PRELIMINARY STUDIES OF A WC-Co-H13 STEEL FUNCTIONALLY GRADED MATERIAL MANUFACTURED BY MEANS OF SPS

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Abstract. *The employ of cemented carbide for tooling is well known and have been widely used in industrial applications. However, the high cost of WC powders suggests a new approach for the production of surface coated parts, which is represented by functionally graded materials, where a gradual transition between the substrate and the coating is used in order to minimize thermo-mechanical stress during the production and the use in application. In the case of WC-Co based tools a steel substrate can be used to increase mechanical properties required by the application. These properties may be provided by H13 steel, which has good toughness, impact strength and also thermal fatigue resistance. There are several techniques to manufacture the WC-Co. A new approach for the production of surface coated parts made of WC-Co by means of spark plasma sintering (SPS) is proposed in this work. The SPS is a novel sintering technique at relatively low temperatures and short dwell times. SPS differs from conventional hot pressing methods since the powder is heated by a direct pulsed current that flows through punches, die and the processed material. The Joule heat due to the electric current rapidly leads to the sintering of the powder under pressure. The main objective of this work is to evaluate the sintering process of a functionally graded material made of WC-Co and H13 steel by means of SPS. Preliminary experiments were carried out to evaluate the interaction between the cemented carbide and the steel. Some dilatometer tests were also carried out to determine the coefficient of thermal expansion of the materials studied since there is a great difference between them, and the thermo-mechanical stress mainly on the interface can lead to failure. Subsequently, two different samples were manufactured. The first was a two-layer made of WC-Co and H13 steel and the second sample was a three-layer sample made of WC-Co, WC-Co-H13 steel and H13 steel. Although, the FGM consolidated samples showed cracks near the interfaces, which occurred during the cooling after consolidation, the three-layer sample showed interesting results since the intermediate layer changed the distribution and decreased the thermal-mechanical stress during SPS consolidation. Consequently, the existence of a gradual transition in the physical and mechanical properties is very important to avoid stress concentration.*

Keywords*: spark plasma sintering, FGM, cemented carbide, steel, manufacturing*

1. INTRODUCTION

Cemented carbides have favorable combination of properties to be used as wear resistant material (Zhao *et al.* (2009)). Therefore, the employ of cemented carbide for tooling is well known and it have been widely used in industrial applications (Lou *et al*. (2003)). However, the WC-Co presents high cost as compared to tool steels. Thus, materials consisting of multilayers and/or metal matrix reinforced with WC, providing better mechanical and physical properties have been studied (Lou *et al.* (2003); Giménez *et al.* (2007); Pascal *et al.*(2009)). In the case of WC-Co based tools, these properties could be provided by H13 steel, which has good toughness, impact strength and also thermal fatigue resistance. Nevertheless, the sintering temperature cannot be higher than 1100°C, since there is a ternary eutectic Fe-WC-Fe_3C between 1120 and 1140ºC (Pascal *et al.* (2009)). Above 1100°C, other phase transformations are also expected such as: W_2C (Lou *et al*. (2003); Guilemany *et al.* (1999)), M_6C (M=W, Fe) (Lou *et al.* (2003); Giménez *et al.* (2007); Pascal *et al.* (2009)), Co_3W_3C (Guilemany *et al.* (1999); Lou *et al*. (2003); Li *at al.* (2005)) and/or Co_6W_6C (Guilemany *et al.* (1999)). These phases are brittle, leading to a loss of toughness, and they have to be avoided. It is worth mentioning that the different expansion coefficients of the materials enlarge the thermal stress during the sintering process. Therefore, a gradual transition between the substrate and the coatings has to be used to minimize thermo-mechanical stress, tailoring a functionally graded material.

There are several techniques to manufacture the WC-Co-steel (Guilemany *et al.* (1999); Lou *et al*. (2003); Li *at al.*, (2005); Pascal *et al.* (2009); Zhao *et al.* (2009)). An approach for the production of surface coated parts made of WC-Co by means of spark plasma sintering (SPS) is proposed in this work. Hence, this work deals with evaluation of the sintering process of a functionally graded material (FGM) made of WC-Co and H13 steel by means of SPS. The SPS is a novel sintering technique characterized by lower temperatures and shorter dwell times than conventional pressure assisted technology. The powder is heated by a direct-pulsed current that flows through punches, die and the processed material. The Joule heat due to the electric current rapidly leads to the sintering of the powders under pressure (Tokita,

2005). Because of the low global thermal load, the interaction between the materials during the sintering can be different with respect to conventional sintering technologies.

