

WC–(Fe,Ni,C) hardmetals with improved toughness through isothermal heat treatments

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The influence of carbon additions on densification during liquid phase sintering of WC–(Fe,Ni,C) hardmetals, and of subsequent heat treatments on some mechanical properties, like hardness and fracture toughness, have been investigated. The relation between total carbon content in the mixtures and final density of the specimens has been determined, together with its effect on the structure of the resulting metallic binder phase. In addition, the relationship between hardness and toughness and WC grain size in these hardmetals has shown to be similar to that in the traditional WC–Co system. Nevertheless, the effect of isothermal heat treatments which bring about a modification of the microstructure of the metallic binder has proved to be beneficial for increasing toughness without an appreciable influence on hardness.

1. Introduction

Because of their unique combination of hardness and fracture toughness, materials within the tungsten carbide–cobalt (WC–Co) system are indispensable at present in a variety of industrial applications [1, 2]. However, other systems have been reported to have superior transverse rupture strength as well as resistance to abrasive wear [3, 4]. The substitution of Co by Fe-based alloys has been widely studied [3–10] due to the high cost of Co and its scarcity of supply.

The study of the relationship between microstructural parameters and mechanical properties such as hardness, and particularly, fracture toughness in the WC–Co system, indicates that the resistance to fracture manifests primarily from the constrained deformation behaviour of the ductile Co phase between the rigid WC grains [10–12]. This means that the substitutes of Co have not only to wet the carbide during liquid phase sintering, have limited solubility for tungsten (W) and carbon (C), form a liquid with W and C at not too high a temperature and present ductile behaviour, but also have a composition adjusted so that neither free C nor mixed eta carbides (M_6C) are formed [4].

In the case of Fe–Ni alloys, C additions are indispensable for achieving full density at low sintering temperatures [4, 5, 9]. This results in WC + (Fe, Ni, C) cermets, in which the microstructure of the metallic binder phase may be modified by heat treatments in order to increase its toughness.

Though stress-induced martensitic transformations have been reported in similar cermets [9], this paper shows that heat-induced phase transformations may also alter the microstructure of the binder phase with little or no effect on the carbide grains, resulting in improved toughness without a significant decrease in hardness.

2. Experimental procedure

The materials examined in this study are WC hardmetals whose metallic binder consists of an Fe alloy containing 10 wt% of Ni and C amounts up to 3.5 wt%. The metallic binder represents 10 wt% of the cermet itself, which results in a 19% volume ratio. To obtain the experimental materials, conventional powder metallurgy routes were used. Fully carburized WC and high purity Fe, Ni and C powders were weighed to achieve desired compositions for each cermet. The powders were mixed in a planetary ball mill with isopropyl alcohol and 1.5 wt% of solid paraffin wax for 20 h. The powders were subsequently dried at 100 °C, granulated in a mortar and sieved through 0.2 mm mesh. The sieved powders were uniaxially pressed in the form of cylinders or bars at 150 MPa pressure and dewaxed in an argon atmosphere at 450 °C for 1 h. The green compacts were then densified by liquid phase sintering at 1250 °C in vacuum.

Density was measured by immersion in mercury and compared to the theoretical density calculated by the rule of mixtures. Specimens were polished up to a 1 µm finish for optical and scanning electron microscopy (SEM), phase identification by X-ray diffraction (XRD) and measurements of Vickers hardness (H_V) with a 30 kg load. Polished sections were etched with a 2% nitric acid solution for 45 s in order to distinguish the constituents of the metallic binder phase under the optical microscope. The microstructural parameters such as average grain size \bar{D} , contiguity C_t and carbide phase volume fraction V_{WC} were measured by point counting and the binder mean free path was estimated using the following equation:

