

Steel binder cermets processed by combination of colloidal processing and powder metallurgy

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Abstract

Cermets constituted by a high-speed steel matrix reinforced with 50 vol. % Ti(C,N) present a great potential due to its combination of properties, such as high wear and oxidation resistance, together with high values of hardness and toughness. However, the consolidation of these materials by conventional powder metallurgy processing presents two main problems: The agglomeration of Ti(C,N) particles, leading to non-homogeneous microstructures, and the low compressibility of the blends due to the small size and morphology of the starting powders.

In this work, colloidal techniques are proposed to overcome these issues. Aqueous suspensions of steel powders and Ti(C,N) particles are prepared followed by spray-dry to obtain spherical granules able to be processed by pressing and sintering, avoiding oxidation of powders. The agglomerates present higher compressibility than blends, and sintered materials show higher density and hardness.

1. Introduction

TiCN-based cermets with steel matrix are a new promising group of composite materials which could be an alternative to conventional TiCN cermets with Ni and or Co as metallic matrixes used in the manufacturing of cutting tools. The advantages in the use of steel as metallic phase are related with its lower toxicity and price besides the ability to be hardened by heat treatment. Previous studies of cermets with several types of reinforcements and a high-speed steel (M2 grade) as matrix have shown high wear and oxidation resistance, as well as high values of hardness and toughness [1-3]. These composite materials were processed by conventional powder metallurgy route: blending of starting powders, uniaxial pressing and sintering. Despite the good properties achieved, some difficulties are found during the processing of the samples: 1) The trend to agglomeration of TiCN particles, leading to non-homogeneous microstructures, 2) the low flowability and low compressibility of blends due to the particle size and shape of starting powders. This low compressibility not only leads to worse sintering performance but also limits the amount of reinforcement that can be added by this conventional processing route.

To overcome these difficulties it is proposed the replacement of the conventional blending of powders used in traditional powder metallurgy by the colloidal processing of the powders in aqueous media followed by spray dry. The use of aqueous suspensions permits to obtain homogeneous distribution of metal and ceramic powders, and the spray-dry of the suspension permits to transform small and irregular particles into "easy-to-press" agglomerates, suitable to flow which could improve the compressibility and could be the way to add higher amount of reinforcement particles.

The colloidal processing has been used for long in ceramics to achieve complex shapes and microstructures [4, 5] being less common its use in metals. Recently this technique has being used in the processing of metallic materials as Ni and Ni-ceramic

composites for structural or energetic applications [6, 7]. Moreover by the synergism of colloidal and powder metallurgy techniques dense Ti parts have been obtained with smaller grain size, lower oxygen content and low porosity than Ti processed by conventional PM techniques [8, 9].

In this work a steel matrix cermet reinforced with Ti(C,N) particles is obtained by combination of colloidal techniques with powder metallurgy in order to obtain samples with higher density and better reinforcement particles distribution which will be reflected on a higher hardness. Also this alternative processing is used to obtain a steel matrix cermet with higher amount of reinforcement particles which is not possible by conventional powder metallurgy.

2. Experimental procedure

The characteristics of the starting powders used are shown in Table 1. It is observed that the relation of the average particle size of the steel powders and the reinforcement powders is 2:1 and their morphologies are quite different, being the water atomized steel particles spherical whereas the TiCN particles are irregular as it is shown in Figure 1.

Table 1. Characteristics of raw materials.

Figure 1. Morphology of High speed steel particles and Titanium carbonitride particles.

The composition of the studied systems and the processing carried out is summarized in Table 2. Two systems have been studied, one with 50 vol. % of reinforcement particles (50/50 system) and other with 70 vol. % of reinforcement particles (70/30 system). Both systems have been processed by conventional powder metallurgy (PM) and by a combination of colloidal techniques and powder metallurgy (SDPM).

Table 2. Composition of the studied systems and processing.

The main difference between the two processes is the mixing stage. In the case of conventional powder metallurgy the mixing is by conventional blending in Turbula during 4 hours with the addition of 2 wt. % of wax (Acrawax C: Ethylene bis stearamide). In the case of combination of colloidal techniques and powder metallurgy, agglomerates or granules of the raw powders were obtained by Spray Dry.

