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Hot isostatic pressing of ultrafine tungsten carbide-cobalt hardmetals

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Hot Isostatic Pressing (HIP) has been successfully used to consolidate tungsten carbide-10 weight% cobalt (WC-10 wt% Co) powders mixtures with WC powder particle sizes in the range of 100 nanometers. Fully dense specimens of this composition have been obtained by HIP at 1000°C, a temperature well below those usually required for reaching the closed porosity stage in the WC-Co system. Conventional processing by vacuum sintering has also been carried out to study the individual effects of high isostatic pressure and vanadium carbide additions on densification and WC grain growth control of these hardmetals. The finest WC mean grain size after sintering has been obtained for the combined action of applied isostatic pressure and vanadium carbide (VC) additions. These results show that VC additions are effective in controlling WC grain growth even at temperatures as low as 1000°C.

1. Introduction

Presently, the use of finer WC powders for producing WC-Co materials with finer microstructures represents one of the most active fields of research in the hardmetal industry. These so-called superfine grained hardmetals, with WC mean grain sizes from 0.3 to 0.4 μm, show not only a significant increase in hardness with respect to the finest commercial WC-Co grades (with WC mean grain sizes about 0.5 μm), but also higher strength and toughness [1–3]. Although the advantages of reducing WC grain size in hardmetals are generally recognized, the fabrication of these materials on industrial scale presents a number of unresolved processing difficulties. A higher specific surface area means a stronger tendency to agglomeration, larger interparticle friction and higher oxidation rate and moisture absorption. On the other hand, it has been confirmed that nanometric WC powders show a higher sintering activity, which allows the use of lower processing temperatures [2]. Nevertheless, these fast sintering kinetics are more difficult to control, especially those phenomena leading to grain growth [4–7]. Until now, the most successful way of controlling WC grain growth during sintering is the addition of small amounts (about 1–2 wt%) of several metallic carbides (as VC, Cr_3C_2, Mo_2C, TaC, etc) to the powder mixtures [5]. However, the physical mechanisms of grain growth control are still unclear. There are some evidences that relate this phenomenon to the formation of eutectics of lower melting point than those typically occurring in the WC-Co pseudobinary system [2, 8], which allows processing at lower temperatures. Other data suggest that the solubility of WC grains in these liquids containing Co, V and Cr is lower than in pure liquid cobalt [8], thus inhibiting solution-reprecipitation mechanisms. In practice, the key for microstructural control in these compositions is the homogeneous distribution of cobalt and the rest of additives in the powder mixtures. Best results are obtained via chemical routes where Co, Cr and V are introduced by simultaneously dissolving salts of these compounds followed by spray drying and co-carburization [9, 10]. In addition to the use of grain growth inhibitors, research is also focused on the development of new sintering techniques as Microwave Sintering (MS) [11] or Spark Plasma Sintering (SPS) [12]. These methods, still not well documented, are based on the application of ultra high heating rates and short dwelling times to avoid long exposure of nanocrystalline powders at high temperatures. In recent years, powder production technologies have been continuously reducing the mean particle size of WC powders the actual limit being below 100 nm [13]. Nevertheless, the use of these ultrafine powders has not led to a proportional decrease in the WC mean grain size of the sintered specimens due to grain growth. In this work, a technique based on Hot Isostatic Pressing (HIPing) has been evaluated as a mean for effective densification and grain growth control in hardmetals processed by using these ultrafine WC powders.

2. Experimental procedure

Characteristics of raw materials are given in Table I. Powder mixtures include WC-Co pre-combined powders, vanadium carbide (VC) as grain growth inhibitor and different organic binders. The experimental compositions used are given in Table II. A planetary

TABLE I Characteristics of starting powders

Supplier	Reference	Composition	FSSS (μm)	O_2 (wt%)
Union Miniere	Microcarb®	WC-10 wt%Co	0.1	0.135
H.C.Starck	VCHV100	VC	1.25	0.65

