Microstructure and mechanical properties of WC and Ti(C_{0.7}N_{0.3}) modified NbC solid solution cermets

S. G. Huang^{a,*}, J. Vleugels^a, B. Tunca Altintas^a, J. H. Huang^a, B. Lauwers^b, J. Qian^b

^aDepartment of Materials Engineering, KU Leuven, Belgium

^bDepartment of Mechanical Engineering, KU Leuven and Member Flanders Make, Belgium

Abstract

Eight NbC solution matrix cermets were prepared by liquid phase sintering of mixtures containing NbC, WC, Ti(C_{0.7}N_{0.3}), Mo₂C, Co and Ni powders. The influence of the WC and Ti(C_{0.7}N_{0.3}) content on the microstructure and mechanical properties of the cermets was investigated. Microstructural investigation was supported by thermodynamic equilibrium calculations to predict the composition of the constituent phases as a function of WC content at 1420 °C. The results indicated the variation in WC and Ti(C_{0.7}N_{0.3}) content had a significant influence on the phase content, the in-situ formed (Nb,W,Ti,Mo)(C,N) solution grain growth and concomitant mechanical properties. The NbC solution cermets with 12-32 wt% WC were composed of a core-rim (Nb,W,Ti,Mo)(C,N) phase, Co-Ni alloy binder, and rimless Ti(C_{0.57}N_{0.43}) phase. XRD phase analysis and simulations revealed that the composition of the cubic structure (Nb,W,Ti,Mo)(C,N) and Ti(C,N) solid solutions depend on the WC content. The NbC matrix cermets with 12-32 wt% WC exhibited a Vickers hardness (HV₃₀) of ~1500 kg/mm² and indentation toughness of ~ 9 MPa.m^{1/2}.

Keywords: Niobium carbide, Carbonitride, Sintering, Microstructure, Thermodynamics

1. Introduction

Ti(C,N) based cermets are characterized by a high temperature creep and diffusion wear resistance. These properties make them suitable for high speed machining of steels. Due to their modest toughness and flexural strength, Ti(C,N) cutting tools are restricted to low feed rate finishing operations [1-4]. Ti(C,N) cermets are generally produced by sintering powder mixtures of Ti(C,N), metallic binder, and carbides such as WC, Mo₂C, NbC or TaC [2,4]. A small amount of WC added to Ti(C,N) cermets decreases Ti(C,N) grain growth and increases the creep resistance of the binder [5,6]. The effect of WC on the microstructure and mechanical properties of Ti(C,N) cermets has been reported in numerous studies, such as Ti(C_{0.5}N_{0.5})-(0-25 wt%) WC-Mo-Ni [5], Ti(C_{0.6}N_{0.4})-(0-9 wt%) WC-Mo-Ni [6], Ti(C_{0.7}N_{0.3})-(0-25 wt%) WC-Ni [7], (Ti,W)(C,N)-(0-20 wt%) WC-Co [8] and Ti(C_{0.7}N_{0.3})-(0-30 wt%) WC-Mo₂C-(Co,Ni) cermets [9]. Beside WC, a small amount of cubic carbides, i.e. NbC or TaC are doped into Ti(C,N) cermets to improve the thermal shock resistance and hot hardness [10,11]. Optimal thermal shock resistance and flexural strength were observed in Ti(C_{0.5}N_{0.5})-Ni cermets with 3 wt% NbC addition [11]. Moreover, a clear effect of NbC addition on the morphology of Ti(C,N) grains was

reported for $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -(5-40) NbC-20 Ni (wt%) cermet, resulting in either core-rim $\text{Ti}(\text{C},\text{N})$ or rimless $\text{Ti}(\text{C},\text{N})$ grains, depending on the NbC content [12].

Unlike for the wear resistant $\text{TiC}/\text{Ti}(\text{C},\text{N})$ - and WC-based materials, the technological applications of NbC have been mainly focused on the microstructural refinement of steels, although NbC possesses a unique combination of high melting point, high hardness and good chemical stability against iron/steels at elevated temperatures [13,14]. Recently, NbC matrix materials were reported to have a pronounced wear resistance and increased tool life when compared to uncoated WC-Co inserts [14]. Similar to $\text{Ti}(\text{C},\text{N})$ based cermet, the NbC grain growth and morphology as well as mechanical properties of NbC based cermet can be adjusted by secondary carbides (WC, TiC, VC, Mo/Mo₂C), carbonitrides ($\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ or $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$) or a combination of these compounds [15,16]. However, the microstructural and mechanical properties evolution in NbC- $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -WC-Mo₂C-Co-Ni cermet has not yet been reported. In the present study, the microstructure and mechanical properties of NbC solid solution (NbC_{ss}) cermet with the addition of different ratio of WC/ $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ were investigated. The NbC content was fixed at 30 wt% to form solid solution niobium carbide (NbC_{ss}) matrix cermet. The evolution of the phase composition was explained by thermodynamic simulation.

