



HOT ISOSTATIC PRESSING OF NANOSIZED WC-Co HARDMETALS

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SUMMARY

A new technique based on Hot Isostatic Pressing (HIP) has been developed to produce dense nanosized WC-Co hardmetals without the addition of grain growth inhibitors. The glass encapsulation process is the key for the effective application of isostatic pressure at temperatures well below those usually required for reaching the closed porosity state in the WC-Co system. Fully dense WC-Co samples with cobalt contents ranging from 10 to 12 wt. % have been obtained by this technique at temperatures between 1000°C and 1200°C with 150 MPa of applied isostatic pressure for 30 minutes. The role of isostatic pressure on the activation of densification mechanisms is discussed.

KEYWORDS: Hardmetals, Tungsten Carbide, Hot Isostatic Pressing, Nanocrystalline Structure.

1. INTRODUCTION

Presently, the use of nanosized 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 grain WC grain sizes from 0.3-0.4 μm , show not only a significant increase in hardness with respect to the finest commercial WC-Co grades (so far, with WC mean grain sizes from 0.4 to 0.5 μm), but also higher strength and toughness (1-6).

Although the advantages of reducing WC grain size in hardmetals are generally recognised, the fabrication of these materials on industrial scale presents a number of unresolved processing issues. Higher specific surface areas enhance sintering activity, which allows the use of lower processing temperatures. However, the fast sintering kinetics of nanometric powders are more difficult to control, especially grain growth phenomena (7-10). In addition, a higher specific surface area also means higher tendency to agglomerate, higher interparticle friction and higher contamination (higher moisture adsorption and oxygen content). Therefore, all processing steps must be adapted to these new powder characteristics, especially those concerning safe manipulation and leakage control due to their high reactivity.

So far, the most successful way of WC grain growth control during sintering is the addition of small amounts (below 1 wt. %) of some metallic carbides (as VC, Cr₃C₂, Mo₂C, TaC, etc) to the powder mixtures. 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 that occurring in the WC-Co pseudobinary system (4, 11). These authors have suggested that the solubility of WC grains in these liquids containing Co, V and Cr is poorer than in pure liquid cobalt. Nevertheless, most densification and significant grain growth occurs in solid state (11), and therefore, solid diffusion inhibition should also be involved.

In practise, the homogeneous distribution of cobalt and the rest of additives is critical for final product performance. 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 (12,13). Apart from the use of grain growth inhibitors, research is also focused on the development of new sintering techniques as Microwave Sintering (MS) (14) or Spark Plasma Sintering (SPS) (15). These are based on the application of ultra high heating rates and short dwelling times to avoid long exposure of nanocrystalline powders at high temperatures. However the results of these techniques are still not well documented.

In the last years, powder production technologies have been continuously reducing the mean particle size of WC powders, being the present limit about 0.03 μm (Nanocarb®) (16). However, this has not been reflected on a substantial decrease of WC mean grain size in sintered hardmetals. So far, the actual lower limit for this magnitude is about 0.3-0.4 μm .

These ultrafine WC powders have been selected in the present work to evaluate several pressure assisted sintering routes with the aim of producing fully dense hardmetals with better grain growth control.

2. EXPERIMENTAL PROCEDURE

Characteristics of raw materials are given in Table 1:

Provider	Reference	Composition	FSSS (μm)	O ₂ (wt.%)
Union Miniere	Microcarb®	WC-10 wt.%Co	0.1	0.135
Union Miniere	Nanocarb®	WC-12 wt.%Co	0.03	0.198
H.C.Starck	VCHV100	VC	1.25	0.65
H.C.Starck	Cr3C2-160	Cr ₃ C ₂	1.55	0.59

Table 1: Characteristics of starting powders

Powder mixtures include WC-Co pre-combined powders, vanadium carbide (VC) as grain growth inhibitor and different organic binders. The compositions used are given in Table 2:

Ref.	WC mean particle size (μm)	Co (wt.%)	VC (wt.%)	C (wt.%)	Organic binder (wt.%)
1	0.1	10	0	0	0
2	0.1	10	0.4	0	2.5
3	0.03	12	0	0	0
4	0.03	12	0.4	0	2.5

