Synergistic effect of Nb and Mo on the microstructural formation of the Ti(C,n)-high chromium ferrous-based cermets


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Synergistic effect of Nb and Mo on the microstructural formation of the Ti(C,N)-high chromium Ferrous-based cermets

H. S. Maurya¹,²,* , K. Juhani¹, M. Tarraste¹, M. Viljus¹, F. Sergejev¹, T.H. Pampori¹, A.Hussain¹, Jakob Kübarsepp¹

¹ Department of Mechanical and Industrial Engineering, Tallinn University of Technology, Ehitajate Tee 5, 19086 Tallinn, Estonia
² Luleå University of Technology, Department of Engineering Sciences and Mathematics, SE 97187 Luleå, Sweden
*Corresponding authors email: himaur@taltech.ee; himanshu.singh.maurya@associated.ltu.se
Abstract: In this study, Ti(C,N)-Fe-based green cermets with different metallic alloying elements have been consolidated by pressureless liquid-phase sintering. The addition of different metallic binders on Ti(C,N)-based cermet such as Nb and Mo on high chromium Ferrous based binder has been investigated. Detailed analysis of the phase constitution was conducted using thermodynamic calculations and experiments, as well as a systematic study of the microstructure evolution and room temperature mechanical properties including hardness and fracture toughness was conducted. The Nb and Mo addition to the binder system affects the sintering temperatures and can significantly affect the phase formation and microstructural development. A Scanning electron microscope (SEM) and Energy dispersive spectroscopy (EDS) technique were used to examine the microstructure, composition, and fracture surface of cermets. The addition of Mo, and Nb reveals lower porosity and finer microstructure as compared to the reference material (Ti(C,N)-Fe-Cr). The refinement of microstructure improves mechanical properties such as hardness and fracture toughness of Ti(C,N)-Fe-Cr-Mo-Nb-based cermets. Further, the addition of these binder elements may reduce the formation of Fe-Cr-based intermetallic complex carbides, allowing cermets to perform better in terms of toughness and corrosion resistance. As a result of the experiments, it is evident that Nb and Mo dissolve in Ti(C,N) and form solid solutions during sintering. The increased number of coreless grains, spinodal decomposition, and crack deflection in cermet further enhance fracture toughness.

Keywords: Ti(C,N)-Fe-based cermets; Grain refinement; Microstructure; Mechanical properties.
1. Introduction

A new generation of titanium carbonitrides (Ti(C,N))-based cermets is now being successfully introduced to the metal cutting industry because of their superior cutting performance, as well as their mechanical and chemical properties such as excellent wear resistance, high edge strength, high-performance reliability, and better thermodynamic stability at elevated temperatures [1–5]. Cermets containing iron and their alloys as binder materials are interesting and could be potential candidates that could compete in cutting and forming applications with conventional hardmetals based on WC-Co/Ni [6–9]. These so-called “green” cermets materials are of interest for health and environmental reasons, since Co and Ni, W are declared as scarce, expensive, and strategic resources; in particular, these materials are included in the list of critical raw materials (CRMs) and also reported as carcinogens to human health according to European REACH program (Registration, Evaluation, Authorization, and Restriction of Chemical Substances) and US NTP (National Toxicology Program) [10–12]. Moreover, the International Agency for Research on Cancer (IARC) has classified nickel compounds in the 1st group as well as nickel metallic and their alloys in the 2B group (conceivable carcinogenic)[13]. It has been suggested that Fe-based binders may be a viable replacement for these toxic and critical raw materials because of their low cost, nontoxicity, abundant availability, and ability to harden with heat treatment, reducing the amount of ceramic content required as compared to conventional cermets [14]. Although there are some advantages to this sustainable approach, there are also some disadvantages, primarily related to sintering, due to the lack of wettability between iron and Ti(C,N) particles as compared to Ni/Co-based binder during liquid phase sintering, as well as the risk of embrittlement caused by reaction products (intermetallic phases).