In this work, samples made of WC-12wt%Co, H13 steel and a mixture of WC-Co and H13 steel were manufactured by means of SPS. The consolidated samples were observed by using optical and scanning electron microscopy. Dilatometry was also conducted to determine the coefficient of thermal expansion (CTE) and the shrinkage since the expansion and contraction between the different materials has to be gradual, minimizing the thermo-mechanical stresses. Subsequently, two samples were manufactured by means of SPS to be compared: a three-layer sample made of WC-Co (coating), WC-Co-H13 steel (intermediate layer) and H13 steel (substrate) and a two-layer sample made of WC-Co (coating) and H13 steel (substrate). Therefore, the effect of the intermediate layer between the substrate and the coating could also be evaluated.

2. MATERIALS AND METHODS

2.1 Materials

The manufacturing of the SPS samples was carried by using WC, Co and H13 steel raw powders. The main features of powders utilized in this study are: WC powder with 99.95 purity and particle size under 0.9 μm; Co powder with 99.95 purity and particle size under 1.5 μm and H13 steel (5wt% Cr, 1wt%V, 0.4wt%C, 1wt%Mo, Fe is the balance) with particle size under 22 μm. Two different mixtures were prepared, according to the composition shown in Tab. 1.

Table 1. Composition of the raw powders and powder mixtures to manufacture the SPS samples.

Material	WC (vol%)	WC (wt%)	Co (vol%)	Co (wt%)	H13 steel (vol%)	H13 steel (wt%)
H13	-	-	-	-	100	100
WCCo	80	88	20	12	-	-
WCCoH13	40	57	10	8	50	35

2.2 Methods

2.2.1 Powders and powder mixtures

The WCCoH13 powder mixture was carried out in two steps. In the first step, 30g of WCCo powder mixture were placed in a polymeric bottle (50ml) containing acetone and four 100Cr6 balls (8 mm diameter). The material was mixed by means of Turbula® for 10 hours. Thus, the mixture was dried at 50°C for about 5 hours in a double boiler. In the second step, 35g of the powder WCCoH13 mixture were placed in a polymeric bottle (50ml) with three 100Cr6 balls (8 mm diameter) and dry mixed by means of Turbula® for 4 hours.

2.2.2 SPS consolidation

The SPS consolidations were carried out using SPS-1050 system, produced by Sumitomo Coal Mining Co. Ltd. The samples were 20 mm diameter and 10 mm height. 60 MPa of maximum pressure was applied; sintering was carried out at 1100°C. A pyrometer, which focuses on the surface of the graphite die, was used for temperature process control. The SPS-1050 is connected to an acquisition system. Hence, the processing parameters control and measurements are carried out throughout the SPS consolidation. The data, such as temperature, vacuum level, displacement and pressure applied, is recorded as function of the time. Therefore, changes during the consolidation process can be detected and they are recorded to later evaluation, such as gas formation, causing a decrease in the vacuum level, and displacements due to consolidation and phase transformations (Zhao *et al*. (2009); Machado *et al* (2009)). Figure 1 shows the temperature as a function of time throughout the SPS consolidation.

The analysis of the SPS consolidation was carried out in different steps. First, the WCCo, H13 steel and WCCoH13 samples (Tab. 1) were consolidated by means of SPS. The evaluation of the sintering process was carried out throughout the analysis of the SPS data recorded during the consolidation of these samples. The second step of the SPS consolidation consisted in consolidating samples made in layers of WCCo, H13steel and WCCoH13. The same process parameters (Fig.1) were applied to all samples in order to compare the results.

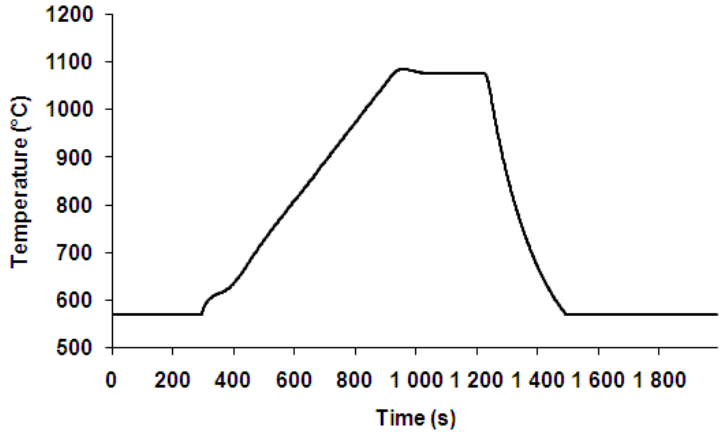


Figure 1. Temperature (ºC) vs time (s) throughout SPS consolidation of all samples. The dwell time was 5 minutes at 1100ºC. The temperature measurement was conducted above 600°C, since a pyrometer was used.

