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ScienceDirect
Ceramics International 35 (2009) 369–372
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Carbide phases formed in WC–M (M = Fe/Ni/Cr) systems

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Received 16 September 2007; received in revised form 3 October 2007; accepted 11 November 2007
Available online 21 February 2008

Abstract

The effect of composition in the formation of carbides in the WC–M (M = Fe/Ni/Cr) system has been studied. Three conventional compositions have been prepared with 10 wt.% of metallic binder. Fe as a metallic binder was first studied and its partial substitution by Ni and Cr was also investigated. A WC powder coated with a similar binder (Fe/Ni/Cr) amount was also investigated. The XRD results, after thermal treatment at 1400 °C, reveal that the substitution of half percent of the iron content by Ni stabilized the austenite Fe(γ) formation. The introduction of Cr in the binder composition induces the formation of Cr_2C carbide. With the decrease of Cr amount in the binder composition of the coated powder, Cr_2C carbide was not formed, but instead other carbide, M_6C, was detected. In order to eliminate this carbide a small excess of carbon (3.6 wt.%) was added to the coated powder. The results are discussed in terms of the phases formed, the binder composition and the final carbon content.

Keywords: Tungsten carbide; Coated powders; Fe/Ni/Cr; η-Phase

1. Introduction

For the production of hardmetals tungsten carbide (WC) is the basic and the most widely used hard compound, whereas cobalt was found to be the optimal binder metal for the largest part applications.

Other cobalt neighbor's group metals (nickel and iron) have been employed but to a very limited extent [1–4] due to the difficulty to attain simultaneously a high hardness and toughness equivalent to the Co bonded WC composites [5–9].

The complete substitution of Co by Ni leads to composites with high ductility, but brings a strong reduction of the hardness [9,10]. Fe and Ni alloys were also investigated for total or partial Co substitution and it was found that the structure of the crystalline phases in the sintered composites has a strong influence on the technological properties [9]. Cr is also used within limited amounts in some hardmetal compositions to control the grain growth and to improve oxidation and corrosion resistance [11]. Both Fe and Cr possess a strong affinity to carbon leading to the formation of carbide phases presenting normally a brittle behavior and reducing, so, the mechanical resistance of the composite [11,12]. However, a systematic study of the thermal reactivity between metallic elements used for Co substitution and WC, aiming the control of brittle phases, is yet missing. Therefore, the aim of the present work has been to investigate the thermal reactivity between WC and transition metals with different carbon affinity Cr/Fe/Ni. This study was carried out using conventional-prepared powders and a coated powder processed by an innovative way of sputter-coating WC particles. The sputter-coated powders have a large potential interest due to its unique particle surface characteristics [13–15], presenting among others, a much higher surface reactivity [16].

2. Experimental

WC powder (241881 Aldrich) with a particle size <10 μm and 99% purity was used to prepare conventional mixtures with iron (Goodfellow FE006020, <60 μm), chromium (Goodfellow CR006021/22, <38 μm) and nickel (Goodfellow NI006021/11, 3–7 μm), all with 99% of purity. Three compositions with 10 wt.% of binder amount were prepared having different contents of iron (Table 1). The mixings were performed with 1.5 wt.% of paraffin wax, using isopropyl alcohol as solvent in a

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0272-8842/$34.00
doi:10.1016/j.ceramint.2007.11.001

Table 1
Percentage of metallic binders in the prepared powders

Sample	Fe (wt.%)	Ni (wt.%)	Cr (wt.%)	Sum (wt.%)	Ni/(Ni + Fe)
M–WC1	10.0	–	–	10.0	–
M–WC2	5.0	5.0	–	10.0	0.5
M–WC3	3.3	3.3	3.3	9.9	0.5
C–WC3	3.9	4.4	1.0	9.3	0.5

Table 2
Weight losses and carbon content of sintered composites at 1400 °C

Sample	Weight losses (wt.%)	Final WC[a] amount (wt.%)	C[b] (wt.%)	C[c] (wt.%)
M–WC1	4.6	92.2	5.61	5.67
M–WC2	5.2	92.1	5.61	–
M–WC3	3.3	92.2	–	5.58
C–WC3	2.0	–	–	–
C–WC3 + C	4.0	–	–	–

[a] ICP analysis.
[b] Estimated carbon.
[c] LECO.

stainless steel mill with WC–Co balls for 6 h, subsequently dried at 60 °C, granulated and sieved. A composite powder was also prepared by coating the WC particles with a stainless steel (SS) AISI 304 target with attached Ni discs (in order to increase the sputtered Ni content relatively to the AISI 304 SS composition), using a modified dc magnetron sputtering process and the deposition parameters reported before [13]. This coated powder has a similar Ni/(Ni + Fe) ratio and binder amount, comparatively to the M–WC3 composition, and was designated by C–WC3 (Table 1). The chemical compositions of the coated powder and of the sintered compositions were carried out by inductively coupled plasma–atomic emission spectrometer (ICP, Isa JY70Plus).