2. Methodology and experiment

2.1. Thermodynamic simulation

For $\text{Ti}(\text{C},\text{N})$ cermet, the microstructure mostly contains core-rim $\text{Ti}(\text{C},\text{N})$ solution grains, dispersed in a metal binder [2-4]. The $\text{Ti}(\text{C},\text{N})$ core and $(\text{Ti},\text{W},\text{Mo},\text{Nb})(\text{C},\text{N})$ rim are usually considered as one cubic structure phase, although the compositions are clearly different. NbC and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ have an identical NaCl type fcc structure and form a continuous solid solution between NbC and TiC [17, 18]. Due to the high solubility of WC and Mo₂C in the cubic NbC and TiC phase as well as in the Co/Ni binder, it is expected that the phase equilibrium of the investigated NbC cermet are considerably more complicated when a high fraction of WC and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ are present. Although some microstructural and phase analysis of low NbC content $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -WC cermet have been published [7,9], no phase diagrams and systematic investigations addressing the effect of the WC and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ content on NbC matrix cermet have been reported. Therefore, thermodynamic simulations were performed to estimate the equilibrium phases and their composition at the sintering temperature using the TCNi8 database of the Thermo-Calc software V2020a (Thermo-Calc Software Inc., Solna, Sweden) [19]. The obtained knowledge can also be transformed to the design of multi-components $\text{Ti}(\text{C},\text{N})$ matrix cermet with/without NbC addition.

2.2. Materials preparation

Based on the simulation, compositions of the cermet were designed to facilitate the investigation on the influence of the WC and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ content on the phase constitution and microstructure of NbC

based cermets. Powder mixtures with a 30NbC-4Mo₂C-7Co-7Ni (wt%) base composition, and balanced variable Ti(C_{0.7}N_{0.3}) and WC content were prepared, hereafter referred to as 12WC, 16WC up to 52WC respectively, as listed in Table 1. The Ti(C_{0.7}N_{0.3}) content evolved from 40 to 0 wt% with increasing WC content from 12 to 52 wt%. The theoretical density (T.D.) was calculated based on the mixture rule, applied to the starting powder composition. Both the theoretical density and the volume of metal binder are increased with increasing replacement of Ti(C_{0.7}N_{0.3}) by WC due to the higher density of WC.

Table 1 Chemical composition of the investigated NbC-WC-Ti(C_{0.7}N_{0.3}) based cermets in wt%

Cermet	NbC	WC	Ti(C _{0.7} N _{0.3})	Mo ₂ C	Co	Ni	Binder (vol%)	NbC (vol%)	T.D. (g/cm ³)
12WC	30	12	40	4	7	7	10.96	26.83	6.90
16WC	30	16	36	4	7	7	11.36	27.84	7.16
20WC	30	20	32	4	7	7	11.81	28.92	7.44
24WC	30	24	28	4	7	7	12.28	30.08	7.81
28WC	30	28	24	4	7	7	12.80	31.35	8.04
32WC	30	32	20	4	7	7	13.36	32.73	8.49
36WC	30	36	16	4	7	7	13.98	34.23	8.85
52WC	30	52	0	4	7	7	17.13	41.95	10.89

The NbC matrix cermets were made of the following starting powders, NbC (CBMM, FSSS=1.52 μm, Brazil), WC (Umicore, CW5300, FSSS=2 μm, Belgium), Ti(C_{0.7}N_{0.3}) (H.C. Starck, FSSS=3.0 μm, Germany), Mo₂C (Langfeng, FSSS=3.50 μm, China), Co (Umicore, Co-HMP, FSSS=0.55 μm, Belgium) and Ni (Vale, T123TM, FSSS=3-7 μm, UK). The NbC powder has a total C and O content of 10.99 and 0.21 wt%. The WC powder has a total C and O content of 6.14 and 0.08 wt%. The C, N and O content of the Ti(C_{0.7}N_{0.3}) powder are 13.2, 6.8 and 0.6 wt%, respectively. All powder mixtures were uniformly mixed on a multi-directional mixer (Turbula, WAB, Switzerland) in isopropanol for 48 h using WC-6 wt% Co balls. After drying and sieving the powder mixtures, green compacts were prepared by cold isostatic pressing at 200 MPa and sintered for 90 min at 1420 °C in a graphite furnace in dynamic vacuum (~ 50 Pa), using a heating rate of 10 °C/min from room temperature to 1250 °C and 3 °C/min from 1250 to 1420 °C.