TABLE II Compositions (in weight percent) of the WC-Co alloys

Reference	Cobalt (Co)	Vanadium Carbide (VC)
1	10	0
2	10	0.4

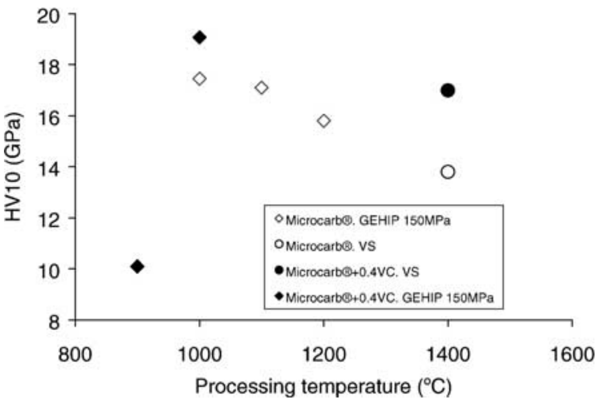


Figure 1 Vickers hardness (HV10) of WC-10wt%Co materials vs. processing temperatures for vacuum sintering and hot isostatic pressing cycles.

mill was used for the milling-mixing step. Mixtures were loaded into 500 cm^3 WC-Co vessels containing 20 vol% of 15 mm diameter WC-Co balls as milling media, 2.5 wt% of organic binder and a variable amount of a dissolving agent. The rotation speed was 200 rpm. After milling, the slurries were dried by heating at 110°C in a container under slightly over atmospheric pressure. These aggressive milling conditions are required to break powder agglomerates and avoid organic binder segregation during drying. Green compacts were produced by uniaxial pressing at 250 MPa using hardened steel dies and punches. Green densities were in the range of 50 to 55% of the theoretical density. Sintering was carried out by two different routes: Vacuum sintering (VS: 10^{-1} mbar) at 1400°C for 1 hour in a furnace with graphite heating elements and glass-encapsulated HIPing (GEHIP) from 900°C to 1200°C at 150 MPa for 1 h. In all sintering cycles, a step is included where the organic binder is burned out in a vacuum of 0.1 mbar at 450°C for 1 hour. The microstructures of the sintered materials have been characterised by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersion Spectroscopy (EDS). The mean WC grain size after sintering has been measured by using standard image analysis software on back-scattered SEM micrographs. A better estimate of the crystalline size for the finest part of the WC grain size distribution has been calculated by the Scherrer law [14]:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

Where "D" is the average crystallite dimension, "λ" the X-rays wavelength, "β" the pure diffraction broadening, "θ" the Bragg angle and "K" is a constant depending on the crystallite shape. A material with WC mean grain size in the micron range has been used as an standard for determining the instrumental broadening. Porosity is a critical property for quality control of hardmetals. Conventional procedures based on Archimedes principle are not precise enough for these materials, since porosity levels below the resolution limit of this technique (about 1 vol%) are fatal for mechanical properties. Therefore, in this work porosity has been measured by using a specific standard developed for hardmetals with a resolution limit about 0.02 vol%. This technique is based on quantitative metalography of polished surfaces via optical microscopy (ISO 4505-1978(E)) [15]. Vickers hardness measurements were carried out applying a load of 10 kg (ISO-3878-1983(E)) [16].

3. Results and discussion

Table III summarizes the hardness and porosity values obtained for compositions with and without additions of vanadium carbide (VC) by using conventional (VS) and GEHIPing sintering cycles. These data show that the application of isostatic pressure (150 MPa) to a glass encapsulated compact allows full densification of WC-10wt%Co with and without VC additions (compositions 1 and 2) at temperatures as low as 1000°C. This temperature seems to be the lowest temperature limit for composition 2, since the cycle carried out at 900°C leads to a material with significant porosity which results in a drastic hardness decrease (about 50%). Conventional vacuum sintering of both compositions leads to similar levels of residual B-type porosity (i.e., mean pore size between 20 and 30 microns). Vacuum sintering experiments at 1400°C (open and solid circles in Fig. 1) show that materials of composition 2 (solid circle: WC-10Co-0.4VC) are significantly harder than