Ti(C,N) based cermets are composed of two phases: ceramic phase (Titanium carbonitride) and metal phase (nickel, cobalt, iron, etc.). Certain limitations can be adjusted in the physical and mechanical properties of cermets to meet the high-temperature performance. Some binder elements or compounds, such as Cr, Mo, Ta, etc, have been reported to improve the sintering ability of Ti(C,N)-based cermets [15–18]. Furthermore, the addition of those alloying elements in the binders improves the hardness and hardenability of the cermets, as well as the volumetric percentage of carbides that are formed during sintering and overall increases ceramic phases. Increased Cr content in FeCr alloy reduces contact angles and improves TiC-FeCr adhesion.
advantageous to use Cr as an alloying element in TiC/Ti(C,N)-based cermets because it promotes corrosion resistance [19–24]. However, chromium also degrades the mechanical properties and sinter ability of cermets due to its strong affinity for oxygen. Several factors contribute to the sintering problems in high chromium cermets, including chrome oxides. The sintering atmosphere plays an essential role in the microstructure’s formation, densification, and mechanical properties of TiCN-based cermets[25,26]. A study by Cao et al. showed that Ti(C0.5N0.5) based cermets exhibit finer microstructure and better strength by introducing nitrogen gas during the sintering process. Moreover, nitrogen addition may also weaken the denitrification process [27].

Several studies report the possibility of fabricating TiC- and Ti(C,N)-based cermets with straight-chromium steels as binders instead of bonded Ni or CrNi austenite cermets [7,16,28–33]. Most of the work was directed towards a binder element with a lower Cr volumetric percentage (< 18 wt %). As a highly active alloying element in a steel matrix, chromium determines the properties of the composites. A low chromium content (5 wt%) can lead to an increase in steel matrix hardenability. A composite made with a steel alloy matrix enriched with chromium 10–13 wt% is corrosion resistant, heat resistant, and temper resistant. Corrosion and rust resistance can be achieved by increasing the chromium content of the steel matrix by over 18 wt%. Only a few papers have reported the fabrication of cermets (mostly TiC-based) in which the binder contains a high chromium content (>18 wt%) [7,34]. Higher Chromium's affinity for carbon results in the formation of secondary chromium-rich carbides (M7C3 and M23C6) during sintering, leaving the chromium distribution in the metallic matrix heterogeneously and depleted of chromium volume percentage[15,35,36]. As a result of these chromium-rich intermetallic carbides formation and chromium uneven distributions in the binder phases, cermets may lose their toughness and corrosion resistance [37,38].

During heat treatment, welding, and high-temperature application of high-chromium stainless steels, carbides rich in chromium can form in their grain boundaries, leading to sensitization. The stabilization of Cr-rich precipitates can be reduced substantially by adding alloying elements that form carbides and/or nitrides that are more stable than those formed by chromium. A strong carbide-forming element such as Ti, Nb, Zr, Ta, and V can serve as a stabilizing agent [39–43]. The addition of these elements to steel, especially Nb, Ti, and Ta results in stable MC-type carbides or carbon-nitrides that effectively reduce Cr-rich precipitate
Moreover, alloying TiC and Ti(C,N) with Mo or Mo$_2$C increases interphase bond strength and enhances the homogeneity of the microstructure [47–49]. For example, the wettability between liquid Fe and TiC improves when Mo is added to the system FeMo with 3-5 wt% [50]. As a result of the addition of these elements, the grain size was reduced and a rim phase of (Mo, Ti) (C,N) formed during solid-state sintering, which impeded Ti(C,N) dissolution during liquid-state sintering. ThermoCalc phase diagram calculations show that at least 2wt.% percent additional niobium ensures a two-phased structure comprising (Ti,Nb) CN and iron-based solid solution without Cr-rich intermetallic carbides forming. Consequently, this study examines cermets with two different compositions and similar Nb contents under theoretically stable equilibrium conditions. Further, this study presents an in-depth investigation of the different metallic binder elements (Mo and Nb) on the microstructural formation, distribution of the Cr in the binder, and formation of the Cr-rich carbide and their mechanical properties of the high chromium Ti(C,N)-Fe-based cermets.