To investigate the thermal reactivity, the powders were uniaxially pressed at 190 MPa and heat treated at a maximum temperature of 1400 °C, during 1 h, in a vacuum atmosphere of 20 Pa. The structural characterization of heat-treated samples was performed by X-ray diffraction (XRD, Rigaku PMG-VH) using a Cu Kα radiation ($\lambda = 1.5418$ Å). The microstructural characterization of polished surfaces was performed with scanning electron microscopy (SEM, Hitachi-S4100). The carbon content of WC powder and sintered samples was determined by automatic direct combustion (LECO CS 200 IH).

3. Results and discussion

The first composition under study was M–WC1 with 10 wt.% of Fe which was heat treated at 1400 °C, during 1 h. The XRD spectra, presented in Fig. 1, reveal three phases: hexagonal WC, bcc ferrite, Fe(α) and fcc austenite, Fe(γ). No carbide phases were detected which, taking into account the phase diagram for this system [17] suggests a carbon content near the stoichiometric one and that no significant decarburization occurred during sintering. The amount of determined C in the starting WC powder, 6.09 wt.% reveals that the deviation from the stoichiometric value, 6.13 wt.% is effectively negligible. The final C amount in the M–WC1 sintered sample is presented in Table 2, together with the estimated value assuming the final WC amount (Table 2), and the initial WC carbon content of 6.09 wt.%. As suggested, comparable calculated and experimental values were found. Considerable weight losses occurred during the heat treatment as presented in Table 2, mostly due to the removal of the paraffin wax and to the loss of binder by volatilization. From the ICP analysis of the sintered M–WC1 sample (Table 2), ~2 wt.% of binder loss was determined, contributing also for the placement of the final composition in the two-phase field (WC and Fe(α)) [17].

When half percent of the iron content is replaced by nickel (M–WC2) and the powder is submitted to the same heating cycle, the austenitic Fe(γ) was formed (Fig. 1) due to the known stabilization effect of Ni [18,19]. No carbide phases were really expected for this composition, because Ni is not a carbide former and, so, extends the limit of the two-phase field until C contents lower than the stoichiometric ones [18,19]. The SEM microstructures of these compositions (in Fig. 1 (right side)), show the binder phase spread among the WC grains, since it

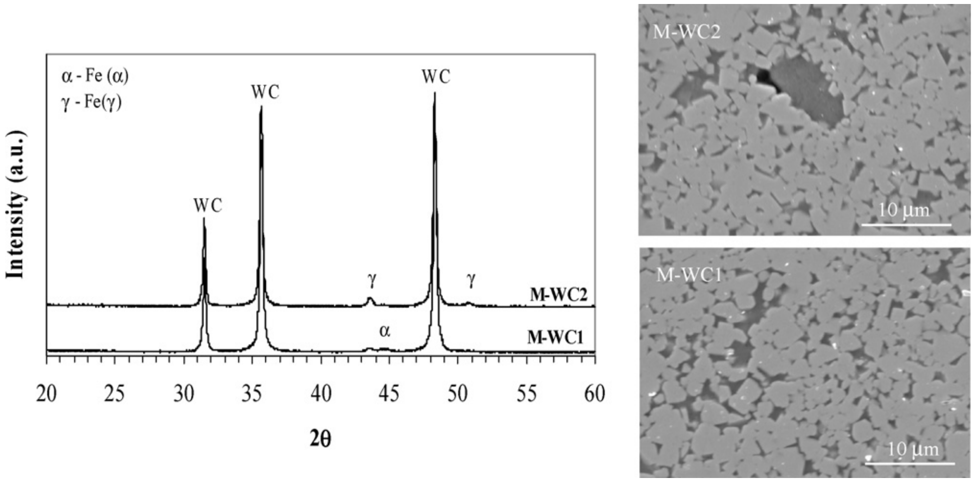

Fig. 1. X-ray diffraction pattern of M–WC1 and M–WC2 heat treated at 1400 °C, during 1 h, and respective SEM micrographs.

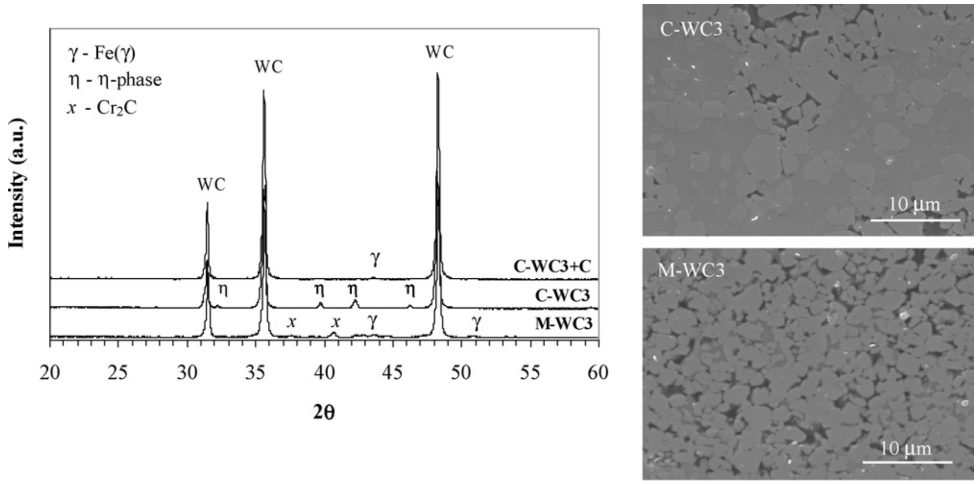

Fig. 2. X-ray diffraction pattern of M–WC3, C–WC3 and C–WC3 + C heat treated at 1400 °C, during 1 h, and respective SEM micrographs.

constituted a viscous phase at the sintering temperatures. The binder distribution is not homogeneous, presenting an accumulation of binder in some regions (see M–WC2 microstructure in Fig. 1).