TABLE III Hardness, porosity and mean WC grain size of WC-10wt%Co compositions

Ref.	Processing	T (°C)	WC grain size (μm)	HV10 (GPa)	Porosity[a]	
1	GEHIP @ 150 MPa	1200	0.7 ± 0.3	15.8 ± 0.3	<A02	<B02
1	GEHIP @ 150 MPa	1100	–	17.1 ± 0.4	<A02	<B02
1	GEHIP @ 150 MPa	1000	0.4 ± 0.2	17.4 ± 0.4	<A02	<B02
1	VS @ 10^{-1} mbar	1400	1.0 ± 0.3	13.8 ± 0.3	<A02	B04
2	GEHIP @ 150 MPa	1000	0.2 ± 0.1	19.1 ± 0.5	<A02	<B02
2	GEHIP @ 150 MPa	900	–	10.1 ± 0.3	A04	B04
2	VS @ 10^{-1} mbar	1400	0.3 ± 0.1	17.0 ± 0.4	A02	B06

[a] According to the standard ISO 4505-1978(E), the codes X02, X04 and X06 (with X = A or B) correspond to 0.02 vol%, 0.06%vol and 0.2 vol% of porosity respectively. Letter A corresponds to pores with sizes below 5 microns and letter B is used to describe larger pores (in the range of 10–30 microns).

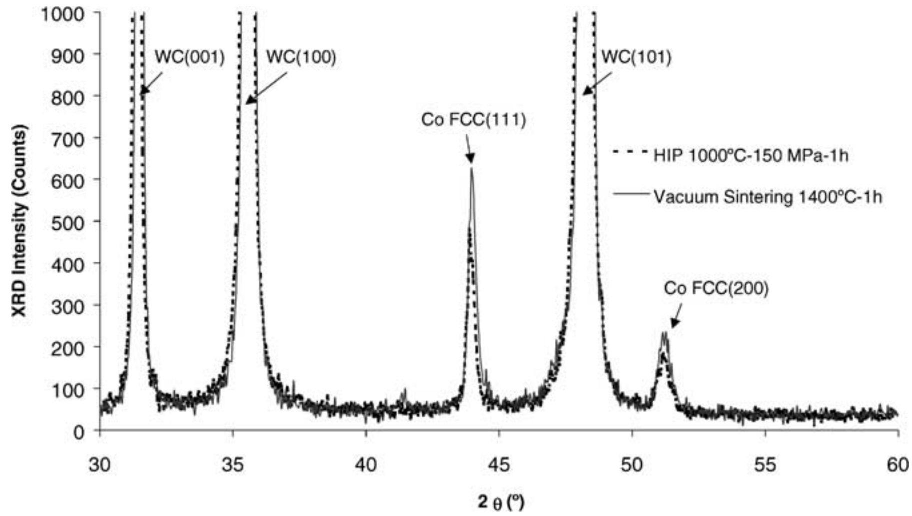
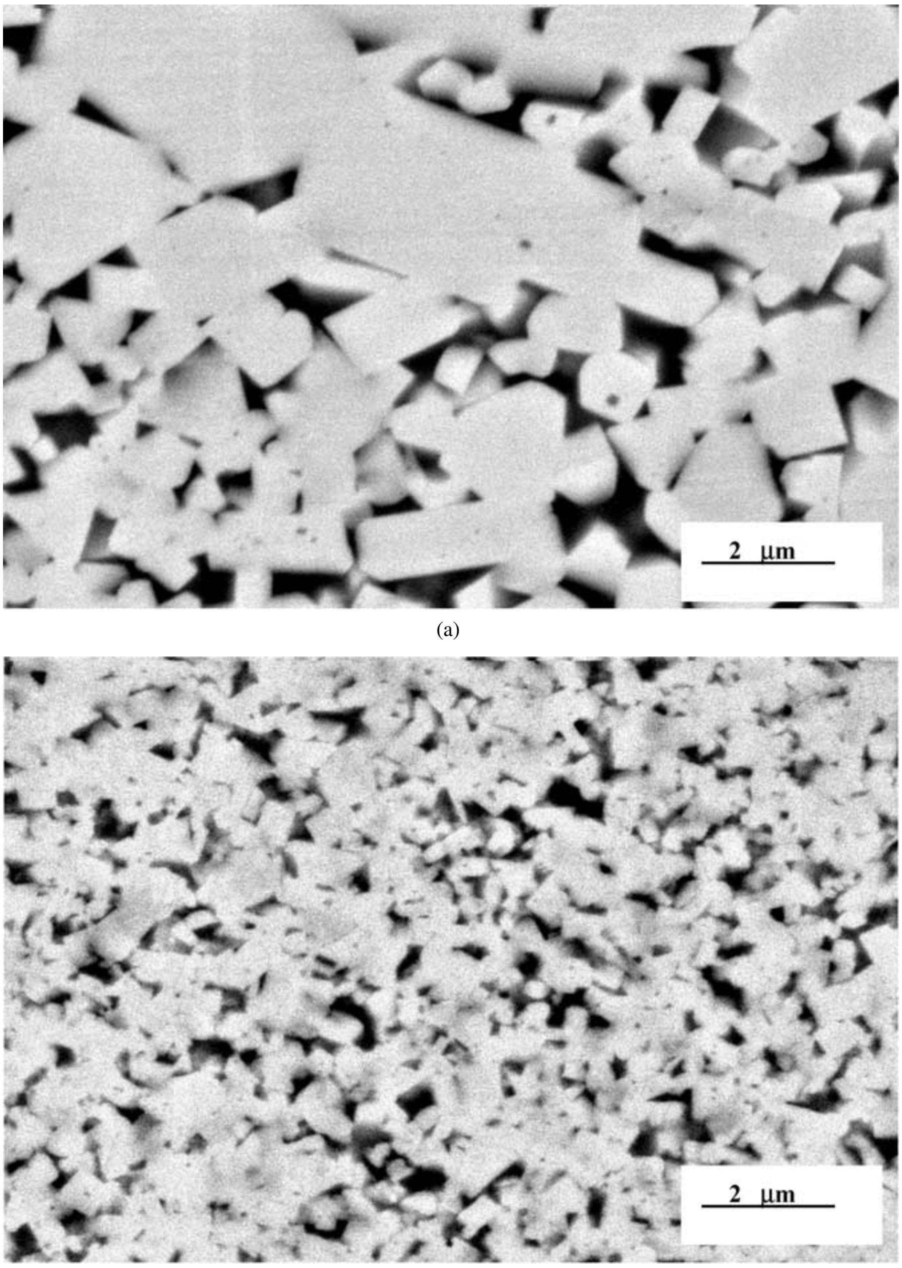