2. Experimental Procedures

2.1 Materials preparation

Fig. 1. Scanning electron microscopy images of initial raw powders: (a) TiC, (b) Fe, (c) Cr, (d) Mo, and (e) Nb.
The starting materials used in this research are listed in Table 1. The raw materials used to fabricate green Ti(C,N)-Fe-based cerments with different metallic binders along with their optimized sintering temperatures are depicted in Table 2. Conventional powder metallurgy procedure has been adapted to fabricate the cerment parts with pressureless liquid phase sintering. All the compositional powders were weighed and then milled in ethanol for 72 hours with WC-Co balls using a 10:1 ball-to-powder weight ratio and a 70-rpm milling speed. The milled mixture was placed in a drying box after milling. A 12-hour drying process was conducted at 60°C. After the composite powders had dried, 145 mesh sieves were used to sieve them. A mixture of paraffin and gasoline was blended with the powder mixture, dried, and sieved again. Uniaxial pressing with 200 MPa pressure was used to prepare green cuboidal-shaped samples (20 mm × 6.5 mm × 5.2 mm). An illustration of the morphology of the original raw powders of the adapted cerment compositions can be seen in Fig. 1. It can be seen that there are irregularities in the sizes of the raw particles.

Table 1. Characteristics of the starting powders used to fabricate Ti(C,N)-Fe-based cerments.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Source</th>
<th>Particle size</th>
<th>Purity (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(C₀.₅N₀.₅)</td>
<td>Pacific Particulate Materials Ltd.</td>
<td>Irregular; ≤3 μm</td>
<td>&gt; 98.71</td>
</tr>
<tr>
<td>Fe</td>
<td>TLS Technik GmbH</td>
<td>Spherical; ≤50 μm</td>
<td>≥ 99.8</td>
</tr>
<tr>
<td>Cr</td>
<td>Pacific Particulate Materials Ltd.</td>
<td>Irregular; ~6 μm</td>
<td>&gt; 99.5</td>
</tr>
<tr>
<td>Mo</td>
<td>Pacific Particulate Materials Ltd.</td>
<td>Irregular; 2-3 μm</td>
<td>&gt; 99.80</td>
</tr>
<tr>
<td>Nb</td>
<td>NPM Silmet</td>
<td>Irregular; 4-6 μm</td>
<td>≥99.79</td>
</tr>
</tbody>
</table>
Fig. 2. Liquid phase sintering regime adapted for the processing of the Ti(C,N)–Fe-based cermets.

The liquid phase sintering was carried out using a RED DEVILTM furnace (R. D. Webb Company, Inc. USA). Fig. 2 illustrates the sintering parameter for fabricating Ti(C,N)-Fe-based cermets. Sintering of green compacts under vacuum conditions was carried out in a sintering furnace set to heat at a rate of 10° C/min. Several dwellings have been performed to burn out the paraffin wax and to reduce oxides at higher temperatures. Additionally, nitrogen atmospheres were introduced at temperatures over 1200°C to lower the loss of the N during the sintering.

Table 2. Nominal chemical composition of the investigated Ti(C,N)-Fe-based cermets with different metallic alloying elements.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition (wt%)</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cermet 01 (Ref. material)</td>
<td>70Ti(C,N)-30(Fe-26Cr)</td>
<td>1500</td>
</tr>
<tr>
<td>Cermet 02</td>
<td>70Ti(C,N)-30(Fe-26Cr-2Nb)</td>
<td>1550</td>
</tr>
<tr>
<td>Cermet 03</td>
<td>70Ti(C,N)-30(Fe-26Cr-5Mo-2Nb)</td>
<td>1550</td>
</tr>
</tbody>
</table>

2.2 Microstructural and phase characterizations

As part of the microstructural investigation, sintered cermets were ground, mounted, and polished in accordance with the preparation procedures for hard metal samples. Analyzing the phase formation of sintered samples was performed using an X-ray diffractometer (XRD) Rigaku.
SmartLab using Cu-Kα radiation. Samples were scanned at a scan step of 0.02° in the 2θ range of 30°–90°. Using Thermo-Calc software and the TCFE13 database, a thermodynamic simulation was conducted for the equilibrium phase diagram of Cermet. Microstructural analysis was performed using a scanning electron microscope (SEM) Zeiss EVO MA15 equipped with an energy-dispersive spectrometer (EDS) INCA.