Based on a previous study [10], where parameters for preparing stable aqueous suspensions of iron powders and Ti(C,N) powders were optimized, slurries of high speed steel and TiCN with high solid contents (50 vol. %) were prepared separately in water adding 0.4 wt. % of Polyethyleneimine (PEI) as dispersant. Then slurries were milled during 1 hour with nylon and Si₃N₄ balls, respectively, for its homogenization. Later they were mixed at the fixed solid compositions (50/50 and 70/30 v/v Ti(C,N)/M2, in order to obtain a unique stable suspension.

After milling, 2 wt. % of polyvinyl alcohol (PVA) was added as binder [9]. These suspensions were spray-dried using an atomizer Labplant SD-05. Procedure and spray drying optimum conditions were described in [8].

The rheology of the formulated slurries was also characterized determined. Rheological behavior of slurries was determined using a Haake Mars rheometer (Thermo Scientific, Germany) with a double-cone plate fix of 60 mm of diameter and angle of 2° (DC60/2°). Test were performed in the control rate mode (CR) shearing from 0 to 1000 s⁻¹ in 2 minutes, dwelling at 1000 s⁻¹ for 1 minute and shearing down to 0 s⁻¹ in 2 minutes at 23°C. Then the flow curves presented are the down-ramp in log-log plot and fitting to the Cross model (Equation 1):

$$\eta = \eta_{\infty} \frac{\eta_0 - \eta_{\infty}}{1 + (CY)^n}$$

Equation 1

where η_0 is the extrapolation of the viscosity to zero, and indicates the stability of the suspension at rest, η_{∞} is the extrapolation of the viscosity to infinity, and Y is related to the effectively of the homogenization, C is a time constant and n is the rate constant.

Samples from blended powders and from atomized powders were processed by pressing and sintering. Pressing was performed in a double-effect uniaxial press into cylinders of 16 mm diameter. The green compacts were sintered in high vacuum (10^{-5} mbar) at 1400 °C for 60 min.

The characterization of the samples was performed by: dimensions of the green compacts measurement to obtain the green density, density measurement of the sintered samples by He pycnometer, hardness measurement and carbon and oxygen analysis by LECO. The microstructure evaluation was performed by Scanning Electron Microscopy and image analysis was performed by Image J software.

3. Results

3.1. Suspension characterization

In colloidal processing, the rheological properties of the suspensions determine the viability of its processing. The Figure 2 shows the flow curves of the 50/50 and 70/30 Ti(C, N)/M2 slurries, before and after PVA addition. The 50/50 Ti(C, N)/M2 slurry shows a pseudoplastic behavior for low shear rates ($< 100 \text{ s}^{-1}$), which turn to Newtonian as the shear rate increases. However, the 70/30 Ti(C, N)/M2 slurry exhibits a clear thickening behavior, where viscosity increases with shear rate. Pseudoplastic behavior is typical for high solid content suspensions of spherical and uniformly charged particles, evidencing the predominance of the metal phase in the flow behavior

of the 50/50 Ti(C,N)/M2 slurry (Figure 1a). When the amount of Ti(C,N) particles increases, the slurry behavior reverses. In fact, Ti(C,N) particles have an irregular morphology (Figure 1b) and then promotes the thickening flow. After the binder addition, the viscosity increases for both slurries. The shear thickening of the 70/30 Ti(C,N)/M2 slurry reduces considerably and both, 50/50 and 70/30 Ti(C,N)/M2 slurries, exhibits a pseudoplastic flow behavior for low shear rates.

Figure 2. Flow curves of Ti(C,N)/M2 slurries, before and after the addition of PVA.

As an example, the Figure 3 shows the evolution of viscosity with the shear rate in a log-log plot, for the 50/50 Ti(C,N)/M2 slurries before and after the PVA addition. The fitting of the data to the Cross model (Equation 1) was also plotted. Table 3 collects rheological parameters which determine the slurry behavior. For higher accuracy, the fitting was performed separately for the high and low shear rate regions in all cases.