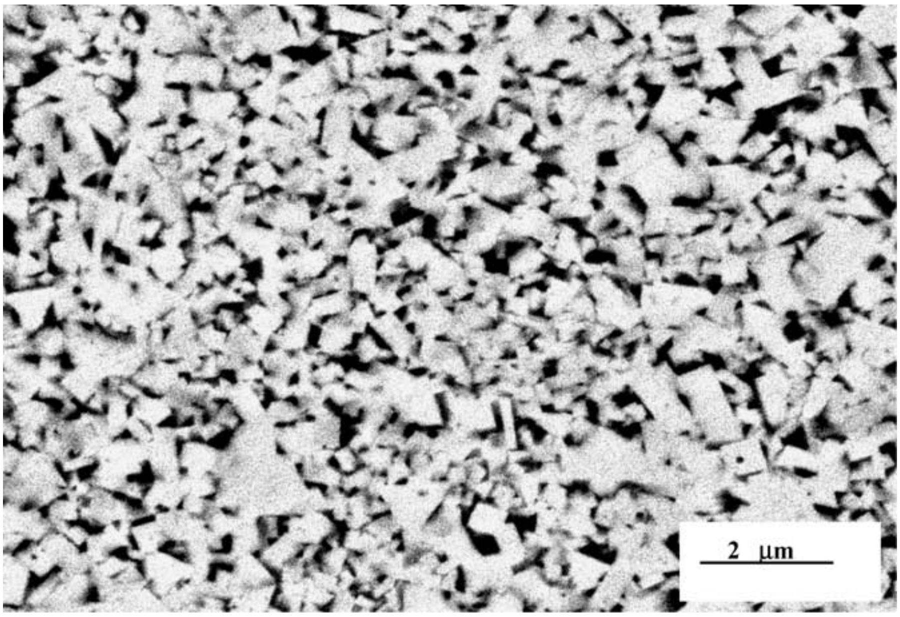
Figure 2 X-Ray diffraction patterns corresponding to WC-10wt%Co-0.4wt%VC: (a) Vacuum Sintered at 1400°C for 1 h and (b) HIPed at 1000°C and 150 MPa for 1 h.



