Effect of Processing Routes on Physical & Mechanical Properties of Advanced Cermet System

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Article

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Abstract: Present research focus on the effect of different processing routes on physical and mechanical properties of nano Ti(CN) based cermet's with metallic binders. Tungsten carbide (WC) is added as secondary carbide and Ni-Co are added as metallic binders in nano Ti(CN) based cermet processed via Conventional and Spark Plasma Sintering (SPS). Systematic comparison of composition and sintering conditions for different cermet's' systems is done to design the novel composition and sintering conditions. Nano TiCN powder was prepared by 30hr of ball milling. Highest density of >98.5% percent was achieved for SPS processed cermet's sintered at 1200°C and 1250°C for 3 min. at 60 MPa pressure in comparison to conventionally sintered cermet's at 1400°C for 1hr with two stage compaction process, uniaxially at 150 MPa and isostatically at 300 MPa pressure respectively. Comparison of XRD analysis of milled powders of different time intervals was done to understand the characteristics of the as received and milled powders. Peak broadening was observed after 5 hr. of ball milling, and it increased till 30hr. Also, peak broadening and refined carbide size was observed in XRD and SEM micrograph of SPS processed cermet. TEM analysis of milled powder showed internal structure having regular periodic arrangement of planes. SEM (BSE) images of all cermets primarily showed three major microstructural phases of core-rim-binder with black, grey and white contrast respectively. In the present sintering conditions high hardness of ~16 GPa and fracture toughness of ~9 MPa $m^{1/2}$ was obtained for SPS processed cermets sintered at higher temperature.

Keywords: cermet system; spark plasma sintering; metal-ceramic bond; ball milling; ceramics

1. Introduction

Titanium carbonitrides based cermet's are considered as candidate materials for machining purposes in the tool industry, because they possess high mechanical properties and high wear performance [1,2].

An attempt has been made to process densified "micro" and "nano" Ti(CN) base cermet with secondary carbides and metallic binders additions [3,4]. Generally, with ceramics, nickel (Ni) and cobalt (Co) are used as binders as they have high wettability with ceramic phase though the fundamental binder with the maximum wettability in the ceramic phase is Ni. During sintering at high temperature, liquid Ni-Co spread over the surface of hard phase, resulting in strong metal ceramic bond. In Ti(CN) cermet, WC is added as secondary carbide – it gets readily wetted by both

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molten nickel and cobalt during sintering and improve sinterability [4-6]. Ahn and Kang et al. [7,8] in their research reported that during sintering core-rim-binder morphology arises. Conventional processing, a cost-effective technique, is always preferred for processing as it is suitable for bulk production and different size and shape component can easily be fabricated [9]. Higher compaction load leads to increase in densification by eliminating large pores [10]. Design of an apparatus used for processing is provided by Yoo et al. [11, 12]. It includes a chamber, a punch and die assembly for supporting a particle material, plungers for applying shear and/or axial pressures, and a power supply for applying a current. In today's time Spark Plasma Sintering (SPS) technique is becoming popular as it fabricate densified product in short processing time and at lower sintering temperature [13-15]. Alvarez et al. [13] processed densified Ti(C,N) cermets with metallic binders having submicron particle size via SPS at 100 MPa uniaxial pressure for 2 min at 1400°C sintering temperature. Ping et al. [14] processed nano Ti(CN)-Mo/Ni cermet via SPS at 1050°C to 1450°C for 3min. at 30MPa pressure. Porosity is found to be negligible at 1200°C. Perfect external appearance of the sintered samples under 1350°C was observed and cracks were visible above 1430°C. Zheng et al. [15] processed nano Ti(CN) cermet having WC, Ni, Mo, VC and graphite addition via SPS. Nanoparticles size and plasma pressure for compaction also effects the properties of processed materials. In case of processing of bulk tungsten samples it is observed that under identical processing conditions (pressure applied, temperature and processing time) there is presence of porosity randomly distributed through the microstructure and density of 92 pct to 96 pct is achieved. For the tungsten sample that was obtained by consolidating powders of initial size 275 nm the porosity was evident through an agglomeration of both the macroscopic and fine microscopic pores [16,17]. Literature survey recommends that processing field of nano Ti(CN) based cermets is still to be explored. There are some challenges also in nano materials development. Selection of economical route of synthesis, to have non-agglomerated nanocrystalline ceramic powders is the primary concern. Nanoparticles compaction to obtain dense compact with avoidance of cracks and inhibition of grain growth to achieve full densification is also a major issue. In regard to nano composite, mechanical properties yet to show improvement upto expectation, that's why they are not yet penetrated commercial market in a big way. Spark Plasma Sintering (SPS) is a fast densification route which prevents excessive grain growth encountered by Nanocrystalline powders during sintering. Suppression of particle/grain coarsening while augmenting densification is essential. Lowering of sintering time and temperature is the solution in which SPS proves to be suitable. Utilizing nano-scale tungsten carbide (WC) and graphene nanosheets (GNSs) as additives, cermets were created via spark plasma sintering (SPS) [38]. Hardness and fracture toughness were found greatly increased by 44.58% and 92.73%, respectively, when compared to the specimen without GNSs. By promoting the migration of hard phases in the liquid phase and preventing their solubility and grain development, a specific concentration of GNSs can significantly boost the fracture toughness of ceramic materials. The characteristics of cermets appeared improved and the creation of a (Ti,W) (C,N) rim phase is encouraged by the addition of nano-WC. Ti(C,N) and WC progressively dissolve into the liquid phase Co during the liquid phase sintering stage, and they precipitated as (Ti,W) (C,N) solid solution to produce a rim phase. It was concluded by the authors that cermets mechanical characteristics can be enhanced, and elements diffusion and densification encouraged by the creation of this rim phase and sample densification can also be accelerated, with enhancement in mechanical characteristics using SPS and adding nano-WC. Development of different core-rim morphologies in processed cermets were observed by reinforcing the produced ceramics with cubic β-cobalt (β-Co) as the binder phase [39]. Powders of (Ti, W, Mo, Ta) and (C, N) were added simultaneously to generate two different core-rim morphologies in an effort to improve the microstructure. Here, high-energy ball milling produced β-cobalt powders with face-centered cubic structures through a solid-phase reaction. The (Ti, W, Mo, Ta) (C, N) powders were made using a carbothermic reduction-nitridation process and a solid-phase chemical reaction. To create Ti(C, N)-based ceramics with two types of core-rim structures—black core/white rim and white core/gray rim, the cobalt and (Ti, W,Mo,Ta)(C,N) powders were mixed, pressed and were conventionally sintered resulting in improved toughness and performance. TiN and nano-TiB2 additions to titanium carbonitride (TiCN-WC-Cr3C2-Co)-