Figure 3. Log-log plot for the 50/50 Ti(C,N)/M2 slurry after adding PVA. Dotted and dashed lines represent the Cross fitting at high shear rate and low shear rate respectively.

Table 3. Rheological parameters determined for Ti(C,N)/M2 suspensions.

The yield point (τ_0), determines the minimum stress that is necessary to communicate to the suspension to promote its flow. The yield point (τ_0) is a characteristic parameter of the pseudoplastic behavior. When PVA was added to the 50/50 Ti(C,N)/M2 slurry, the yield stress decreases two orders of magnitude, from 1.16 to 0.06 Pa. In fact, both slurries exhibit a low yield point after the PVA addition (0.06 Pa and 0.24 Pa for the 50/50 and 70/30 Ti(C,N)/M2 slurries respectively), which extremely favors its spraying.

The η_0 is the extrapolation of the viscosity at shear zero and it quantifies the stability of the suspension at rest. The 50/50 Ti(C, N)/M2 slurry have a η_0 as low as 0.22 Pa·s.

Although, the η_0 increases with PVA addition (i.e. from 0.18 to 0.22 for the 50/50 Ti(C,N)/M2 composition), the registered value can be considered still too low. Then the slurries can undergo sedimentation and phase segregation phenomena, and therefore it is necessary spraying them under agitation. Oppositely, the 70/30 Ti(C,N)/M2 slurry have a η_0 higher than 10 Pa·s, which clearly prevents powders sedimentation and segregation. Other relevant Cross parameter is the extrapolation of the viscosity to shear infinite (η_∞). From this parameter the effectiveness of the homogenization process can be estimated. In our case, the lower values of η_∞ of the 50/50 Ti(C,N)/M2 slurries (28 mPa s and 66 mPa s) indicate an intimate mixing and high dispersion of both powders at this suspension. Contrarily, the thickening behavior at high shear rates of the 70/30 Ti(C,N)/M2 compositions questions the correct homogenization of the metal and ceramic phases in the suspension. In this case the addition of PVA, which diminishes the shear thickening, makes improve the uniform distribution of both particles, and then allows the spraying of a homogeneous mixture of powders in suspension.

In addition to the Cross parameters, the viscosity measured at a shear rate of 100 s^{-1} ($\eta_{100\text{s}^{-1}}$) provides information about the viability and stability of the suspension during its colloidal processing. In our case, the viscosity values measured after PVA addition were 67 and 144 mPa·s for 50/50 and 70/30 Ti(C,N)/M2 compositions, respectively. Those values are lower enough to assure the slurry flow when they pass through the nozzle, and then they guarantee the correct processing of those slurries by spray drying.

3.2. Samples characterization

Both suspensions 50/50 and 70/30 Ti(C,N)/M2 were spray dried to shape granules, for further compacting by PM processing, and compared to samples with powder mixtures with the same composition processed by conventional powder metallurgy route.

In Table 4 are shown the green density values of the compacts after pressing. In both systems, 50/50 and 70/30, the green density is higher for the compacts from powders mixed by colloidal techniques followed by Spray Dry than in compacts from conventionally blended powders. The improvement in the green density using these techniques is 7.9 % and 7.4 % respectively. The main reason for this increase in the compressibility of the powders is the formation of granules after the atomization of the aqueous suspensions as it can be seen in Figure 4b) and d). These granules improve the compressibility and also improve the phases distribution in the green compact avoiding the agglomeration of Ti(C,N) reinforcement particles.

Table 4. Green density of the samples after uniaxial pressing at 750 MPa.

Figure 4. Powders morphology of a) Blended 50/50 system, b) Spray dried 50/50 system, c) Blended 70/30 system and d) Spray dried 70/30 system.

In Table 5 density and hardness of the sintered samples is observed. Both compositions present an increase in the density when they are processed by combination of Spray Dry and Powder Metallurgy, SDPM. The hardness of the 70/30 sample is not improved after the processing by SDPM while the hardness of the sample 50/50 shows an improvement of 50 % after the processing by combination of techniques.

Table 5. Hardness and density of samples after sintering under high vacuum at 1400 °C.