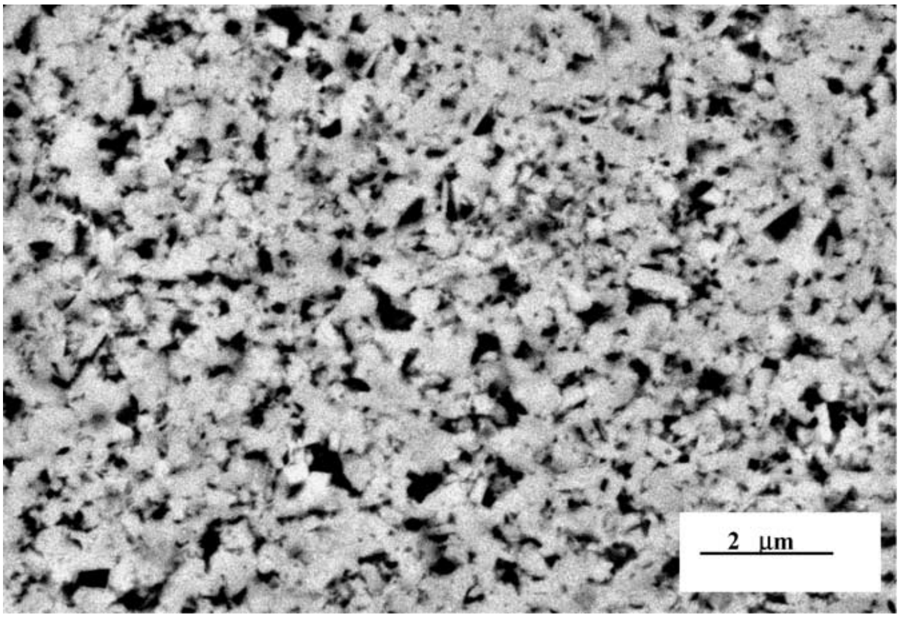
(a)

(b)

Figure 3 Back-scattered SEM micrographs corresponding to: (a) WC-10wt%Co vacuum sintered at 1400°C for 1 hour, (b) WC-10wt%Co HIPed at 1000°C and 150 MPa for 1 hour, (c) WC-10wt%Co-0.4wtVC vacuum sintered at 1400°C and (d) WC-10wt%Co-0.4wtVC HIPed at 1000°C and 150 MPa for 1 hour. (*Continued.*)



(c)



(d)

Figure 3 (*Continued*).

those of composition 1 (open circle: WC-10Co). It is well known that hardness of WC-Co materials is mainly affected by porosity, cobalt content, presence of η phase and WC mean grain size [17]. X-Ray diffraction analysis has confirmed that neither η phase nor graphite (that has similar effect as porosity) appear in both types of specimens: vacuum sintered or HIPed. (Fig. 2). SEM micrographs of both materials have confirmed that VC additions allow obtaining materials with a much finer WC grain size (Fig. 3a and c), although these additions also induce a slightly higher amount of porosity than the composition without VC (Table I). The hardening effect of vanadium carbide on the WC-10wt%Co alloy has also been observed for HIPed specimens obtained in a fully dense form at 1000°C, a temperature well below the "solidus" temperature for this composition which is around 1340°C as measured by DSC [8, 18]. As before, SEM analyses have confirmed that WC mean grain size is clearly smaller for composition 2 (Fig. 3b and d).