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based ceramics subjected to spark plasma sintering (SPS) processing have been found to have specific effects [40]. TiN and nano-TiB2 additions together affected the mechanical properties, in 0 to 15 weight percent. When TiN was added, the fracture toughness value increased more than when nano-TiB2 was added. On the other hand, the cermets generated with the inclusion of nano-TiB2 had higher hardness values. The outcomes indicated that the new ceramics function and are extremely tough. Also, sintered Ti(C,N)-primarily based cermets had been suggested to have advanced oxidation resistance, which may be further stepped forward via the addition of alloyed Cr [41]. Four united cermets comprised by Ti(C,N) as the earthenware stage and four high entropy combinations as the folio stage were synthesized by Obra et al.[42]. Mechanical alloying was used to create the four HEAs—CoCrCuFeNi, CoCrFeNiV, CoCrFeMnNi, and CoFeMnNiV—which resulted in the formation of a single (face centred cubic) fcc phase. Cold welding caused the materials to become highly agglomerated, however the particles are made up of misoriented nanocrystalline domains that are roughly 10–50 nm in size. Porosity persisted in majority of the cermets even though a high temperature of 1575°C was needed to achieve the maximum cermet densification through pressureless sintering. Distinct compositional shifts were noted in the ceramic and binder phases during liquid phase sintering with a core-rim microstructure in processed cermets. It is accounted that cermet is a sophisticated class of material that combines the benefits of both the metal and ceramic phases [43]. It is composed of a hard ceramic phase and a metallic binding phase. This class of materials' outstanding qualities are especially helpful in tribological, machining, and high temperature applications. Powder metallurgy (PM), reaction synthesis (RS), thermal spray (TS), cold spray (CS), and laser-based additive manufacturing techniques are the most widely used processing methods for cermet systems. Cermet's are a type of materials that minimize the drawbacks of both the ceramic and the metals while combining the benefits of both the ceramic phase and the metallic binder. Modern technologies have partially addressed the inherent challenges of producing components with both metal and ceramic phases. Research on nano Ti(CN) based cermet's is still in progress and yet to make more advances in regard to their processing and mechanical properties in regard to microstructural development. The present work deals with processing of nano Ti(CN) based cermet via conventional and SPS route followed with study of their physical and mechanical properties. The composition, processing routes and sintering parameters are defined on the basis of literature review on the work done by other researchers in the field of nano cermet systems. **Table 1**, **Table 2** and Table 3 presents the summary of compositions, sintering routes and conditions with physical and mechanical properties.

Table 1. Composition and sintering conditions summary of investigated cermets' systems.