To explain the differences in the properties of these samples processed by PM or by SDPM it is necessary to understand how the processing of these compound materials is. The processing is performed by Liquid Phase Sintering (LPS) and during which several processes of dissolution and reprecipitation of carbides occur. During the process the liquidus temperature of the metallic matrix is achieved and the liquid metal partially dissolves the particles of Ti(C,N) and the carbides of alloying elements from the high speed steel matrix (which had precipitated during heating). After that the

dissolved Ti(C,N) reprecipitate around undissolved Ti(C,N) particles together with the carbides of the alloying elements [2]. Being this the sintering mechanism is clear that the microstructure and the final properties of these compound materials depend on the reinforcement particles distribution and the liquid phase formation.

In the case of the system 70/30 the amount of metallic matrix is lower than in the system 50/50 and, therefore, the amount of liquid phase. When this sample is processed by SDPM the ceramic and metallic particles distribution is better than in the processed by PM, it can be detrimental to the formation of liquid phase because it is easier to achieve liquid phase when the particles are closer because the heat transfer between particles is better. This could be the main reason for the lower hardness achieved in the 70/30SDPM sample than in the 70/30PM sample despite of its better particles distribution.

The sample 50/50 processed by SDPM shows a higher density and hardness than the sample 50/50 processed by conventional PM being one of the main reasons the better particles distribution, however it is necessary to study in deep this system due to the large increase in the hardness values.

It is important to analyze the content of C and O in such materials because the final properties of them are very sensitive to the C content [11, 1]. In the work [1] it was concluded that an increase of 0,5 wt. % in the system M2/TiCN leads to an increase of the double in the hardness value. This increase is due to: firstly an increase in the C content decreases the liquidus temperature of the high speed steel matrix [12] improving the liquid phase formation and moreover an increase in the C content enhances the formation of carbides of alloying elements that increase the material hardness.

Table 6 presents the carbon and oxygen content of 50/50 cermet processed by PM and by SDPM before and after the sintering. It is observed a decreasing in carbon and oxygen during the sintering in both samples. This decreasing is due to the

decarburizing reaction typical of sintering of powders. It is observed higher oxygen content in the SDPM green compacts than in PM green compacts probably due to the addition of PVA as binder before the spray drying of the powders while in the blending of the powders for PM the lubricant used was Acrawax C.

Table 6. Carbon and oxygen content in green compacts and sintered samples.

The main difference between these two samples is the carbon content of the sintered samples. It is observed that the C content of the SDPM sample is 0.25 wt. % higher than the C content of the PM sample. The C content is the responsible of the hardness of the compound material as is observed in Table 7. In this table is showed the hardness of the M2/TiCN cermet with different carbon additions to study the changes in the hardness values by increasing the carbon content. The presence of higher carbon content involves an increase in hardness because C decreases the liquidus temperature [11] improving the densification of the sample during sintering and, also higher carbon content increases the formation of secondary carbides.

Table 7. Relation between hardness and carbon added in the cermet M2/TiCN.

In Figure 5 the microstructures of 50/50 PM and 50/50 SDPM samples after sintering are shown. In both microstructures three phases can be observed: the black one correspond with Ti(C,N) particles, the grey one corresponds with the steel matrix and the bright phase corresponds with the carbides of the alloy elements from the high speed steel matrix. Comparing both microstructures it is observed a more homogeneous distribution of reinforcement particles and higher amount of carbides of alloying elements in the sample 50/50 SDPM both features are the consequence of the higher carbon amount and are the responsible of the higher density and hardness found on SDPM samples.

Figure 5. Microstructures of samples 50/50 PM and 50/50 SDPM after sintering at 1400 °C.

The amount of carbides of alloying elements in both samples was quantified by image analysis. The binary image of the microstructures in Figure 6 reveals a higher amount of carbides in 50/50 SDPM sample than in 50/50 PM sample, 1.99 % and 4.57 %, respectively.

Figure 6. Binary image of the 50/50 PM and 50/50 SDPM microstructure used to analyze the amount of carbides of alloying elements.