A detail of the microstructure obtained by the combined effect of HIPing and VC additions is shown in Fig. 4. The WC mean grain size of this material (measured by digital processing of SEM images) is of $0.25 \pm 0.10\ \mu$m (Fig. 5). The reflection corresponding to WC (101) with a Bragg angle of 48.266° (for Cu K_α wavelength) has been used to measure the line broadening produced by the finest grains present in the HIPed material. Fig. 6 shows the different peak widths of XRD patterns corresponding to the HIPed and VS material. The half maximum intensity width method was selected for the calculations. In this case, the crystallite shape parameter "K" has a constant value of 0.9. Special care has to be taken for correction of Kα-doublet separation and determination of instrumental broadening. For the latter, the material of composition 1 processed by vacuum sintering at 1400°C is taken as standard due to its large WC mean grain size. The application of the Scherrer equation to these data gives a value of $0.124\ \mu$m for the average WC crystallite size.

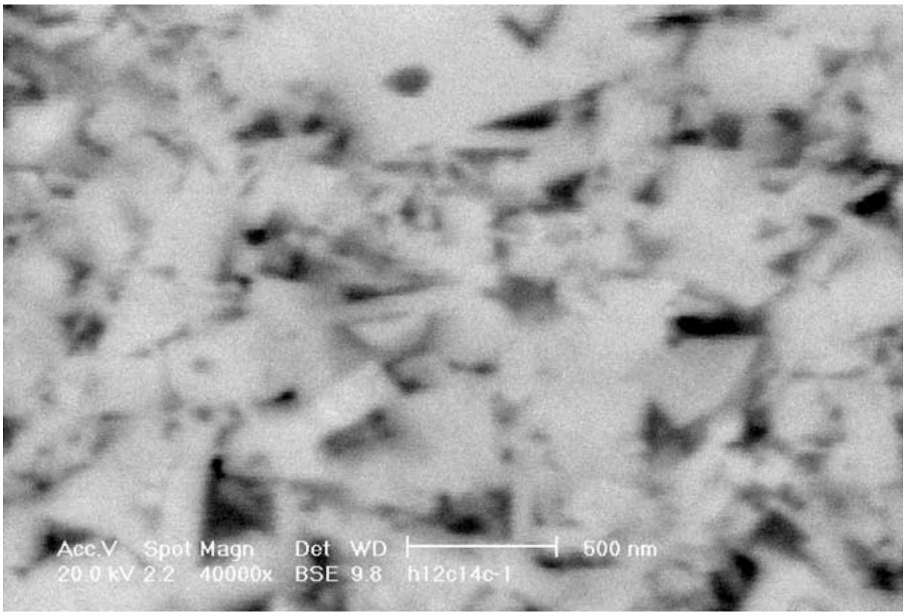


Figure 4 Back-scattered SEM micrograph of WC-10wt%Co-0.4wtVC HIPed at 1000°C and 150 MPa for 1 hour showing the extremely fine WC grains obtained by this sintering procedure.