Powder Info			Composition Info	Milling Parameters		Sintering				Paper Info (Year)	Ref
TiCxN1-x, µm	X	WC, µm		Velo (RPM)	Time (h)	Tech Used	Pressure (MPa)	Sintering Temp	Holding Time (min)		
>0.1	0.7	0.85	TiCN-43,WC-6.9,Ni-32, Mo-16,VC-0.6,C-1.5	200	24h	SPS	20	1350	3	2004	[15]
3-4	0.5	1-4	TiCN-65,WC-15,Ni-20	250	20	VS	150	1510	60	2004	[19]
1	0.7	0.8	TiCN–WC–Mo2C–(Co,Ni)	*	80	VS	100	1360	60	2008	[20]
0.1	0.5	1.14	TiCN-(47.5-57.5),WC-20,Co-15,Mo-(5-15), C-2.5	*	24h	VS	170	1430	60	2006	[21]
<1	0.7	<1	TiCN-59,WC-15,Co+Ni-17,Mo2C-9	304	50h	VMS	300	1400	5	2009	[22]
0.8-3	0.5	5.9	TiCN-50,WC-21.22,Ni-20,{Mo+Ta(Nb)}-8.47	*	24h	VS	125	1510	60	2012	[23]
0.7-0.95	0.5	0.4	TiCN-55,WC-25,Ni-20	*	24h	VS	100	1510	60	2001	[24]
0.13	0.7	0.45	TiCN-53.5,WC-15,Co+Ni-14.5,TaC-7,Mo2C-10	*	45h	VS	*	1450	60	2008	[25]
0.5-0.8	0.5	200 nm	TiCN-51.87,WC-16,Ni-11,Co-9,Mo2C-12,VC-0.13	30	72h	VS	120	1450	90	2010	[26]
0.3	0.7	0.2	TiCN-55,WC-25,Ni-20	*	24h	VS	100	1510	60	2003	[27]

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0.13	0.7	0.45	TiCN-X, Ni+Co-14.5,Mo2C-10, (WC-15/TaC-10)	68	48h	VS		*	*	2006	[28]
1	0.7	0.2	TiCN-51.4,WC-15,Co+Ni-15,Mo2C-10,TaC-8,Ce/Co-0.6	*	72h	VS	100	1465	60	2012	[29]
*	0.5	*	TiCN-85,Co-15	400	30min	SPS	80	1300	1	2012	[30]
*	0.5	*	TiCN-80.75,Al2O3-14.25,Mo-2.5,Ni-2.5	*	*	SPS	50	1450	2	2003	[31]
0.7	0.8	3.52	TiCN-65,WC-15,Ni-7.5,Co-7.5,Mo-4,C-1	150	24h	VS	180	1430	60	2006	[32]
1*	0.7	0.72	TiCN-43,WC-6.9,Ni-32,Mo-16,Cr3C2-0.6,C-1.5	150	12h	VS	300	1450	60	2004	[33]
TiC-3.87, TiN-0.04	0.5	3.25	TiCN-X,WC-15, Co+Ni-24, Mo-8/15,	*	24h	VS	170	1450	60	2004	[34]
0.5	0.7	0.45	TiCN-53.5,WC+TaC-22,Ni+Co-14.5,Mo2C-10	68	48h	VS		*	*	2005	[35]
TiC-1.5, TiN-2.9	0.5	*	TiCN-70,Ni-20,Mo2C-10	*	24h	VS	100	1550	120	2008	[36]
0.21	0.7	*	TiCN-76,Ni-12,Mo2C-12	*	36h	SPS	30	1250	3	2003	[37]

Table 2. Summary of physical and mechanical properties of investigated cermets' systems.