2.3. Characterization

The density of the sintered cermets was measured in ethanol by the Archimedes method. The specimens were cross-sectioned with a diamond saw and polished with diamond pastes of 1-15 μm . Polished and fractured surfaces were observed by high resolution scanning electron microscopy (NanoSEM, Nova 450, FEI). Two representative samples for transmission electron microscopy (TEM) examination were prepared by focused ion beam microscopy (FIB, Nova NanoLab 600 DualBeam, FEI), using 30 kV Ga ions for milling and 5 kV Ga ions for cleaning. Selected area electron diffraction (SAED) patterns and high angle annular dark field (HAADF) scanning TEM (STEM) images were collected using JEOL ARM200F. Elemental mapping of polished cermets were performed by electron probe microanalysis (EPMA, JXA-8530F, JEOL Ltd, Japan). The accelerating voltage and beam current were fixed at 15 kV and 100 nA, respectively. The average grain size of the NbC solutions was measured by the line intercept method using back-scattered images, without applying a correction factor. The diffraction patterns from polished surfaces were recorded from 20 to 80° 2θ with a angular step of 0.02° and a counting time of 1 s per step using a θ - θ X-ray diffractometer (Seifert 3000, Ahrensburg, Germany) and Cu K_α radiation (40 kV, 40 mA). The lattice parameters of the constitute phases were refined by Rietveld analysis [20]. Vickers (HV_{30}) hardness was determined with a load of 294 N for 15 s. Indentation fracture resistance, K_{IC} , was calculated according to the Shetty formula [21]. Five indentations on each cermet were made to obtain the mean and standard deviation.

3. Results and discussion

3.1. Thermodynamic simulation

For the simulation, NbC, WC, TiC, TiN, Mo_2C , Ni, Co, and C were defined as input compounds. Fig. 1.a plots the calculated isothermal section of the NbC-WC-Ti($\text{C}_{0.7}\text{N}_{0.3}$) system at 1420 °C and an atmospheric pressure of 50 Pa, equivalent to the sintering vacuum pressure. The Mo_2C , Co and Ni content is fixed at 4, 7 and 7 wt%, respectively. The proposed compositions, indicated by the red dashed line and dots are in different phase regions, depending on the WC content. Beside the equilibrium liquid binder and gas phases, NbC_{ss}, Ti(C,N) and WC are also indicated as constituent phases in the diagram. Three major hard phase constituents, i.e. NbC_{ss}-Ti(C,N), NbC_{ss}, and NbC_{ss}-WC are expected along the WC/Ti($\text{C}_{0.7}\text{N}_{0.3}$) compositional range. For conventional Ti(C,N) cermets, the compositions are generally located in the red square area, where the stable ceramic phases are usually Ti(C,N) and a small amount of rim composition (Ti,W,Mo,Nb)(C,N) solutions [4,11,12,22].

The influence of the WC content on the phase constitution in the NbC cermets is shown in Fig. 1.b. At 1420 °C, the substitution of Ti($\text{C}_{0.7}\text{N}_{0.3}$) by WC has a clear effect on the phase evolution. 45-75 wt% NbC_{ss} forms the matrix of the cermets and a small amount of gas phase is always present. At a WC content below 29 wt%, the cermets contain NbC_{ss}, liquid binder and Ti(C,N) phases. A combination of NbC_{ss} and liquid binder is found in the 29-40 wt% WC composition range. At higher WC content,

NbC_{ss}, liquid binder and WC phases are predicted to co-exist in the cermets. The NbC_{ss} and metal binder phase content increased gradually with increasing WC content, until Ti(C_{0.7}N_{0.3}) is completely substituted by WC.

Figs. 1.c and d show the influence of the WC content on the composition of the liquid binder and NbC_{ss} phases. In the binder phase, the main compounds are Co, Ni and WC, as compared to the other compounds NbC, Mo₂C, TiC, TiN and C. A significantly lower TiN content is estimated in the binder, as compared to WC and other carbides. At 1400 °C, the solubility of WC, Mo₂C, NbC, TiC and TiN in liquid Ni is 27, 36, 7, 11 and < 0.5 wt%, respectively [2]. The simulation is therefore consistent with the experimental data. With increasing WC content, more WC is dissolved in the binder. A maximum WC content of 51 wt% is predicted in the binder when the total WC content is close to 35 wt%. A negative C value is estimated in the binder in order to reduce the extra C from the carbides, implying that the C from the carbides can not be completely dissolved in the binder. In the NbC_{ss} phase, the main dissolved compounds are NbC, TiC and WC, whereas the TiN content is significantly lower. Therefore, the NbC_{ss} can be described as a nitrogen-poor (Nb,Ti,W,Mo)(C,N) solution. With increasing WC content, more TiC is replaced by WC in the NbC_{ss} phase.