2.3 Mechanical and physical properties
Room temperature Vickers hardness tests have been conducted on the cross sections of sintered cermets with a load of 30 kgf for a dwell time of 10 seconds. A 30 Kgf load was used to test the room temperature fracture toughness ($K_{IC}$ (MPa·m$^{1/2}$)) of the sintered specimen using the indentation fracture toughness (IFT) method (EN-ISO 28079:2009). The fracture toughness was subsequently measured by applying the Shettly et al. equation [51].

$$K_{IC} = 0.0028 \sqrt{\frac{HV \cdot P}{\Sigma l}}$$

(1)

where $HV$ refers to Vickers hardness, $\Sigma l$ (mm) corresponds to the sum of the crack tip length from the indenter load, and $P$ is the load in (N). The density of sintered cermets was measured by Archimedes' principle using an analytical balance (Mettler Toledo ME204) at room temperature. To ensure accuracy and reduce experimental error, each sample was tested three times. An optical microscope Axiovert25 at 200-time magnification was used to determine the porosity of the cermets (ISO 4499–4:2016). SEM images of sintered cermets were analyzed using Image J software by using the standard intercept method to determine grain size.
3. Results and discussion

3.1 Phase analysis of the cermets

Fig. 3 exhibits the XRD pattern of the Ti(C,N)-Fe-based cermets with different metallic binders. When Mo and Nb dissolve in Ti(C,N) or in a Fe-based binder, the lattice parameter of Ti(C,N) or α-Fe will decline or increase, respectively. An expanded FCC lattice will shift diffraction to low angles Fig. 3 (b). There are some lower-intensity peaks resulting from the formation of intermetallic complex carbides. Intermetallic carbide phases have been observed as $M_xC_y$ (x/y: 7/3, 23/6, 2/1, 3/1) due to the greater affinity of Cr for carbide formation which has been reported in the relevant literature of the TiC-Fe-based cermet. Microstructure inhomogeneity, component segregation, and defects presence in the cermets affect the α-Fe peak of Cermets 01-03.

The temperature-composition phase diagrams of TiCN-Fe-based cermets were generated using Thermo-Calc software. Fig. 4 (a) illustrates the phase diagram of the ref. material (Cermet 01) while Fig. 4 (b, c) corresponds to the cermets with the addition of different binder elements (Cermet 02 and Cermet 03), calculated with the aim of determining their impact on the phase
formation and microstructure. Although the initial nitrogen and carbon levels in the cermets are predetermined based on the Ti(C$_{50}$N$_{50}$) starting powder, the actual values can change due to the processes occurring during sintering. For instance, the reduction of the carbon in the form of CO/CO$_2$ during the reduction of oxides and reduction of nitrogen through evaporation. Therefore, the carbon content on the x-axis on the phase diagrams was plotted in such a way that the carbon value is dependent on nitrogen, while maintaining constant values for other elements (Ti, Fe, Cr and Nb/Mo). Thus, the C/N ratio increases from left to right, as illustrated in Fig. 4 (d). Red line at 6.8 wt.% carbon denotes the chemical composition which corresponds to the equimolar ratio of C and N.

According to the phase diagrams, the following solid phases are stable in the region around equimolar C/N ratio in all cermets: TiCN (fcc), Fe-based binder (bcc), intermetallic sigma (σ) and secondary carbide (M$_{23}$C$_6$). With the introduction of Nb in cermet 02 the secondary fcc phase, (Ti,Nb)C, is predicted. This is due to the negligible dissolution of Nb in carbonitride and binder phases. The addition of Mo in cermet 03 shows that additional intermetallic phases (laves phase (Lav.) and chi phase (χ)) are stable under equilibrium conditions at lower temperatures. All phases besides main carbonitride (TiCN) and Fe-based binder are stable at lower temperatures and therefore they might not have time to form during relatively fast cooling, especially intermetallic sigma, laves, and chi phases which are known for their sluggish formation. Nonetheless, these findings still demonstrate that variations in the C/N ratio can significantly affect the phase composition of TiCN-FeCr(M) cermets. It is evident that the stability and therefore possible formation of chromium based M$_{23}$C$_6$ carbide increases considerably with higher C/N ratio. The presence of small fraction of M$_x$C$_y$ phases observed in XRD patterns (Fig. 3) confirm that these alterations in chemical compositions occurred.
Figure 4. Phase diagrams (a) Cermet 01, (b) Cermet 02, (c) Cermet 03) and changes in carbon and nitrogen content (d) calculated using Thermo-Calc® 2023b software and TCFE13 database.
3.2 Effect of different metallic alloying elements on the microstructural formation of the cermets

Figure 5. Scanning electron microscopy of the Ti(C,N)-Fe-based cermet with different metallic alloying elements (a,b) Cermet 01, (c,d) Cermet 02, (e,f) Cermet 03, and (j) Schematics of microstructural formation of the TiCN-Fe-based cermets.