Composition	Properties of sintered cermets						Ref.
	% Density	Relative Density (gm/cm3)	Grain Size (μm)	Hardness (Gpa)	Fracture Toughness (Mpa.m1/2)	Trans R.S MPa	
TiCN-43,WC-6.9,Ni-32,Mo-16,VC-0.6,C-1.5	*	6.48	>100nm	14.2	*	879.5	[15]
TiCN-65,WC-15,Ni-20	98.8	6.16	30-100nm	12.2	12	*	[19]
TiCN–WC–Mo2C–(Co,Ni)	*	*	*	*	*	*	[20]
TiCN-57.5,WC-20,Co-15,Mo-5, C-2.5	*	*	1.17	15.98	13.2	870	[21]
TiCN-52.5,WC-20,Co-15,Mo-10,C-2.5	*	*	1.15	17.39	11.9	990	[21]
TiCN-47.5,WC-20,Co-15,Mo-15,C-2.5	*	*	0.79	17.87	11	1030	[21]
TiCN-59,WC-15,Co+Ni-17,Mo2C-9	99.5	*	>1	17.36	*	*	[22]
TiCN-50,WC-21.22,Ni-20, {Mo+Ta(Nb)}-8.47	*	*	1-4	~11	~10	*	[23]
TiCN-55,WC-25,Ni-20	*	6.5	0.7-0.9	14.2	8.8	*	[24]
TiCN-53.5,WC-15,Co+Ni-14.5,TaC-7,Mo2C-10	*	6.39	>1	17.54	*	965	[25]
TiCN-51.87,WC-16,Ni-11,Co-9,Mo2C-12, VC-0.13	99.5	6.74	0.5-1	14.7	10.1	2210	[26]
TiCN-55,WC-25,Ni-20	*	*	1.2	14	7.3	*	[27]
TiCN-60.5,WC-15,Ni+Co-14.5,Mo2C-10	*	*	0.5	18.63	*	1500	[28]
TiCN-75.5,Ni+Co-14.5,Mo2C-10	*	*	0.5	18.7	*	1320	[28]
TiCN-50.5,WC-15,Ni+Co-14.5,Mo2C-10, TaC-10	*	*	0.5	18.65	*	1600	[28]
TiCN-51.4,WC-15,Co+Ni-15,Mo2C-10, TaC-8, Ce/Co-0.6	*	*	1-2	17.06	9.21	1639	[29]
TiCN-85,Co-15	99	*	>1	17.1	5.51	904	[30]
TiCN-80.75,Al2O3-14.25,Mo-2.5,Ni-2.5	*	5.115	0.5>	14.45	*	*	[31]
TiCN-65,WC-15,Ni-7.5,Co-7.5,Mo-4,C-1	*	6.258	>1	18.63	14.5	1623.5	[32]
TiCN-43,WC-6.9,Ni-32,Mo-16,Cr3C2-0.6,C-1.5	98>	*	>1	12.3	*	2884	[33]
TiCN-53,WC-15,Mo-8,Co+Ni-24	*	*	1	12.5	17	1425	[34]
TiCN-46,WC-15,Mo-15,Co+Ni-24	*	*	1	12.74	18.2	1600	[34]
TiCN-53.5,WC+TaC-22,Ni+Co-14.5,Mo2C-10	*	6.7	0.3	19.5	10.6	1740	[35]
TiCN-70,Ni-20,Mo2C-10	>98	5.56	3.2	*	14.2	*	[36]
TiCN-76,Ni-12,Mo2C-12	*	*	0.42	16.78	*	295	[37]

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Table 3. Summary of patents of investigated cermets' systems.

S.No.	Patent Ref.	Filing date	Publication date	Applicant	Title	Ref No.
1	US2033513	Jun 12, 1935	Mar 10, 1936	Firth Sterling Steel Co	Hard cemented carbide material	[44]
2	US4145213	May 17, 1976	Mar 20, 1979	Sandvik Aktiebolg	Wear resistant alloy	[45]
3	US4942097	14 Oct 1987	17 Jul 1990	Kennametal Inc.	Cermet cutting tool (TiCN,WC,TiC,Mo2C,Co,Ni)	[46]
4	US4948425	Apr 6, 1989	Aug 14, 1990	Agency Of Industrial Science And Technology	Titanium carbo-nitride and chromium carbide-based ceramics containing metals (TiC.5N.5, Cr3C2, Mo2C, B4C,Co,Ni,Si)	[47]
5	US5186739	Feb 21, 1990	Feb 16, 1993	Sumitomo Electric Industries, Ltd.	Cermet alloy containing nitrogen	[48]
6	US5370719	Nov 16, 1993	Dec 6, 1994	Mitsubishi Materials Corporation	Wear resistant titanium carbonitride-based cermet cutting insert (TiCN,WC,Cr3C2, Mo2C,ZrC,TaC,NbCN,VC,Ni,Co)	[49]
7	US5395421	30 Sep 1993	7 Mar 1995	Sandvik Ab	Titanium-based carbonitride alloy with controlled structure (TiC,TiN, WC,Mo2C,TaC,VC, Co,Ni)	[50]
8	US5766742	31 Oct 1996	16 Jun 1998	Mitsubishi Materials Corporation	Cutting blade made of titanium carbonitride-base cermet, and cutting blade made of coated cermet (TiCN,TiN,TaC,NbC,WC,VC,ZrC, Cr3C2,Mo2C,Co,Ni,graphit powder C)	[51]
9	US6004371	19 Jan 1996	21 Dec 1999	Sandvik Ab	Titanium-based carbonitride alloy with controllable wear resistance and toughness (TiC,TiN, WC,Mo2C,TaC,VC,Co,Ni)	[52]
10	US 6129891 A	23 Aug 1999	10 Oct 2000	Sandvik Ab	Titanium-based carbonitride alloy with controllable wear resistance and toughness (TiC,TiN, WC,Mo2C,TaC,VC,Co,Ni)	[53]
11	EP1043414A1	5 Apr 2000	11 Oct 2000	Mitsubishi Materials Corporation	Cermet cutting insert	[54]
12	US7332122	7 Oct 2003	19 Feb 2008	Sandvik Intellectual Property Ab	Ti(C,N)-(Ti,Nb,W)(C,N)-Co alloy for milling cutting tool applications	[55]
13	US7588621	23 Aug 2007	15 Sep 2009	Sandvik Intellectual Property Aktiebolag	Ti(C,N)-(Ti,Nb,W)(C,N)-co alloy for milling cutting tool applications	[56]
14	US7645316	30 Oct 2006	12 Jan 2010	Sandvik Intellectual Property Aktiebolag	Ti(C,N)-(Ti,Nb,W)(C,N)-Co alloy for finishing and semifinishing turning cutting tool applications	[57]
15	US8007561	13 Jun 2006	30 Aug 2011	Ngk Spark Plug Co., Ltd.	Cermet insert and cutting tool	[58]