The chemical composition of the Ti(C,N) phase is plotted in wt% and mol% in Figs. 1.e and f, respectively. The dominant components are TiN and TiC, whereas the other carbides are not found. According to the TiC/TiN molar ratio, the [C]/([C]+[N]) ratio of the Ti(C,N) phase decreases with increasing WC content and is lower than that of the Ti(C_{0.7}N_{0.3}) starting powder. The estimated [C]/([C]+[N]) ratio is 0.48, 0.45 and 0.42 at a WC content of 12, 20 and 28 wt%, respectively. Therefore, a N-rich Ti(C,N) phase will remain in the sintered cermets. Based on the simulation, the expelled gas phase contains N-rich compound, consistent with the phenomena that N₂ is outgassed during the sintering of Ti(C,N), WC, Mo₂C and NbC powder mixtures in vacuum [2,4]. The formation of CO is not expected since O₂ was not considered in the simulation. The influence of N₂ gas pressure on the phase formation of the 16WC cermet is shown in Fig. 1.g. According to the simulation, the gas phase content increases with decreasing N₂ gas pressure at 1420°C. There is no Ti(C,N) decomposition, i.e. the in-situ gas formation when the gas pressure is above 2000 Pa. A small amount of Ti(C,N) however is decomposed into TiC and N₂ when the pressure is 50 Pa at 1420 °C.

Fig. 1. Calculated isothermal section of the NbC-WC-Ti(C_{0.7}N_{0.3}) system at 1420 °C (a). Influence of WC content on the phase constitution in the investigated cermets (b), composition of the metal binder phase (c), NbC_{ss} phase (d) and Ti(C,N) phase (e (wt%) and f (mol%)) and influence of sintering furnace gas pressure on the phase content of the 16WC cermet, sintered at 1420 °C (g).

3.2. Microstructural analysis

Microstructures of the sintered NbC-WC-Ti(C_{0.7}N_{0.3}) cermets with 12-52 wt% WC are compared in Fig. 2. All cermets were fully densified, regardless of the WC content. Despite the difference in composition, the microstructure of the 12-28 wt% WC cermets looks fairly similar in terms of phase distribution, grain morphology and grain size. Three contrasting phases can be differentiated in the cermets, i.e., core-rim structured NbC, dark contrast Ti(C,N) and metallic binder. WC and Mo₂C were completely dissolved in the ceramic and/or the binder phases. The NbC grains exhibited a bright core-grayish rim morphology and form the matrix of the cermets. Composition analysis on both the core and rim of the NbC solution grains indicate the presence of Nb, Ti, W and Mo, consistent with the thermodynamic simulation in Fig. 2.d. The rim area is richer in Ti than the core and the bright core has a higher concentration of W and Mo, as compared to the rim area. The chemical composition of the grey contrast core-rim grains was reported for Ti(C_{0.7}N_{0.3})-19Mo₂C-20NbC-24Ni (wt%) cermet, indicating a higher level of Mo and Nb in the core than in the rim [22]. Similar results were reported for Ti(C_{0.7}N_{0.3})-(15-25)NbC-20Ni (wt%) cermets, where the grey contrast grains had 30 at% Nb in the core and 20 at% Nb in the rim area [23].

For core-rim structured grains, the precipitation sites of the rim on the core are mainly determined by the surface energy. The surface energy of NbC in Ni is higher than that of Ti(C,N) [12]. Therefore, a rim phase preferentially precipitated on the surface of the NbC-rich core rather than on the Ti(C,N) grains. Since WC and Mo₂C already completely dissolved in the metal binder at a much lower

