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Solid state and liquid phase sintered Mo_2C, WC and TiC modified NbC-Ni cermets

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ABSTRACT

NbC-12 vol% Ni cermets were solid state and liquid phase sintered by pressureless sintering at 1300°C and 1420°C. The effects of 5 vol% secondary carbides (Mo_2C, WC and/or TiC) additions on the microstructure and mechanical properties of the NbC-Ni cermets were investigated. Solid-state sintering at 1300°C revealed an interconnected (NbC) microstructure with isolated or clustered nickel phase. Liquid phase sintering on the other hand exhibited fully dense cermets with a homogeneously distributed binder. Liquid phase sintering in the NbC-12 vol% Ni system resulted in abnormal grain growth which was suppressed by secondary carbide additions. The pseudo-binary phase diagrams were calculated using Thermo-Calc software. Microstructure and phase analysis were carried out using SEM/EDS and XRD. The best combination of hardness and fracture toughness was found in the NbC-Ni cermets co-doped with 5 vol% Mo_2C and WC.

1. INTRODUCTION

The use of cemented carbides and cermets for wear resistance applications is ubiquitous since the discovery of WC-Co composites in 1922 by Schröter [1,2]. However, due to health, economic and supply risk concerns associated with tungsten and cobalt elements, serious efforts both at industrial and academic levels are directed towards finding an alternative for this remarkable composite material [2,3]. After its initial exploration by R. Warren [4,5] in the 1960s, NbC received hardly any attention as main hard phase in hardmetals probably because of its scarcity. Nevertheless, the discovery of new deposits of niobium ore in Brazil revived the interest in NbC as a potential alternative to WC and Woydt and Mohrbacher reported the possibilities of utilizing NbC in cutting tools in 2013 [6–8]. The NbC-Co system was reported to offer inferior mechanical properties due to extensive NbC grain growth and modest wetting between binder and hard phase [9]. NbC-Ni cermets on the other hand have better yet not good enough mechanical properties unless doped with secondary carbides like Mo_2C, VC, WC or a combination thereof [10]. This is usually accompanied by a typical core-rim structure with a NbC core surrounded by a W and Mo enriched rim [11]. Similar to the Ti(C,N)-Ni system, where the addition of Mo_2C improves the wettability, NbC has a high surface free energy and dissolution of secondary cubic carbides lowers its surface free energy by forming a cubic solid solution rim [12]. A systematic study on pure and Mo_2C, WC, TiC modified NbC-Ni systems under solid state and liquid phase sintering regimes has not been reported yet. In this work, pure NbC-12 vol% Ni and systematically-modified 5 vol% secondary carbide containing variants were pressureless solid state and liquid phase sintered and their microstructure and mechanical properties were studied.

2. EXPERIMENTATION

The starting powder composition and theoretical densities for different cermets are summarized in **Table 1.** The cermets were prepared from NbC (CBMM, Brazil; FSSS 1.68 μm), Ni (Vale, T123™, U.K.; FSSS 3-7 μm), Mo_2C (Langfeng Metallic, China; FSSS 3.5 μm), WC (Umicore, CW5300, Belgium; FSSS 1.7-2.3 μm), and TiC (H.C. Starck, Germany; FSSS 1-1.5 μm) powders. The carbon and oxygen content in the NbC powder were 10.6 wt.% and 0.61 wt.% respectively. After weighing, the powder mixtures were wet mixed in ethanol with 10:1 BPR WC-6Co balls in a polyethylene container for 48 h on a multidirectional mixer (Turbula, WAB, Switzerland). Afterwards, the powder suspensions were dried on a rotary evaporator at 78°C. Shaping of powders into solid cylinders was carried out through cold isostatic pressing at 200 MPa for 1 min. The green compacts were pressureless sintered in an actively pumped vacuum (~20 Pa) at 1300°C or 1420°C for 90 mins, with a heating rate of 20°C/min from room temperature to 1050°C, 5°C/min up to 1250°C and 3°C/min up to the sintering temperature followed by a cooling rate of 20°C/min. The pseudo-binary phase diagrams were simulated using Thermo-Calc software (TCFE7 database). The sintered cermet density was measured in ethanol via the Archimedes method while the theoretical density was calculated according to the rule of mixture applied to the starting powder composition. Phase identification was carried out by X-ray diffraction (XRD, Seifert 3003 TT, Germany) and X'pert Highscore plus software was used for indexing the diffraction patterns and extracting the lattice parameters. The cermets were

cut with a diamond saw and cross-sections were ground on a 15 µm diamond plate and polished using 6 and 1 µm diamond paste. The microstructures were studied by scanning electron microscopy (SEM, XL-30-FEG, FEI, The Netherlands). The Vickers Hardness, HV_{30}, (FV-700, Future Tech Corp. Japan) was measured with an indentation load of 30 kg for 15 sec, and the indentation toughness was measured from the radial crack lengths around the HV_{30} indentations using Shetty's formula [13]. The values presented are the mean and standard deviation of five indentations.