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16	US 8202344 B2	21 May 2007	19 Jun 2012	Kennametal Inc.	Cemented carbide with ultra-low thermal conductivity (TiC,WC,Cr3C2,TaNbC,Mo2C,Ni,Co)	[59]

2. Materials and Methods

Commercially available Ti(CN), WC, Ni, Co powders of sub-micron particle size from Stark and Aldrich were used and following cermet composition (wt%): 75TiCN-10WC-15(Ni-Co) was designed for investigation. Nano Ti(CN) powder ranging from 200 nm to 350 nm particle size was prepared via ball milling. Ti(CN) (1-2 μm) size powder was systematically milled consecutively for 1, 5, 10, 15, 20, 25, 30 hr to obtain unagglomerated, ultra-fine (nano) powder with narrow size distribution and minimum contamination. For the conventional sintering, the mixed powders were uniaxially compacted at 150 MPa and further pressed cold isostatically at 300 MPa to achieve uniform density in the compacts. Sample of 4-6 mm thickness were prepared and subsequently sintered at 1400°C temperature for 60min holding time in inert atmosphere. The spark plasma sintering experiments were performed at 1200°C and 1250°C for 3 min. at 60 MPa pressure. Sintering in SPS was a multiple-stage regime (non-linear) with holding periods at 800°C (4 min.) with constant 60MPa. Multistage SPS promotes activation of grain boundaries and their diffusion leads to densified bonded structure. Cermet samples were thoroughly polished. Vickers Hardness was taken at 10 kg load. Indent images were seen on optical microscope and hardness is calculated by formula given in eqn. 1. Shetty et al. [18] formula given in eqn. 2. is applied to calculate fracture toughness value. Average values of five readings are reported. Using a Vickers diamond pyramid indenter, indentation fracture of a number of well-characterized cermet's was investigated. The obtained crack length-indentation load data were examined using relationships typical of fully developed radial/median crack geometries and radial crack geometries. For every alloy under investigation, the radial crack model provided a better fit to the data. It is demonstrated that the observed linear relationship between the radial crack length and the indentation load is consistent with an indentation fracture mechanics analysis predicated on the assumption of a wedge-loaded crack. A straightforward relationship between the alloys' hardness (H), Palmqvist toughness (W), and fracture toughness (Kic) is also predicted by the research.

$$\text{Hardness(GPa)} = \frac{(1.8544 * \text{load})}{\text{diagonal average}^2} \quad (1)$$

Where load of Indentation (N) and diagonals average (mm).

$$\text{Fracture Hardness } (K_{Ic}) = 0.025 \left(\frac{E}{H}\right)^{0.4} (H.W)^{0.5} \quad (2)$$

Where KIc is the indentation fracture toughness (MPa.m1/2); $W = \frac{P}{4a}$, Where P is load of Indentation (N) and 2a is Vickers diagonal (D), E=Elastic Modulus (GPa), H=Hardness (GPa).

3. Results and Discussion

XRD of milled powder of different time periods is shown in Figure 1. Peak broadening is observed after 5 hr. of ball milling and it increased till 30 hr. of ball milling. Peak broadening indicates size reduction. SEM (EDS) and TEM analysis is done of 30 hr. milled powder shown in Figure 2 (a, b, c, d). SEM with EDS is shown in Figure 2 (a, b) revealing nano particle size and confirming the presence of basic elements of Ti, C and N. TEM analysis image Figure 2 (c, d) showed regular periodic arrangement of planes showing crystalline phase. Thereafter powders of the present composition were mixed in a WC jar at 500 rpm for 4 h.