2.2.3 Microstructural characterization

The metallographic sample preparation consisted on grinding followed by polishing (up to 1-µm diamond paste) and etching with Nital 2% reagent. The consolidated samples were observed by using optical (Optical Microscope Zeiss - Leica) and scanning electron microscopy (Environmental Scanning Electron Microscope TMP ESEM). Energy dispersive analysis (EDAX) was also performed in order to evaluate the microstructures of the consolidated samples.

2.2.4 Dilatometry

FGMs made of materials with very different coefficients of thermal expansion (CTE) enlarge the thermal-mechanical stresses during cooling after consolidation. Therefore, this physical property has to be considered in FGMaterial's design. Dilatometer measurements were carried out to measure and compare the CTE of the WCCo, H13, and WCCoH13 samples consolidated by means SPS. The shrinkage and the shrinkage rate were also evaluated since these results can show phase transformations during heating and cooling, which also can enlarge the thermo-mechanical stresses.

The samples for dilatometer tests were about 11 mm in length and 4x4 mm^2 square section. The tests were conducted in the range of temperatures between the room temperature and 1100ºC. The heating rate was 20ºC /min in order to have accurate measurements. The sample was maintained at 1100ºC for 5 min and the cooling rate was about 2ºC/s. The measurements were carried out using a Baehr dilatometer (type 805 A/D). It is worth mentioning that CTE measurements on heating are the same on cooling. Therefore, the results presented can be related to the cooling of samples after consolidation.

3. RESULTS

3.1 SPS consolidation of WCCo, H13 steel and WCCoH13 samples.

The evaluation of the sintering process throughout the SPS consolidation can be performed by analyzing the data recorded since the SPS-1050 is connected to an acquisition system. Therefore, changes during the consolidation process can be detected such as displacement and displacement rate, which is derivative of displacement with respect to time. The displacement rate as a function of temperature is shown for WCCo, H13, and WCCoH13 samples in Fig. 2.

Phase transformations and the consolidation of the material can be detected (see peak (2) and (3) in Fig. 2). In Fig. 2, peak (2), at about 860°C in the H13 steel graph, is related to the bonding of adjacent particles and also to the ferrite-austenite transformation. Peak (3) in the WCCo graph is due to the beginning of the consolidation and the complex carbide formation (W_4Co_2C). On the other hand, peak (3) also indicates the complete consolidation of the H13 steel (Machado *et al.* (2009)). Finally, peak (1) indicates the very beginning of SPS process consolidation, the displacement observed is related to the powder rearrangement in the matrix. A similar peak due to the same phenomenon can be observed during the SPS processing of all samples.

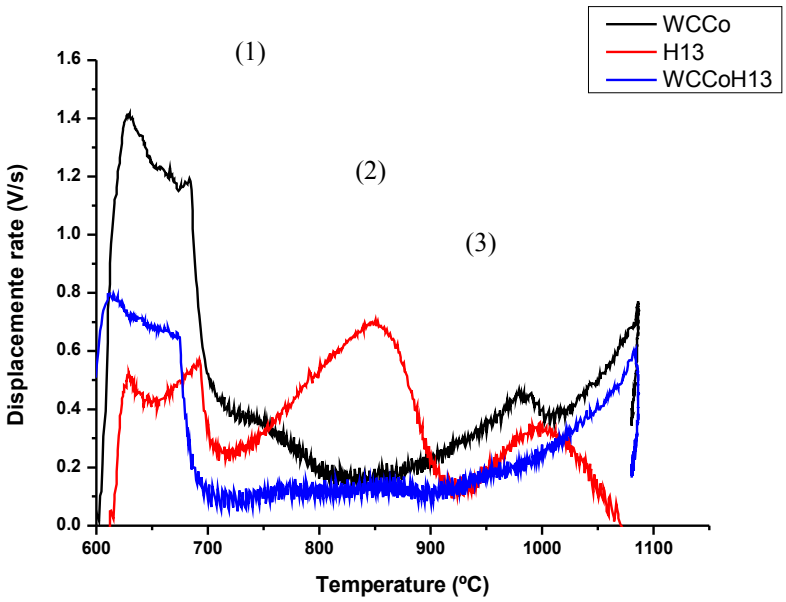
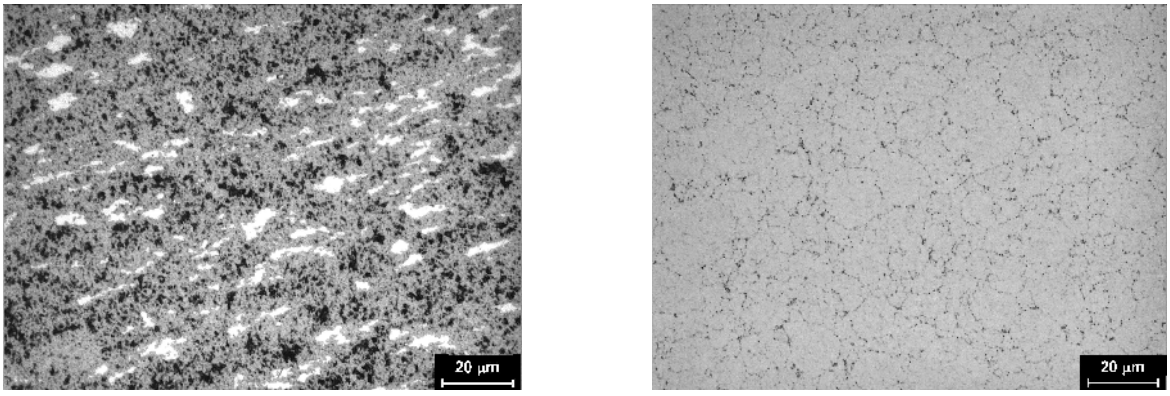


