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Properties of Ti(C,N) cermets synthesized by mechanically induced self-sustaining reaction☆

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Abstract

The properties of TiC_xN_{1-x}/(Ni or Co) cermets sintered by a pressureless method from powder mixtures, and obtained for the first time by a mechanically induced self-sustaining reaction process (MSR), were studied. The hardness, toughness, friction and wear coefficients, and oxidation resistance were determined. It was shown that cermets obtained from powdered materials synthesized in one single MSR step possessed improved mechanical properties, similar to those obtained in cermets with more complex bulk compositions. Higher wear resistances were observed in cermets whose hard phase was richer in carbon. The oxidation resistance of the cermets depended primarily on the binder composition. This resistance was better for those cermets with cobalt as the binder. Superior oxidation resistance was displayed when small amounts of W or Mo were incorporated into the binder.

Keywords: Ti(C,N); Cermets; Hardness; Wear resistance; Milling; Oxidation resistance

1. Introduction

The hard components in modern cermets are made of Ti(C,N) solid solutions with secondary carbides such as Mo_2C, WC, TaC or NbC, which are added to improve sinterability, abrasion resistance or thermal shock resistance.[1,2] Ti(C,N)-based cermets are currently employed in cutting tool operations due to their excellent wear resistance and good chemical stability at high temperature.[3,4]

The main difficulty in using Ti(C,N)-based cermets as competitive materials for WC–Co (hard metal) on a larger industrial scale lies in their inferior toughness, which depends on the amount of ductile binder and increases with the grain size of the ceramic phase. This toughness can be improved at the expense of hardness, which increases with the volume portion of the hard constituent, but also by decreasing the grain size and increasing the particle contiguity.[5,6] An appropriate toughness is attained with a lower amount of binder in WC–Co than in cermets, without excessively damaging the hardness.[7]

Manufacturers have proposed a wide variety of hard metal inserts, which can be coated with TiN, TiC_xN_{1-x}, TiC, Al_2O_3, ZrC_xN_{1-x}, or TiAlN[8] in order to improve the wear resistance and fracture resistance, while maintaining the toughness.[9] Depending on the machining requirements (high-speed, interrupted turning, milling, grooving, threading, among others) and work material, the wear resistance-to-toughness compromise is different. In some cases, high hardness is not required and cermets that are less expensive than coated carbides and equipped with a long tool life, provide a cost-efficient solution to many machining applications.[10,11]

The machinability of materials is a dynamic field with enormous implications in different industrial sectors because manufacturers are constantly looking for improvements that can increase the overall productivity. Manufacturers of cutting tool inserts need to develop products that can perform at higher speeds and last longer under increasingly rigorous operating conditions. Some strategies that can drive material development include shrinking particle sizes and employing more complex compositions. A recent advance in cermet capabilities has been

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made possible by the introduction of new micrograin cermet grades that feature a bending strength equal to that of hard metal.[12]

The main interest in using finer particles lies in the excellent sintering behaviour of powders producing smaller voids and a denser finished material. The finer particles result in significantly higher hardness for a given binder level. In general, insert tools made with submicron materials have excellent wear resistance and bending strength. Currently, researchers are exploring the potential benefits of nano-phase materials. Several authors have found a significant toughness improvement in the case of nano-systems compared to those of the corresponding micrometer and ultrafine systems.[13,14] However, the development of these nano-systems requires the development of new production technologies.

High energy ball milling has been shown to be a powerful technique for obtaining ultrafine powders and, in some cases, nanostructured materials.[15] In previous works,[16,17] we have shown that transition metal carbonitrides, the principal component of cermets, can be obtained from mixtures of elemental powders by a particular milling process called a mechanically induced self-sustaining reaction (MSR).[18] It has been demonstrated that MSR can be an appropriate method for preparing the pre-reacted hard components as raw materials for the cermet fabrication.[19] Recently, this process has allowed the synthesis of powdered cermets in a short time with nanometric characteristics and good stoichiometric control.[20] As previously indicated, these two features can be key factors for obtaining cermets with improved properties. Therefore, the capacity of this synthesis method to develop new materials for insert products must be explored.

In this work, we present the characterization of cermets first obtained through a mechanically induced self-sustaining reaction and subsequently sintered through a classical pressureless method. Details of the synthesis process and the microstructural characterization of densified cermets have been shown in a previous paper.[20] Hardness, which is measured by microindentation, toughness, which is calculated from the cracks departing from the indentation corners, tribological behaviour and oxidation resistance at 1000 °C are studied in this work.

2. Experimental

Cermets were fabricated by means of a pressureless process from powders synthesized by MSR. The experimental details on the MSR synthesis in a nitrogen atmosphere are described in a previous work.[20] Two set of cermets were prepared. Cermets labelled as HCB were obtained from titanium carbonitride powders produced by MSR, and subsequently blended with the metal binder (Ni or Co). In some cases, a second ceramic phase (WC or Mo_2C) was added. Cermets labelled as HC were obtained from powdered cermets produced by a one-step MSR process without any other treatment. In this case, the metal binder and the second phase (W, WC or Mo_2C) were added to the starting titanium/graphite mixture (necessary for TiC_xN_{1-x} formation) before the MSR process was performed. Flow chart describing cermet processing is presented in Fig. 1.

Powdered cermets were cold isostatically pressed at 200 MPa for 5 min to give cylinders of 12 mm in diameter. The green bodies were sintered at 1400 °C during 60 min (heating rate 10 °C/min, free cooling) under inert atmosphere (helium gas, $H_2O \leq 3$ ppm, $O_2 \leq 2$ ppm and $C_nH_m \leq 0.5$ ppm, Air Liquide) in a horizontal furnace (Thermolyne Type 59300 model no. F-59340-CM, Thermolyne). Table 1 shows the raw powders employed and different phases present in the cermets after sintering as observed by XRD in a previous work.[20] The same number in HCB and HC labels of cermets in Table 1 corresponds to the same gross composition of the raw materials.