Fig. 5 exhibits the SEM images of the Ti(C,N)-Fe-based cermets with different alloying elements revealing that ceramic phases are embedded in metallic binder. In the BSE-SEM mode, the contrast of the phase depends on the average atomic number of the sample. Three main phases are evident in sintered cermets: dark grey, bright, and light grey. The dark grey phase
corresponds to the Ti(C,N) grain, bright to the binder, and light grey to the intermetallic carbide of the binder alloy elements. As a result of contamination from the milling body, a white bright phase is also observed in all cermets related to tungsten. Cermets exhibit a variety of non-core Ti(C, N) phases, which are primarily solid solutions of (Ti, M)C, N (M = Mo, Nb). In the liquid phase sintering process, the complex intermetallic carbides gray phase forms predominantly at the interface between the metallic matrix and ceramic Ti(C,N) particles due to the dissolution-precipitation mechanism [52–54]. Ti(C,N) particles mainly exhibit angular and globular shapes and are distributed evenly throughout the cermets with bimodal distribution (coarse and fine grains). However, variation in the Ti(C,N) particle can be seen with the introduction of the different elements in the Fe-based binder systems. Two different magnifications are presented in Fig.5 to better illustrate the morphology of the consolidated cermets parts.

Cermet 01 (Ref. material) exhibits mainly spherical and angular Ti(C,N) particles with an average gain size of 2.39 microns (Fig. 5 (a, b, c)). The reference material exhibits a smaller Ti(C,N) particle without any additional binder element which could be attributed to the lower solubility of the Ti(C,N) in the binder phase. Ti(C,N) is inherently insoluble in ferrous binders, and Mo and Nb-free cermet does not show apparent grain growth. However, the addition of the Nb in the binder system of Cermet 02 led to the coarsening of the Ti(C,N) particle with a slight variation in the Ti(C,N) particle shape. Moreover, some increase in the submicron grain size can also be observed due to the inclusion of Nb in the binder system, which displays bimodal distribution. (Fig. 5 (d, e, f)). An average Ti(C,N) particle of 3.19 microns was computed for Cermet 02. The coarsening of the Ti(C,N) particle could be attributed to the adsorption of the Nb into the particular plane and limit the growth of that plane. A second consequence of the addition of Nb to the binder phase is that it leads to an increase in the sintering temperature i.e.,1550°C, which could cause grain coarsening. Therefore, the introduction of Nb on the binder phases had only a slight effect on the cermet grain size.

However, the addition of Nb and Mo to the binder system of Cermet 03 at the same sintering temperature (1550°C) has an obvious effect on the grain size and decreased the growth of the Ti(C,N) particle and exhibited a lower average particle size i.e., 2.04 microns (Fig. 5 (g, h, i)). Ti(C,N) particles are transformed largely into spherical shapes by adding these two binder elements. However, some grains of Ti(C,N), mostly larger ones, had tetragonal shapes. Calculated percentages of sub-micron Ti(C,N) particle sizes for Cermet 01, 02, and 03 are 2, 8,
and 16 %, respectively. Adding Mo to a binder system improves wettability and prevents the coarsening of the grains. A possible explanation for this observation is that the Mo and Nb diffused into the Ti(C,N) phases during high-temperature sintering, resulting in homogeneous Ti(C,N) particles that slowed grain growth and preserved the ceramic phase's original shape. Generally, when Mo, Cr, and Nb are added to ceramic in the form of pure metallic powder, they react with graphite carbon to form carbide at lower sintering temperatures, and then completely dissolve in the binder at an eutectic point. Liquid phase sintering results in dissolved elements from the binder phase precipitating on the surface of ceramic particles and thus improving the wettability of the ceramic phase with metallic binder. Fig. 5 (j) exhibits a schematic representation of the microstructure of sintered Ti(C,N)–Fe-based cermet. The Ti(C,N) particle shape of cermet was probably influenced by Mo content, sintering temperature, and holding time. Ti(C,N) particle shapes of cermet 02 and 03 are probably determined by Nb and Mo content, sintering temperature, and holding time. In extremely harsh operating conditions, ceramic materials with angular or tetragonal particles are preferred. Based on our observations, both Mo and Nb are primarily responsible for improving the wettability of the Ti(C,N) phase with the Fe-based binder as well as strengthening the bond between these phases in the Ti(C,N)–high chromium ferrous-based cermets.