temperature ($< 1300\text{ }^{\circ}\text{C}$) as compared to the rapid dissolution temperature of $\text{Ti}(\text{C},\text{N})$ ($>1400\text{ }^{\circ}\text{C}$) [2, 24-26], the formation of the Nb-rich $(\text{Nb},\text{W},\text{Mo})\text{C}$ cores already occurred at solid state sintering temperatures around $1300\text{ }^{\circ}\text{C}$ by the dissolution of WC and Mo_2C in the binder phase and concomitant diffusion and dissolution in the NbC phase. With increasing temperature, there is a preferential solubility of TiC from $\text{Ti}(\text{C},\text{N})$ grains due to the much higher solubility of TiC than TiN in Ni [2]. In this study, TiC from the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ grains partially dissolved into the binder and reprecipitated as a Ti-rich $(\text{Nb},\text{Ti},\text{W},\text{Mo})(\text{C},\text{N})$ solid solution rim on the Nb-rich $(\text{Nb},\text{W},\text{Ti},\text{Mo})\text{C}$ core grains at liquid phase sintering temperatures. The overall surface energy of the cermets is decreased upon formation of the Ti-rich $(\text{Nb},\text{Ti},\text{W},\text{Mo})(\text{C},\text{N})$ rim on the NbC solution core. The total N content of the core-rim NbC grains is expected to be negligible according to the simulation.

Although the 12-32 wt% WC cermets show a similar NbC_{ss} morphology, some gradual microstructure changes can be observed as a function of the WC content. With increasing WC content, the width of the core increases, whereas the thickness of the rim decreases, indicating that more W dissolves to form W-rich NbC cores. When the WC content is above 36 wt%, it becomes difficult to distinguish the core and rim of the NbC_{ss} grains. Further substitution of $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ by WC promotes the formation of a $(\text{Nb},\text{W},\text{Mo})\text{C}$ solid solution through the dissolution of WC and Mo_2C into NbC. As shown in Figs. 2.g and h, the 36 and 52 wt% WC cermets contain an interconnected structure of larger $(\text{Nb},\text{W})\text{C}$ grains with dispersed bright WC grains. The Co-Ni binder phase was found to be mainly located at the WC/WC grain boundaries, whereas it was hardly detected at the $(\text{Nb},\text{W},\text{Mo})\text{C}/(\text{Nb},\text{W},\text{Mo})\text{C}$ and $(\text{Nb},\text{W},\text{Mo})\text{C}/\text{WC}$ grain boundaries. The change in microstructure with an increase in WC content is consistent with observations in cubic phase containing cemented carbides [27,28].

Compared to the NbC starting powder, coarsening of NbC_{ss} grains is observed in these cermets. As summarised in Table 2, the average NbC_{ss} grain size, as determined by the line intercept method, is in the $1.30\text{--}1.60\text{ }\mu\text{m}$ range in the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ containing cermets (12-32WC) and substantially increased to $3.65\text{ }\mu\text{m}$ in the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ free cermet (52WC). A much smaller average NbC grain size is observed in the current WC and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ modified NbC matrix cermets, as compared to NbC-Ni cermets [16]. Due to the dissolution of WC, Mo_2C and TiC in the NbC and binder phases, the surface energy of the liquid binder, as well as the in-situ formed core-rim NbC solution grains, was changed during sintering, influencing the grain growth behaviour of the solution carbide.

The $\text{Ti}(\text{C},\text{N})$ particles in the 12-28 wt% WC cermets exhibit a rimless structure, characteristic of some $\text{Ti}(\text{C},\text{N})$ cermets with high nitrogen or high cubic carbide content [4, 12, 23]. Previous studies of the low NbC content $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -WC/ Mo_2C -NbC-Co-Ni cermet system demonstrated that $\text{Ti}(\text{C},\text{N})$ grains always exhibit a typical core-rim structure [6-9]. A $\text{Ti}(\text{C},\text{N})$ core and $(\text{Ti},\text{Nb})(\text{C},\text{N})$ rim were reported in $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -NbC-Ni cermets with less than 10 wt% NbC, whereas rimless $\text{Ti}(\text{C},\text{N})$ grains were found in the cermets containing 15-40 wt% NbC [12, 23]. The misfit strain between $\text{Ti}(\text{C},\text{N})$ and $(\text{Ti},\text{Nb})(\text{C},\text{N})$ was explained as the key factor for the separation of core/rim structures in the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -

NbC-Ni cermets [23]. According to the simulation in Fig. 1, the composition of the Ti(C,N) phase is clearly different from the NbC solution phase. A large misfit strain is therefore expected between the two phases, resulting in the formation of rimless Ti(C,N) grains.

Fig. 2. Backscattered electron micrographs of the NbC-WC-Ti(C_{0.7}N_{0.3}) cermets, sintered at 1420 °C. (a) 12WC, (b) 16WC, (c) 20WC, (d) 24WC, (e) 28WC, (f) 32WC, (g) 36WC and (h) 52WC.