Table 2: Compositions of powder mixtures

Mixtures were loaded into a 500 cm³ vessel containing 20 vol.% of 15 mm ϕ WC-Co balls as milling media and a variable amount of dissolving agent. Two mixing machines were used: a conventional ball mill with polyethylene containers and a planetary mill (Netzch PM4) with WC-Co containers, the main difference being the higher acceleration given to the

balls by the planetary mill. After milling, drying of the slurries was carried out by “overpressure” drying, a new method consisting in heating the slurry at 110°C in a sealed container till a slightly over atmospheric pressure is achieved. The gas is released maintaining this overpressure during drying avoiding binder segregation. Spray drying was also used to produce granulated powders with good flowability. Green compacts were produced by uniaxial pressing using steel dies at 250 MPa. Green densities were in the range of 50-55 % of the theoretical density. Sintering was carried out by two different routes: Vacuum sintering (VS) at 1320°C and 1400°C for 1 hour in a furnace with graphite heating elements (10^{-1} mbar) and glass-encapsulated HIP from 900°C to 1200°C at 150 MPa for 0.5 h (GEHIP). 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). Vickers Hardness measurements were carried out applying a load of 10 kg (17).

3. RESULTS

3.1. Vacuum Sintering (VS)

The main problem found in these cycles is the presence of macro-porosity (B04-B06) (20), independently of the sintering temperature (Fig. 1).

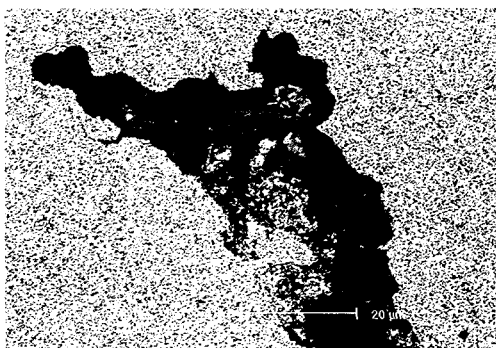


Fig. 1 SEM micrograph showing B-type porosity found in composition 3 after VS (10^{-1} mbar) at 1400°C for 1 hour.

This phenomenon has been related to the formation of organic binder agglomerates during mixing. These agglomerates have been detected by SEM of green compacts (Fig. 2). After debinding, such large pores cannot be closed during vacuum sintering.



Fig. 2 SEM micrograph of a compact of composition 3 showing a large agglomerate of organic binder ($> 100 \mu\text{m}$).

These large binder islands have been found in compacts with very different organic binder contents (1.5 or 2.5 wt. %). Therefore, it is thought that are formed during drying due to the strong tendency of nanocrystalline powders to agglomerate. This type of porosity can be considerably reduced by using more aggressive milling (Fig.3). The binder is better distributed in the mixtures if powder aggregates are effectively broken.

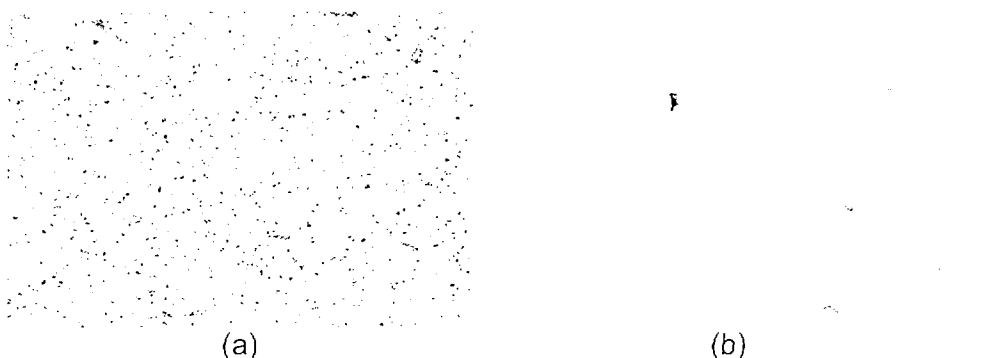


Fig. 3 Composition 4, VS at 1360°C for 1 h. Porosity obtained by two milling techniques: (a) conventional ball mill (72h) and (b) planetary mill (6h)

The effect of WC powder particle size on sintering is clearly observed in hardness data (Table 3). Hardness of composition 2 (based on Microcarb®) is significantly reduced when the sintering temperature is changed from 1400°C to 1320°C whereas that of composition 4 (based on Nanocarb®) is not affected (Fig. 4).

