The Use of NbC20Ni Hard Materials for Hot Rolling Applications

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Abstract

The WC-Co Hard Materials are well-established considering applications as machining cutting tools or steel hot rolling rolls. This paper focused on the hot rolling hard material grade development, investigating the replacement of the WC-Co by NbC-Ni. The Ni content was around 20wt.% and the process variables were adjusted to get a sintered product with hardness close to 1000 HV, typical value for WC-Co for this application. Mixtures of NbC and Ni powders were milled in an attritor mill, uniaxially pressed and sintered. The addition of WC was considered. Prior to the roll production in a high temperature vacuum furnace, thermal analysis (DSC and dilatometry) were carried out to outline the high temperature liquid formation and the shrinkage during sintering. Guide rolls were produced considering previous lab scale results. The samples and rolls were characterized in terms of density, hardness and microstructure. Results were presented and discussed. To evaluate performance, larger rolls will be produced and tests will be carried out under industrial conditions.

Keywords

NbC, cermets, cemented carbides, hard materials, hot rolling

Introduction

The replacement of the Tungsten Carbide (WC) by Niobium Carbide (NbC) is not new [1]. More recently, preliminary results show promising potential, considering applications for components subject to intense wear [2, 3].

The market for cutting tools produced by sintering has been dominated by Tungsten Carbide (WC) since 1930 [4]. Alternative materials for cutting tools such as Titanium Carbide (TiC), called cermets, have been explored for decades [4]. Currently, 80% of the world's Tungsten production, which is 100,000 tons per year, comes from China [5]. It is estimated that 66% of the produced Tungsten is converted into carbides or hardmetals [6, 7], mainly to be used in the manufacture of the "hard metals".

Unlike Tungsten, the economically exploitable Niobium is found almost entirely in Brazil, that has the world's largest reserves of Nb, more than 95% [7]. Also, the world reserves of Niobium are superior to those of Tungsten [6,7,8, 9].

In order to consolidate Niobium Carbide as a substitute for Tungsten Carbide, some challenges must be overcome. It is necessary to explore more fundamental properties that have a relevant technological impact. Thermodynamic and kinetic aspects may direct both the synthesis of Niobium Carbide from the oxide as well as the sintering process in order to obtain microstructures and properties that allow high performance for several applications.

This paper considers the replacement of WC for NbC for hot rolling applications, as illustrated in Figure 1. The binder content used here was close to 20wt% and coarse (or extra-coarse) grain size was the goal to be achieved. Densities higher than 8.0 g/cm^3 and Vickers Hardness (HV_2) close to 1000 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.