$$\bar{L} = \frac{\bar{D}(1 - V_{WC})}{V_{WC}(1 - C_t)} \quad (1)$$

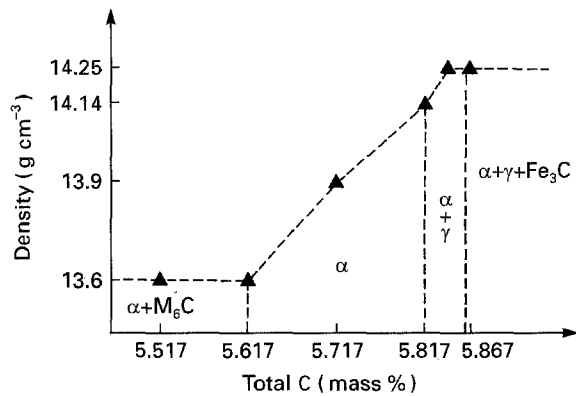


Figure 1 Density versus total C and corresponding structure of WC + 10% (Fe, Ni, C) alloy after sintering at 1250 °C for 1 h.

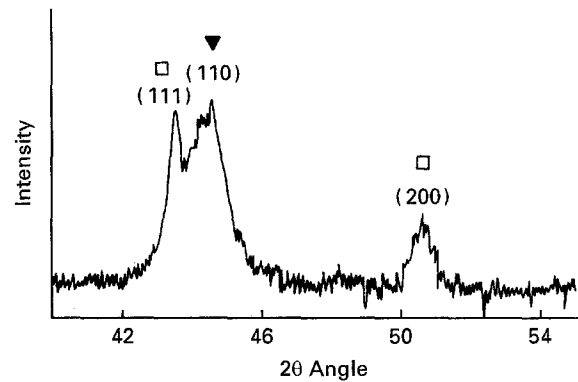


Figure 2 XRD pattern of the binder of WC + 10% (Fe, Ni, C) alloy (□ austenite, ▼ ferrite) after sintering.

To analyse the metallic binder phase in detail, the WC phase was completely removed from the polished surfaces by etching in a solution of 10% sodium carbonate at a current density of 1 A cm^{-2} [13]. This allowed XRD and energy dispersive X-ray spectrometry (EDS) measurements of the binder itself, without any interference by the WC grains. Also, thin foils for transmission electron microscopy (TEM) were prepared by standard ion beam milling.

Fracture toughness values from several specimens were calculated measuring the length of the cracks produced by Vickers indentations [14] or by four point bend tests on beams pre-cracked by the bridge indentation method [15, 16].

Heat treatments carried out on sintered specimens consisted in austenitizing at 800 °C followed by oil quenching and ageing at temperatures ranging from 500 to 600 °C.

3. Results and discussion

Sintering experiments carried out with these hardmetals were performed up to a temperature of 1500 °C, varying C additions and sintering time. However, at temperatures above 1250 °C an excessive weight loss was noticed due to the evaporation of the constituents in the binder phase. Thus, sintering was usually carried out at 1250 °C. The effects of the total amount of C contained in the specimens on the final density of these hardmetals is illustrated in Fig. 1, showing that C additions are beneficial to obtain fully dense materials. Fig. 1 also shows that the amount of carbon contained in these materials not only has an

effect on their density but also, as could be expected, on the phases present after sintering. It is noteworthy that fully dense materials can be produced with binders consisting of a combination of Fe–Ni ferrite and austenite. Nonetheless, it has also to be noted that iron carbide (Fe_3C) can be formed when the total C content in the specimens exceeds a critical value of about 5.867 wt %. Additionally, it must also be pointed out that although densities higher than 98% can be reached at extremely short times after reaching the sintering temperature (for specimens with a total C content of 5.842 wt %) full density can only be achieved after a 1 h holding period.