HAADF STEM images of the 16WC and 52 WC grade cermets were collected to study the phases at higher magnification for better identification of the phases, as seen in Fig. 3. In this imaging mode, the contrast is proportional with the atomic weight of constituent elements, thus enables easy identification of the phases. As shown in Fig. 3.a, Ti(C,N) with the smallest molecular weight appears the darkest and WC grains appear the brightest in Fig. 3.b. SAED patterns used for identification of the hard phases are given in Fig. 3. Multiple interfaces, including NbC/NbC, NbC/binder, Ti(C,N)/binder and NbC/Ti(C,N) interfaces can be clearly observed in the 16WC cermet. Interfaces of NbC/WC, WC/WC, WC/binder as well as NbC/binder are observed in the 52WC cermet.

Fig. 3. HAADF STEM images and SAED patterns of the 16WC (a) and 52WC (b) cermets. Dashed circles mark the grains where SAED were collected. Z.A. stands for 'zone axis'.

In order to clarify the phase compositions, EPMA elemental mapping was carried out for the 12WC and 36WC cermets with representative microstructure features, as shown in Fig. 4. In the 12WC cermet, evenly distributed Co and Ni are found only in the binder grains. The elements W and Mo are also observed in the binder. The core-rim NbC_{ss} grains exhibit a gradient distribution of Nb, W and Ti. As

compared to the rim, a higher concentration of W and Nb is found in the core, whereas the Ti content is lower in the core. The rimless Ti(C,N) grains have the highest concentration of Ti, C and N. The elements Nb, W, Mo, Co and Ni are not detected in the Ti(C,N) grains, which further confirms the simulated Ti(C,N) composition in Fig. 1.e. In the 36WC cermet, the binder grains are rich in Co and Ni, as well as some W and Mo. The bright contrast grains are free WC and only contain W and C. The NbC_{ss} grains demonstrate a relatively uniform distribution of Nb, Ti and W.

Fig. 4. Elemental distribution in the 12WC (a) and 36 WC (b) cermets.

3.3. Phase analysis and lattice parameter

Core-rim structured Ti(C,N)-based cermets usually contain two phases, i.e. cubic Ti(C,N) and cubic Co/Ni binder phases. Diffraction peaks of the Ti(C,N) core and (Ti,W,Mo,Nb)(C,N) rim in conventional Ti(C,N) cermets are overlapping due to the identical crystal structure and similar lattice constant [5,8,9,11]. In this study, the XRD phase analysis demonstrated that three cubic phases, i.e. binder, NbC_{ss} and Ti(C,N), in the cermets with ≤ 28 wt% WC, whereas binder, NbC_{ss} and hexagonal WC phases were identified in the 36WC and 52WC cermets. The XRD peak positions of the core and rim of the NbC_{ss} phase could not be distinguished due to the very close composition and identical crystal structure. However, the diffraction peaks corresponding to the NbC_{ss} and Ti(C,N) phases could be differentiated. The experimentally determined lattice parameters of the three cubic phases in the cermets with 12-52 wt% WC are summarized in Table 2. The variation of WC and Ti(C_{0.7}N_{0.3}) significantly modified the lattice parameters of the binder and NbC_{ss} phases due to the change of W, Ti, Mo and Nb content in these phases.

Table 2 NbC_{ss} grain size, and lattice parameters of the binder, NbC_{ss} and Ti(C,N) phases

Grade	Density (g/cm ³)	NbC _{ss} grain size (μm)	Binder lattice (Å)	NbC _{ss} lattice (Å)	Ti(C,N) lattice (Å)	Misfit (%)
12WC	6.92	1.43	3.5905	4.3582	4.2783	1.868
16WC	7.18	1.51	3.5929	4.3586	4.2783	1.877
20WC	7.44	1.60	3.5956	4.3625	4.2783	1.968
24WC	7.75	1.40	3.6020	4.3661	4.2783	2.052
28WC	8.08	1.32	3.6062	4.3716	4.2783	2.181
32WC	8.42	1.50	3.6093	4.3698	/	/
36WC	8.82	2.14	3.5740	4.3771	/	/
52WC	10.82	3.65	3.5605	4.4517	/	/