Ref.	WC particle size (µm)	Co (wt.%)	VC (wt.%)	Sint. Temp. (°C)	HV10 (kg/mm ²)
2	0.1	10	0.4	1400	1700
4	0.03	12	0.4	1400	1620
2	0.1	10	0.4	1320	1570
4	0.03	12	0.4	1320	1620

Table 3: Hardness of WC-Co hardmetals produced by vacuum sintering

XRD analyses and optical microscopy observations have confirmed that neither η phase nor graphite are present in these specimens (Fig. 5). Therefore, these hardness values can be explained by the different densification and grain growth kinetics of WC powders with different specific surface area. At 1400°C, both powders achieve 98% T.D.. However, Nanocarb® is more susceptible to grain growth and, therefore, its hardness is lower than that obtained with Microcarb® (Fig. 6a and 6b).

A reduction of the sintering temperature (up to 1320°C) does not appreciably change the hardness of Nanocarb®, whereas for Microcarb® it is reduced by 8%. The reason for this behaviour can be found in the combination of two phenomena: pooling and porosity. Composition 2 (based on Microcarb®) present large cobalt pools and higher porosity than composition 4 (based on Nanocarb®). Thus, it is clear that a higher WC specific surface area favours cobalt spreading among WC particles and subsequently higher densification.

Unlike Microcarb®, Nanocarb® is active enough at 1320°C for achieving high density without significant WC grain growth (Fig. 6c and 6d).

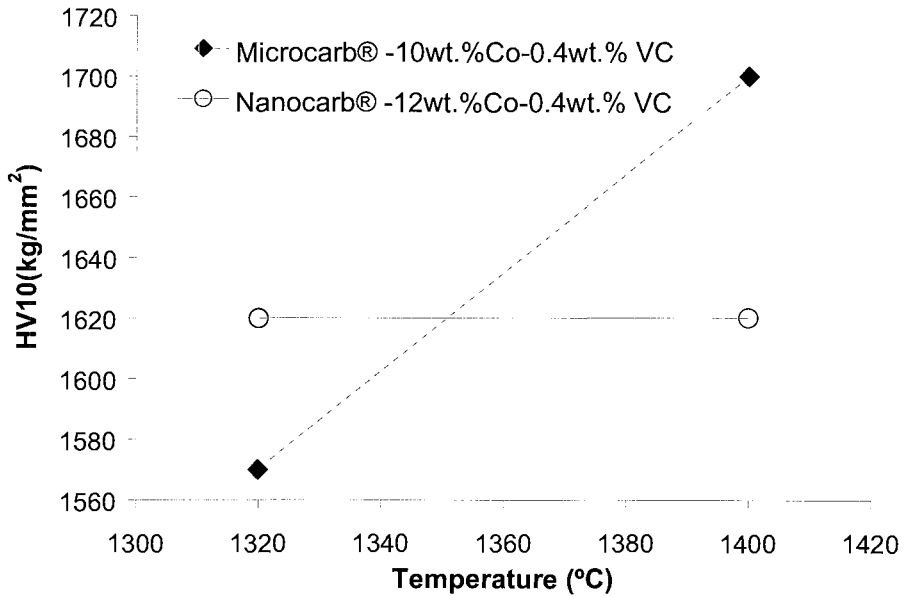


Fig. 4 Vickers hardness (HV10) of vacuum sintered specimens vs. sintering temperature

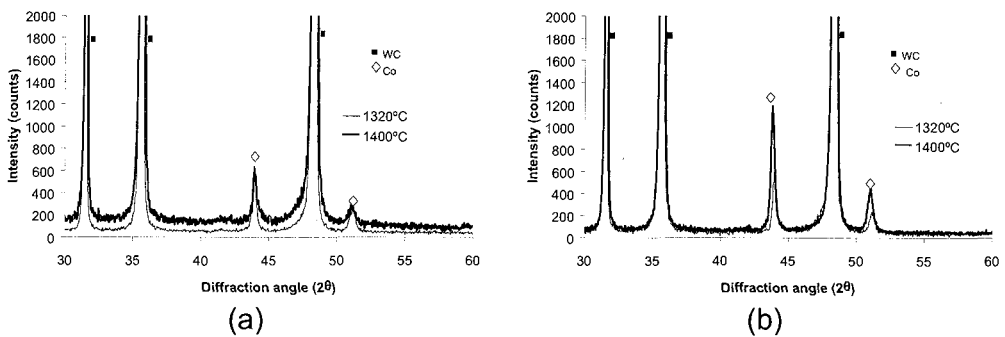


Fig. 5 XRD patterns corresponding to vacuum sintered samples: (a) Composition 2 and (b) Composition 4