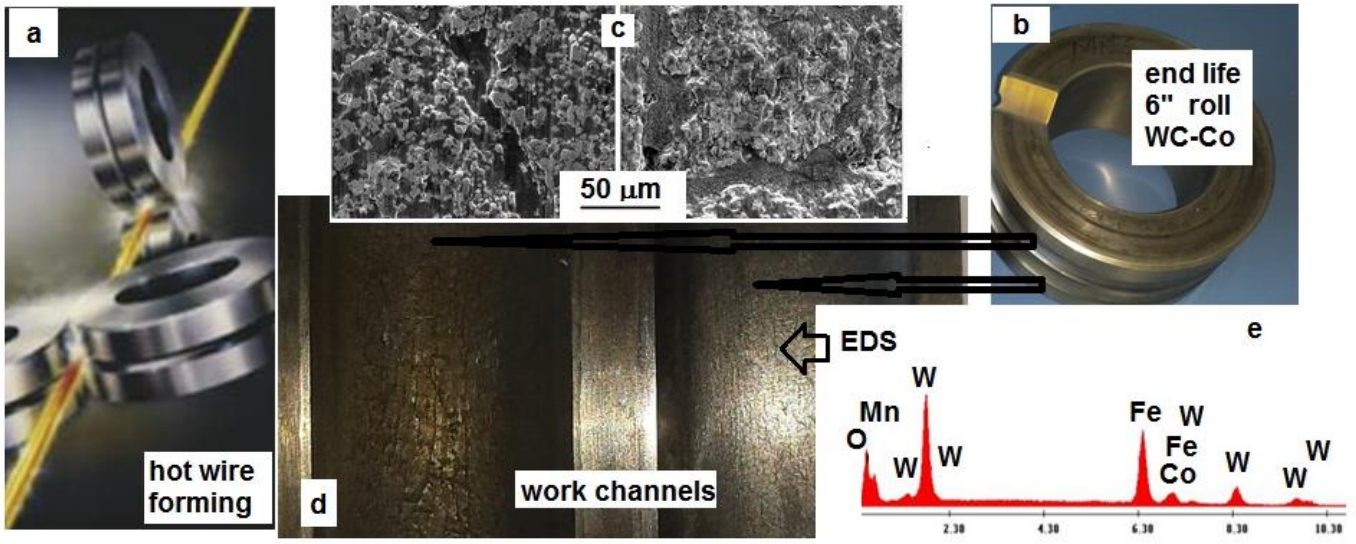


Figure 1 – (a) Illustration of wire hot rolling, (b) commercial WC-Co roll used as reference in this work, (c) Top SEM image for channels indicating thermal cracking, (d) Top optical image for the channel showing a network of cracks, and (e) EDS for a channel, showing the presence of Fe and Mn, from the wire.

Experimental Procedures

Figure 2 shows SEM and EDS for commercial rolls used for wire hot rolling, identified here as CR1 and CR2. It is possible to see a WC grain size close to 5 μm, and a binder content between 15 and 20vol.%. The binder is a mixture of Ni and Co, as identified by EDS, and the usual presence of Cr was detected. The hardness values (HV_2) for CR1 and CR2 are, respectively, 1029±13 and 914±29.

Figure 3 shows SEM for raw materials used here: Ni carbonyl powder with a particle size around 2 μm; NbC produce by carbothermic reduction from Nb_2O_5, and a WC carrier, actually a commercial WC6Co ready-to-press powder. Mixtures of these raw materials were milled under isopropyl alcohol: ball milling for 14/15 hours and attritor milling for 15, 120 or 240 minutes. Cylindrical samples were pressed (30, 50,

or 200MPa) for thermal analysis: 200mg (5.0x1.0mm) for Differential Scanning Calorimetry (DSC); and 2.0g (9.0x8.0mm) for dilatometry. Larger samples and guide rolls were sintered in industrial conditions (high temperature vacuum furnace). All nominal chemical composition mentioned here are in weight percent, so the meaning of NbC20Ni-4WC is: 20wt.% of Ni, 4wt.% of (WC6Co) and 76wt.% of NbC.