4. Conclusions

The combination of colloidal and powder metallurgy techniques (Spray Dry of aqueous suspensions followed by pressing and sintering) to process steel matrix cermets reinforced with Ti(C,N) particles has proven to be a very good alternative to conventional powder metallurgy. Thanks to this combination of techniques the following improvements have been achieved:

- Increase in the compressibility of the powders.
- Increase in the density after sintering.
- More homogeneous microstructures.
- Higher hardness.

One aspect that must be taken into account when using spray dried powders is the residual carbon coming from the binder used in the aqueous suspension. The presence of a higher amount of carbon in the cermet has consequences for the formation of liquid phase and, therefore, in the sinterability and properties.

5. Acknowledgements

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6. References

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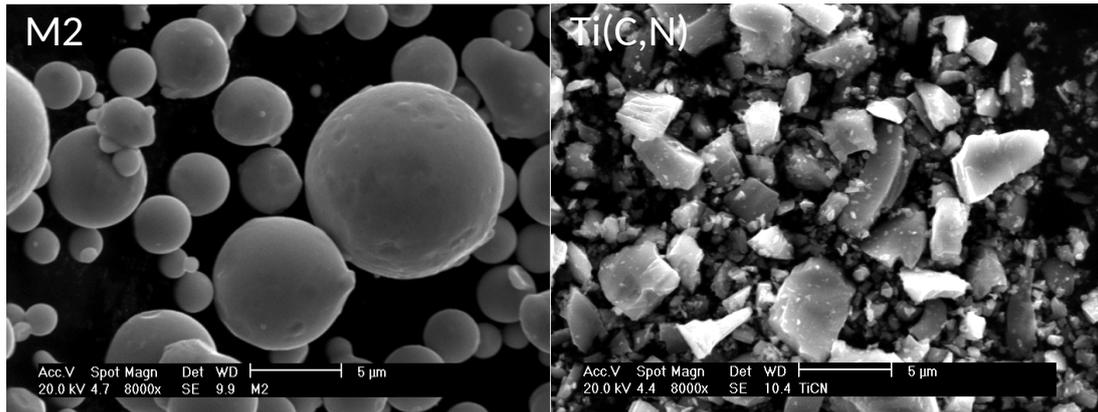


Figure 1. Morphology of High speed steel particles and Titanium carbonitride particles.

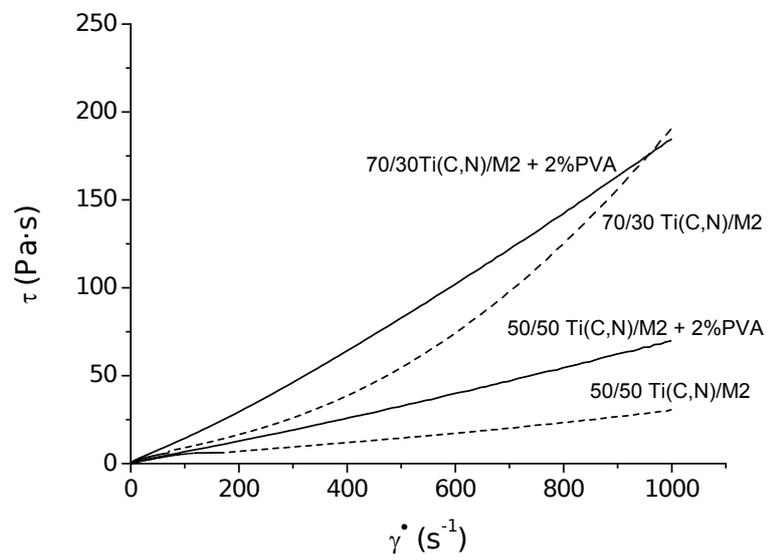


Figure 2. Flow curves of Ti(C,N)/M2 slurries, before and after the addition of PVA.