As compared in Fig. 5, the lattice parameter of the binder initially increased with increasing WC content up to 32 wt% and then significantly decreased at higher WC contents. The binder phase exhibits a larger lattice parameter than that of pure Co (3.5480 Å) or Ni (3.5238 Å). The lattice parameter of the binder phase is controlled by the dissolution of alloying elements [29]. Therefore, the variation in lattice parameter can be explained by the simulated composition of the binder phase, as presented in Fig. 1.c. At 1420 °C, the binder contains mainly Ni, Co, WC and a small amount of Mo₂C, TiC and NbC. A maximum of 21 mol% WC is dissolved in the binder when the total WC content is close to 32 wt%. The atomic radius of Ni (124.6 pm) and Co (126 pm) is smaller than that of W (139 pm), Mo (139 pm), Nb (146 pm) and Ti (144.2 pm) alloying elements. Therefore, the lattice parameter of the binder increased up to a maximum at an overall WC content of 32 wt%, corresponding to the maximum WC+TiC+Mo₂C+NbC concentration in the binder. At higher WC contents, the lattice parameter decreased again due to the decreased dissolution in the binder.

Fig. 5. Influence of WC content on the composition and the lattice parameter of the binder phase.

The lattice parameter the NbC_{ss} phase is also closely related to the WC content, as shown in Fig. 6. All NbC_{ss} showed a smaller lattice parameter than that of the NbC starting powder (4.4671Å). According to the simulation in Fig. 1.d, the dissolved compounds in NbC_{ss} are mainly NbC, TiC and WC, whereas the content of TiN and Mo₂C is significantly lower. Among the alloying elements, Nb has the biggest atomic radius (146 pm), followed by Ti (144.2 pm), W (139 pm) and Mo (139 pm). The lattice parameter of the NbC_{ss} phase decreases with increasing amount of alloying elements. The substitution of Ti(C_{0.7}N_{0.3}) with up to 36 wt% WC in the cermets only resulted in a slight change in the phase composition, and accordingly a small variation of the lattice parameter. On the other hand, the WC+TiC+Mo₂C (mol%) concentration decreased dramatically when Ti(C_{0.7}N_{0.3}) is completely replaced by WC, resulting in a clear increase of the lattice parameter.

Fig. 6. Influence of WC content on the lattice parameter and composition of the binder phase (a) and NbC_{ss} (b) in NbC-WC-Ti(C_{0.7}N_{0.3}) cermets.

The lattice parameter of the rimless Ti(C,N) phase, as listed in Table 2, remains nearly constant at 4.2783 Å with changing WC content, indicating a similar C/N ratio of the Ti(C,N) phase in the cermets. The lattice parameters of TiC and TiN are 4.3274 and 4.2473 Å, respectively [30, 31]. The lattice parameter of Ti(C,N) decreases from 4.2969 Å for Ti(C_{0.7}N_{0.3}) to 4.2797 Å for Ti(C_{0.5}N_{0.5}). Accordingly, the lattice parameter of Ti(C,N) can be expressed as a (Å) = - 0.0857 x + 4.3274, where a is the lattice parameter and x is the atomic ratio of [N]/([C]+[N]) (in mol%) [32]. In this study, the N content of the rimless Ti(C,N) phase was estimated to be 57.3 at%, substantially higher than in the Ti(C_{0.7}N_{0.3}) starting powder and in good agreement with the thermodynamic prediction of 58 at% for the 28WC cermet.

According to Ahn *et al.*, a lattice constant misfit of 0.84% between (Ti,Nb)(C,N) and Ti(C,N) solutions resulted in core/rim separation in Ti(C_{0.7}N_{0.3})-(>15)NbC-20Ni (wt%) cermets [23]. Separation of the core/rim Ti(C,N) grains occurred when the lattice constant of the solid-solution Ti(C,N) exceeded 4.3280 Å in Ti(C_{0.7}N_{0.3})-19Mo₂C-(10-20)NbC-24Ni (wt%) cermets [22]. At this level of misfit and lattice parameter threshold, the misfit dislocations at the interface between the (Ti,Nb,Mo)(C,N) rim and the Ti(C,N) core resulted in the physical separation of the Nb-rich rims from the Ti(C,N) cores [32]. In this study, the lattice parameter of the NbC_{ss} phase is above 4.3580 Å. The misfit level between NbC_{ss} and Ti(C,N) phases, as listed in Table 2, is in the range of 1.86 to 2.18%, which is significantly higher than the critical values [22, 23]. Therefore, NbC cermets would always form rimless Ti(C,N) grains and a core-rim structured NbC matrix.