Table 1. Chemical composition, theoretical, actual and relative densities of different cermets.

Cermet	Cermet composition (vol.%)	T.D (g/cm^3)	Actual (g/cm^3) and Relative Density (%)	
			1300°C	1420°C
NbC-0	NbC -12 Ni	7.95	7.85 (98.8)	7.89 (99.4)
NbC-M	NbC -12 Ni - 5 Mo_2C	8.02	7.96 (99.3)	7.96 (99.3)
NbC-W	NbC -12 Ni - 5 WC	8.34	8.22 (98.5)	8.33 (99.9)
NbC-MW	NbC -12 Ni - 5 Mo_2C - 5 WC	8.41	8.31 (98.8)	8.38 (99.9)
NbC-MWT	NbC -12 Ni - 5 Mo_2C - 5 WC - 5 TiC	8.27	7.84 (94.8)	8.11 (98.0)

3. RESULTS AND DISCUSSION

The pseudo-binary phase diagrams of the cermets are presented in **Fig. 1**. The selected compositions corresponding to their starting powder carbon content are indicated by the black dashed lines. The thermodynamically stable phases above the liquidus temperature (~1300°C) are liquid nickel binder and cubic NbC or cubic solid solutions of (Nb,X)C with X=Mo,W,Ti. The FCC phase below the liquidus temperature is the nickel binder alloy. With increasing temperature, the number of stable phases evolves to a binary system, i.e. metal binder and carbide hard phase.

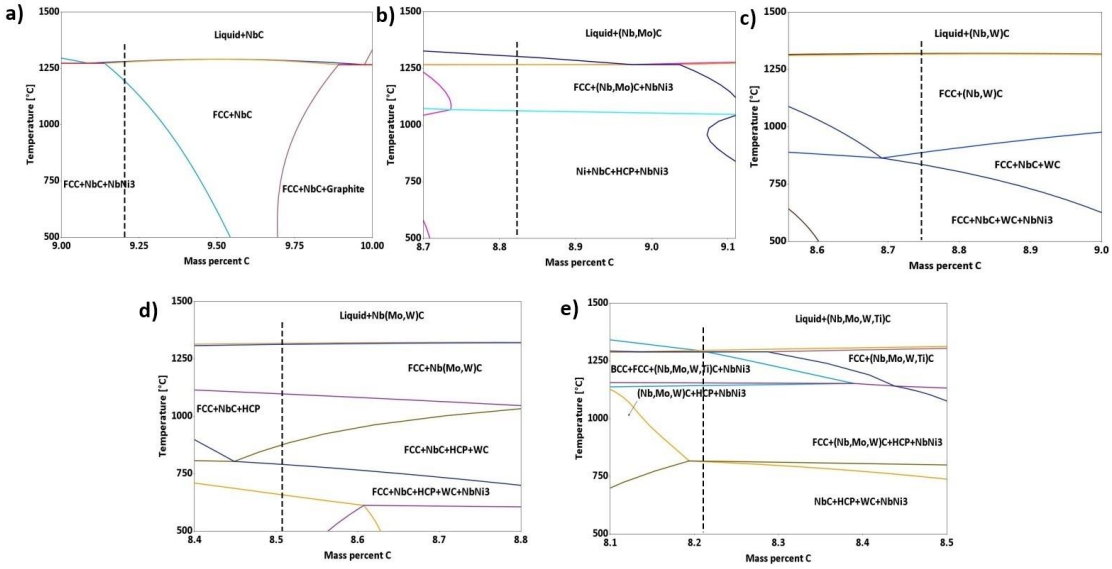

Figure 1. Pseudo-binary phase diagrams of NbC-0 (a), NbC-M (b), NbC-W (c), NbC-MW (d) and NbC-MWT (e).