Optical microscopy and SEM were carried out as part of the microstructural characterization of the specimens along with phase content determination by XRD. Table I presents a summary of the measured microstructural parameters such as average WC grain size \bar{D} , contiguity C_t , binder phase volume fraction $1 - V_{\text{WC}}$ and mean free path \bar{L} , as a function of the initial WC particle size used. From this table it can be appreciated that both \bar{D} and \bar{L} systematically increased as the initial WC particle size was also increased. Additionally, Fig. 2 is presented as a verification of the b.c.c.–f.c.c. mixed character of the binder phase after sintering, which is constituted in quantitative terms by 75% b.c.c. + 25% f.c.c. The microstructure of the specimen after etching with nitric acid is shown in Fig. 3. The binder phase, which corresponds to the dark and white areas in the optical micrograph are clearly distinguishable after etching and correspond to ferrite and austenite respectively. As may also be expected, both the morphology and appearance of

TABLE I Measured microstructural parameters, hardness and toughness of WC + 10% (Fe, Ni, C) alloy for different WC mean particle sizes

WC Particle size (μm)	\bar{D} (μm)	C_t (%)	V_{WC} (%)	\bar{L} (μm)	H_V (kg mm^{-2})	K_{IC} ($\text{MPa m}^{\frac{3}{2}}$)
≈ 1	0.5 ± 0.05	40	80.5 ± 0.5	0.2 ± 0.02	1603 ± 58 1572 ± 72^a	10 15 ^a
≈ 4	1 ± 0.1	40	80.5 ± 0.5	0.4 ± 0.04	1380 ± 42	12
~ 6	1.5 ± 0.15	40	80.5 ± 0.5	0.6 ± 0.06	1200 ± 30	16

^aHeat-treated.

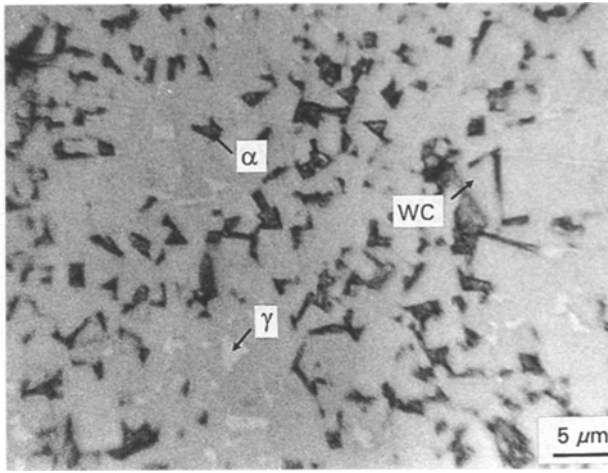


Figure 3 Optical micrograph of as-sintered sample etched with nitric acid.

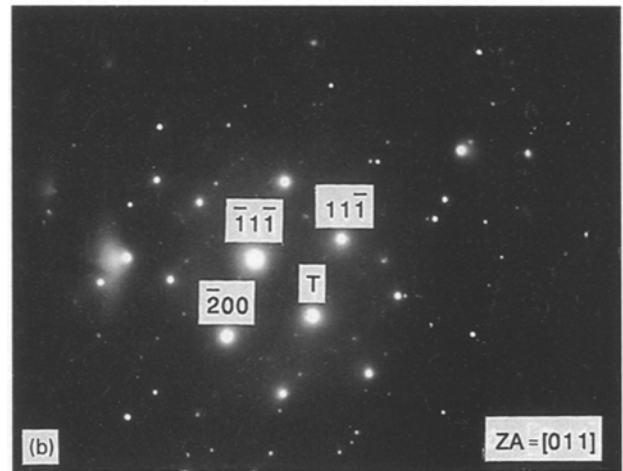


Figure 5 (a) TEM micrograph of an austenite grain (γ phase) and (b) corresponding diffraction pattern.