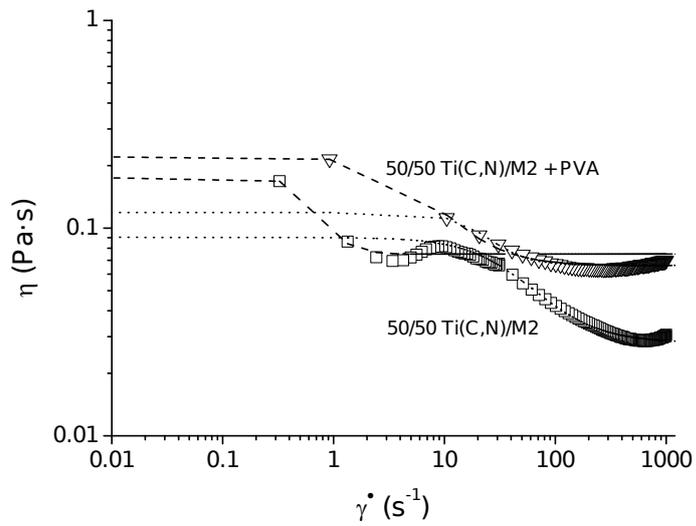


Figure 3. Log-log plot for the 50/50 Ti(C,N)/M2 slurry after adding PVA. Dotted and dashed lines represent the Cross fitting at high shear rate and low shear rate respectively.

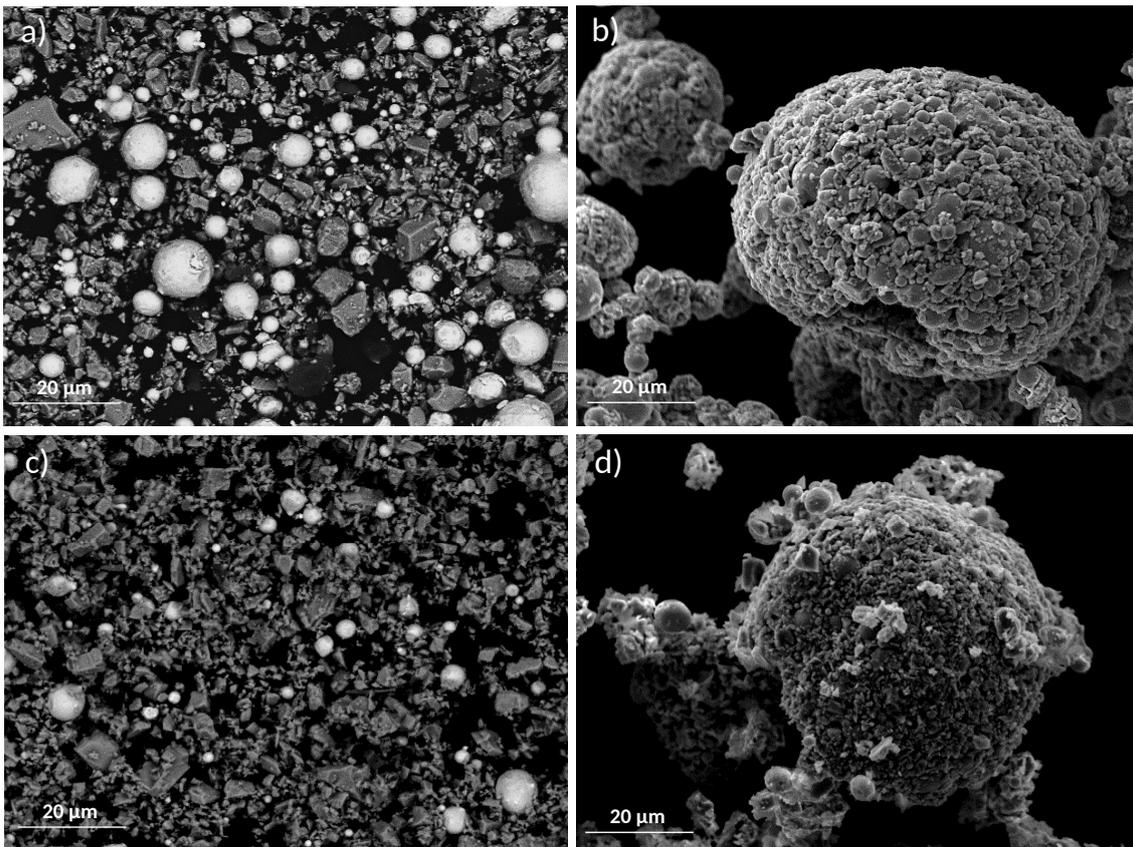


Figure 4. Powders morphology of a) Blended 50/50 system, b) Spray dried 50/50 system, c) Blended 70/30 system and d) Spray dried 70/30 system.