Table 3. Chemical compositions of Ti(C,N) and binder phases of the cermets 01,02, and 03 with different alloying elements in wt.% (Spots are measured from the location depicted in SEM image of Fig. 5 (b,e,h))

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position</th>
<th>C</th>
<th>N</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Nb</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>1</td>
<td>7.62</td>
<td>11.77</td>
<td>77.91</td>
<td>0.64</td>
<td>0.51</td>
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<td>-</td>
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<tr>
<td>2</td>
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<td>11.29</td>
<td>78.41</td>
<td>0.84</td>
<td>0.61</td>
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<td>-</td>
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<tr>
<td>3</td>
<td>2.54</td>
<td>-0.68</td>
<td>3.71</td>
<td>7.35</td>
<td>81.92</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>4</td>
<td>2.35</td>
<td>-0.12</td>
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<td>82.52</td>
<td>-</td>
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<td>5</td>
<td>8.83</td>
<td>2.97</td>
<td>8.62</td>
<td>40.54</td>
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<td>41.50</td>
<td>33.55</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>02</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>1</td>
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<td>12.54</td>
<td>77.54</td>
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<td>0.47</td>
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<tr>
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<td>78.44</td>
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<td>6.88</td>
<td>81.26</td>
<td>-0.34</td>
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</table>
Table 3 depicts the chemical composition of Ti(C,N)-Fe-based cermet with different alloying elements revealing that Nb and Mo exist in the Ti(C,N) phases (EDS position 1 and 2 of Fig. 5 (b, e, h)). Ti(C,N) reacts with Mo and Nb to form (Ti,M) C, N (Mo, Nb) solid solutions, improving the wettability of ceramic phases with metallic binders. Additionally, Nb and Mo can be seen in the binder phase, which may be used to strengthen the cermet (EDS position 3 and 4 of Fig. 5 (b, e, h)). The presence of Mo, Nb, C, and other elements in the binder generally modifies the mechanical properties of cermet positively. Furthermore, the dissolved elements may form carbides and/or complex intermetallic carbides which may affect the mechanical properties of the cermets (EDS position 5 and 6 of Fig. 5 (b, e, h)).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<tr>
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<td>2.47</td>
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<td>1.68</td>
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<td>41.58</td>
<td>33.73</td>
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<table>
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<tr>
<th>Cermet 03</th>
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<td>8.26</td>
<td>6.20</td>
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<td>25.70</td>
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<tr>
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<td>24.00</td>
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Figure 6. Elemental mapping of the Ti(C,N)-Fe-based cermets with different metallic alloying elements (a) Cermet 01, (b) Cermet 02, (c) Cermet 03.

Fig. 6 depicts the elemental distribution mapping of the Ti(C,N)-Fe-based cermets with different alloying elements. In all the cermet distribution of the Ti and Fe elemental distribution
is quite predictable. Due to the Chromium's high affinity for forming carbides, segregation of the Cr can be observed in all cermets, resulting in intermetallic carbides forming. However, Chromium dissolves partially in titanium carbide, but much remains in the binder phase as a complex secondary metal carbide. In Cermet 01 denser Cr-rich intermetallic carbides can be observed as compared to Cermet 02 and 03. The addition of the Nb may suppress the formation of these secondary metal carbides. Some parts of the Nb dissolve in the phase and some remain in the binder. Cermet 03 exhibits a better distribution of the Cr in the binder phases and also a less dense formation of the secondary metal carbides which also corroborates with XRD analysis.