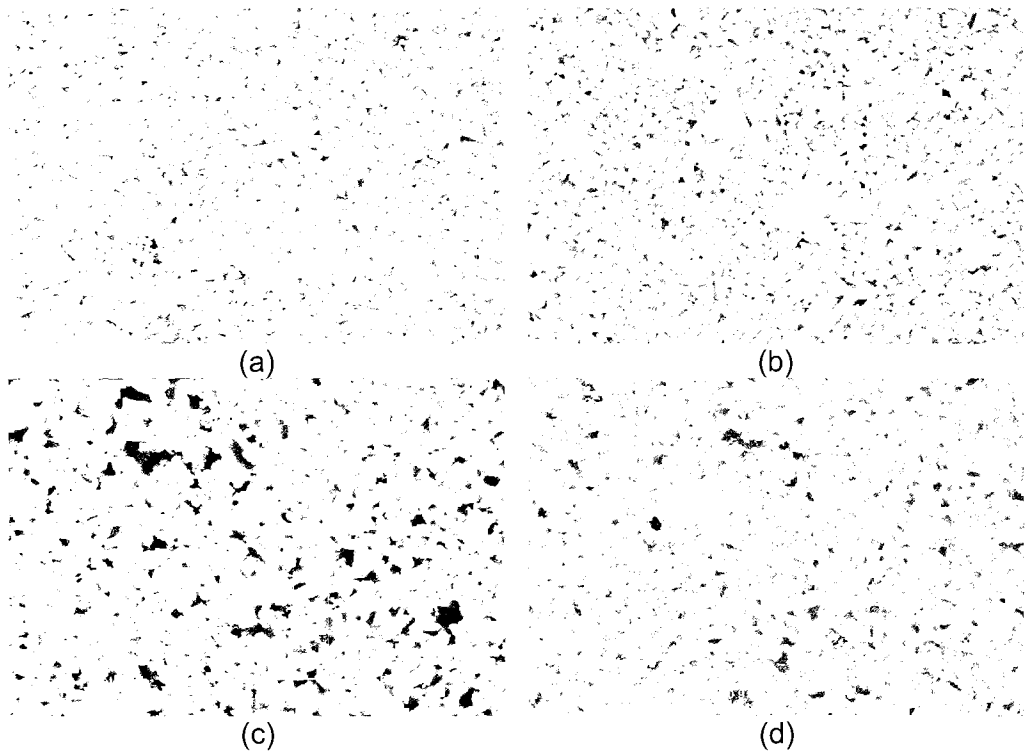


Fig. 6 Back-scattered SEM micrographs of vacuum sintered: (a) Composition 2 vacuum sintered at 1400°C, (b) Composition 4 vacuum sintered at 1400°C, (c) Composition 2 vacuum sintered at 1320°C and (d) Composition 4 vacuum sintered at 1320°C

3.2. Hot Isostatic Pressing (HIP)

As observed in the previous section, the two main issues concerning conventional processing of nanosized WC-Co powders are porosity and grain growth. Thus, pressure assisted techniques are the natural choice for densification of these materials, specifically hot isostatic pressing. The most critical step of the selected technique is glass encapsulation. Glass melting point must be selected to avoid capsule closure before out-gassing (due to oxides reduction) has been completed.

Hardness and porosity of HIPed materials have been summarised in Table 4.

Ref.	Co (wt.%)	VC (wt.%)	Encap. Method	T (°C)	η phase	HV10 (kg.mm ⁻²)	Porosity	
							A02	<B02
3	12	0	vacuum	1200	no	1550	A02	<B02
1	10	0	vacuum	1200	no	1580	A04	<B02
3	12	0	vacuum	1100	no	1630	A02	<B02
1	10	0	vacuum	1100	no	1710	<A02	B02
3	12	0	H ₂	1100	yes	1660	<A02	<B02
4	12	0.4	vacuum	1000	no	1790	<A02	<B02
2	10	0.4	vacuum	900	no	960	A04	B04
2	10	0.4	vacuum	900	no	1010	A04	B04
4	12	0.4	vacuum	900	no	1580	A04	B04

Table 4: Properties of materials produced by HIP at 150 MPa

The highest hardness has been obtained for Nanocarb®+0.4%VC+12wt%Co by HIPing at 1000°C, HV10 = 17.9 GPa. This value is one of the highest reported so far for this composition (7). The microstructure of this material is extremely fine with needle-like grains (Fig. 8). Cobalt distribution is not perfectly homogeneous, showing some micro-pooling. However, the mean size of cobalt islands is below 1 μ m.