Accordingly, the XRD patterns of the sintered cermets in **Fig. 2** contain only peaks of the cubic carbide solid solution and the fcc binder alloy, whereas the characteristic XRD peaks of the secondary carbides in the starting powder have disappeared. This is indicative of a successful dissolution of the secondary carbides into the NbC and Ni lattices [10]. The change in sintering temperature showed no discernible effect on the XRD results which is in accordance with the thermodynamic simulations whereby most of the cermet systems are dual phase above 1100°C and the secondary carbides are completely dissolved in NbC and binder phases. S.G. Huang et al. [14] reported on the effect of the sintering temperature on NbC-Ni based cermets with different secondary phase contents. Since the dopant content was fixed at 5 vol.% in this work, the sintering temperature showed no effect on the XRD patterns.

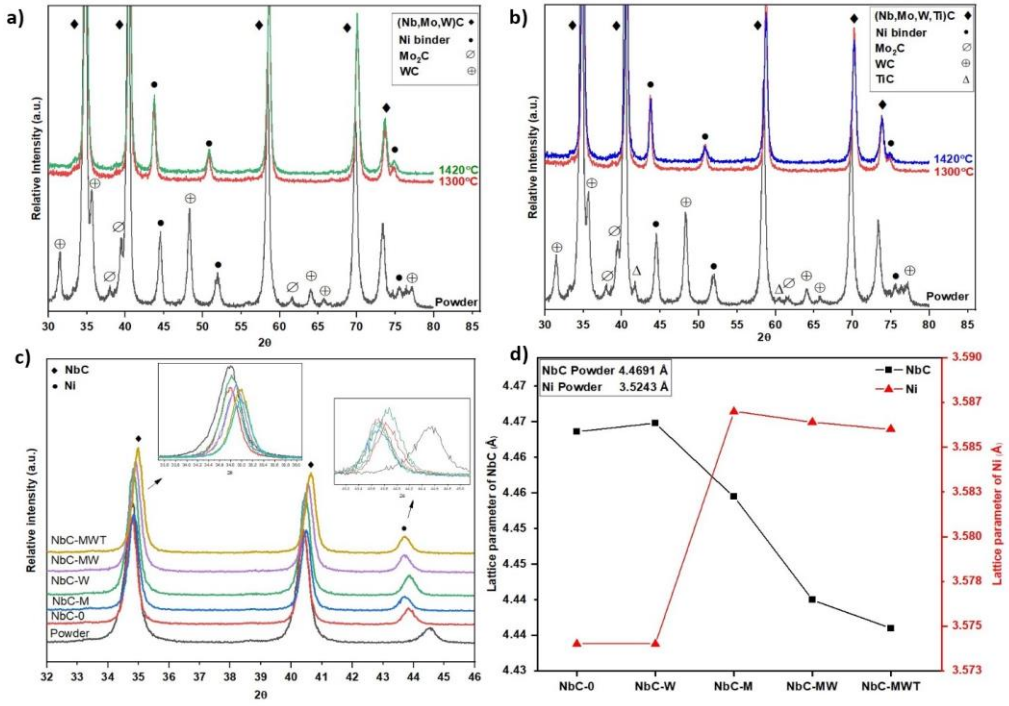

Figure 2. XRD patterns of NbC-MW (a), NbC-MWT (b), detailed XRD pattern segment (c) and constituent phase lattice parameters of all cermets after sintering at 1300°C (d).

Fig. 2 (c) provides a closer view at the peak shifts associated with the solid solution formation during sintering and the changes in the lattice parameters of NbC and Ni binder phase as a function of composition for the cermets sintered at 1300°C. During sintering, the replacement of bigger Nb (146 pm) atoms by smaller atoms Mo (139 pm), W (141 pm) or Ti (144.5 pm) [15] in the NbC lattice causes a decrease in its lattice parameter and a XRD peak shift towards higher 2θ value. Nickel (124 pm) on the other hand has an even smaller atomic radius than Nb, Mo, W and Ti and the dissolution of bigger atoms in nickel during liquid phase sintering causes its lattice to expand which results in a XRD peak shift towards lower 2θ value. The lattice parameter of NbC in NbC-0 decreases slightly as carbon diffuses out of the NbC lattice to dissolve in the nickel binder [16]. In NbC-W, the lattice parameter of NbC is similar as in NbC-0, probably due to the preferable dissolution of relatively less stable WC in the nickel binder which kept the NbC lattice somewhat intact. In fact, a slightly increased lattice parameter suggests that WC may have also acted as a carbon source for NbC. The addition of 5 vol.% Mo_2C in NbC-Ni cermet caused a significant decrease in NbC and significant increase in Ni lattice parameters. This suggests that Mo preferably dissolved into the NbC lattice to form a substitutional solid solution which caused the larger Nb atoms to dissolve in the nickel binder. The lattice parameter of NbC continues to decrease amid solid solution formation by smaller (Mo, W, Ti) atoms.