The introduction of Cr, 3.3 wt.%, maintaining the same Ni/(Ni + Fe) ratio and the total binder amount of 10 wt.% (M–WC3), led to the formation of a chromium carbide, Cr_2C during the thermal cycle (Fig. 2). Although no phase diagram is known for this system (WC–Fe–Ni–Cr) the formation of carbide phases is presumable from the higher carbon affinity of chromium when compared to that of tungsten. The formation of the chromium carbide may result from the following reaction:

$$WC + xCr \rightarrow W + Cr_xC \qquad (1)$$

and the metallic tungsten resultant of the WC decomposition can be solubilized into the binder phase, until the solubility limit is attained. The XRD spectrum of M–WC3, in Fig. 2, shows that Cr_2C is formed to a limited extent. In this case and assuming Eq. (1) small quantities of W will be formed too, its solubilization being possible in the binder phase. The amount of carbon determined in this sintered sample shows a slightly lower value than in M–WC1. The binder phase for this composition presents (in Fig. 2), an austenitic form, not very well crystallized.

Although Cr has been used with beneficial effect on WC-based composite properties due to its grain growth-controlling role, the amount used is normally low (≤0.5 wt.%). This restrainment is related to the previously discussed high carbon affinity of this element and to the difficulty in the remotion of the porosity for WC composites with Cr. Therefore, a sputter-coated powder, C–WC3, with Fe, Ni and Cr in a total of 9.3 wt.% was prepared maintaining the same Ni/(Ni + Fe) ratio and a lower amount of Cr (1 wt.%) than M–WC3. For this powder, no Cr_xC phases were detected, but instead, another type of carbide phase, η-phase, was formed. The η-phase can contain all the binder elements $(Fe,Cr)_3(Ni,W)_3C$ [20]. Accordingly, no other peaks, besides the WC and η-phase peaks, are discernible in the spectra of C–WC3 (Fig. 2). The microstructure presented in Fig. 2 shows higher uniformity. Not very attractive mechanical properties are expected for this composite because M_6C is a brittle phase and, besides, the metallic ductile phase necessary to give enough toughness to the composite is negligible.

However, the formation of η-phase can be avoided by using an excess of C [5]. An excess of 3.6 wt.%, relative to the stoichiometric carbon, was added to the C–WC3 powder, in the sample C–WC3 + C. The XRD spectra, presented in Fig. 2 shows that the composite has the WC major phase and the austenite, Fe(γ). A composite of this type has relevant chemical, structural and microstructural characteristics to attain a combination of very attractive technological properties such as: high hardness, coming from the WC phase, high toughness, coming from the austenitic phase and high oxidation and corrosion resistance, coming from the Cr content and the austenitic metallic structure. Moreover, the very uniform binder distribution due to the sputter-coated process [13–16] and the controlled final grain size due to Cr addition will be also beneficial in the mechanical properties.

4. Conclusions

No carbide phases were detected for the conventionally prepared composite with 10 wt.% of Fe, after the thermal treatment at 1400 °C. Besides the WC phase, both bcc ferrite, Fe(α) and fcc austenite, Fe(γ), phases were present. The replacement of half percent of the Fe content by Ni stabilized the austenite, Fe(γ), phase. The introduction of 3.3 wt.% of Cr to the binder composition induced the formation of Cr_2C carbide. The decreasing of the Cr amount in a sputter-coated composite powder led to the formation of $(Fe,Cr)_3(Ni,W)_3C$ phase, η-phase, instead of Cr_xC carbides, which may contain all the metallic elements. In order to eliminate the η-phase, in this composition, an excess of 3.6 wt.% relative to the stoichiometric carbon was added, completely inhibiting the carbide formation and leading to the appearance of the more favourable austenite, Fe(γ) phase.

This composite has relevant chemical, structural and microstructural characteristics to attain a combination of very attractive technological properties such as high hardness, coming from the WC phase, high toughness, coming from the austenitic phase and high oxidation and corrosion resistance, coming from the Cr content and the austenitic metallic structure. The high uniform binder distribution, due to the sputter-coated process, and the controlled final grain size, due to Cr addition are also beneficial characteristics from the point of view of the mechanical properties.

Acknowledgements

The author C.M. Fernandes gratefully acknowledges the financial support of the POCTI programme of the Portuguese Foundation for Science and Technology (FCT) and European Social Fund (FSE).

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