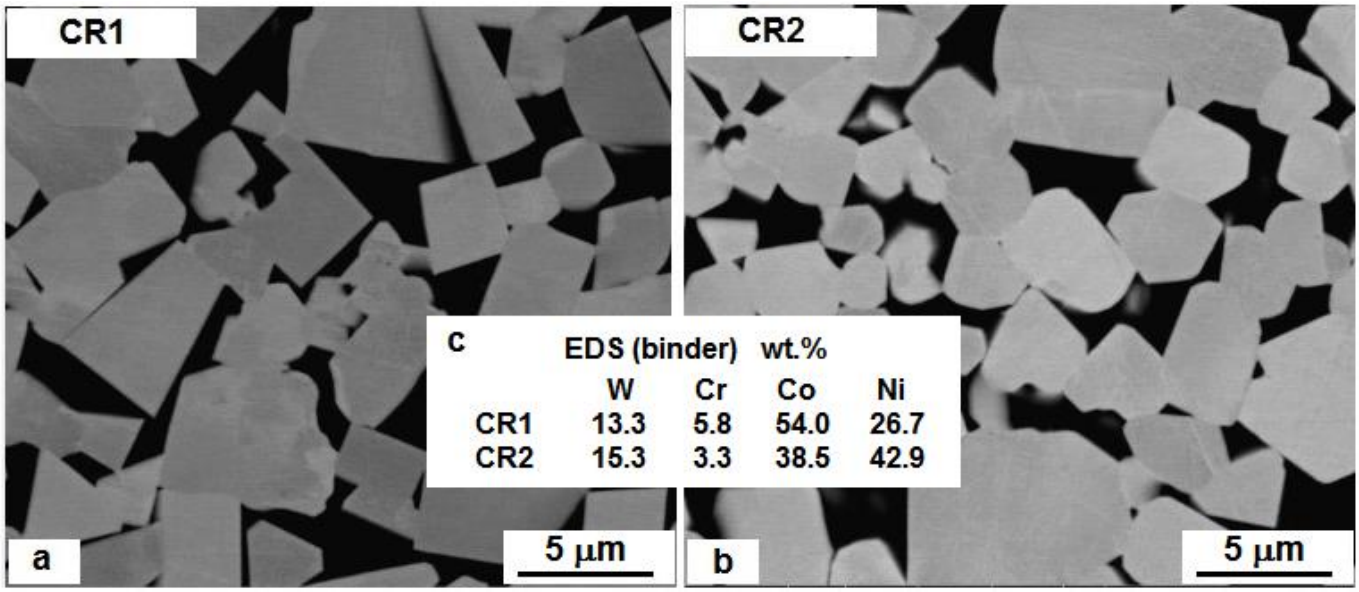


Figure 2 – SEM microstructures for two commercial rolls: (a) CR1, (b) CR2, and (c) qualitative chemical analysis (EDS) for the binder for CR1 and CR2.

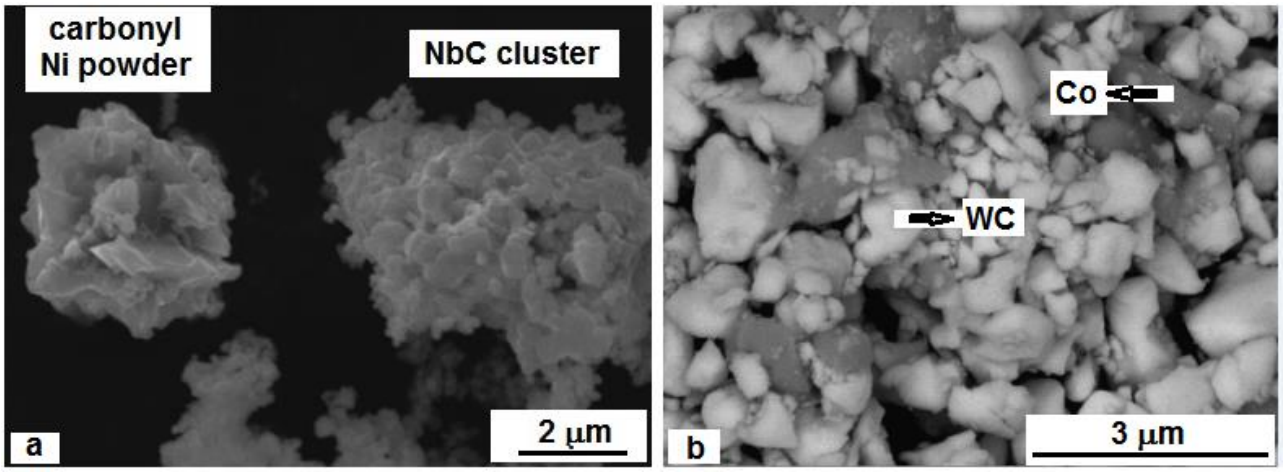


Figure 3 – SEM for raw materials: (a) carbonyl Ni and NbC, and (b) WC carrier, a commercial ready-to-press WC6Co.

Results and Discussion

Thermal Analysis

Table I shows characteristics for thermal analysed samples: Differential Scanning Calorimetry (DSC); and Dilatometry (DIL). The higher density of the WC should be the reason for the higher density for green and

sintered sample. Higher hardness values were obtained for samples with WC, that acts a grain growth inhibitor. DSC measurements are presented in Figure 4 and dilatometric measurements in Figure 5. For "binary" system (without WC) it is possible to observe (Figure 4) an endothermic peak at around 1320ºC, during heating, that should be related to liquid formation. Solidification occurs at around 1340ºC during cooling (exothermic peak). The addition of WC changes these profiles. Two small endothermic peaks (1360 and 1370ºC) were observed during heating. No peaks were observed during cooling, so the formed liquid seems to be transient, in this case.

Table I – Densities (green and sintered) and hardness for thermal analysed samples (DSC and DIL). Powders were ball milled for 14 hours and pressed at 200MPa.

sample	d_g [g/cm³]	d_s [g/cm³]	HV_2 [kgf/mm²]
422_NbC20Ni_DSC	-	-	948±58
425_NbC20Ni-4W_DSC	-	-	1266±49
421_1_NbC20Ni_DIL	4.00	7.32	1019±133
424_1_NbC20Ni-4WC_DIL	4.54	7.98	1176±109