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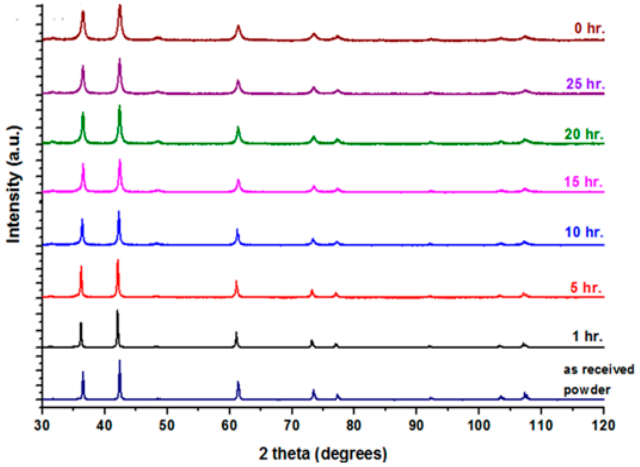

Figure 1. XRD analysis showing peaks of as received and ball milled Ti(CN) powder.

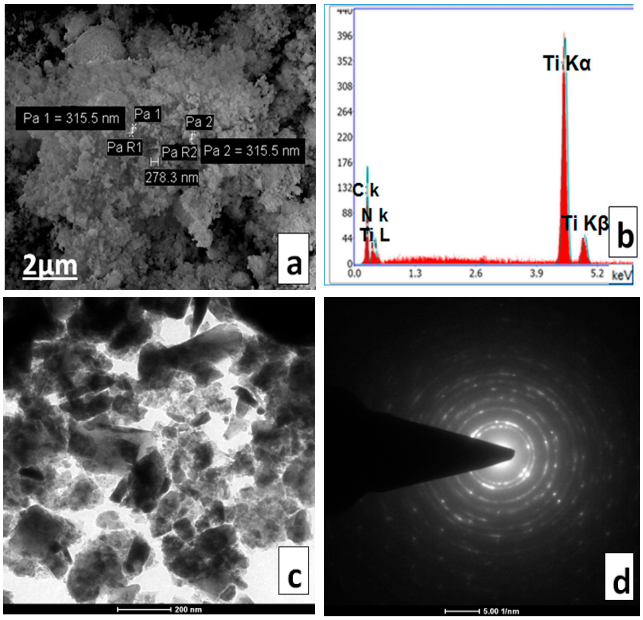

Figure 2. SEM (a), EDS (b) with TEM images of 30 h ball milled Ti(CN) powder (c&d).

Density of the sintered samples was measured by Archimedes principle. Highest density of >98.5% is achieved for SPS sintered cermet at 1250°C (Table 3). The liquid melt comprising of Ni and Co effectively dissolves Ti(CN) and WC ceramic powders and precipitates out ceramic solid solutions. Thus, dissolution and reprecipitation process contributes in the densification [5,6]. The phase evolution in sintered 75TiCN-10WC-15(Ni-Co) cermet is represented in Figure 3 (a, b, c). Fig. 3 (a, b) is XRD of SPS processed cermet at 1250°C and 1200°C. Figure 3 (c) is XRD pattern of conventionally processed cermet at 1400°C. XRD analyses for investigated cermet revealed the presence of constituent elements and solid solution with some broadening in SPS sintered cermet confirming refined carbide size as observed in micrograph after sintering.

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Table 3. Properties of processed sintered nano Ti(CN) based cermet.

Cermet (wt%): 75TiCN-10WC-15(Ni-Co)						
Sintering Technique	**Sintering Temp. (°C)**	**Holding Time (min)**	**Pressure (MPa)**	**Relative Density %**	**HV10 (GPa)**	**K_{Ic} (MPa $m^{1/2}$)**
Conventional	1400	60	150-uniaxial 300-isostatic	~98	15.0± 0.15	7.7± 0.45
SPS	1200	3	60	>98	15.8± 0.23	8.0± 0.30
	1250	3	60	>98.5	16.3 ± 0.34	8.5± 0.21