Figure 2. Displacement rate as a function of temperature for WCCo, H13, and WCoH13 samples during SPS consolidation.

3.2 Microstructural characterization of WCCo, H13 steel and WCCoH13 samples

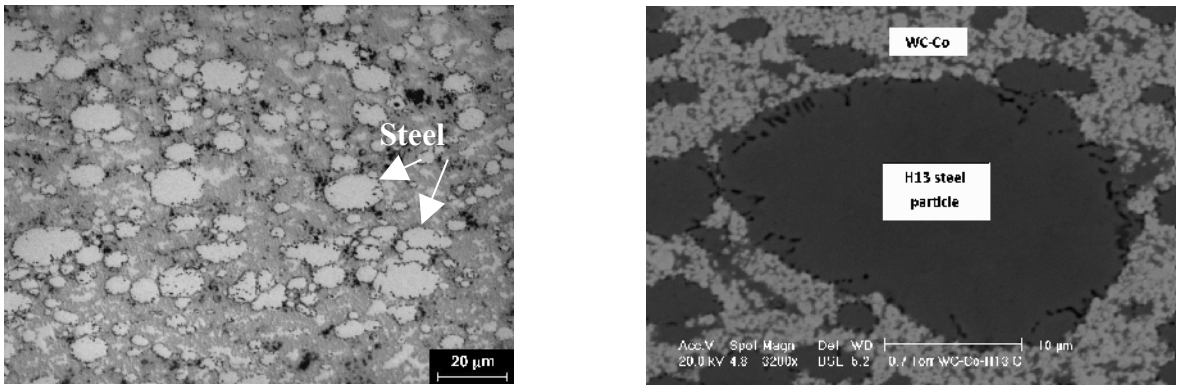
Figure 3 shows the microstructures of the WCCo and the H13 steel samples after SPS consolidation. The black regions or spots in Fig. 3a are due to removed material during metallographic sample preparation since the WCCo sample is not fully densified. The light regions in figure 3a are cobalt rich ones. The sintering temperature was not high enough to allow the fusion and/or diffusion of cobalt through the matrix. On the other hand, the H13 steel presented full density (Fig. 3b), and the black regions are due the presence of oxides in the raw powder.

Figure 4 shows the microstructure of the WCCoH13 sample. The steel particles can be easily identified (Fig. 4a and Fig. 4b). The black and light spots in the WCCo rich regions (Fig 4a) are also identified since the sample was not full density. No cracks were observed after SPS consolidation.



(a) (b)

Figure 3. Microstructures of the (a) H13 steel and the (b) WCCo samples. Optical microscopy.

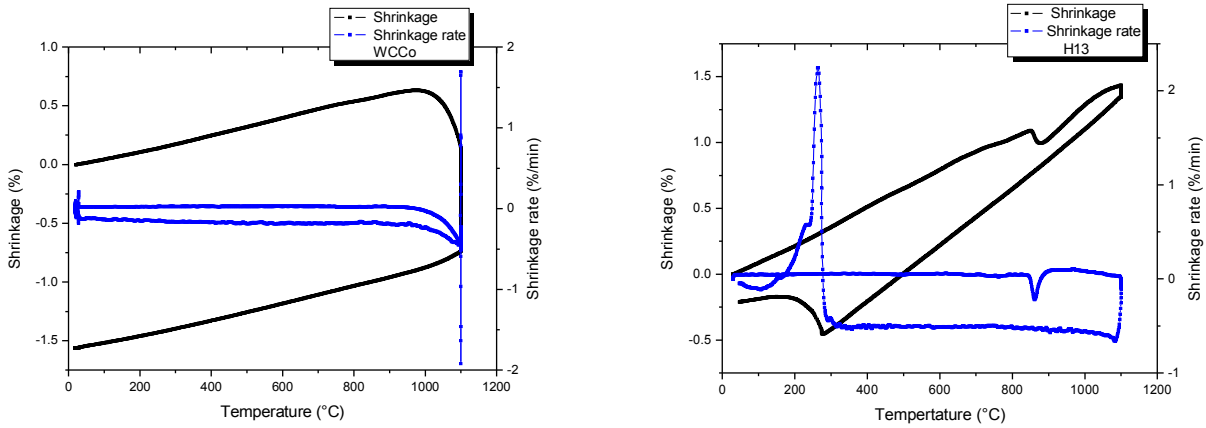


(a) (b)