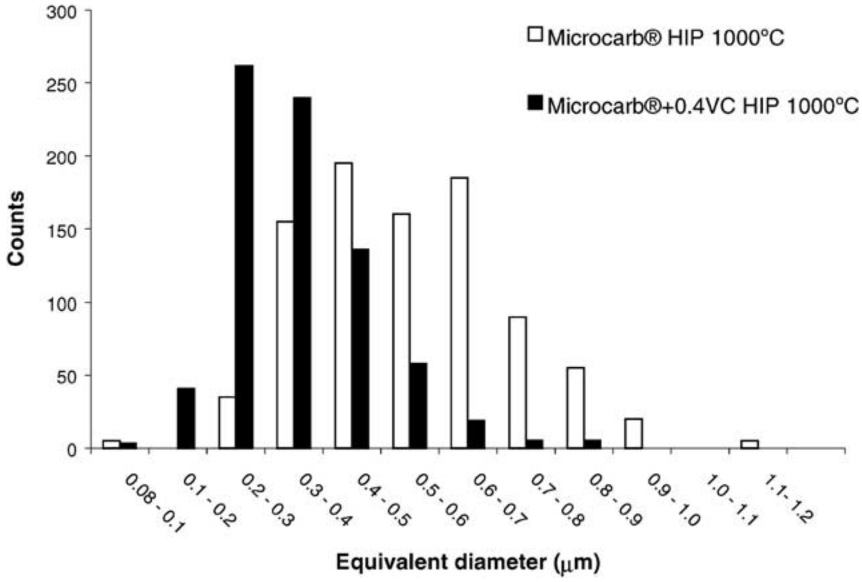


Figure 5 Histograms of WC grain equivalent diameters corresponding to specimens of compositions 1 and 2 produced by GEHIPing at 1000°C for 1 h.

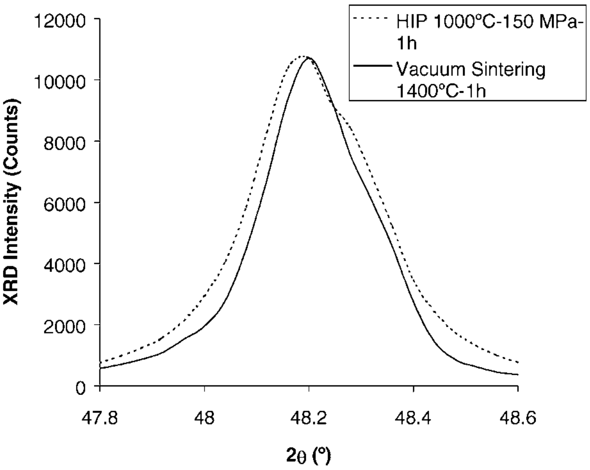


Figure 6 WC (101) lines corresponding to XRD graphs of HIPed and vacuum sintered materials. Line broadening produced by WC crystallite refinement is clearly observed.

This procedure underestimates the actual WC grain size as it does not take into account WC grains larger than 0.5 μm, which are present in the microstructure. However, it is a proof of the presence of very small WC crystallites in the WC-10wt%Co-0.4wt%VC material produced by GEHIP.

So far, the effect of VC on WC grain growth inhibition has been explained by mechanisms based on the presence of a liquid phase during sintering: either, by reducing the temperature of liquid formation [8] or by reducing the solubility of WC grains in this liquid phase [2]. However, these results confirm that vanadium carbide is also effective in inhibiting WC grain growth in the solid state. This observation allows thinking that a more realistic mechanism, than those previously suggested, may be based on solute drag hypothesis [19] by which solute atoms in Co (vanadium and possibly carbon as well) would be expected to concentrate in

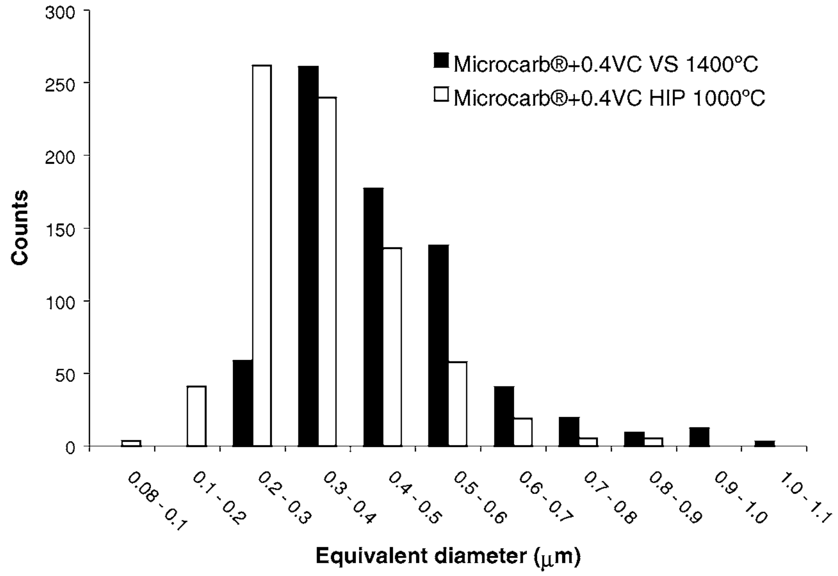


Figure 7 Histograms of WC grain equivalent diameters corresponding to specimens of composition 1 GEHIPed at 1000°C for 1 h and composition 2 processed by VS at 1400°C for 1 h.