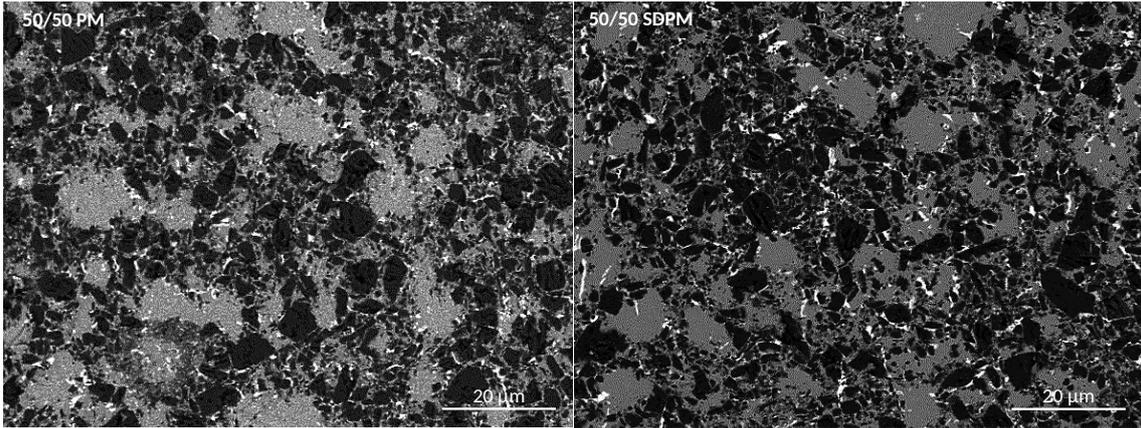


Figure 5. Microstructures of samples 50/50 PM and 50/50 SDPM after sintering at 1400 °C.