The bulk densities of the cermets were measured by the water immersion technique (Archimedes method). The final relative densities were estimated in accordance with the rule of mixtures. The cermets were sectioned and polished until a mirror effect was obtained for the micro-hardness measurements. For a reliable comparison, the specimens were taken from the central part of each cermet. The Vickers test was performed at room temperature in a Microhardness FM-700 (Future-Tech. Corp) with a load of 9.81 N (H_v 1.0) for 15 s. Six micro-indentations were taken at different locations on the polished cermet and the reported value is the average of the measured values. The fracture resistance was evaluated by the direct crack measurement method using the Warren and Matzke expression.[21] Although the toughness value obtained from the length of the radial cracks around the Vickers indentations is fundamentally different from the fracture toughness obtained by conventional methods,[22] it can be used to compare the performances of the studied cermets.

The tribological behaviour of the cermets was studied at room temperature using a reciprocating pin-on-flat configuration under 10 N of applied load without any lubricant. Si_3N_4 balls of 6.0-mm diameter were used as antagonist materials. A new ball position was used for each new test. In all the friction tests, the sliding linear speed was 2 mm/s over a 3.0-mm long wear track for 5000 cycles. The relative humidity was maintained between 30 and 40% in ambient air. The friction force was recorded during the tests leading to the evolution of the friction coefficient versus the number of cycles $f(N)$ for a set of two different experiments on each sample. The friction coefficient was taken as an average over the final part of the curve after the initial period of stabilisation. Profiles of the wear tracks were measured by mechanical profilometer. The specific wear rates of the cermets are estimated as the worn volume/unit load and sliding distance (mm^3/Nm).

The isothermal oxidation behaviour was carried out at 1000 °C (heating rate 10 °C/min, free cooling) for 18 h in static air using a CI Robal electrobalance (C.I. Electronics Ltd.) attached to the support frame of a high-temperature vertical furnace (1500 °C; Severn Furnaces Ltd.). Specimens with dimensions of 2 mm × 3 mm × 5 mm were placed into an alumina crucible, which was centred inside an 8 mm inner diameter ceramic tube in order to minimize the buoyancy effects.

The indentation marks and the oxidized samples were examined by scanning electron microscopy (SEM) in a Philips XL-30 instrument at 20 kV. The instrument was equipped with an EDX analysis system.

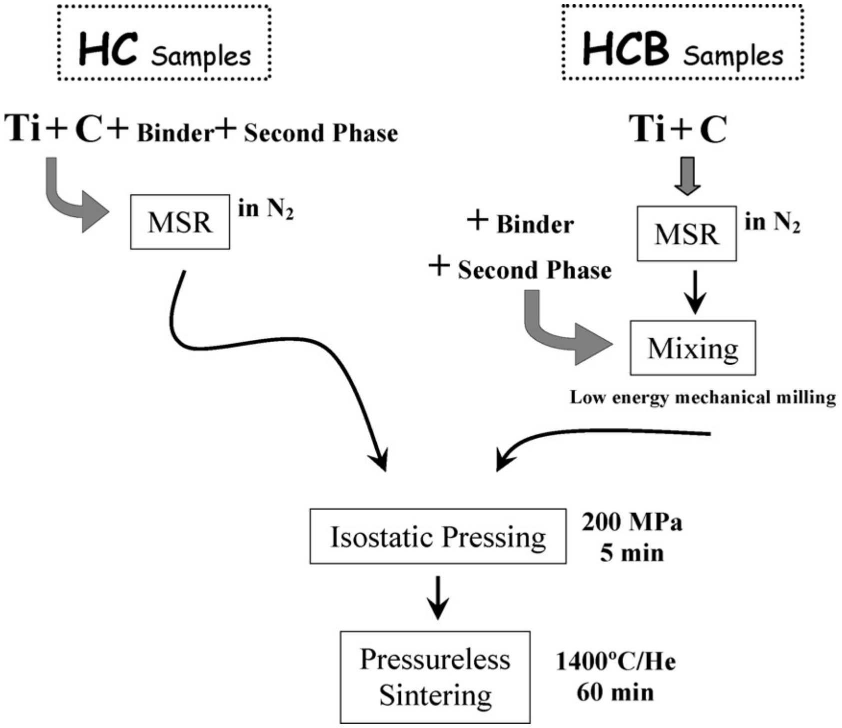

Fig. 1. Flow chart of cermet processing.

3. Results and discussion

3.1. Mechanical properties

Some properties of the studied cermets are given in Table 2. High density values (96–97%) were only achieved in HC samples, which is a reflection of better homogenization of the ceramic and binder phases.

Some representative microindentation marks are shown in Fig. 2, where the microstructure of the cermets can be also appreciated. A detailed description of the cermets' microstructure was provided in a previous article.[20] The hardness in the cermets depends on the intrinsic properties of the separate phases, but it is also influenced by other factors such as ceramic particle size. For the same starting gross composition, HC cermets showed enhanced hardness when compared with HCB cermets, where binder was added to the powdered mixture after MSR. This fact could be explained by the different morphology of the cermets, the hard particles in HCB cermets being coarser as observed in SEM micrographs of Fig. 2. The same trend was also observed in the toughness values, which were higher for those cermets obtained from powders synthesized by a one step MSR process. A considerable spalling of the hard particles at the border of the contact area of the indenter was observed in HCB cermets, which reveals a weaker bond strength at the binder-ceramic boundaries and consequently a cermet that is not as tough.