The comparison between actual and theoretical densities of sintered cermets is presented in **Table 1.** Except for the NbC-MoWT, all cermets were densified at 1300°C, illustrating that the fine size and homogeneity of the powder mixtures facilitated the densification of cermets even in the solid state [14]. The pseudo-binary phase diagram for NbC-MWT in Fig. 1 shows that dual phases exist above 1300°C whereas the additional phases in the other cermet systems tend to dissolve at 900-1200°C to form NbC and fcc nickel phases. This could be attributed to the relatively higher negative heat of formation of TiC which also explains the relatively poor sinterability [17]. However, as the system moves into the liquid phase and Mo_2C (lower negative heat of formation) wets TiC, the cermet densifies [18].

Fig. 3. shows backscattered electron micrographs (BSE) of the NbC-12 vol.% Ni based cermets sintered at 1300 and 1420°C for 90 min. The bright contrast phase represents NbC grains, whereas the Ni binder phase has a dark atomic number contrast, which was also verified by EDS elemental mapping shown in **Fig. 4**. Lower magnification micrographs are presented in **Fig. 5**. The change in sintering temperature is evident in the microstructures, where the isolated/clustered nickel binder in

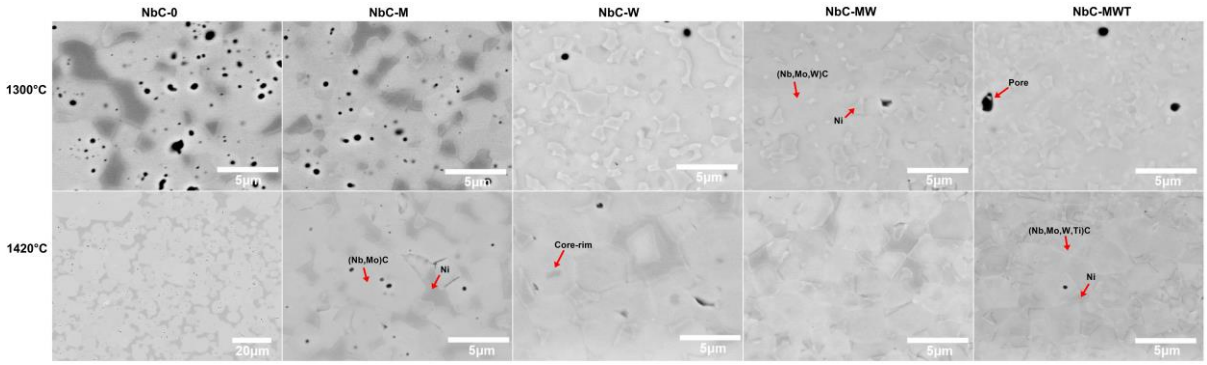

Figure 3. BSE micrographs for NbC-12 vol% Ni based cermets sintered at 1300°C and 1420°C.

the solid state (1300°C) sintered cermets is more dispersed throughout the NbC solid-skeleton after liquid phase sintering. The black spots on the bright contrast NbC grains could be small pores or residual oxide impurities which tend to be reduced with increasing sintering temperature mostly due to the dissolution of less stable Mo_2C and WC which promote the carbothermal reduction of oxides. NbC grain growth in liquid phase sintered systems occurs through a solution and re-precipitation process [19,20]. The smaller NbC grains dissolve in the liquid binder to re-precipitate on bigger ones. Accordingly, the smaller grains turn more spherical while the growing bigger grains remain faceted. The microstructure of NbC-0 in Fig. 3 at 1420°C, shows excessive grain growth with a few abnormally large faceted NbC grains in the micrograph. Such abnormal grain growth was also reported by Kyung-Sik Oh et al. in the NbC-Fe system [21]. Grain growth of NbC in the NbC-Fe system was governed by an interfacial-reaction mechanism and the interfacial structure of the grains has a strong influence on grain growth. Therefore, changing the atomically flat interface to an atomically rough one might eliminate such excessive grain growth. The grain growth inhibiting effect of Mo_2C and WC is evident from the micrographs (Fig. 3 and Fig. 5) of NbC-M and NbC-W. The addition of these secondary carbides has substantially reduced the excessive grain growth of NbC and this could be due to the fact that these carbides upon dissolution into either binder or NbC phase (Fig. 4) reduces the high surface energy of the NbC and improves the wettability [16]. The formation of a typical core-rim structure in NbC-W proves the diffusion of tungsten from the (Nb,W)C rim into the core (NbC).