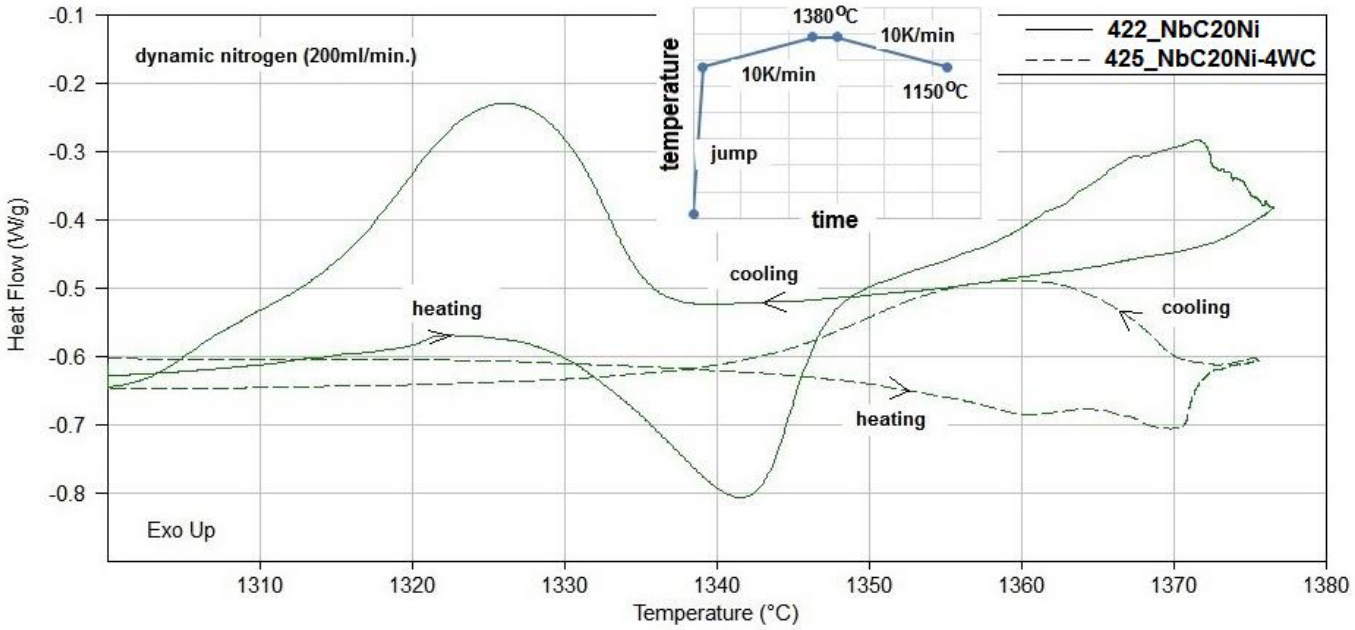


Figure 4 – DSC curve for samples 422 and 425 (see table I). Thermal cycle is presented on the top.

As a tentative to explain the presence of liquid, it is presented in Figure 5 a pseudo-binary NbNi-C, considering 20wt.% of Nickel. There is a broad region for liquid. It is possible to estimate de carbon content looking for the liquidus during DSC experiment. For example, considering Figure 4 and a liquidus around 1340ºC, it is possible to estimate (Figure 5) a carbon content close to 7.5wt.%.