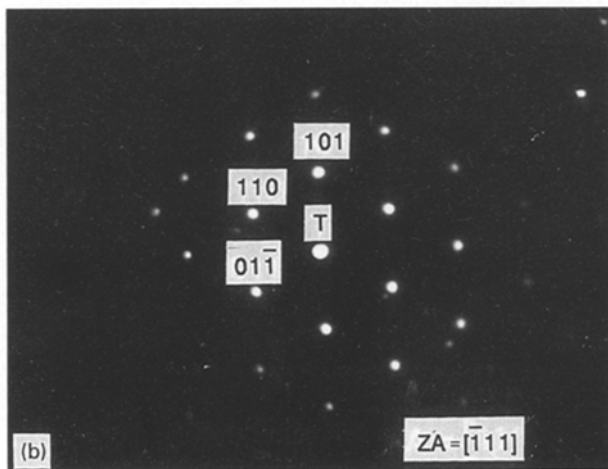
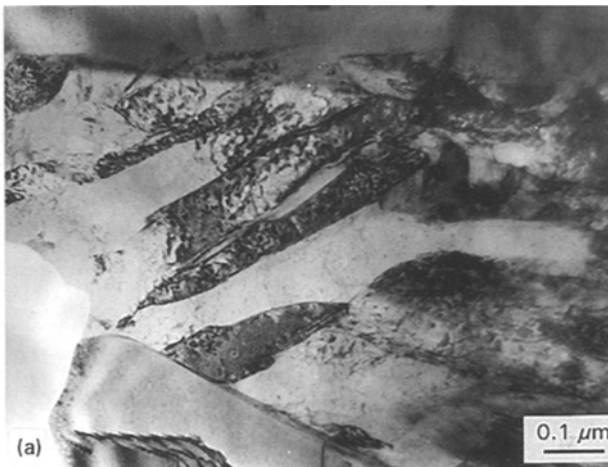


Figure 4 (a) TEM micrograph of ferrite grains (α phase) and (b) corresponding diffraction pattern in an as-sintered specimen.

α -Fe and γ -Fe under the TEM are quite distinct. This is shown, along with their corresponding electron diffraction patterns in Figs 4 and 5.

The morphology of the ferritic phase in Fig. 4 indicates that it corresponds to acicular ferrite or bainite; the possibility of being martensite was ruled out since, as will be seen further ahead, the amount of the phase was increased by isothermal heat treatments.

As shown in Table I, the hardness/fracture toughness combination of the as-sintered specimens is similar to values reported in the literature for hardmetals in the WC-Co system [10]. Considering the equations proposed by Gurland *et al.* [17] for hardness of WC cemented carbides

$$H_C = H_{WC}V_{WC}C_t + H_M(1 - V_{WC}C_t) \quad (2)$$

where H_C , H_{WC} , H_M are the composite, WC and binder hardness respectively. H_{WC} is represented by

$$H_{WC} = 1382 + 23.1 \bar{D}^{-1/2} \text{ (kg mm}^{-2}\text{)} \quad (3)$$

and the results obtained (Table I) yield the following expression for H_M

$$H_M = 366.3 + 12.3 \bar{L}^{-1/2} \text{ (kg mm}^{-2}\text{)} \quad (4)$$

which is very similar to that of a Co binder ($H_M = 304 + 12.7 \bar{L}^{-1/2}$).

In a search for an improvement in mechanical properties, heat treatments after sintering were carried out as described in the previous section. These heat treatments induced the $\gamma \rightarrow \alpha$ transformation which leads to the formation of a fully ferritic binder phase containing precipitation of Fe_3C . This is illustrated in Fig. 6 by the XRD trace. The appearance of the microstructure under the optical microscope is included in

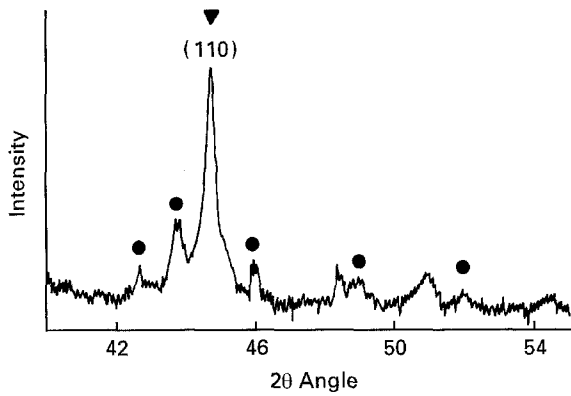


Figure 6 XRD pattern corresponding to the binder phase of an as-heat-treated sample (▼ ferrite, ● cementite).