3.6 Mechanical and Physical Properties

Figure 7. Bulk density and porosity of the cermet sample with different binder system inset optical images of the cermet at 200 magnification (a) Cermet 01, (b) Cermet 02, and (c) Cermet 03.

Fig. 7 exhibits the physical properties of the Ti(C,N)-Fe-based cermets with different alloying elements. Cermet 01 exhibits higher porosity as compared to Cermet 02 and 03 suggesting that Ti(C,N)-Fe-based cermet densification is unfeasible without the introduction of additional binder elements. As a result of the Nb addition to Cermet 02, there was a slight reduction in porosity,
which was attributed to an increase in the sintering temperature as well as refinement of the hard phase due to Nb diffusion, which could result in improved wettability of the ceramic and binder phases. A binder system consisting of Mo and Nb has been found to significantly enhance densification for Cermet 03. As discussed previously, both elements helped refine the microstructure and improve the wettability and sinterability of the cermets.

Fig. 8 depicts the mechanical properties of the cermets with different metallic alloying elements. Cermet 01 exhibits a lower hardness that could be attributed to the higher porosity and coarser Ti(C,N) particles that can affect the hardness of the material. However, the introduction of the Nb in the binder for the Cermet 02, led to an improvement in the hardness of the material due to the increment of the sub-micron particle and lower porosity as compared to Cermet 01. Submicron grain size generally affects the hardness of the material, higher smaller grain size leads to higher hardness. Cermet 03 exhibits a reduction in the hardness value even though it shows a lower porosity and finer particles of the Ti(C,N). The reduction in value could be attributed to the reduction in intermetallic carbide formation due to the diffusion of Mo and Nb in the Ti(C,N) phase as well as the dual morphology of the ceramic particles.
Figure 8. Mechanical properties of the Ti(C,N)-Fe-based cermets with different metallic alloying elements.

The fracture behavior of the cermets with different metallic alloying elements has been depicted in Fig. 8. Cermet 01 exhibits a lower fracture toughness value due to higher porosity and coarser Ti(C,N) particles. Moreover, the formation of the Cr-based intermetallic carbides also leads to lower toughness value due to their brittle nature that can facilitate crack propagation [33,38,55–57]. The finer grain size and improved densification of Cermet 02 result in an increase in fracture toughness. The presence of the sub-micron Ti(C,N) grain aids the strength and toughness of the material. Cermet 03 exhibits similar behavior as well. The maximum toughness value has been achieved for the be Cermet 03 due to submicron Ti(C,N) grain and lower porosity of the cermets. In addition, it has been reported that dual morphology (fine and coarse grain) plays a significant role in improving the toughness of the cermet [58]. Hardness and fracture toughness values are in agreement with previously reported Ti(C,N)-Fe cermets [4,7,59–64]. However, the addition of the binder elements leads to enhancing the mechanical properties of the cermet.

Figure 9. Optical image of the indentation mark on Ti(C,N)-Fe-based cermets under 30 kgf load (a) Cermet 01, (c) Cermet 02, and (e) Cermet 03, and SEM images of the crack propagation of the Ti(C,N)-Fe-based cermets with different metallic alloying elements (b) Cermet 01, (d) Cermet 02, and (f) Cermet 03.
The crack propagation path of Ti(C,N)-Fe-based cermets observed with SEM with different alloying elements is shown in Fig. 9. The crack propagation in all the cermets indicates a brittle fracture of the Ti(C,N) particle. It is clear that brittle fracture dominates the fracture mechanism of Ti(C,N)–Fe-based cermets, with almost no ductile fracture observed in the matrix. In addition, the above figure depicts mixed trans- and intergranular fractures that occurred in tandem with one another. In all the cases, the transgranular fracture was evident and dominant because numerous Ti(C,N) particles break under fracture energy, indicating that the bond between ceramic particles and binders was strong [65,66].