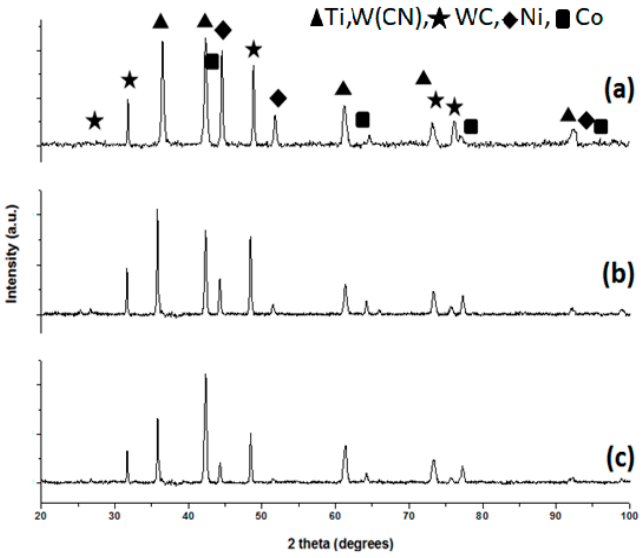

Figure 3. XRD pattern of sintered TiCN based cermets, (a) SPS processed at 1250 °C. (b) SPS processed at 1200 °C. (c) Conventionally sintered at 1400 °C.

Figure 4a represents the micrograph of conventionally sintered cermet at 1400°C. Micrograph revealed core-rim morphology evolved due to dissolution and reprecipitation process. Generally there are three phases in cermets: one is hard phase which is core, second is surrounding phase rim and the third one is a metal binder phase. EDS confirming the typical core and rim structure are shown in Figure 4 (b, c, d). Figure 4b. reveal Ti, C, N elements presence in core, in addition W is also present in rim (Figure 4c). Figure 4d revealed majorly Ni and Co elements presence in binder. Figure 5 (a, b) revealed the micrograph of investigated cermet processed via spark plasma sintering at 1200°C and 1250°C. Figure 6 (a, b, c, d) present the results of EDS for SPSed cermet micrograph with region of core, rim and binder with the respective chemical compositions. It is observed that SPS processing helps in achieving high density in reduced sintering time. Good bonding with clean boundaries is the benefits with SPS. In the simultaneous presence of pressure and electric current, sintering occurred very fast and consequently the temperature raises and densification completes within few minutes. The novelty of multistage SPS is that activation of grain boundaries, their diffusion followed with lattice diffusion occurs resulting in good grain to grain bonding.

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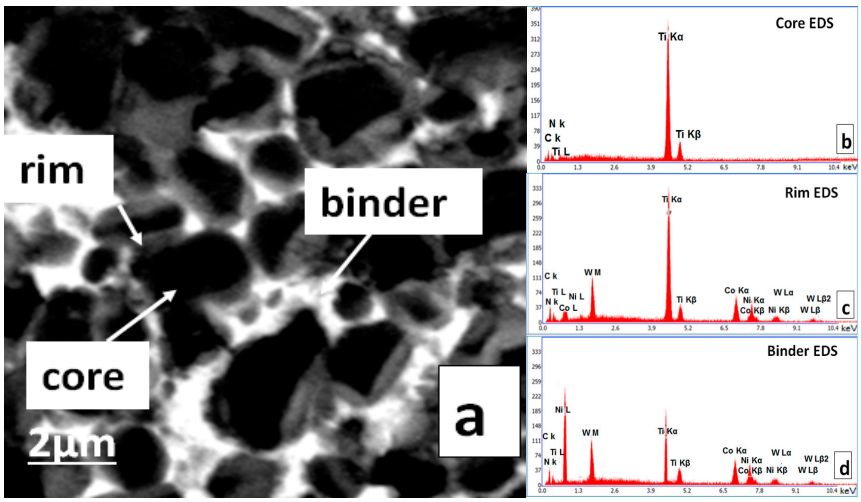

Figure 4. SEM(BSE) (a) and EDS (b,c,d) of core-rim-binder phases of conventional processed Ti(CN) based cermet at 1400 °C for 3 min. .

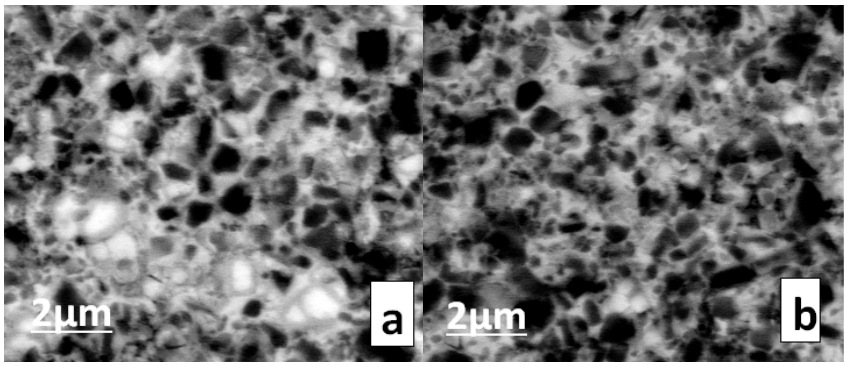

Figure 5. Micrograph of SPS sintered cermet processed at 1200 °C (a) and 1250 °C (b).