Table 1
Raw powders used for cermet fabrication (the powder mixture subjected to the MSR process in a nitrogen atmosphere is marked by square brackets), and phases observed after sintering as determined from XRD measurements.

Specimen	Raw powders	Cermets	
	Ti/C (atomic ratio) + binder (wt%) + 3rd phase (wt%)	Hard phase	Binder
HCB2	[Ti/C (1/05)] + Ni (15%)	$TiC_{0.67}N_{0.33}$	Ni_3Ti
HCB4	[Ti/C (1/0.5)] + Co (15%)	$TiC_{0.68}N_{0.32}$	CoTi, Co_2Ti (m)
HCB7	[Ti/C (1/0.5)] + Co (15%) + WC (5%)	$TiC_{0.71}N_{0.29}$	CoTi, Co_2Ti, W (m)
HCB8	[Ti/C (1/0.5)] + Co (15%) + Mo_2C (5%)	$TiC_{0.67}N_{0.33}$	CoTi, Co_2Ti, Co_7Mo_6 (m)
HC1	[Ti/C (1/0.25) + Ni (15%)]	$TiC_{0.36}N_{0.64}$	$NiTi_2$
HC2	[Ti/C (1/0.5) + Ni (15%)]	$TiC_{0.75}N_{0.25}$	Ni_3Ti, (Ni,Ti) (m)
HC3	[Ti/C (1/0.75) + Ni (15%)]	$TiC_{0.79}N_{0.21}$	Ni_3Ti
HC4	[Ti/C (1/0.5) + Co (15%)]	$TiC_{0.85}N_{0.15}$	Co_3Ti
HC5	[Ti/C (1/0.5) + Ni (7.5%) + Co (7.5%)]	$TiC_{0.75}N_{0.25}$	(Co,Ni)Ti
HC6	[Ti/C (1/0.5) + Co (15%) + W (5%)]	$TiC_{0.75}N_{0.25}$	CoTi, W (m)
HC7	[Ti/C (1/0.5) + Co (15%) + WC (5%)]	$TiC_{0.74}N_{0.26}$	CoTi, W (m)
HC8	[Ti/C (1/0.5) + Co (15%) + Mo_2C (5%)]	$TiC_{0.76}N_{0.24}$	CoTi, Mo (m)

m: minor phase.

Table 2
Density, Vickers microhardness (H_v 1.0), toughness (K_{IC}), wear rate (k), friction coefficient (f), and oxidation mass gain of cermets

Specimen	Density (g/cm^3)	Relative density (%)	H_v 1.0 (GPa)	K_{IC} (MPa m$^{1/2}$)	k (10^{-6} mm^3/Nm)	f	Mass gain (wt%)
HCB2	5.0	92	11.6	5.3	–	–	–
HCB4	5.1	94	10.5	5.0	–	–	–
HCB7	5.1	91	11.9	5.6	–	–	–
HCB8	5.1	92	12.1	6.1	–	–	–
HC1	4.9	90	9.8	5.7	5.6	0.89	29
HC2	5.2	96	12.6	9.6	4.7	0.83	27
HC3	5.3	97	12.7	7.5	4.9	0.85	23
HC4	5.2	96	14.1	8.8	3.0	0.86	20
HC5	5.1	94	12.8	9.0	4.6	0.81	30
HC6	5.5	97	12.2	6.5	4.8	0.86	13
HC7	5.4	96	12.5	8.6	4.5	0.85	14
HC8	5.4	97	12.9	6.5	5.2	0.89	11

The Vickers microhardness of the HC cermets (Table 2) proved to be particularly sensitive to hard phase stoichiometry. The hardness was found to increase with increasing carbon content, and close values were observed for similar C/N ratios in the titanium carbonitride phase. These results are in agreement with a lower hardness for TiN than TiC. In this sense, the lower and higher hardness values were observed in cermets HC1 (with the lowest carbon content) and HC4 (with the highest carbon content), respectively. HC1 also had the coarsest ceramic particles, which is a detrimental factor for hardness as well.