3.4. Mechanical properties

Fig. 7 compares the room temperature Vickers hardness (HV₃₀) and indentation fracture resistance (K_{IC}) of the NbC-WC-Ti(C_{0.7}N_{0.3}) based cermets, sintered at 1420°C. The hardness of the 12-32 wt% WC cermets slightly varies around 1500 kg/mm² and decreases almost linearly with further increasing WC content. Mechanical properties of Ti(C,N) based cermets are dependent on microstructural features, such as composition, binder content, hard phase grain size, etc. [2, 4]. Generally, the addition of a proper amount of WC to Ti(C,N) cermets decreases the hard phase grain growth, resulting in improved hardness and toughness [5, 6]. As discussed above, the microstructures of the investigated cermets, i.e. phase constitution, binder content, and hard phase grain size are closely related to the WC content. In the cermets with 12-32 wt% WC, a similar NbC_{ss} + Ti(C,N) + binder phase constitution, NbC_{ss} grain size, as well as binder content were observed, resulting in a comparable hardness. The other microstructural factors, such as composition of the NbC_{ss} and metal binder phases did not significantly

affect the hardness. Upon further increasing the WC content to 36 and 52 wt%, both the binder content (vol %) and hard phase grain size increased, resulting in a linearly decreased hardness.

The fracture toughness of the cermets with 12-32 wt% WC was around 9.0 MPa m^{1/2} and increased to 10.2 MPa m^{1/2} for the 52 wt% WC cermet. For Ti(C,N)-Ni and NbC-Ni based cermets, there exists an antagonistic correlation between the hardness and fracture toughness [2, 15]. The hardness decreases and fracture toughness increases with increasing ceramic grain size and binder content. In this study, the combined addition of WC and Ti(C_{0.7}N_{0.3}) effectively limits the NbC_{ss} grain growth in combination with an only slightly increasing binder content within the 12-32 wt% WC content window, and the similar hardness is also reflected in a comparable toughness. At higher WC contents of 36 and 52 wt%, a combined effect of coarse ceramic grains and increased binder content contributed to the improved toughness.

Fig. 7. Influence of WC content on the hardness and fracture toughness of the NbC-WC-Ti(C_{0.7}N_{0.3}) cermets.

To correlate the microstructure and fracture toughness, the crack propagation paths originating from the indentation corners of three representative cermet microstructures (12WC, 24WC and 52WC) are shown in Fig. 8. The 12WC and 24WC cermets had a similar toughness and both microstructures contain three phases, core-rim structured NbC_{ss}, rimless Ti(C,N) as well as Co-Ni alloy binder. The local modes of fracture in the 12WC and 24WC are almost the same as shown in Figs. 8.a and b, respectively. Multiple crack paths are present, i.e., cracks propagate through coarse NbC_{ss} grains, along the fine NbC_{ss}/NbC_{ss} grain boundaries, along the NbC_{ss}/binder interface, with binder bridging. It is evident that the many coarse NbC_{ss} grains are fractured in a transgranular mode, whereas most of the fine NbC_{ss} grains are fractured in an intergranular mode. The coarse Ti(C,N) grains effectively deflect the propagating crack. At a higher WC content of 52 wt%, transgranular fracture of the coarse

(Nb,W,Mo)C grains as well as intergranular fracture of both the WC/Ni-Co interface and (Nb,W,Mo)C/WC grain boundaries are observed. However, as shown in Fig. 6, the fracture toughness of the 36 and 52WC cermets are much higher than for the lower WC grade cermets. The increased metal binder content (see Table 1) and presence of WC/Ni-Co interfaces form the basis for an improved fracture toughness by increasing the metal crack bridging effect.

Fig. 8. Indentation crack propagation path in the NbC-WC-Ti(C_{0.7}N_{0.3}) cermets with 12 wt% WC (a), 24 wt% WC (b) and 52 wt% WC (c).

4. Conclusions

The influence of 12 up to 52 wt% WC addition on the microstructure and mechanical properties of pressureless liquid phase sintered NbC solution cermets was investigated. The dissolution of WC, Mo₂C and TiC into the metal binder as well as the NbC solution phase was confirmed by XRD analysis and thermodynamic simulations. Core-rim structured NbC solution grains with a Nb, Mo, W-rich core and a Ti-rich rim, together with rimless Ti(C_{0.43}N_{0.57}) grains, were formed at WC contents ranging from 12 to 32 wt. At WC contents of 36 and 52 wt%, the microstructure contained relatively large homogeneous (Nb,W,Mo)C solid solution grains, a metal binder and dispersed WC grains.

The cermets with 12-32 wt% WC exhibited a similar HV₃₀ hardness of 1500 kg/mm² and indentation toughness of ~ 9.0 MPa.m^{1/2}. Due to the increased binder content and coarse WC grains,

the fracture toughness of the cermet with 52 wt% WC increased to 10.2 MPa m^{1/2} accompanied by a hardness decrease to 1230 kg/mm².

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