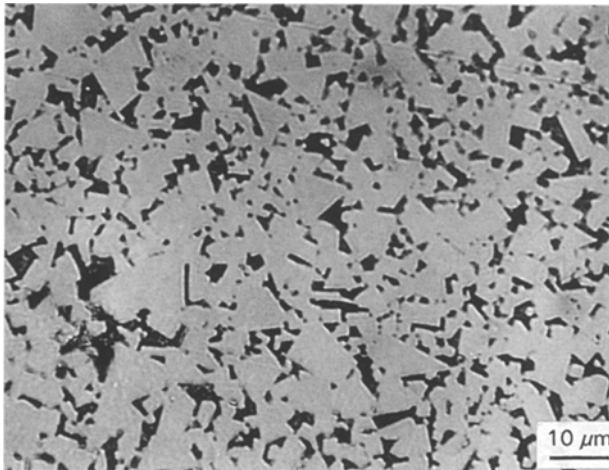


Figure 7 Optical micrograph of an as-heat-treated sample etched with nitric acid. The dark component corresponds to bainite.

Fig. 7, which after etching did not show any remnants of the previous austenite.

The influence of these heat treatments on the fracture toughness of the materials (Table I) can be appreciated in Fig. 8 (a) and (b) by the length of the cracks produced after indentation under a load of 30 kg. It is apparent in these figures that heat treatments have a beneficial effect on the fracture toughness of this material as shown by the shorter cracks generated (Fig. 8(b)).

Based on the results obtained after sintering of WC hardmetals, it may be seen, in agreement with previous reports [4, 5, 9], that the use of binders within the Fe–Ni–C system leads to fully dense materials under the sintering conditions reported in this work. From Fig. 1 it is apparent that the optimum temperature for sintering of the experimental materials is about 1250 °C, which results in a microstructure (e. g. Fig. 3) with the typical appearance of WC-based hardmetals, in which the liquid binder phase at the sintering temperature exhibits good characteristics for material transport and a relatively good wettability. With this experimental composition it may be noticed from Fig. 1 that a certain degree of control can be exerted on the phase content of the binder, depending on C content, from being 100% ferritic to a combination

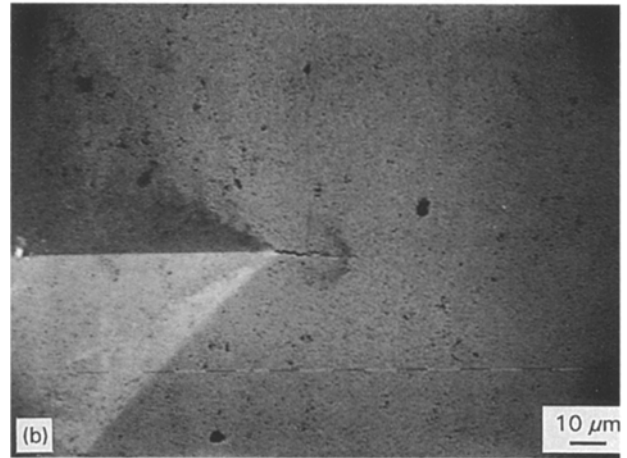
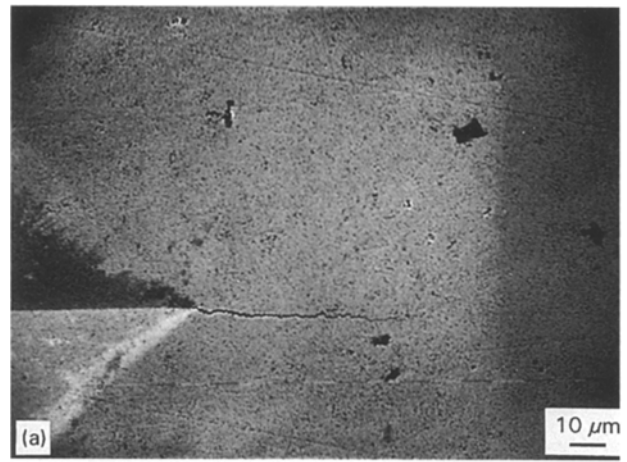