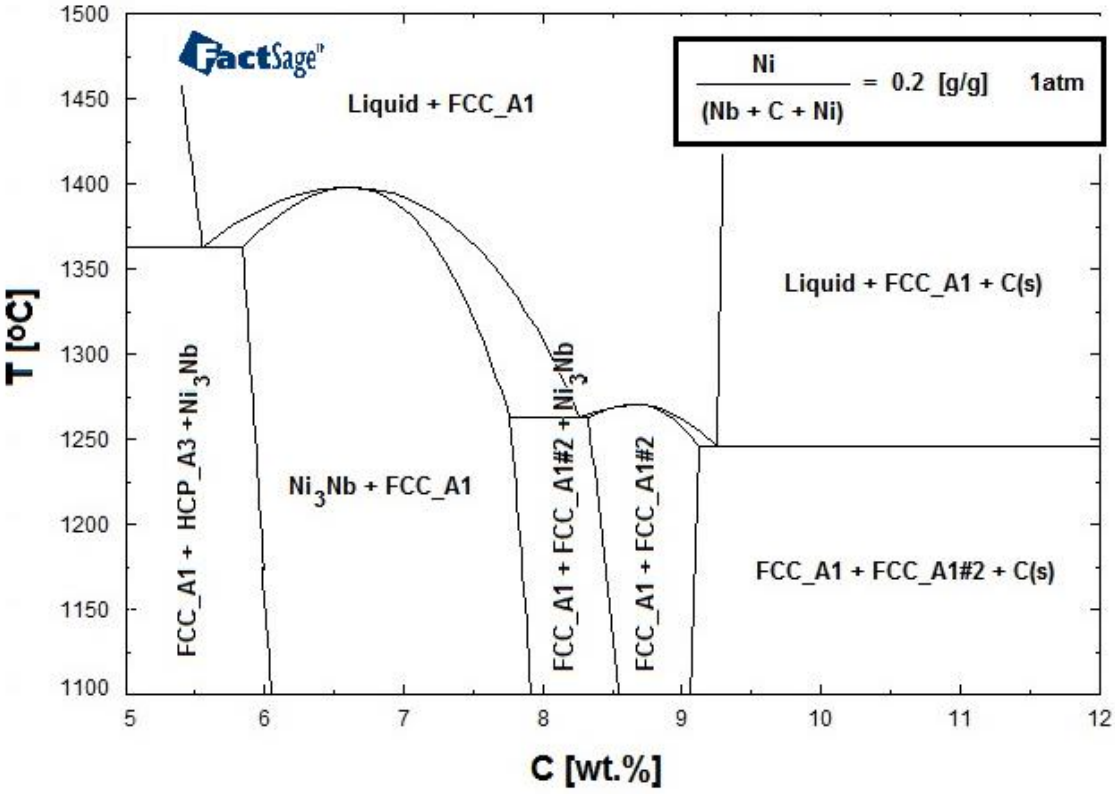


Figure 5 – Pseudo-binary Nb-Ni-C equilibrium diagram for 20wt.% Ni. Figure was created at IPT (Institute for Technological Research - São Paulo)".

Figure 6 shows dilatometric curves considering the effect of WC addition. Shrinkage starts at around 1100ºC for both samples (with and without WC). The presence of WC reduces the total linear shrinkage at 1350ºC, lower than 20%. At this sintering temperature, and with the addition of WC, there is no liquid to the rearrange the NbC particles. The presence of liquid improves shrinkage. Figure 7 presents optical micrographs for these samples, and it is possible to observe the effect of WC on the NbC grain size.

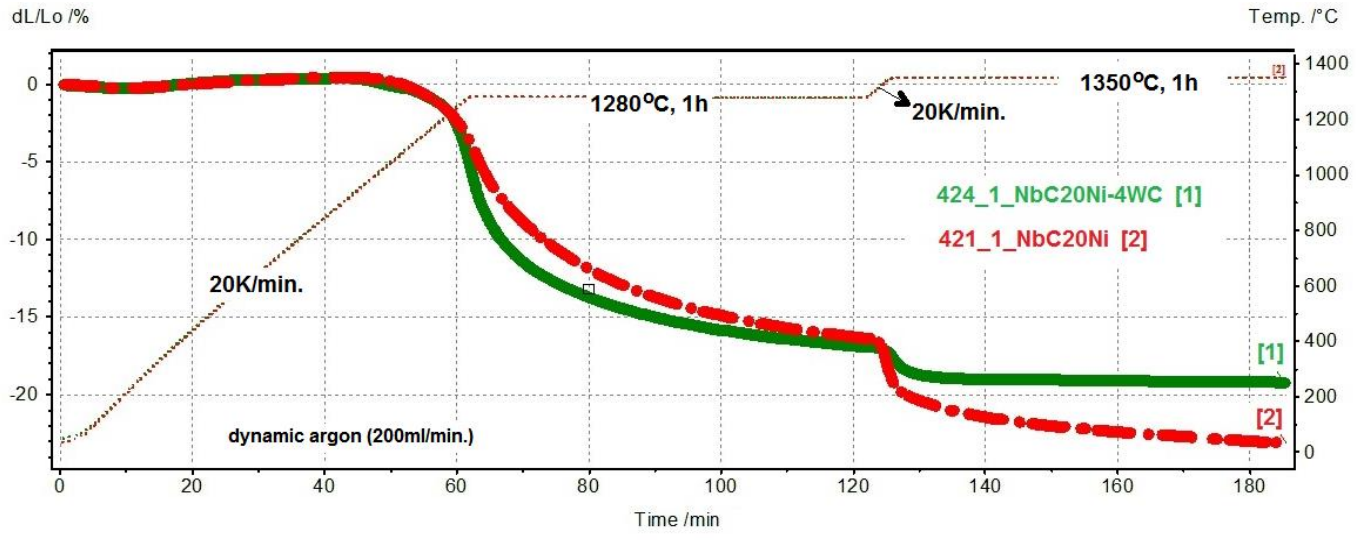


Figure 6 – Dilatometric measurements for 424_1 and 421_1 samples (see table I). Thermal cycle can be achieved at temperature versus time curves.