Figure 4. Microstructure of the WCCoH13 sample. (a) Optical microscopy, and (b) Scanning electron microscopy, back scattered electrons.

3.3 Dilatometer measurements of WCCo, H13 and WCCoH13 samples.

Figure 5 and 6 show the shrinkage and the shrinkage rate (derivative shrinkage with respect to the time) as a function of temperature during heating and cooling of the WCCo, H13 and WCCoH13 samples after being consolidated. The WCCo sample (Fig. 5a) presented a linear behavior, excepted above 1000ºC. Probably, interactions between the particles and phase transformations occurred, causing the shrinkage. Phase transformations also occurred in the steel during heating and cooling, as shown in Fig. 5b. The ferrite-austenite transformation occurred at about 860ºC during heating, and during cooling at about 200ºC, the martensite formation also verified. The WCCoH13 sample (Fig. 6) is made of a mixture of materials. Therefore, it was expected the same behavior and temperature transformations. The ferrite-austenite transformation (Fig. 6) was identified at the same temperature found in Fig. 5b during heating. However, the austenite-pearlite transformation occurred at about 800ºC and the martensite formation occurred at higher temperature (about 400ºC) during cooling. The main explanation for the changes in the temperature transformation in the steel sample can be related to the dissolution of Co in the steel, which was verified in previous work (Machado *et al.*, 2009), changing the Ms temperature. The change observed in WCCo sample (Fig 5a) above 1000 ºC was also detected in WCCoH13 sample (Fig. 6), and it can be related to the WCCo phase transformations.



(a) (b)

Figure 5. Shrinkage and shrinkage rate as function of temperature. (a) WCCo sample and (b) H13 steel sample.

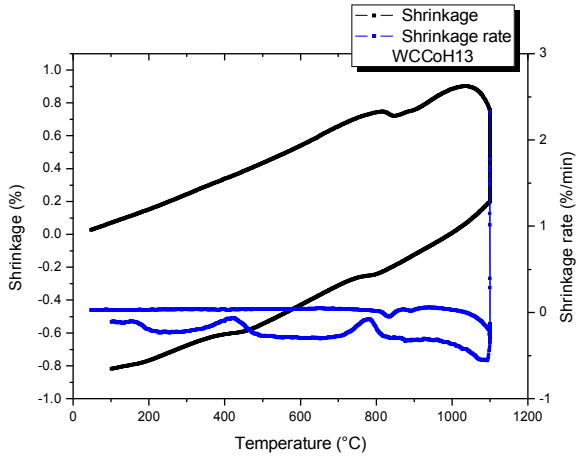


Figure 6. Shrinkage and shrinkage rate as function of temperature. WCCoH13 sample.

The coefficient of thermal expansion (CTE) of WCCo, H13 and WCCoH13 samples were determined (Fig. 7) after SPS consolidation by means dilatometry. CTE changes are expected with the temperature. However, a great variation occurred in the H13 sample at about 860ºC due to ferrite-austenite transformation. A similar behavior is observed WCCoH13 sample, and it can also be related to ferrite-austenite transformation of the steel during heating. The results also showed a decrease in the CTE of the WCCo and WCCoH13 samples above 1000ºC. This phenomenon occurred only in the samples containing WCCo, which were not fully densified. Probably, interactions between the particles and phase transformations occurred, causing this shrinkage. In order to design the functionally graded material sample (item 3.4), the maximum CTE value obtained was adopted since it will be the critical one during cooling. Table 2 displays the CTE adopted for the WCCo, H13 and WCCoH13 samples.

