Sintering, Shrinkage and Microstructure of NbC-20Ni Cemented Carbide

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The well-established cemented carbides are composites of tungsten carbides (WC) bonded with cobalt, nickel or a mixture of these two binders. Additives as chromium, titanium, molybdenum or vanadium carbides are used to tailor microstructure and mechanical properties. Two general applications for these hardmetals are for machining and mechanical forming tools, and the binder content and grain size are the main adjustable variables regarding the compromise between hardness and toughness. The use of other carbide replacing WC, like NbC, has been hardly investigated. Nickel binding NbC carbides, during liquid phase sintering, works properly and full densification should be obtained. Mixtures of very fine carbides and carbonyl Ni powders were produce by intense ball and attritor milling. WC was used to adjust microstructure. These mixtures were pressed using uniaxial pressures, 50 or 200MPa. Shrinkage was evaluated using dilatometric measurements under an atmosphere of dynamic argon. Samples were also sintered in a DSC/TG equipment. The sintered samples were characterized in terms of microstructure, density, and hardness. Results were presented and discussed. A relationship between sintering cycles and microstructure was established.

Introduction

Cemented carbides, as WC-Co, can be used as tools for machining purposes or for processes involving plastic deformation of metals [1, 2]. The carbide provides hardness and the binders, usually cobalt or nickel, are the responsible for the toughness. Lower binder contents and small carbide grain size are used in applications that require very high hardness and high friction properties, like machining tools. On the other hand, the cemented carbides for plastic deformation (metal forming) should have higher binder concentration and large grain size, tailoring hardness and toughness in according the application of the component. These cemented carbides are produced by powder metallurgy, using as starting materials mixtures of carbides (WC, and other carbides) and binder (Co or Ni). Ken Brookes [3] published a very nice review about tungsten based materials, including history and trends for cemented carbides.

The replacement of WC for other carbides has been hardly investigated. Warren [4] tested different metals to bind niobium carbides (NbC). More recently, aspects like the addition of other carbides to control microstructure of NbC-Ni systems [5 and 6], the use of new techniques of sintering, as SPS [7], and the use of intermetallic binders [8], has been pointed out.

This paper considers the replacement of WC for NbC for hot rolling applications. The binder content used here was close to 20wt% and coarse grain size was the goal to be achieved. Densities close to 8.30g/cm^3 and Vickers Hardness (HV_2) close to 1100 were expected. Two chemical compositions and two milling processes were investigated. The sintering was monitored in a dilatometer and also by thermal analysis. The presence of a liquid phase, the shrinkage and the microstructural aspects are presented and discussed in the present work.

Experimental procedures

The initial raw material powders used in the present work were the following: NbC S3; carbonyl Ni powder and a ready-to-press WC-6Co powder. Two mixtures were prepared:

- A 76wt%NbC, 6%wtWC (actually 6wt% of WC-6Co) and 18wt% Ni mixture that was ball milled for 15 hours, identified as NbC-18Ni-6WC;
- A 76wt%NbC, 4%WC (actually 6wt% of WC-6Co) and 20%wtNi mixture that was attritor milled for 15 and 120 minutes, identified as NbC20-Ni-4WC.

Ball mill: 1.0kg of the mixture was milled with 8.0kg of WC balls (~20mm in diameter), in a 160x240mm stainless steel vessel, internally coated with Ti, under 1l of isopropyl alcohol, for 15 hours at 130rpm. Attritor mill: 1.0kg of the mixture was milled with 2.0kg of stainless steel balls (~8mm in diameter), in a 180x200mm stainless steel vessel, under 2l of isopropyl alcohol, for 15 and 120 minutes at 200rpm. Fig. 1 shows details of the attritor mill: the milling vessel (attritor mill) and accessories to dry the milled mixture and to recover the isopropyl alcohol. Figs. 2 and 3 show images for ball milled and attritor milled

mixtures. The interaction between carbides and carbonyl nickel powder seems to be more intense for attritor milled mixture, i.e., the nickel particle appear to be coated with carbides.