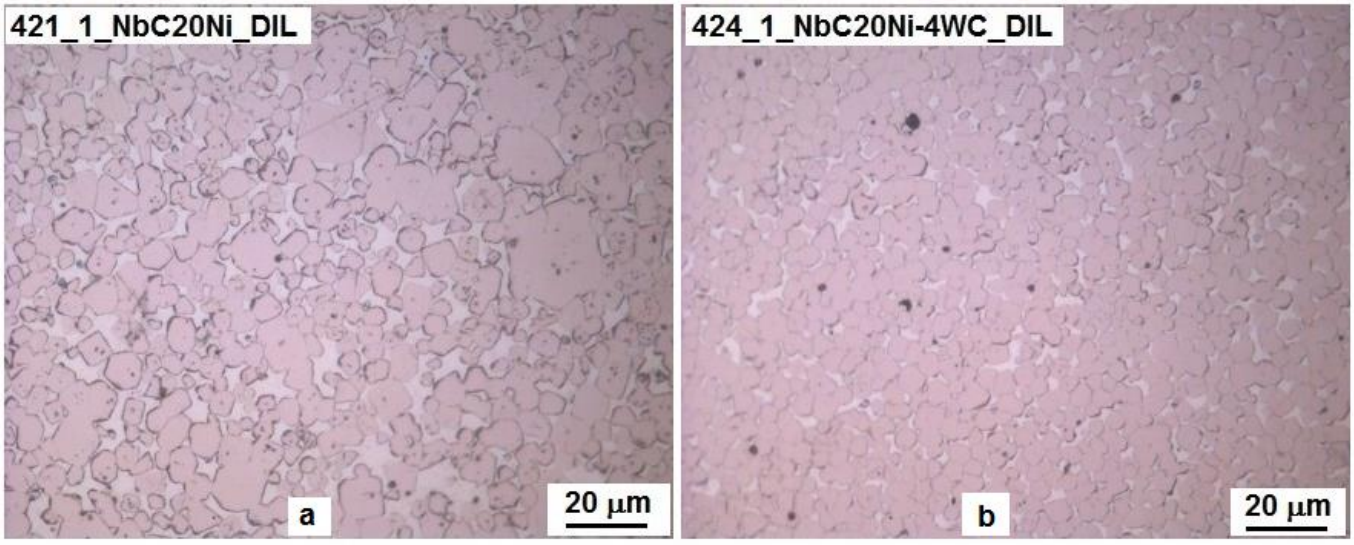


Figure 7 – Optical micrographs (etched) for samples: (a) 421_1, and (b) 424_1, as Table I and Figure 5.

To investigate the use of attritor milling compared with previous long time ball milling, and also to reach an thermodynamic equilibrium condition, a higher temperature (1390ºC) and longer time (3h) DSC measurement was carried out, as showed in Figure 8(a). As pointed out for Figure 4, more than one endothermic peak (liquid) was observed during heating. Two peaks were also observed during cooling: a very small one, close to 1310ºC, that is probably related to the Ni-C eutectic transformation (1316ºC); and a well-defined exothermic peak, bellow to 1300ºC, that should be related to a ternary Nb-Ni-C eutectic phase, probably with a carbon content around 8.5 wt.% (see Figure 5). Figure 8(b) shows an optical micrograph for this DSC sample, that is similar to presented in Figure 7(b).