The hardness of samples HIPed without grain growth inhibitors substantially increases as the process temperature decreases. This hardening effect is more pronounced on Nanocarb®, though it leads to lower absolute hardness values than Microcarb®. Thus, both materials present similar hardness when processed at 1100°C (Fig. 9).

The low hardness values found in samples HIPed at 900°C show that the lower limit for densification by this new HIP technique should be between 900°C and 1100°C.

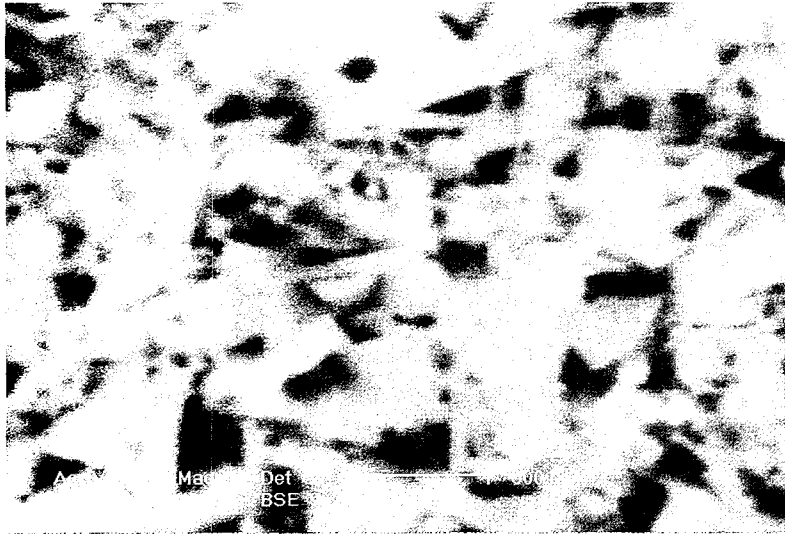


Fig. 8 Back-scattered SEM micrograph corresponding to Nanocarb®+0.4%VC+12wt%Co sintered by HIP at 1000°C for 0.5 hours.