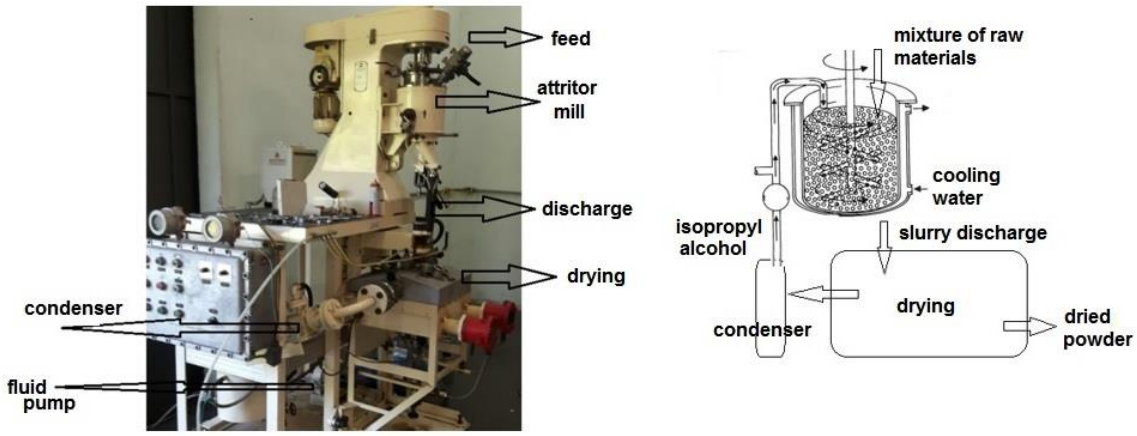


Fig. 1 - Aspects of the semi-continuous attritor mill.

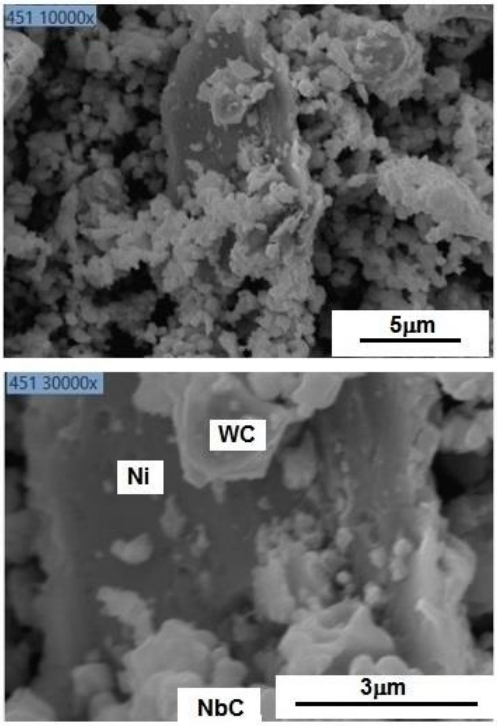
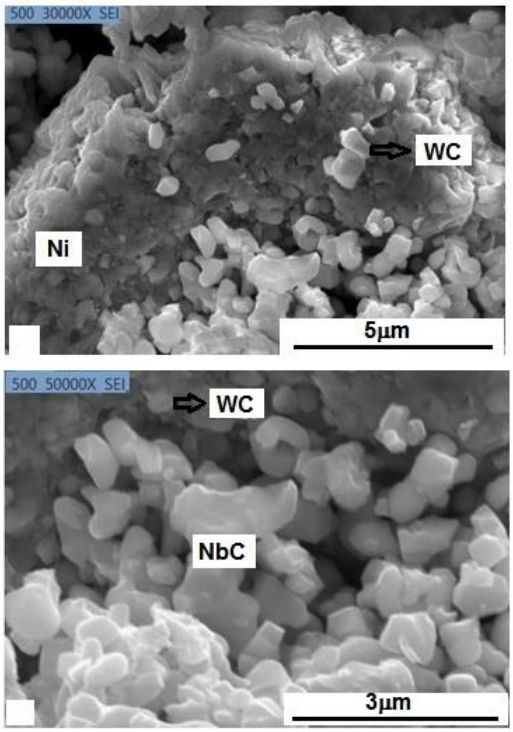


Fig. 2 - The 76wt%NbC, 6%wtWC and 18wt% Ni mixture ball milled for 15 hours. Secondary Electrons Image – SEI.