the neighborhood of WC-Co interfaces as a means of lowering their free energy as compared to that in the perfect lattice. According to this hypothesis, the solute atoms concentrated at the WC-Co interfaces would act as an atmosphere that has to be dragged by the moving boundary, thus decreasing its mobility. This implies that grain boundary migration (i.e., grain growth) may be very much reduced for low temperatures (since the net driving force on the boundary diminishes) and also for increasing concentrations of vanadium. These arguments also find support by recently published observations, by high resolution transmission electron microscopy (HRTEM) [20] and energy filtering transmission electron microscopy (EFTEM) [21], of vanadium segregation at WC-Co interfaces, thus becoming facetted and consequently less mobile. WC grain growth control can also be achieved by reducing the HIPing temperature even in the absence of vanadium carbide as shown in Fig. 3a and b. Both microstructures correspond to fully dense specimens of composition 1 that exhibit a significant difference in hardness (from 13.8 to 17.5 GPa respectively) (open symbols in Fig. 1). Nevertheless, reducing the HIPing temperature is less efficient in controlling WC grain growth than using VC additions. WC grain size distributions, obtained from SEM micrographs, show that vacuum sintering composition 2 at 1400°C for 1 hour, results in a smaller WC grain size than composition 1 HIPed at 1000°C for 1 h. (Fig. 7). Nevertheless, the hardness of both materials is very similar due to their different porosity levels (Table I). Samples HIPed at 1000°C undergo a linear shrinkage of about 20%, which is similar to that of vacuum sintered specimens processed at 1400°C, thus a similar amount of mass transport must occur in both situations.

The application of pressure during HIPing starts at 850°C, temperature at which no appreciable shrinkage occurs under vacuum (at this point, the sample contains about 50% of porosity). Although pressure is isostatically applied, local shear stress components appear at WC particle contact points. This effective stress, caused by the high-pressure difference between the outside (1500 bar) and the inside of the glass capsule (10^{-8} bar), can lead to cobalt plastic deformation and the collapse of the pore structure. At this stage, the ultrafine WC particles, considered as perfectly rigid, can undergo substantial rearrangement due to plastic deformation of the cobalt phase (which occupies about 15 vol% of the sample). Apart from the high-applied pressure, HIPing temperatures as selected in this work are in the range of those used in hot rolling of cobalt alloys (≈1000°C) [22], where large plastic deformation is produced. Once WC particles form a solid skeleton in mechanical equilibrium, other mechanisms, as cobalt creep flow or diffusion, need to be taken into account to explain the removal of residual porosity. Both phenomena are possible for cobalt at 1000°C (>1/2 Co melting point). Nevertheless, the micrographs of Fig. 3 show that cobalt distribution is not perfect, reflecting poorer spreading when compared with liquid phase sintering. As described in fast sintering technologies [23], the production of nanometric structures requires that microstructural homogenisation is carried out during powder processing, since mass transport produced by the sintering cycles (characterised by low temperatures and short times) is not enough to eliminate compositional microgradients.

4. Conclusions

Hot Isostatic Pressing has been demonstrated as a very efficient method for obtaining fully dense ultrafine hardmetals at temperatures as low as 1000°C. Extremely fine microstructures (about 0.2 μm) have been obtained by the combined action of low processing temperature and vanadium carbide additions. The results obtained suggest that grain growth inhibition may be explained by a mechanism based on solute drag as the segregation of vanadium to WC-Co interfaces reduces their mobility. Cobalt plastic deformation leading to rearrangement of WC nanograins is proposed as the dominant densification mechanism during the first sintering stage. Final densification must require the contribution of diffusion-based phenomena as creep flow and solution reprecipitation mechanisms, being the latter responsible for WC grain growth.

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