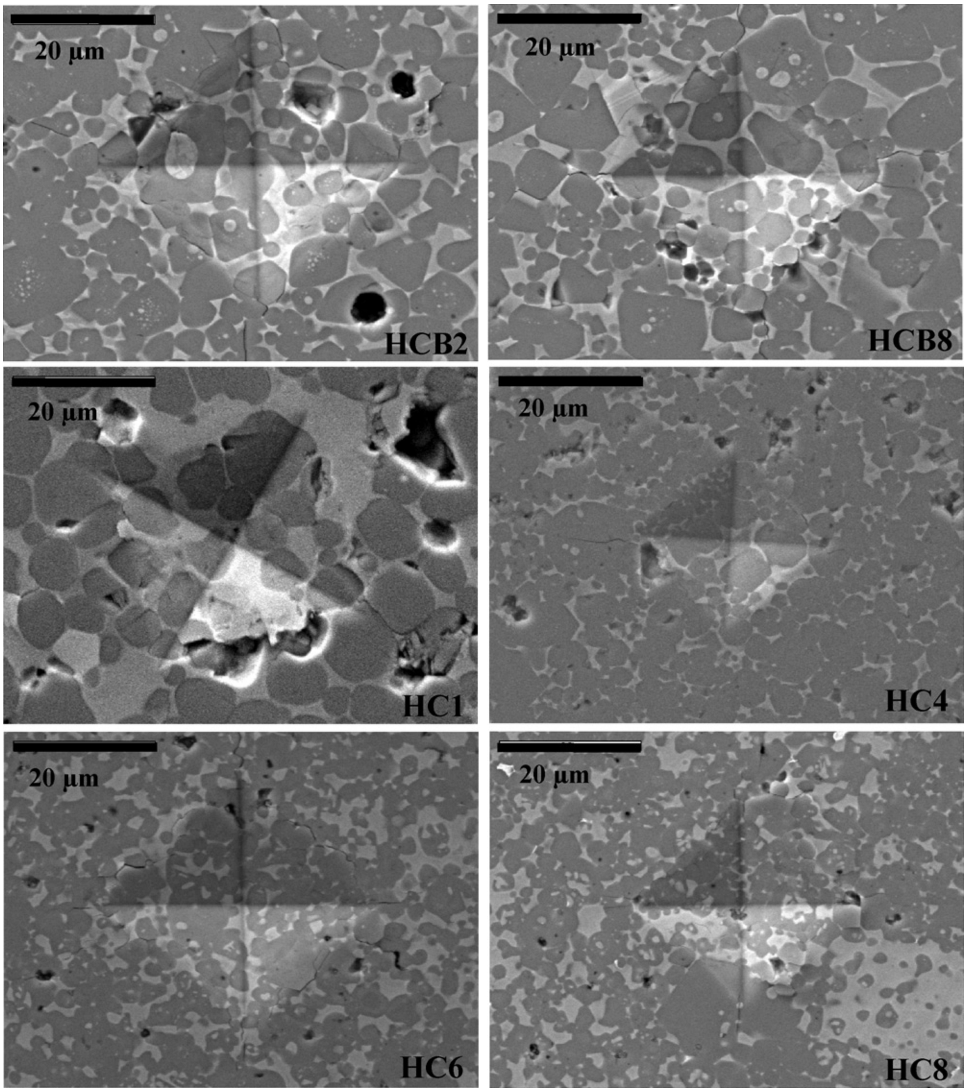

Fig. 2. SEM micrographs of microindentation marks for some representative HCB and HC cermets.

The influence of the binder nature on the hardness of HC cermets is not evident from the results presented in Table 2. A more detailed study focused on the effects of these intermetallic phases on the mechanical properties of the cermets would be necessary. On the other hand, the addition of small amounts of secondary phases, such as W, WC, and Mo_2C, did not produce significant effects on the hardness values, and were comparable to those of cermets with a similar TiC_xN_{1-x} stoichiometry. However, addition of W and Mo_2C resulted in cermets that were not as tough. However, cermet HC7 maintained a good toughness value with WC additions.

In summary, cermet HC4, containing $TiC_{0.85}N_{0.15}$ as the hard phase and Co_3Ti as the intermetallic binder, had the highest hardness (14.1 GPa), and cermet HC2, containing $TiC_{0.75}N_{0.25}$ and Ni_3Ti, the highest toughness (9.6 MPa $m^{1/2}$). Cermet HC1, with the lowest relative density, showed the lowest toughness value. An optimal combination of hardness and toughness was obtained for cermets HC2, HC4, HC5, and HC7, with values larger than 12.5 GPa and 8.6 MPa $m^{1/2}$, respectively. These hardness and toughness values are comparable to those found in the bibliography[23–25] for cermets with high contents of secondary carbides and the typical core-rim microstructure, which are accepted as being responsible for the improvement of the mechanical properties.

3.2. Tribological behaviour

Some papers provide the microstructural and tribomechanical characteristics of Ti(C,N)-based cermets, but as far as the tribological aspect is concerned, investigations focus mainly on cutting tests and practical performance at high temperature.[2,23,26–29] So far, there is less information available regarding the effect of the composition on the tribological behaviour under the dry sliding conditions where often bearings and seals operate.[6,30,31] Therefore, the tribological behaviour of the Ti(C,N)-based cermets was evaluated in reciprocating friction unlubricated tests under 10 N of applied load. As the HC specimens exhibited better physical and mechanical properties, they were selected for tribological testing. The wear resistance of different samples was estimated by measuring the worn volume of the track after testing. Fig. 3 displays the calculated wear rates (k) for the set of samples ordered by increased wear resistance together with the microhardness values. The k values vary in the range of (3–6) × 10^{-6} mm^3/Nm, and appear to correlate with the hardness properties (Table 2). Similar trends have been reported in other samples such as WC–Co and Ti(C,N)–NiMo cermets.[2,31] As a general trend, an increment in the wear resistance can be noticed when the hardness of the cermet increases. This behaviour agrees with the Archard's wear equation that predicts that the material loss is inversely proportional to the bulk hardness. The tribological properties have been compared regarding the chemical composition of the samples. In Fig. 4, the tribological properties have been plotted as a function of the stoichiometric x value in the TiC_xN_{1-x} formula. Three different situations can be distinguished for the wear rate values attending to the C/N content. Thus, the lowest and highest wear rates correspond to the samples with the maximum and minimum x values, (i.e. HC4 and HC1), respectively. This indicates that an increment on the carbide character improves the wear resistance, as this fact entails also an augmentation of the hardness. An influence of the hard grain size is likely in cermet HC1 since it is well known that coarse-grained cermets usually have lower abrasive wear resistance those that of fine or medium grain size.[6] The remaining samples, with a chemical composition closer to that of $TiC_{0.75}N_{0.25}$, exhibit very similar hardness and wear resistance values as denoted in Fig. 3. The friction coefficients are not directly related to the wear rates or stoichiometric composition, and the values span in a range between 0.81 and 0.89 for the set of samples (Table 2). No clear differences are noticed in the tribological behaviour when a second ceramic phase (WC or Mo_2C) was added (up to 5 wt%), probably because it did not significantly change the hardness and the amount of interface boundaries, which can result in potential sites for grain detachment.[30]

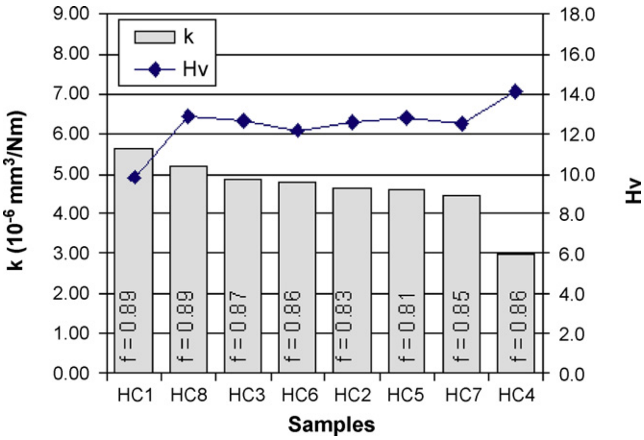

Fig. 3. Specific wear, friction coefficients, and microhardness values for the series of HC cermets.