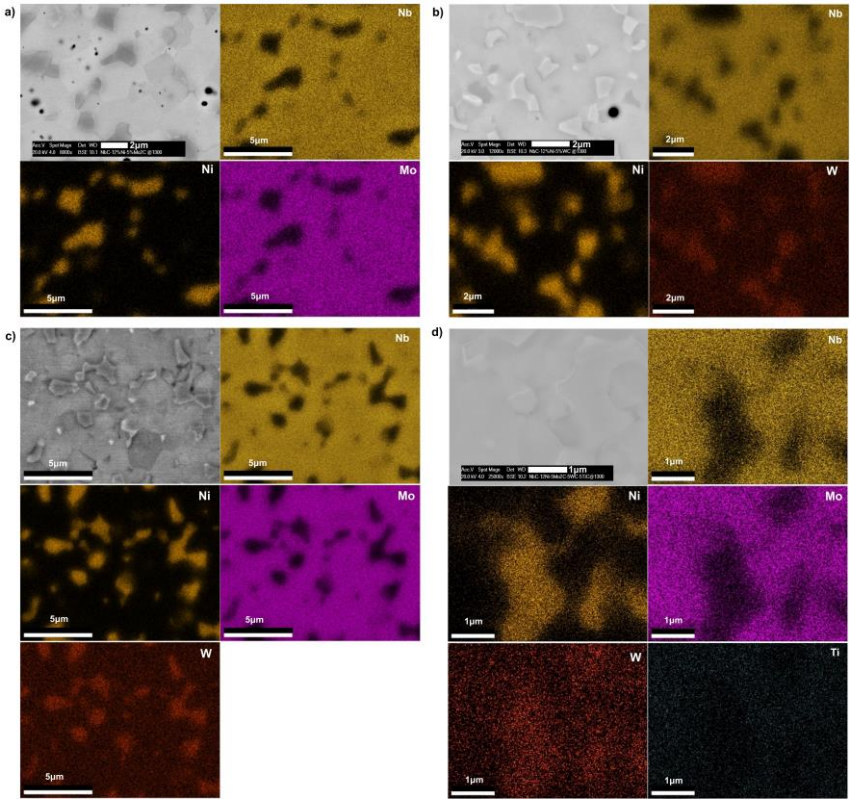

Figure 4. EDS elemental maps of NbC-M (a), NbC-W (b), NbC-MW (c) and NbC-MWT (d) sintered at 1300°C.