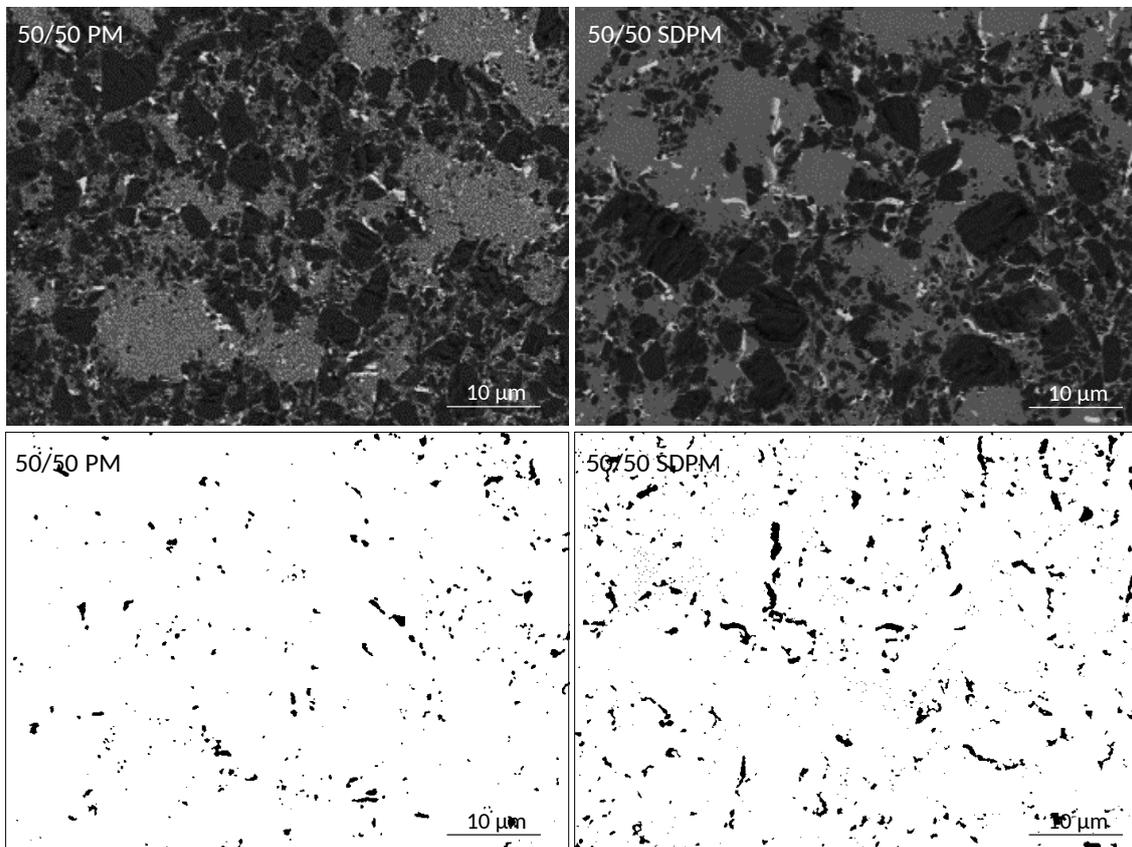


Figure 6. Binary image of the 50/50 PM and 50/50 SDPM microstructure used to analyze the amount of carbides of alloying elements.

Table 1. Characteristics of raw materials.

Raw material	Supplier	Supplier data		Experimental data	
		Density (g/cm ³)	Particle size (μm)	Density (g/cm ³)	Particle size (μm)
Ti(C _{0.5} ,N _{0.5})	H.C. Starck	5.03	D50 = 2.0 - 4.0	5.12	D50 = 3.9 D90 = 8.6
High Speed Steel, M2	Osprey	8.56	D90<16	8.09	D50= 8.1 D90 = 15.8

Table 2. Composition of the studied systems and processing.

Sample	Ti(C,N) (Vol. %)	High speed steel, M2 (Vol. %)	Mixing	Pressing & Sintering
50/50 PM	50	50	Conventional blending	Uniaxial press + Vacuum sintering
50/50 SDPM	50	50	Colloidal techniques + Spray Dry	
70/30 PM	70	30	Conventional blending	
70/30 SDPM	70	30	Colloidal techniques + Spray Dry	

Table 3. Rheological parameters determined for Ti(C,N)/M2 suspensions.

Composition	τ_0 (Pa)	η_0 (Pa·s)	η_{100s-1} (mPa·s)	η_∞ (mPa·s)
50TiCN	1.16	0.18	119	28
70TiCN	-	-	90	-
50TiCN + PVA	0.06	0.22	67	66
70TiCN + PVA	0.24	13.02	144	-

Table 4. Green density of the samples after uniaxial pressing at 750 MPa.

Sample	Green density (g/cm ³)	Increase (%)
50/50 PM	4.61 ± 0.01	7.9
50/50 SDPM	4.98 ± 0.01	
70/30 PM	4.07 ± 0.01	7.4
70/30 SDPM	4.37 ± 0.01	

Table 5. Hardness and density of samples after sintering under high vacuum at 1400 °C.

Sample	Sintered density (g/cm ³)	Hardness
50/50 PM	6.39 ± 0.18	448 ± 12
50/50 SDPM	6.68 ± 0.03	920 ± 33
70/30 PM	5.75 ± 0.06	379 ± 9
70/30 SDPM	5.90 ± 0.13	329 ± 2

Table 6. Carbon and oxygen content in green compacts and sintered samples.

Sample	C content	C content	O ₂	O ₂
	Green compacts (wt. %)	Sintered sample (wt. %)	content Green compacts (wt. %)	content Sintered sample (wt. %)
50/50 PM	6.15	4.57	0.57	0.11
50/50 SDPM	5.85	4.72	1.27	0.09

Table 7. Relation between hardness and carbon added in the cermet M2/TiCN.

C addition (wt. %)	Hardness (HV30)
0	448 ± 16
0.25	647 ± 87
0.5	1004 ± 77
0.75	1223 ± 25
1.0	1333 ± 35