The 76wt%NbC, 4%wtWC and 20wt% Ni mixture atritor milled for 120 minutes. Secondary Electrons Image – SEI.

The mixtures were uniaxially dry pressed, 50 or 200MPa, and the sintering was carried out inside a dilatometer (Netzsch 402 c) or inside a DSC/TG (TA Q600 SDT). Electronic images were obtained from a FEI QUANTA FEG 600, DRX spectruns were determined in a Shimadzu difratometer. Density was determined by Archimedes method and microhardness was determined with a HMV Shimadzu equipment, using high-load microindentation (2.0kg).

Results and discussion

Figs. 4 and 5 present the DSC curves for samples ball milled (15h) and for samples milled using an attritor mill, for 15 and 120 minutes. It was used a “quick” thermal cycle and a thermal cycle similar to a typical sintering process, as showed in the legends. Despite of small differences in nominal chemical composition, the liquid phase formation occurred, during heating, at around 1350^{o}C, considering the “quick” cycle. In this case, the liquid was no transient, and the solidification (exothermic peaks) occurred at lower temperature (~1360^{o}C) for sample with higher binder content (20wt%), as shown in Fig. 4. For

longer sintered cycles, as showed in Fig. 5, the liquid phase formed was transient only for sample with lower binder content (and higher WC content), seen that no exothermic peak was observed during cooling. For samples with higher binder content, the liquid phase appeared at around 1350ºC, and it solidifies at around 1310 ºC. Considering the double peak appearance, we concluded that the liquids formed have different chemical compositions. The measured microhardness (HV_2) of the 510_1 sample was 1260 (Fig. 5), and of the 482_1 sample was lower (1090), and the reason should be the higher temperature (1430ºC) used to sinter this sample (Fig. 4).

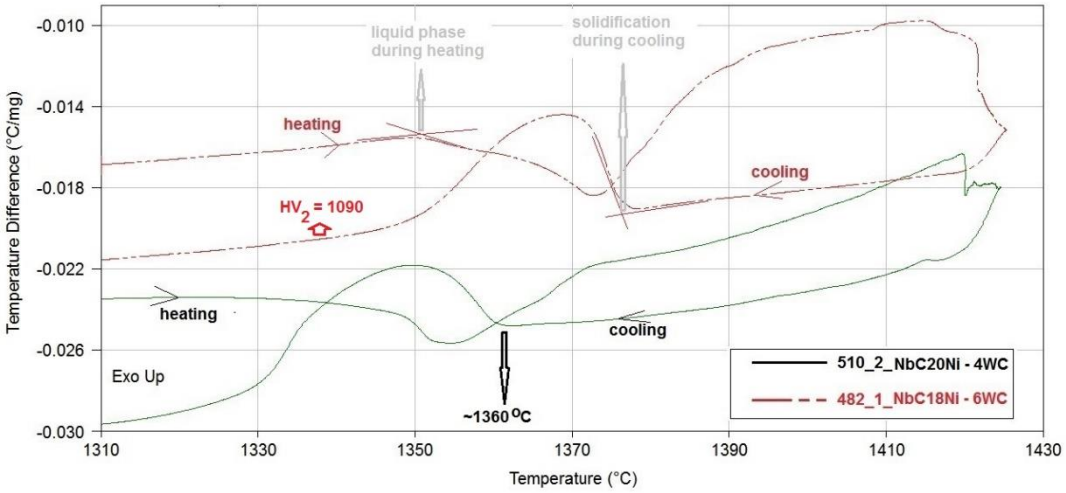


Fig. 4 - DSC curves for NbC-18N-6WC ball milled and NbC-20Ni-4WC attritor milled (15min.), pressed (50MPa) samples. Very quick heating up to 1200ºC, heating up at 10ºC/min. up to 1430ºC, 5 min. at 1430 ºC, and cooling down at 10ºC/min. up to 1200ºC. Dynamic atmosphere of Nitrogen, 200ml/min.