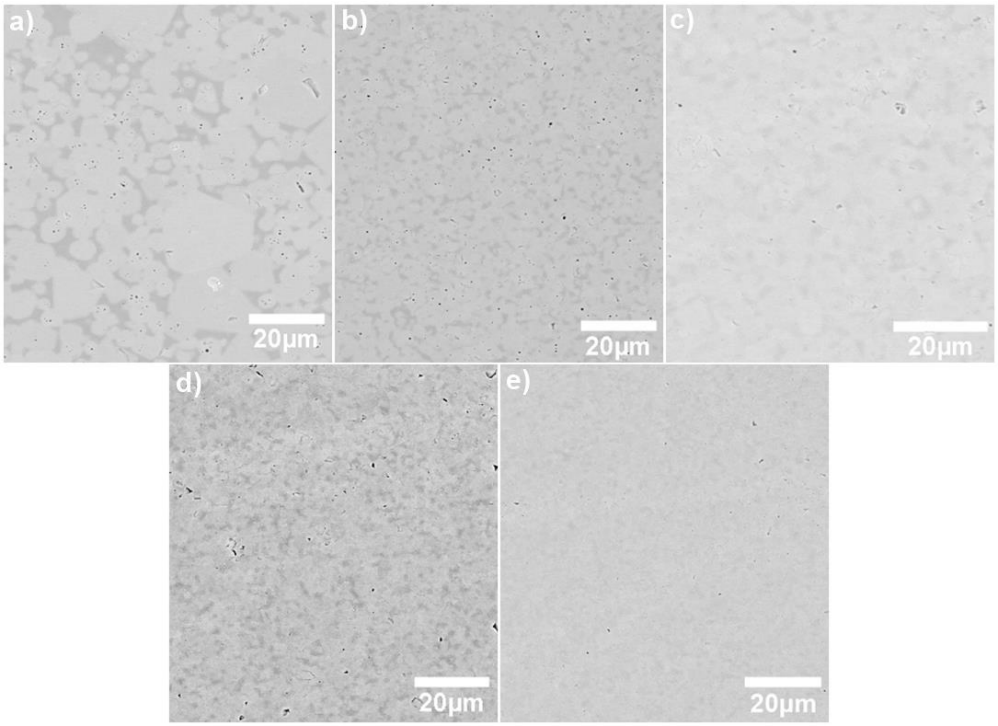

Fig. 5. BSE micrographs of NbC-0 (a), NbC-M (b), NbC-W (c), NbC-MW (d) and NbC-MWT (e) sintered at 1420°C.

Hardness and fracture toughness data for the cermets sintered at 1300°C and 1420°C are presented in **Table 2.** The hardness of NbC-0, NbC-M and NbC-MW remained similar at different sintering temperatures, but a significant increase in hardness was measured for NbC-MWT sintered at 1420°C. This is due to the fact that NbC-MWT only completely densified during liquid phase sintering which drastically improved the hardness. Generally, hardness and fracture toughness have an inverse relationship and therefore the NbC-MWT with highest hardness of 13.70 ± 0.16 GPa had the lowest fracture toughness of 8.6 ± 0.8 MPa. √m. The hardness of the cermets clearly increased with increasing secondary carbide phase addition and accompanying grain size reduction. When sintered at 1300°C, the relatively higher fracture toughness of NbC-0 could be due to the larger grains and relatively wider grain size distribution which enhanced crack deflection during intergranular cracking. When sintered at 1420°C, the NbC-M and NbC-W had a comparable hardness and fracture toughness, which was higher than for NbC-0. The hardness increased whereas the toughness decreased with higher secondary carbide addition (NbC-MW and NbC-MWT).

Table 2. Hardness and fracture toughness of cermets sintered at 1300°C and 1420°C.

Cermet	Hardness (GPa)		Fracture Toughness (MPa. √m)	
	1300°C	1420°C	1300°C	1420°C
NbC-0	12.00 ± 0.26	11.1 ± 0.20	11.0 ± 0.9	11.8 ± 1.0
NbC-M	12.90 ± 0.12	12.5 ± 0.10	9.1 ± 0.2	12.4 ± 0.6
NbC-W	12.60 ± 0.17	12.3 ± 0.12	8.4 ± 0.3	12.0 ± 1.6
NbC-MW	13.80 ± 0.11	13.2 ± 0.12	8.3 ± 0.8	10.1 ± 1.1
NbC-MWT	10.70 ± 0.26	13.7 ± 0.16	8.1 ± 0.3	8.6 ± 0.8

4. CONCLUSIONS

NbC-12vol%Ni-X (X=Mo_2C, WC, TiC) were solid state and liquid phase sintered at thermodynamically evaluated sintering temperatures. NbC showed good sinterability with a Ni binder and all cermets were almost fully densified even in the solid state at 1300°C. The Mo_2C+WC+TiC containing cermet however only fully densified in the liquid phase sintering regime at 1420°C, due to the TiC addition. In the solid state, the nickel binder was found to be clustered in-between connected NbC grains whereas the binder impregnated through the solid skeleton which showed good wettability during liquid phase sintering. The abnormal grain growth of the liquid phase sintered NbC-Ni cermet was suppressed by the individual as well as combined addition of Mo_2C and/or WC. The effect of a finer grain size and full densification was also reflected in the mechanical properties, where all doped cermets had a higher

hardness than the pure NbC-Ni cermet while the addition of Mo_2C+WC+TiC resulted in the highest hardness but lowest fracture toughness. The liquid phase sintered cermets with Mo_2C or WC had a comparable hardness around 12.5 GPa and a fracture toughness of ~12.4 MPa √m.

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