The changes in friction coefficient as a function of number of cycles are presented in Fig. 5 for three representative samples (HC1, HC2, and HC4) corresponding to the three cases identified. The friction behaviour is very similar, exhibiting a first running-in period where the friction coefficient rises quickly and then stabilises in a steady-state around 0.8–0.9. This high value is not surprising considering the test severity due to the absence of lubrication conditions and the ceramic nature of the mating

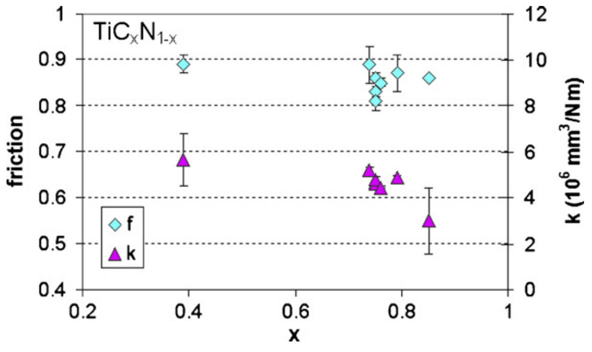

Fig. 4. Dependence of the friction and wear coefficients versus the stoichiometry of the TiC_xN_{1-x} hard phase.

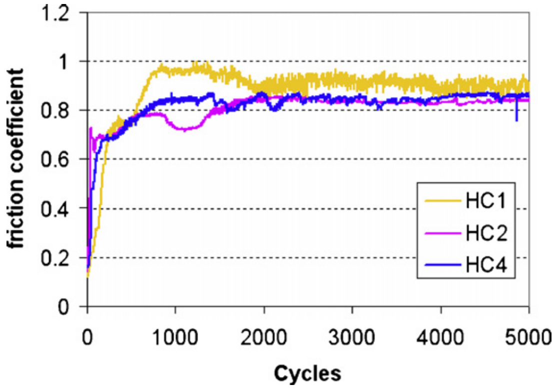

Fig. 5. Variation of the friction coefficient for three representative cermets HC1, HC2 and HC4 in a reciprocating pin-on flat friction test.

surfaces. The slight increment in friction for sample HC1 might be attributed to the presence of coarser hard grains.

3.3. Oxidation resistance

The mass gain evolution during the isothermal stage at 1000 °C in air for some representative HC cermets is shown in Fig. 6. All cermets mainly followed a parabolic oxidation trend, but the net mass gain was quite different (Table 2). The results shown in Table 2 indicate that the degree of oxidation decreases slightly with increasing carbon content in the titanium carbonitride phase. The presence of cobalt instead of nickel improves the oxidation resistance, which is significantly better for cermets containing W or Mo in the binder. These results suggest that the oxidation resistance of the cermets is primarily dependent on the nature of the binder. It must be taken into account that the binder constitutes the continuous skeleton in which ceramic particles are embedded and, therefore, the oxidation process needs to progress through the binder.

The oxidation resistance (the smallest weight gains) of the cermets improved remarkably when a small amount of W or Mo was present in the binder. This cannot be explained by the fact that 5 wt% less of the hard phase was present in these cermets, or by the formation of volatile species such as the tungsten oxides. The beneficial effect of employing W as the alloying element on the oxidation behaviour of some alloy systems, such as TiAl, can be found in the literature.[32] However, the explanation of this influence is not simple because of many synergistic effects.[33] In general, the presence of W or Mo is advantageous for the oxidation resistance of many alloy systems, provided that they are added in a reduced amount, acting as doping elements and reducing the oxygen solubility.[34]

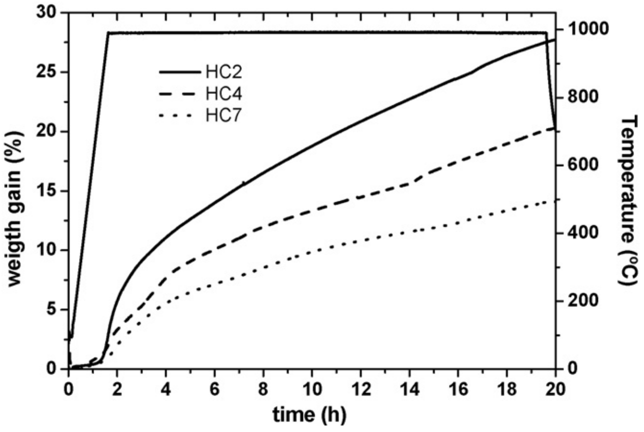

Fig. 6. Isothermal oxidation curves in static air at 1000 °C for three representative cermets HC2, HC4, and HC7.