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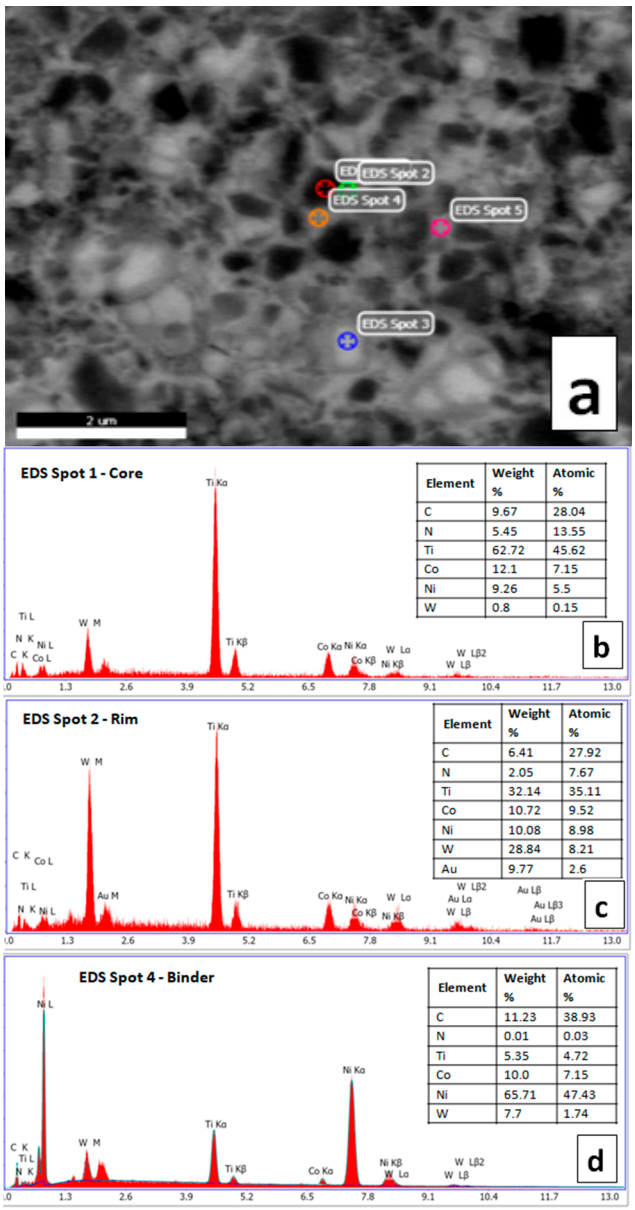

Figure 6. EDS for SPSed cermet micrograph (a) with region of core (b), rim (c) and binder (d) with the respective chemical compositions.

It was found that Vickers hardness for Ti(CN) based cermet processed via SPS at 1250°C is ~16GPa, at 1200°C is >15GPa and cermet processed via conventional sintering at 1400°C is ~15 GPa (**Table.1**). Fracture toughness value of 8.5 MPa $m^{1/2}$ is achieved highest for cermet processed via SPS at 1250°C (Table 3). Spark Plasma Sintering (SPS) is a fast densification route which prevents excessive grain growth and shortens the sintering temperature and time and improves the properties of processed cermet.

4. Conclusions

Present work focus on effect of conventional and spark plasma sintering on physical and mechanical properties of advanced cermet system. Nano Ti(CN) based cermets of following 75TiCN-10WC-15(Ni-Co) composition is sintered via conventional sintering at 1400°C for 60min where powder cermets were compacted win two stages (uniaxially at 100 MPa and further isostatically at 300 MPa), Multi stage Spark Plasma Sintering (SPS) is done at 1250°C and 1200°C for 3 min at 60 MPa in flowing argon. Nano Ti(CN) ranging from 200 nm to 315 nm particle size is prepared by 30 hr of ball milling. . Peak broadening is observed after 5 hr. of ball milling and it increased till 30 hr. of ball

milling. Peak broadening indicates size reduction. TEM results showed regular periodic arrangement of planes showing crystalline phase. Highest density of >98.5 % is achieved for SPS sintered cermets. XRD peaks of SPS processed cermet at 1250 °C show peak broadening, which confirms the refined carbide size. SEM micrographs revealed core-rim morphology evolved due to dissolution and reprecipitation process. Hardness and fracture toughness is found high in SPS sintered cermets.

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