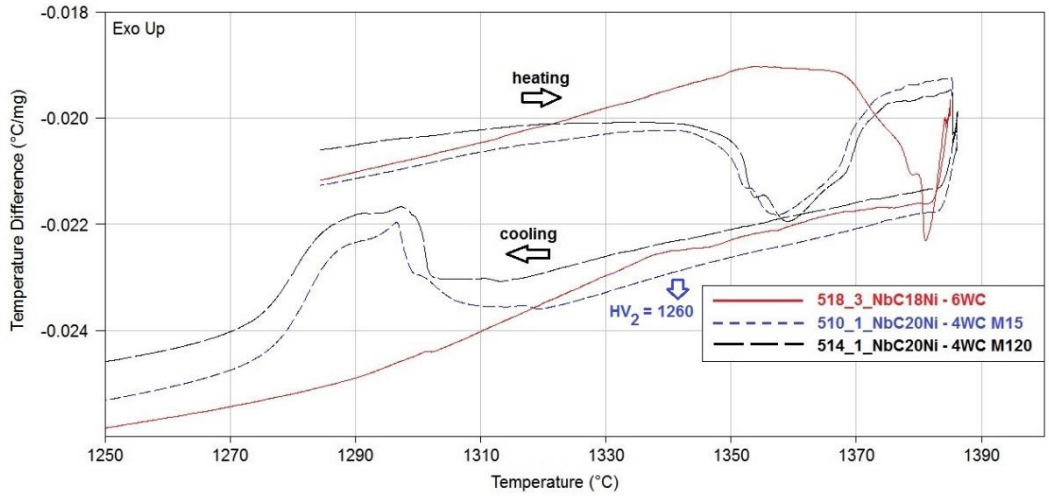


Fig. 5 - DSC curves for NbC-20Ni-4WC attritor milled (15 and 120 min.), and for NbC-18Ni-6WC ball milled, pressed samples. Heating at 20ºC/min. up to 1280 ºC, 60 min. at 1280 ºC, 5ºC/min. up to 1390 ºC, 60 min. at 1390 ºC and colling down at 5ºC/min. up to 1200ºC. A dynamic atmosphere of nitrogen, 200ml/min., was used.

The figure 6 shows dilatometric measurements for samples produced with the ball milled mixture considering two cycles: one with a lower temperature step (1 hour at 1280ºC) and another where the heating up was directly to 1390ºC, with same heating rate (20ºC/min.), staying at this temperature for two hours. The “solid state” sintering (1 hour at 1280ºC) improved shrinkage and final density. Figs. 7 and 8 show the microstructures for these two samples. Microhardness for both samples was similar, close to 1180 (HV_2). Higher level of porosity was observed on the sample sintered directly for 2 hours at 1390ºC. Fig. 9 shows DRX for the mixture (76wt%NbC; 4wt%WC; 18wt%Ni) after 15h ball milling and for sintered samples. It is possible to observe the dissolution of WC, considering the detection limit of x-Ray diffraction. A tungsten content around 10.5wt% was determined by EDS in the binder for 483_3 sintered sample and 3.9wt% for 508_1 sample. This difference should be related to WC nominal content, milling process and the sintering cycle.