Figure 8 Cracks produced by a 30 kg load Vickers indentation on an (a) as-sintered and a (b) as-heat-treated sample.

of ferrite and austenite after sintering. Nevertheless, Fig. 1 also shows that for the Ni content used in this work, the addition of C aids densification due to its effect in decreasing the liquids temperature of the binder, which renders, at the optimum C content (5.842 wt %), a mixed ferritic–ausenitic binder. It should also be pointed out that the numbers reported for the amount of C in the specimens correspond to total C, that is, C contained in the WC powder plus C added to the binder (from 0 to 3.5 wt %). Thus, the C content in the binder itself after sintering is much lower than that added, since C is lost during sintering. This may be understood with reference to the Fe–Ni–C phase diagrams [18, 19], since at the sintering temperature (1250 °C) and binder C content (3.25 wt %) the binder is in the liquid state, but the reduction of oxides lowers the C content until the austenite is stabilized. Although it is difficult to estimate the final C content in the austenite, judging by the results obtained by XRD after sintering, which indicate that binder is constituted of 75% ferrite + 25% ausenite (Fig. 2) without any detectable Fe₃C, it is considered that this steel should be of the hypoeutectoid type. According to previously reported data [18] and considering the amount of Ni used in this work, the maximum C content in this steel could not be higher than 0.2 wt %, since it would lead to the presence of $\alpha + \gamma + \text{Fe}_3\text{C}$ after sintering, which is

contrary to the aforementioned experimental observations. This argument is also supported by the fact that after heating to 800 °C followed by quenching, during the subsequent heat treatment, the binder phase is completely austenitic.

As seen in Table I, both hardness and fracture toughness were measured for the aforementioned hardmetals (initial binder composition 87% Fe–9.7% Ni–3.25% C) in the as-sintered and as-heat-treated condition. The results show the beneficial effect of the heat treatment on fracture toughness without an appreciable decrease in hardness. For higher Ni contents than that used in this work, it has been argued [4, 5, 9] that the stress-induced martensitic transformation of the austenite may be responsible for that behaviour. However, in the present work, the increase in fracture toughness is only observed after an isothermal heat treatment (500 °C for 1 h) which must produce, in this hypoeutectoid steel, a transformation to bainite ($\alpha + \text{Fe}_3\text{C}$) as shown in Fig. 6. Hong *et al.* [20] proposed that crack growth in WC–Co hardmetals proceeds by microcracking of the carbide grains and/or carbide–carbide boundaries ahead of the primary crack, followed by ligament formation and failure in the intervening binder areas which link the microcracks to the primary crack. From this point of view, the failure stress for the individual binder ligaments may be quite high due to the constraint imposed by the carbide grains. For the as-heat-treated condition the bainitic binder could therefore be expected to be stronger than the corresponding ferritic–austenitic binder obtained after sintering. In addition, the formation of bainite as a transformation product of austenite also explains why hardness does not decrease in these materials.

4. Conclusions

It is apparent that Fe–Ni–C binders for WC hardmetals allow full densification at reasonable temperatures and times. In this system it is important to exert stringent control on the amount of C added to the powder mixture, not only because of its influence on the final density, but also because of its effect on the phases formed and to prevent the formation of eta carbides. The relation between hardness and WC grain size obtained with Fe–Ni–C based binders is very similar to the corresponding hardmetals using

Co-binders. The fracture toughnesses of these materials are also comparable, which consequently indicates the suitability of Fe–Ni–C alloys as valid alternatives for Co. By producing a mixed ferrite–austenitic binder after sintering of WC + (Fe,Ni,C) hardmetals, a subsequent heat treatment to induce $\gamma \rightarrow$ bainite transformation, results in an increase in K_{IC} of about 50%. Additionally, it is important to point out that this increase in toughness takes place without an appreciable decrease in hardness.

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