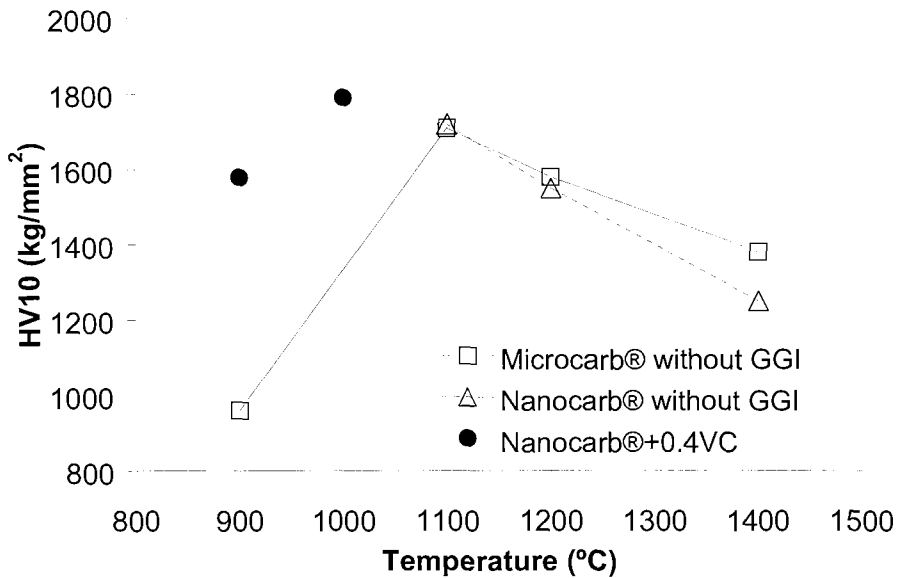


Fig. 9 Vickers hardness (HV10) vs. HIP temperature

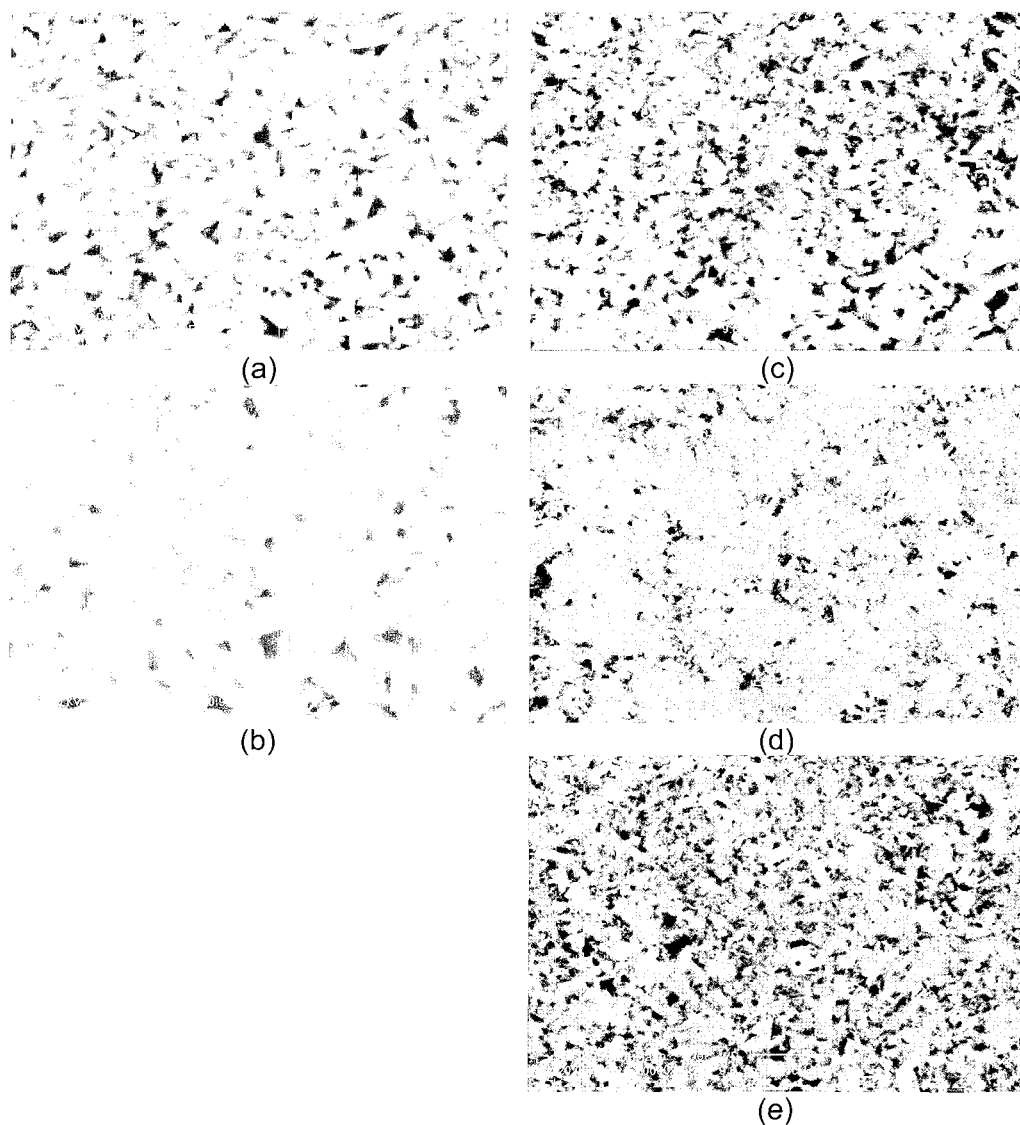


Fig. 10 Back-scattered SEM micrographs corresponding to: (a) Composition 4, VS at 1400°C, (b) Composition 4, VS at 1320°C, (c) Composition 3, vacuum encapsulated and GEHIP at 1100°C, (d) Composition 3, H₂ encapsulated and GEHIP at 1100°C and (e) Composition 4 vacuum encapsulated and GEHIP at 1000°C

The microstructure refinement obtained by using lower processing temperatures is clearly observed in Fig 10. The correlation between these microstructures and their corresponding hardness values is straightforward, except for the material HIPed at 1100°C after H₂ encapsulation (Fig. 10d). This material shows a significant cobalt depletion due to the formation of η phase (Co₃W₃C), clearly identified by XRD (Fig. 11) and EDS of grains with slightly darker grey contrast in Fig. 10d (Fig. 12). This phase is not present in the specimens encapsulated in vacuum.