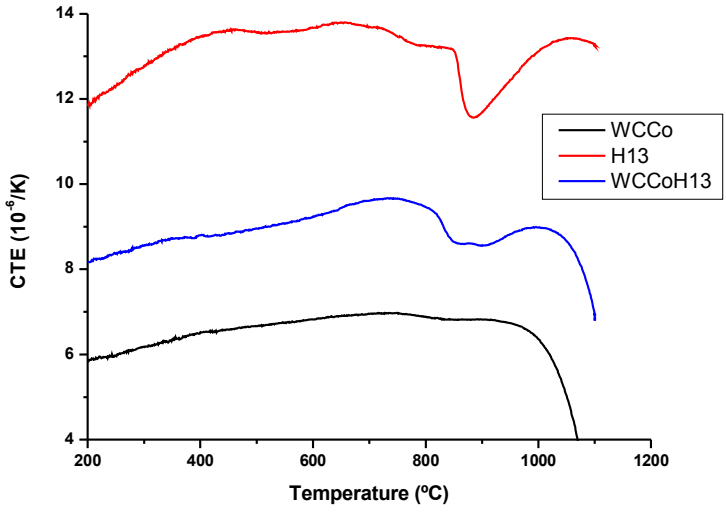


Figure 7. Coefficient of thermal expansion (CTE) obtained by means a dilatometer.

Table 2. Coefficient of thermal expansion (CTE) - maximum values measured.

Sample	CTE (10^{-6}/K)
WCCo	6.9
H13	13.4
WCCoH13	9.6

3.4 The FGM samples design

Since the CTE of the WCCoH13 samples, containing 50% volume of steel, is around the mean value of the CTE of the two base materials, an intermediate layer made of this mixture was included between WCCo and H13 (FGM 3). In order to evaluate and compare the effect of the intermediate layer on the manufacture of the FGM 3, a sample made of two layers (WCCo and H13) was also manufactured, named as FGM 2. The schematic of the FGM 2 and FGM 3 samples are shown in Fig. 8.

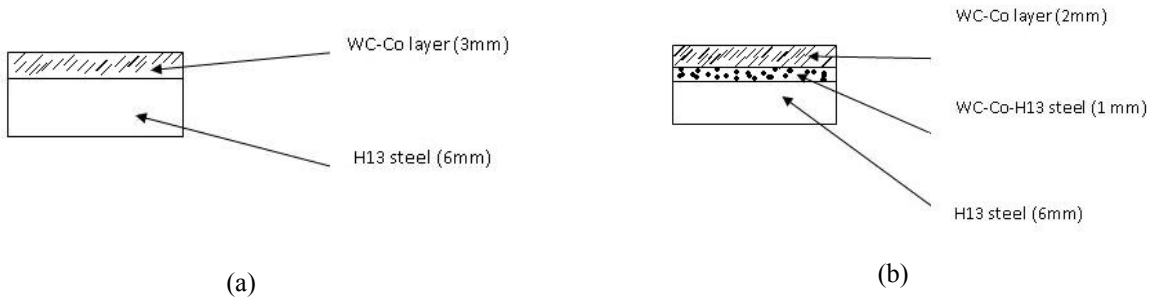


Figure 8. Schematic of (a) FGM 2 and (b) FGM 3 samples.

3.5 Microstructural characterization – FGM samples

The FGM 2 and FGM 3 samples were manufactured by using the processing parameters described previously (Fig. 1). Figure 9 shows the FGM 2 and FGM 3 samples after SPS consolidation.

The interfaces show a binding between the materials, as can be observed in Fig. 10 and Fig.11. Fig. 12 shows details of Fig 11, and the interface between WCCo and WCCoH13 and the interface between WCCoH13 and H13 steel can be observed. The WCCo, H13 steel and WCCoH13 regions in the FGM 2 and FGM 3 samples showed the same features observed, and discussed previously, of the WCCo, H13 and WCCoH13 samples after SPS consolidation.

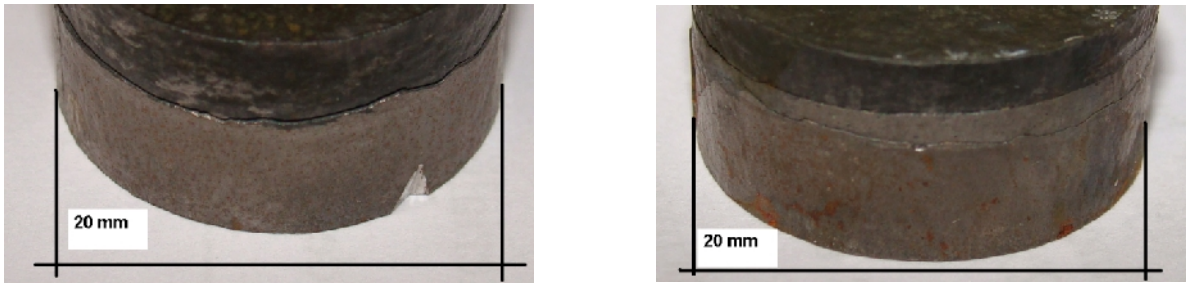


Figure 9. (a) FGM 2 and (b) FGM 3 samples.