These results contrast with those of a previous work, where the addition of WC worsened the oxidation resistance of a Ti(C,N)-based composite.[35] However, it must be taken into account that, in fact, WC additions in our cermets did not remain as a ceramic phase, but metallic tungsten was incorporated into the binder. In this sense, Monteverde and Bellosi have reported that cermets in two different Ti(C,N)–WC based materials showed a lower growth rate of the reaction scale than the ceramic material.[36]

Fig. 7 shows the XRD patterns of the oxide scales formed on cermets HC2, HC4 and HC7 after the isothermal oxidation. The XRD patterns indicate that TiO_2 rutile was the major oxide and, therefore, that the TiC_xN_{1-x} hard phase was unstable under the oxidation experimental conditions. TiC_xN_{1-x} was not detected in the three cermets due to the thickness of the oxide scales (Fig. 8) that impedes the observation of the underlying non-oxidized cermet. Binder phases were also detected in the XRD patterns on the oxide scales: Ni and Ti in cermet HC2, Co in cermet HC4, and CoTi and Co_3Ti in cermet HC7. Oxidized binder phases were also detected in cermets HC4 and HC7: CoO and $CoTiO_3$, respectively. The original intermetallic binder, CoTi (Table 1), was observed in cermet HC7 after oxidation, in agreement with its improved oxidation resistance. This phase, CoTi, seems to be more oxidation-resistant than γ'-Ni_3Ti and Co_3Ti, which were the former binders in cermets HC2 and HC4, respectively. After the oxidation test, the Co_3Ti phase was also observed in cermet HC7 as a consequence of the selective oxidation of titanium in the CoTi phase, which produces its depletion similar to that shown in the oxidation of TiNi equiatomic alloys.[37] The appearance of Ni or Co in the XRD patterns on the surface of cermets HC2 and HC4, respectively, occurs again because of the preferential loss of titanium from Ni_3Ti or Co_3Ti to form TiO_2.[38,39]

The cross-section examination of different cermets by SEM confirmed that those cermets with smaller weight gains had a much-thinner attacked thickness as evidenced in Fig. 8. The three cermets showed an oxide scale with a multilayered structure. Three areas *a*, *b,* and *c* were observed (Fig. 8). The inner zone, *a*, corresponds to the central part of the cermet body, where oxidation had not penetrated. In this region, the hard carbonitride grains surrounded by the binder phase are observed (Fig. 9). The medium zone, *b*, corresponds to an incipient oxidation region, where the microstructure of the cermet was being destroyed (Fig. 9), and it is characterized by a finer-grained microstructure and a pronounced porosity induced by the evolution of N_2 and CO gas species. The bright round particles observed in this region are constituted by the binder metallic elements as evidenced by EDX analysis. The size of these particles was different for the three studied cermets, the smallest ones being found in the

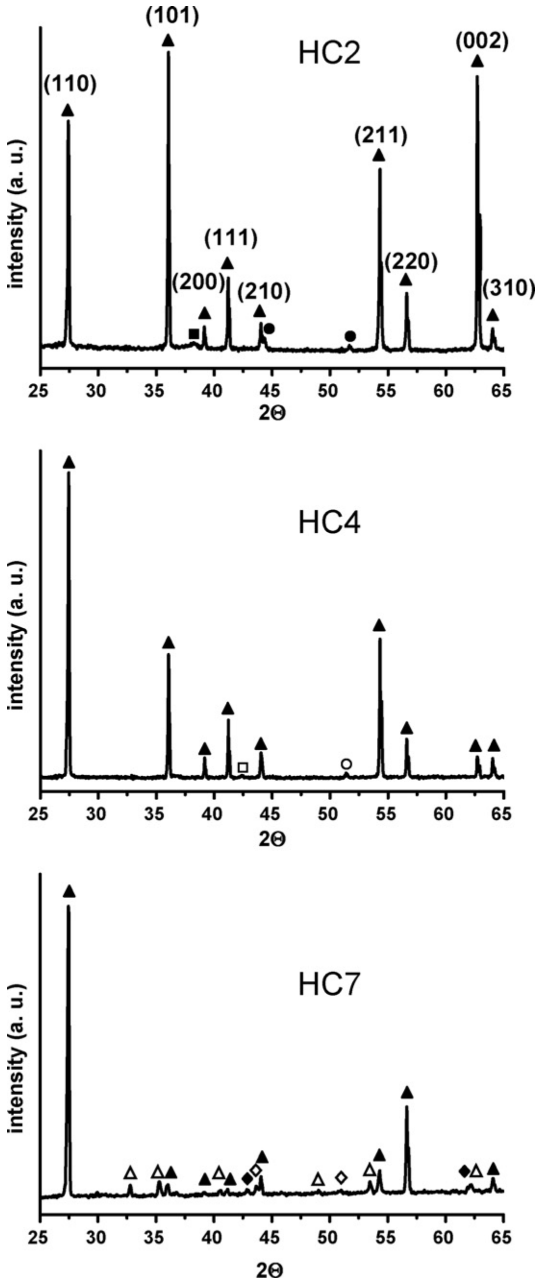

Fig. 7. XRD patterns of oxide scale formed on cermets HC2, HC4, and HC7 after isothermal oxidation at 1000 °C. (▲) TiO_2 (rutile), (●) Ni, (■) Ti, (○) Co, (□) CoO, (◆) CoTi, (◇) Co_3Ti, and (△) $CoTiO_3$.