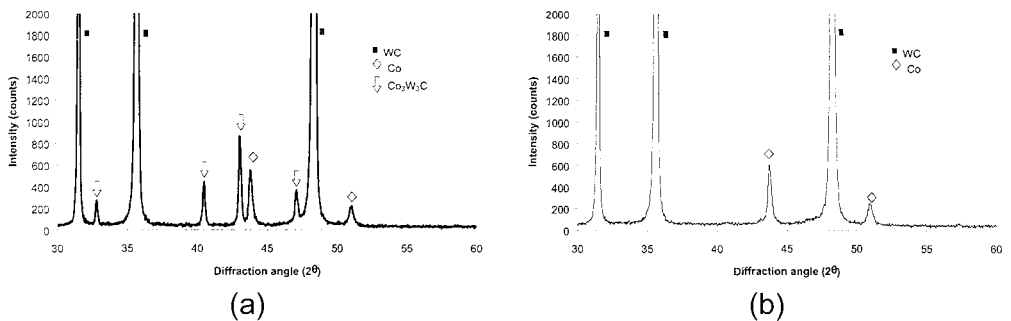


Fig. 11 XRD patterns corresponding to samples HIPed at 1100°C: (a) H₂ encapsulated (b) Vacuum encapsulated

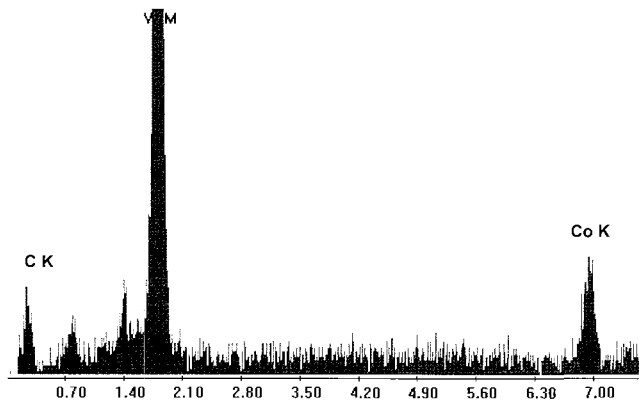


Fig. 12 EDS analysis corresponding to η phase (in grey contrast in Fig.10d)

Temperatures of liquid formation in either WC-Co or WC-VC-Co systems are well above those used in the present HIPing cycles (21). Therefore, densification is completely carried out in solid state. Samples sintered at 1000°C undergo a linear shrinkage about 20 %, similar to that of vacuum sintered specimens at 1400°C, thus a similar amount of mass transport must occur.

The application of pressure starts at 850°C, with no appreciable shrinkage (at this point, the sample contains about 50% of porosity). Although pressure is isostatically applied, locally shear components of stress appear at contacts between WC particles. This effective stress, caused by the high pressure difference between outside (1500 bar) and inside the glass capsule (10^{-8} bar), can lead to cobalt plastic deformation and collapse of the porous structure. At this stage, the nanometric WC particles, considered as perfectly rigid, can undergo substantial rearrangement due to plastic deformation of cobalt, (≈ 18 vol.% of the sample). 1000°C is a typical temperature used for hot rolling of cobalt of high purity (22).

Once the number of contacts between WC particles approaches that corresponding to 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 ($> \frac{1}{2}$ Co melting point). Nevertheless, the micrographs show that cobalt distribution is not perfect, reflecting poorer spreading if compared with liquid phase sintering.

4. CONCLUSIONS

A new HIP technique has been developed for densification of nanosized hardmetals at temperatures as low as 1000°C. Grain growth is avoided at these temperatures even in absence of grain growth inhibitors producing a substantial hardness increase.

Under these conditions, densification is carried out in solid state. Cobalt plastic deformation leading to rearrangement of WC nanograins is proposed as the dominant densification mechanism during the first sintering stage. Final densification should require the contribution of diffusion based phenomena as creep flow.

Processing of these materials by conventional vacuum sintering present two main issues: porosity and grain growth. Porosity is related to milling-mixing conditions, whereas grain growth can be controlled by VC additions.

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