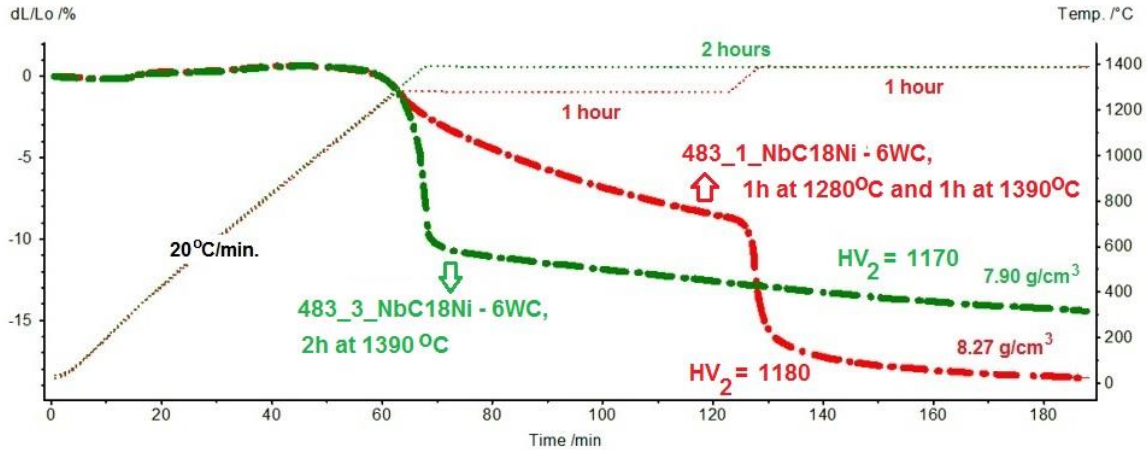


Fig. 6 – Dilatometric curves for NbC-18Ni-6WC ball milled samples pressed at 200MPa. Heating rates of 20°C/min., with (483_1) and without (483_3) a lower temperature (1280°C) step. Dynamic argon (200ml/min.) atmosphere.

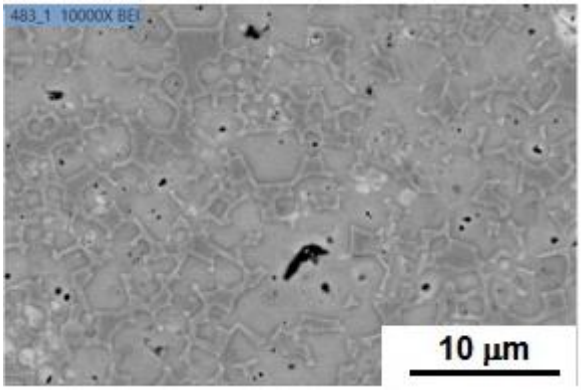


Fig. 7 – Backscattered image of NbC-18Ni-6WC ball milled and pressed (200MPa) sample. Two steps: 1h at 1280°C, and more 1h at 1390°C.

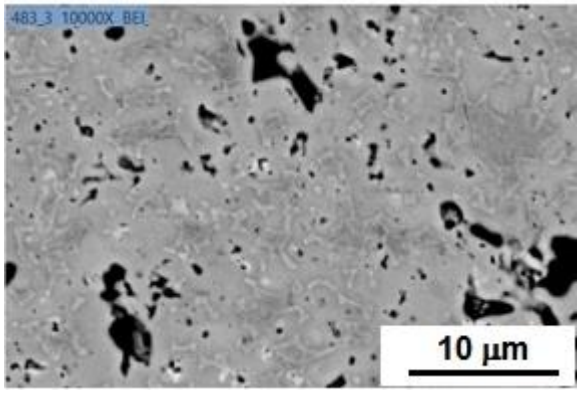


Fig. 8 – Backscattered image of NbC-18Ni-6WC ball milled and pressed (200MPa) sample. One step: 2 hours at 1390°C.