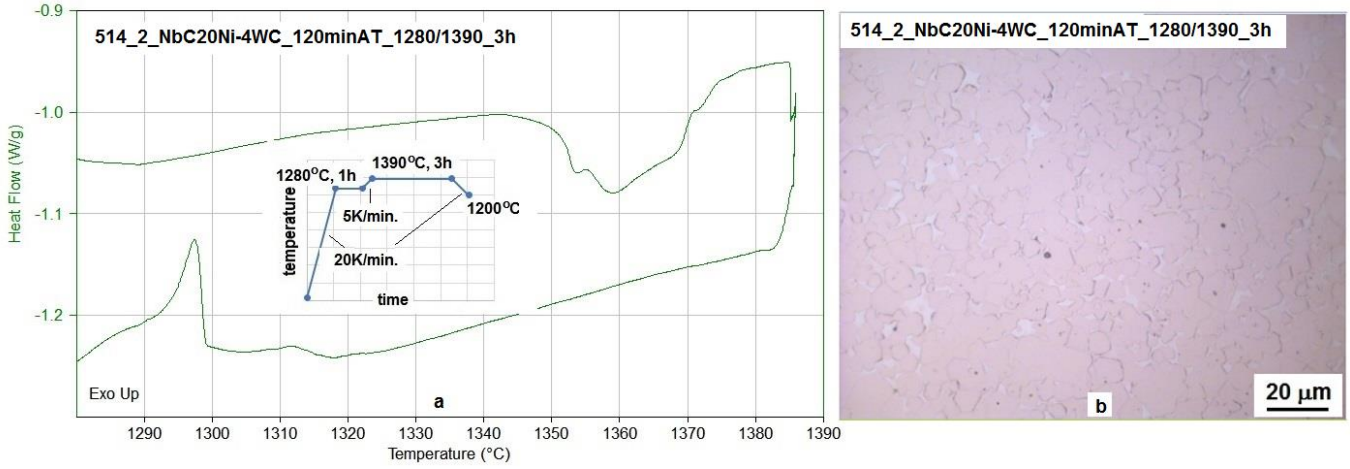


Figure 8 – (a) DSC curve (thermal cycle into the graph) for attritor milled (120 min.) powder pressed at 50MPa, and (b) optical (etched) micrograph for this DSC sample.

To anticipate the behaviour during typical industrial sintering cycles, thermal analysis (DSC and DIL) were carried out using two high temperature steps (1280ºC/1390ºC), as presented in Figure 9 (DSC), simulating a sintering cycle. For the dilatometric measurement (Figure 10), it was also possible to evaluated the

effects of attritor milling time (15 or 120 minutes). The DSC profile presented is like that presented in Figure 8(a).

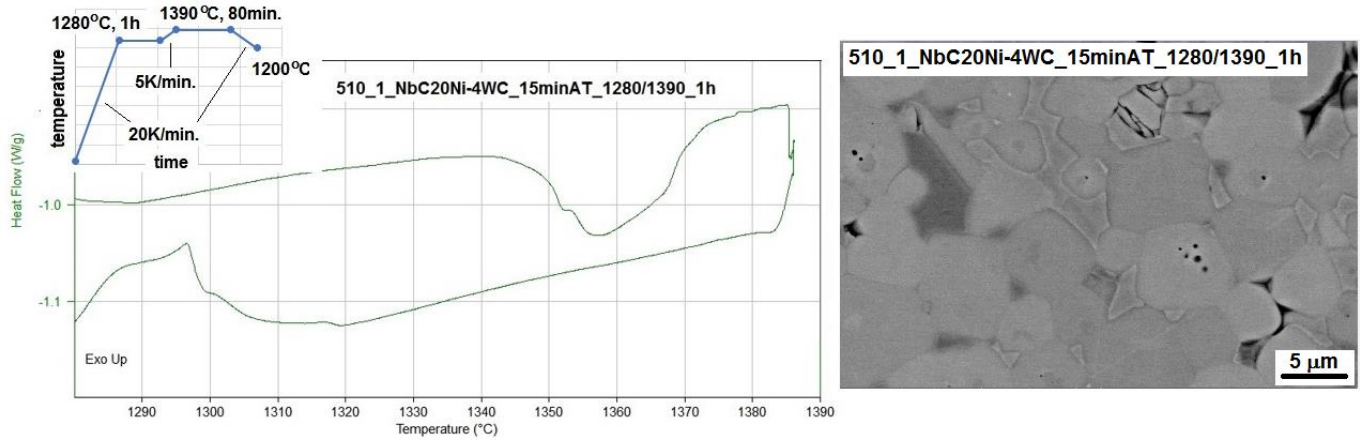


Figure 9 - (a) DSC curve (see thermal on the top, left side) for attritor milled (15 min.) powder pressed at 50MPa, and (b) SEM (etched) micrograph for this DSC sample.