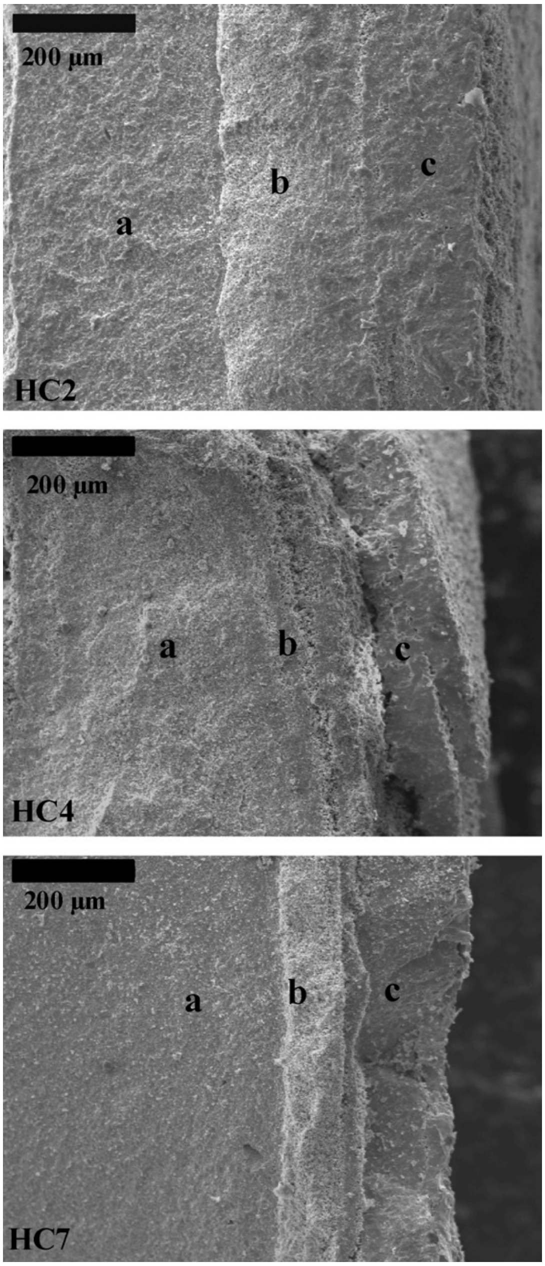

Fig. 8. SEM micrographs of the cross-section of oxide scales after isothermal oxidation at 1000 °C for cermets HC2, HC4, and HC7.

cermet with better oxidation resistance (HC7). Finally, the outer zone, *c*, which is fully oxidized, consists of a continuous rutile layer that exhibits a rather smooth and sintered aspect (Fig. 9). However, this oxide layer presents many cavities, and therefore cannot provide an efficient oxidation protection. In addition, this outer layer did not adhere well to the sample surface and some spalling was observed (Fig. 8). On the other hand, the sharp boundary between different zones implies that the oxide grows at the cermet-scale interface.

Some interesting differences were observed in the features of this outer layer for the three studied cermets (zone *c*, Fig. 9). In cermet HC2, particles containing the binder elements were remarked embedded in this layer as bright round particles. The outer layer in cermets HC4 and HC7 was apparently free from these particles. Cobalt and nickel elemental maps performed by EDX showed the Co and Ni distribution in the oxidized cermets (Fig. 10). It was confirmed that cobalt was missing from this outer region (rutile layer), and was concentrated on the top external surface of cermets HC4 and HC7. These results agree with the XRD patterns on the oxide scales of these cermets, where CoO and $CoTiO_3$ were observed. It has been suggested that the improvement of the oxidation resistance in the cermets is the consequence of the presence of the binder that activates the sintering of the growing TiO_2 particles on the surface.[36] However, this fact fails to explain the differences observed in our work. The reason for the improved oxidation resistance lies,