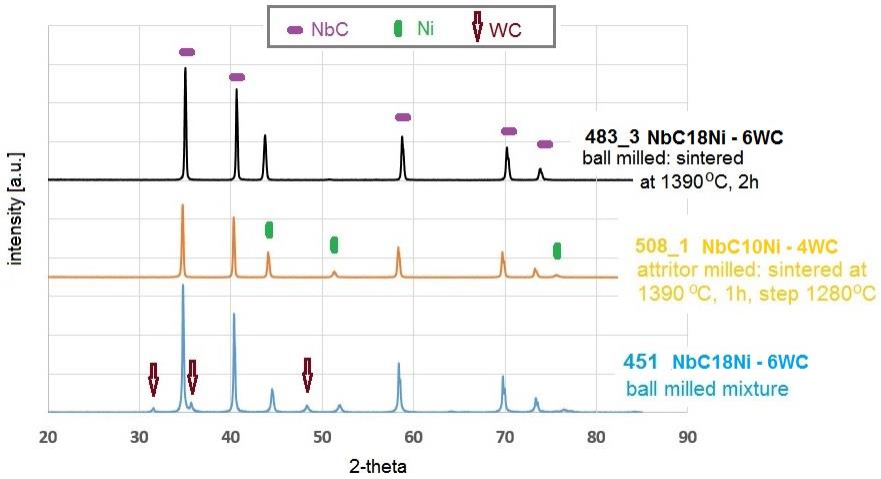


Fig. 9 – DRX for the ball milled mixture and for ball and attritor milled sintered samples. It was used a Cu k-α radiation

The figure 10 evaluates sintering process considering powders ball and attritor milled. For attritor milled pressed sample a lower heating rate (5°C/min.), between 1280 and 1390°C, was used, which allowed to observe the liquid formation at around 1350°C. Fig. 11 shows microstructures of the sintered (as Fig. 10) samples. The coarser grain size for 512_2 sample should be related to the milling process (attritor) and lower heating rate between high temperature soakings.

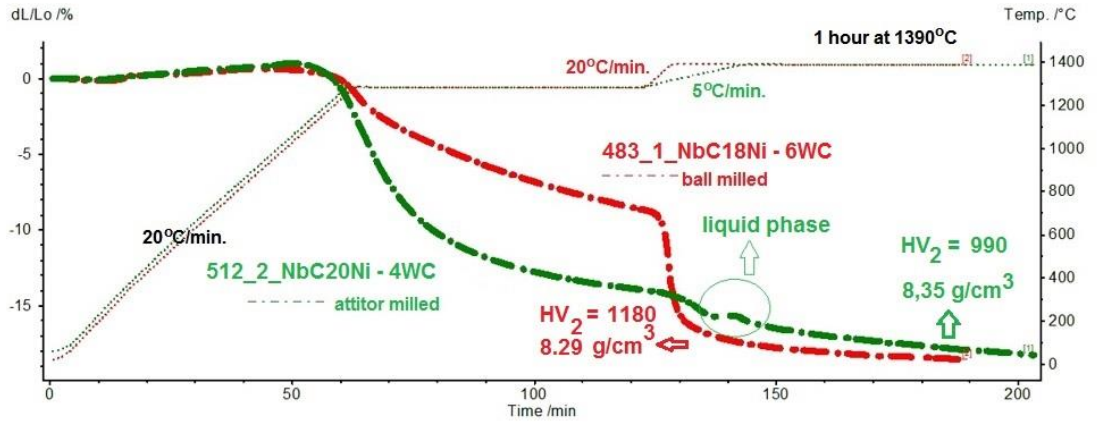


Fig. 10 - Dilatometric curves for NbC-18Ni-6WC ball milled and for NbC20Ni-4W attitor milled pressed (200MPa) samples. Heating rates and high temperature steps as showed on the figure. A dynamic argon (200ml/min.) atmosphere was used.