Nevertheless, the two FGM samples presented cracks near the interfaces (Fig. 11 and Fig. 13), which occurred during the cooling after consolidation. Probably, the crack initiation occurred in the interface but it propagated into the WCCo region in the FGM 3 sample (see Fig. 11). On the other hand, the FGM 2 sample showed many cracks and they occurred both in the WCCo and H13 steel regions, as can be observed in Fig. 13. These results confirm the existence of thermal-mechanical stress, which was higher in the FGM 2 sample, as a result of higher differences of the coefficients of thermal expansion and also due to phase transformations, mainly the martensite formation. The intermediate layer in FGM 3 sample changed the distribution and decreased the thermal-mechanical stress during SPS consolidation, promoting cracking in the WCCo side, which is not fully densified. In FGM 2, cracks are also detected in H13 steel, even if it results well densified. Therefore, the existence of a gradual transition in the physical and mechanical properties is very important to avoid stress concentration.

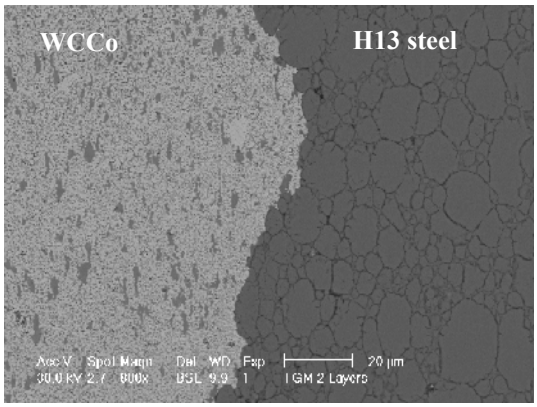


Figure 10. FGM 2 interface after SPS consolidation. Scanning electron microscopy, back scattered electrons.

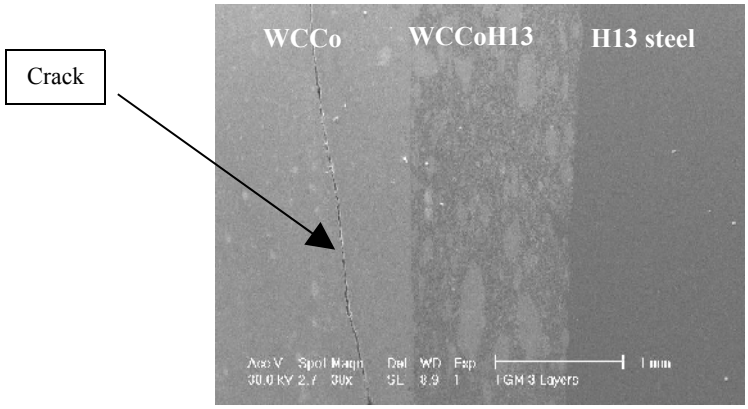
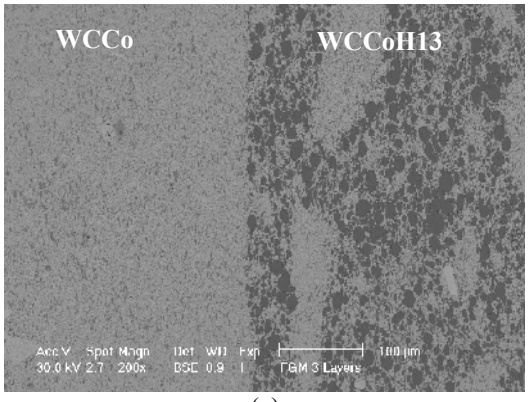
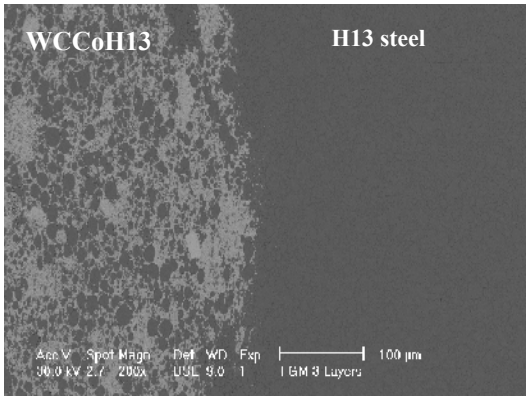


Figure 11. FGM 3 interfaces after SPS consolidation. Scanning electron microscopy secondary electrons.



(a)



(b)

Figure 12. Detail of FGM 3 interfaces after SPS consolidation. Scanning electron microscopy, back scattered electrons.