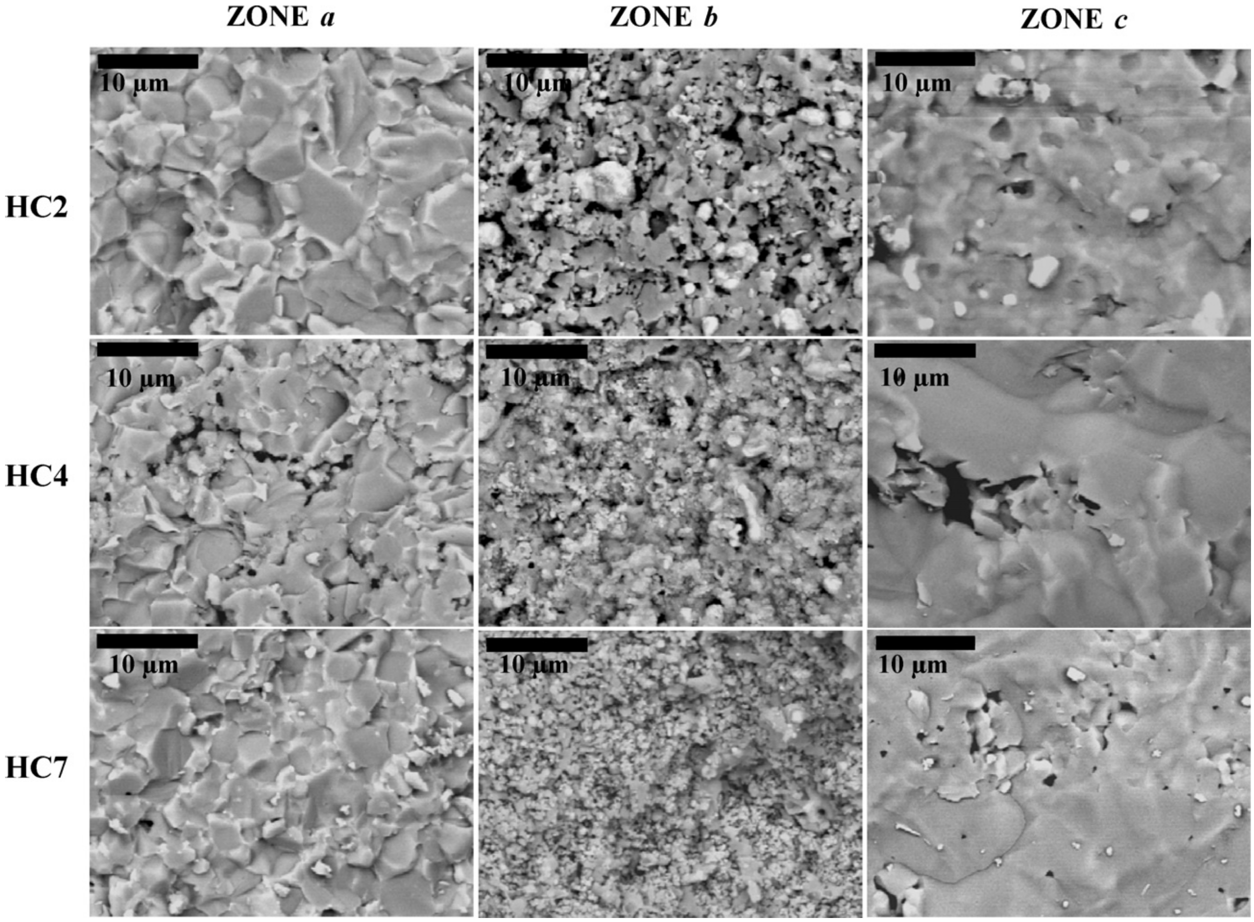

Fig. 9. BSE-SEM micrographs from regions *a*, *b*, and *c* in Fig. 7.

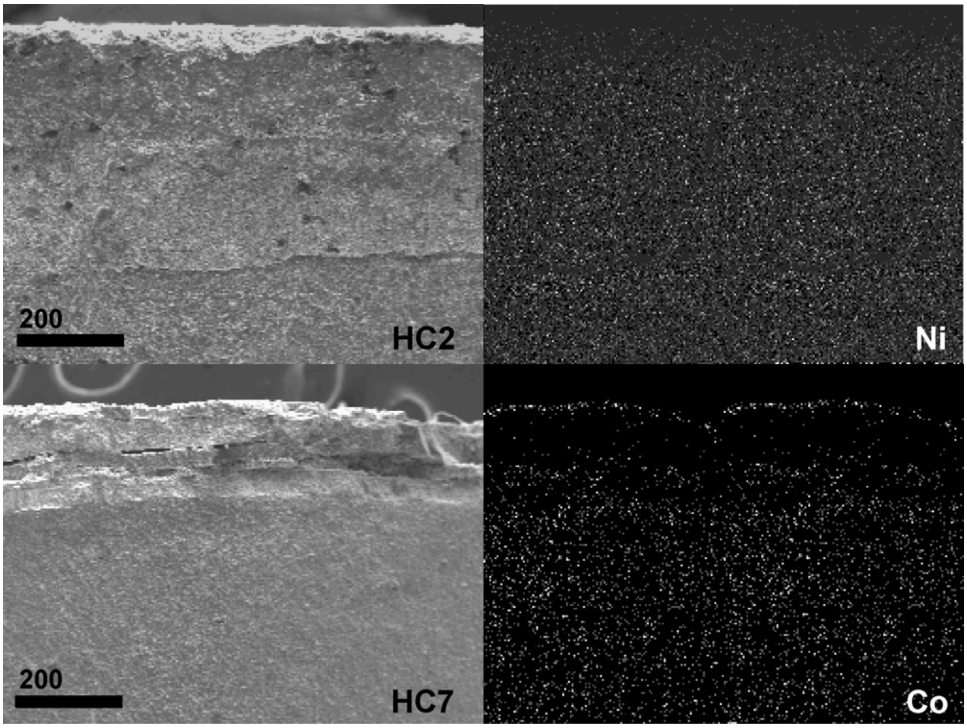

Fig. 10. SEM micrographs of the cross-section of oxide scales in cermets HC2, and HC7, and X-ray mapping of Ni (HC2) and Co (HC7).

rather, in the formation of a superficial oxidized binder row upon the outer rutile layer. This thin layer can act as a diffusion barrier for oxygen species, sealing the communicating paths with the atmosphere and slowing down the oxidation rate.

4. Conclusions

TiC_xN_{1-x}/Ni and TiC_xN_{1-x}/Co cermets fabricated for the first time from powdered cermets synthesized by MSR were characterized. An optimal combination of hardness and toughness was found when powdered cermets were obtained in one step from the mixtures of elemental powders. The hardness and toughness values for these cermets were larger than 12.5 GPa and 8.6 MPa $m^{1/2}$, respectively, and they are comparable to those found in the bibliography for cermets with high contents of secondary carbides and the typical core-rim microstructure. The friction was found to be about 0.8–0.9 for all the compositions although small differences in worn volume were seen. The wear rate at dry sliding conditions follows the bulk hardness and chemical composition. Higher wear resistances are obtained for harder samples containing higher carbon contents in the TiC_xN_{1-x} cermets. The oxidation resistance in the cermets was determined by the nature of the binder phases. A better oxidation resistance was observed in cermets containing only Co as binder. Improved resistance was found in cermets with W or Mo additions. The formation of a Co-containing oxide layer at the top surface of the cermets seemed to be at the origin of this oxidation resistance. Taking into account the analyzed properties, the best performances were found in cermets with a chemical composition of the hard phase closer to that of $TiC_{0.75}N_{0.25}$, containing cobalt as the binder, with small proportions of the binary carbide WC.

The superior properties observed in cermets obtained from powder mixtures synthesized by a one-step MSR process were the consequence of a homogeneous chemical composition and microstructure developed during sintering, which resulted in a good distribution of the binder phase that minimized contiguity of ceramic particles. Taking into account the simplicity of the studied compositions, significant improvement in the overall properties are expected if the starting formulation and the sintering conditions are optimized. In particular, the optimization of the sintering process is crucial in order to inhibit the observed grain growth of hard ceramic, and to maintain the nanometric character of powdered cermets obtained by MSR.

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