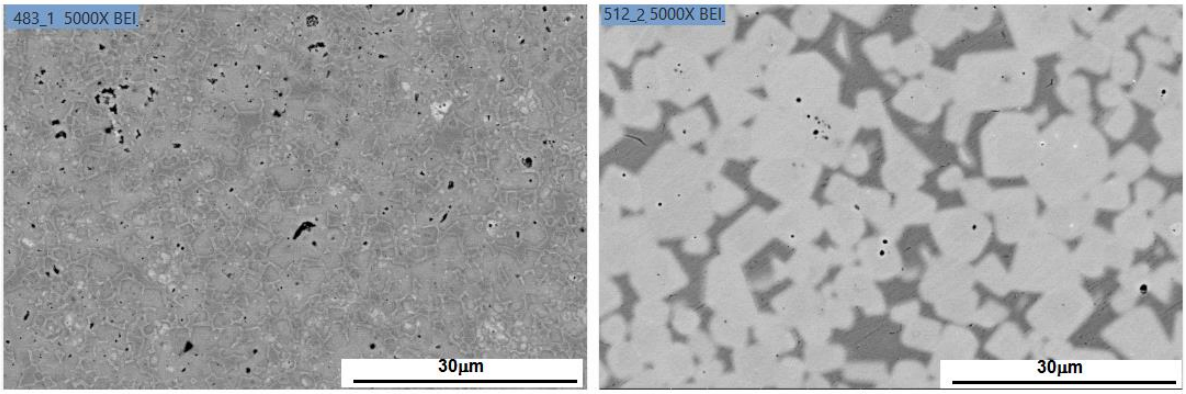


Fig. 11 - Backscattered images for NbC-18Ni-6WC ball milled and for NbC-20Ni-4WC attritor milled pressed (200MPa) and sintered (as Fig. 10) samples.

The figure 12 shows dilatometric curves for attritor milled and pressed samples considering the milling time, 15 and 120 minutes. Figures 13 and 14 show the microstructures of these samples. There were no observed shrinkage differences between samples. The grain size for sample produced with powder milled for longer period (120 minutes) seems to be finer. Figure 15 shows the microstructures of the samples sintered in a DSC/TG equipment. Very small pores can be observed inside NbC carbides. These carbides have different chemical compositions, particularly on their surfaces (interfaces with the binder).

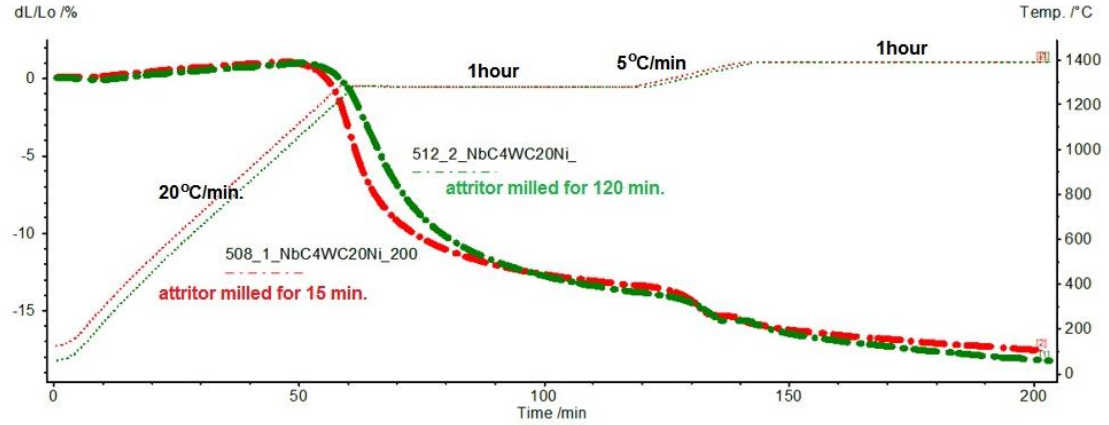


Fig. 12 - Dilatometric curves for NbC-20Ni-4WC attritor milled and pressed (200MPa) samples. Heating rates of 20°C/min., 1 hour at 1390°C and 1hour at 1280°C. The sample 508_1 was from powder milled for 15 minutes and the 512_2 was milled for 120 minutes. A dynamic argon (200ml/min.) atmosphere was used.