Cermet 01 exhibits a smooth and straight crack propagation attributed to the lower toughness of the material (Fig 9 (b)). However, in the case of Cermet 02 and 03 deflections in the crack propagation can be observed which could lead to improved toughness of the material [58,67]. The toughness mechanisms occurring in the Ti(C,N)-Fe-based cermets are intergranular, transgranular, deflection, bridging, and branching. For cermet 01, the dominant fracture mechanism is transgranular. Coarser Ti(C,N) grains are susceptible to crack and lead to easy crack propagation when the crack tip encounters such coarse particles. However, in the case of Cermet 02 and 03, deflection of the crack path can be observed mostly along the finer particle causing an intergranular fracture and making the crack propagation path torturous and improving the toughness of the material (Fig 9 (d, f)). Transgranular fractures consume less fracture energy than intergranular fractures, which makes cermets more susceptible to fracture and affects the toughness of the material. A substantial amount of experimental evidence has shown that grain refinement improves toughness in brittle and brittle/ductile fractures. Moreover, the addition of the high carbide forming element leads to lower the formation of the intermetallic carbide formation in the binder phase which significantly improves the toughness of the material.

4. Conclusion

Ti(C,N) based cermet with high chromium Fe-based binder was prepared by the conventional powder metallurgy route with different metallic alloying elements. The effect of the addition of the different binder elements (Mo and Nb) on the microstructural formation and mechanical properties was investigated in detail, and the main conclusions were:

1. Green and sustainable Ti(C,N) based cermets with high chromium Fe based binder have been consolidated successfully by conventional power metallurgy route.
2. The addition of Nb and Mo in the binder system led to the refinement of the Ti(C,N) grain due to the diffusion of these elements in the Ti(C,N) phases. Moreover, these elements lead to improving the sintering ability of the cermets. Better densification or lower porosity has been achieved for the cermets with composition Ti(C,N)-Fe-Cr-Nb-Mo. The addition of these elements in the binder system lowers the grain coarsening and improves the wettability between ceramic and binder phases.

3. Thermal analysis and thermodynamic calculations of the cermet samples do not appear to be in agreement. Sintering of TiCN in a nitrogen atmosphere can vary the proportions of C and N, and therefore such phase diagrams need to be investigated. Combining these two techniques may facilitate understanding the differences among sintered samples containing differing amounts of carbon.

4. The introduction of these elements to the binder system may lower the formation of the chromium-based intermetallic complex carbide which could be beneficial to improve the toughness and corrosion resistance of the cermets. However, it is not possible to fully or nearly fully depress secondary chromium-rich carbides by the addition of niobium (2 wt%). It is imperative to focus future efforts on increasing the Nb percentage to improve the Cr distribution in the binder.

5. Mechanical properties such as hardness and fracture toughness have been investigated and cermets with Ti(C,N)-Fe-Cr-Nb-Mo composition show a better hardness and fracture toughness i.e. $1365 \pm 13 \text{ HV}_{30}$ and $8.24 \pm 0.10 \text{ MPa} \cdot \text{m}^{1/2}$. Grain refinement, solid solution strength, and lower porosity play a significant role in improving the mechanical properties of the cermets.

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Author’s Disclosure Statement
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Data availability
The present data forms a part of the ongoing study, and the results may be shared upon reasonable request from the corresponding author(s).

5. References


CRediT authorship contribution statement

**H.S. Maurya:** Conceptualization, Methodology, Data curation, Validation, Formal analysis, Investigation, Writing – original draft preparation. **K. Juhani:** Formal analysis, Resources, Investigation, Supervision, Funding acquisition, Writing – review & editing. **M. Tarraste:** Validation, Formal analysis, Writing – review & editing. **M. Viljus:** Validation, Resources. **F. Sergejev:** Validation, Resources, Supervision, Funding acquisition. **T.H Pampori:** Investigation, Writing – review & editing. **A. Hussain:** Writing – review & editing. **J. Kübarsepp:** Validation, Resources, Supervision, Funding acquisition.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Highlights

1. Recent efforts have been made in developing and tailoring advanced “green” TiCN-high chromium Fe-based cermets.
2. The incorporation of alloying elements such as Nb and Mo facilitates the densification of TiCN-Fe based cermets.
3. Thermodynamic calculations and experimental investigation with different alloying elements have revealed the effect on phase formation.
4. Adding Nb and Mo facilitates the formation of Ti(CN) solid solutions, improving the microstructure and mechanical properties of cermets.