1366 ± 8	5.90 ± 0.26
NbC-12 vol.% (Fe-50 at.%Al)	7.42	98.2	1518 ± 17	5.05 ± 0.10
Nickel bonded NbC-MeC cermets				
NbC-12 vol.%Ni	7.90	99.4	1222 ± 15	12.04 ± 0.75
NbC-12 vol.% (Ni-25 at.%Al)	7.94	98.4	1360 ± 14	5.68 ± 0.20
NbC-15 Ni-5 Mo ₂ C (vol.%)	7.93	100	1351 ± 13	8.16 ± 0.57
NbC-15 Ni-8.5 Mo ₂ C-8.5 WC (vol.%)	8.74	100	1357 ± 29	10.11 ± 0.82
NbC-15 Ni-8.5 Mo ₂ C-8.5 WC-8.5 TiC (vol.%)	8.51	100	1553 ± 26	7.78 ± 0.19
NbC-15 Ni-8.5 Mo ₂ C-8.5 WC-17.0 TiC (vol.%)	8.10	98.5	1492 ± 6	8.55 ± 0.48
Cobalt bonded WC-NbC cemented carbides				
WC-12Co-40NbC (wt.%)	10.50	99.9	1523 ± 21	8.26 ± 0.39
WC-12 Co-40 NbC-0.9 VC (wt.%)	10.38	100	1599 ± 14	8.11 ± 0.15
WC-12 Co-40 NbC-1.8 VC (wt.%)	10.06	98.0	1651 ± 14	7.80 ± 0.21
WC-12 Co-40 NbC-3.6 VC (wt.%)	10.06	100	1697 ± 6	7.78 ± 0.10
WC-12 Co-40 NbC-3.6 Cr ₃ C ₂ (wt.%)	10.17	100	1680 ± 15	7.03 ± 0.20

Conclusions

Full densification of Fe, Co and Ni bonded NbC based cermets was achieved by pressureless liquid phase sintering in vacuum for one hour at 1420 °C. The hardness and toughness of the NbC matrix cermets can be mainly tailored by the binder composition and secondary carbide additions. The addition of Al in an Fe or Ni binder based NbC cermets, or the addition of multiple carbides (WC, Mo₂C or TiC) in NbC-Ni cermets, not only influenced the morphology of the NbC grains, but also the NbC grain growth. For a given binder phase, the investigated materials show a similar trend in hardness and toughness, ie the higher the hardness, the lower the fracture toughness. Ni binder based NbC cermets allow the combination of high hardness and improved toughness. The addition of small amounts of VC/Cr₃C₂ in a NbC partially substituted WC-Co cemented carbide increased significantly the hardness in combination with a moderate fracture toughness.

Acknowledgements

We gratefully acknowledge the financial support of the Companhia Brasileira de Metalurgia e Mineração (CBMM), São Paulo, Brazil. The authors thank the Hercules Foundation (project ZW09-09).

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