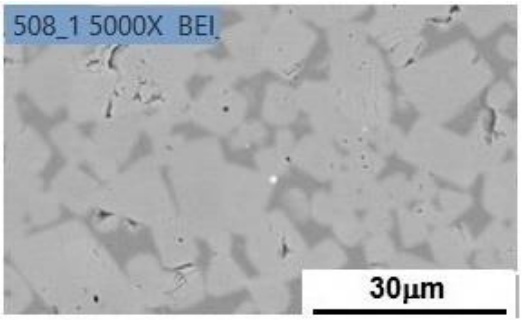


Fig. 13 - Backscattered image for NbC20Ni-4WC attritor milled (15 minutes) and pressed (200MPa) sample. Two steps: 1 hour at 1280ºC, and more 1 hour at 1390ºC.

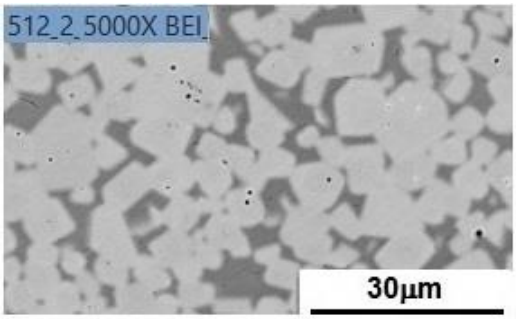


Fig. 14 - Backscattered image for NbC20Ni-4WC attritor milled (120 minutes) and pressed (200MPa) sample. Two steps: 1 hour at 1280ºC, and more 1 hour at 1390ºC.

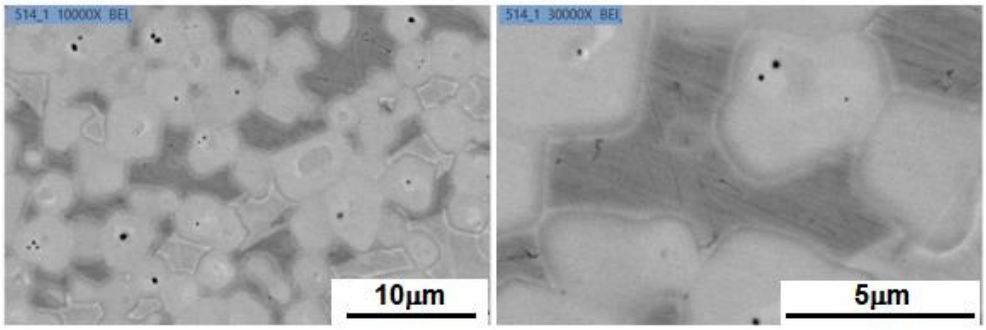


Fig. 15 - Backscattered images for NbC20Ni-4WC attritor milled, pressed (50MPa) and sintered in DSC/TG at 1390ºC with previous lower temperature (1280ºC for 1 hour), sample.

Conclusions

- The interaction between carbides and carbonyl nickel powder seems to be more intense for attritor milled mixture;
- A liquid phase occurs at around 1350ºC during heating up. The chemical composition and sintering cycle affects the behaviour of this liquid phase during cooling;
- The “solid state” (1280ºC) sintering, before sintering step, improves shrinkage and final density for the NbC-18Ni-6WC;
- It was observed that the WC strongly dissolves during sintering, since no DRX peaks for WC were observed on the sintered samples, and a high concentration of tungsten in the binder was determined;
- There are no shrinkage differences, considering dilatometric curves, for attritor milled and pressed samples, considering milling times of 15 and120 minutes. The grain size for sample produced with a longer time milled mixture showed a finer grain size;
- The carbides on the microstructure of the NbC-20Ni-4WC appear to have different chemical compositions, particularly on their surfaces.

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