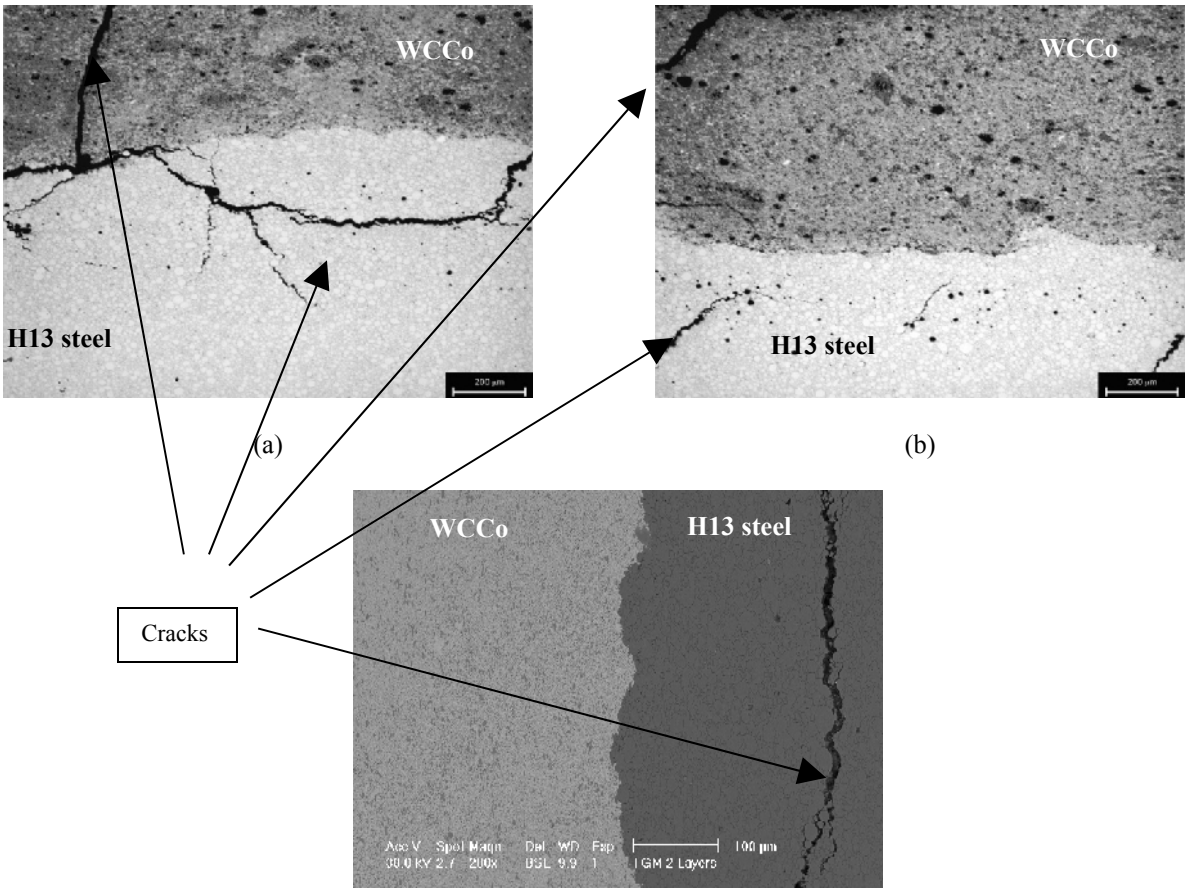


Figure 13. FGM 2 sample interface, cracks near the interface mainly in the steel region. (a) and (b) Optical Microscopy. (c) Scanning electron microscopy, back scattered electrons.

4. Final Remarks

The main objective of this work was the evaluation of the sintering process of a functionally graded material made of WCCo and H13 steel by means of SPS consolidation. An interaction between WC, Co and iron (steel) was observed and dilatometer tests were carried out to evaluate the CTE and design a FGM sample prototype made of WCCo and H13 steel. The results show the manufacture was viable. Hence, two different FGM samples made in layers were consolidated by means of SPS.

Although, the FGM consolidated samples showed cracks near the interfaces, which occurred during the cooling after consolidation, the three-layer sample showed interesting results since the intermediate layer changed the distribution and decreased the thermal-mechanical stress during SPS consolidation. Consequently, the existence of a gradual transition in the physical and mechanical properties is very important to avoid stress concentration.

It is also important to point out that the SPS temperature used was low for WC-Co system consolidation and the materials were not fully densified. However, it was selected considering the existence of a ternary eutectic Fe-WC-Fe_3C between 1120 and 1140ºC. The martensite formation also has to be taken into account since it enlarges the thermal-mechanical stresses. This study was preliminary, and the development of a FGM, by means of SPS containing, made of more layers and/or with different steel chemical compositions have to be performed for its use in industry applications.

5. ACKNOWLEDGEMENTS

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