Figure 10 presents dilatometric measurements considering the effects of variables as attritor milling time and compaction pressure. The shrinkage profile was the same for samples (pressed at 200MPa) attritor milled for 15 or 120 minutes. As it was expected, the shrinkage for samples pressed at lower compaction pressure was higher. Figure 11 presents optical micrographs for samples sintered as Figure 10. Milling time and compaction pressure do not affect the microstructures, that was confirmed by the values of densities and hardness (Figure 10). Figure 12 presents SEM images for two samples sintered in the dilatometer. The qualitative chemical analysis (EDS) shows high concentrations of Nb and W in the binder.

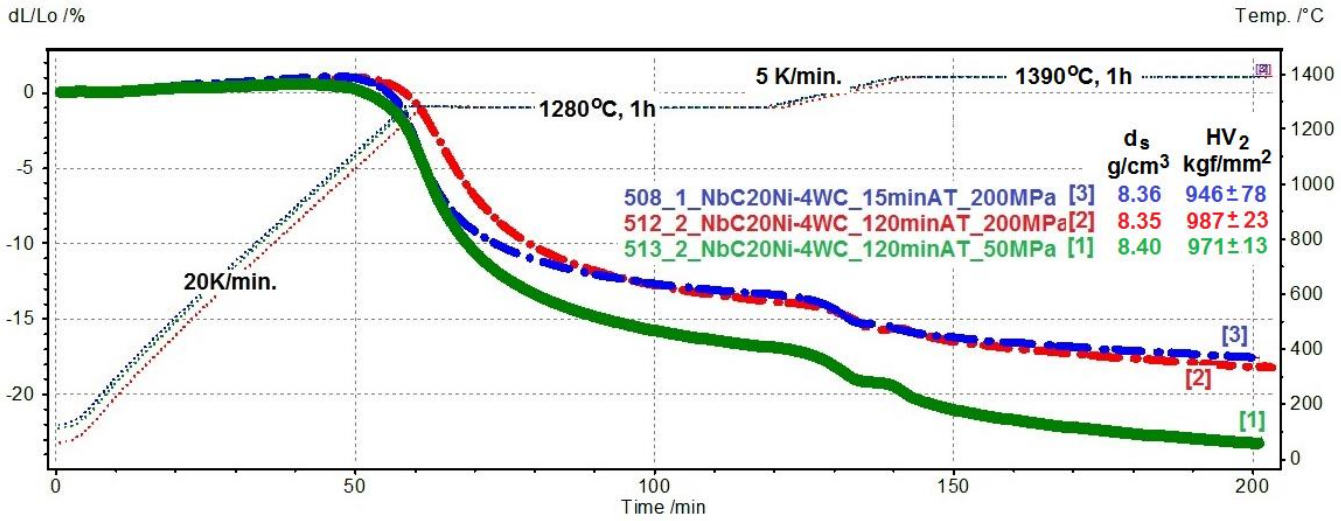


Figure 10 – Dilatometric measurements for 508_1, 512_2 and 513_3 samples. Thermal cycle can be achieved at temperature versus time curves. Densities and hardness are also presented in the figure.

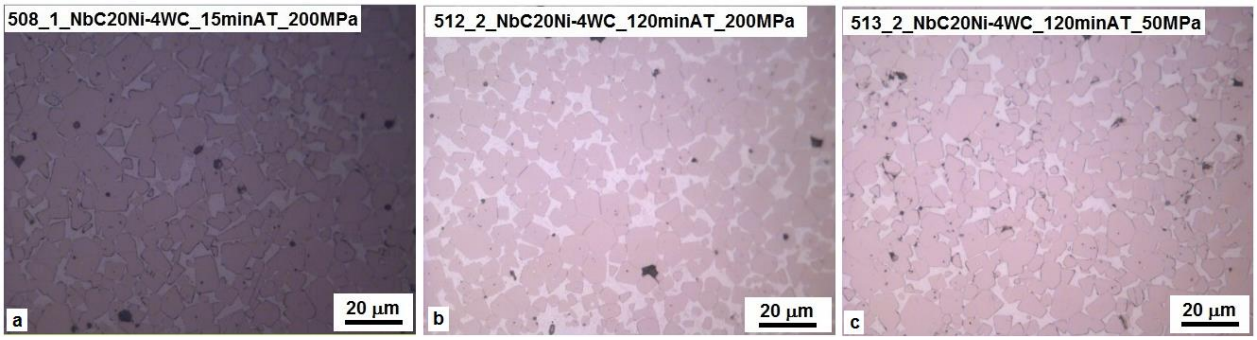
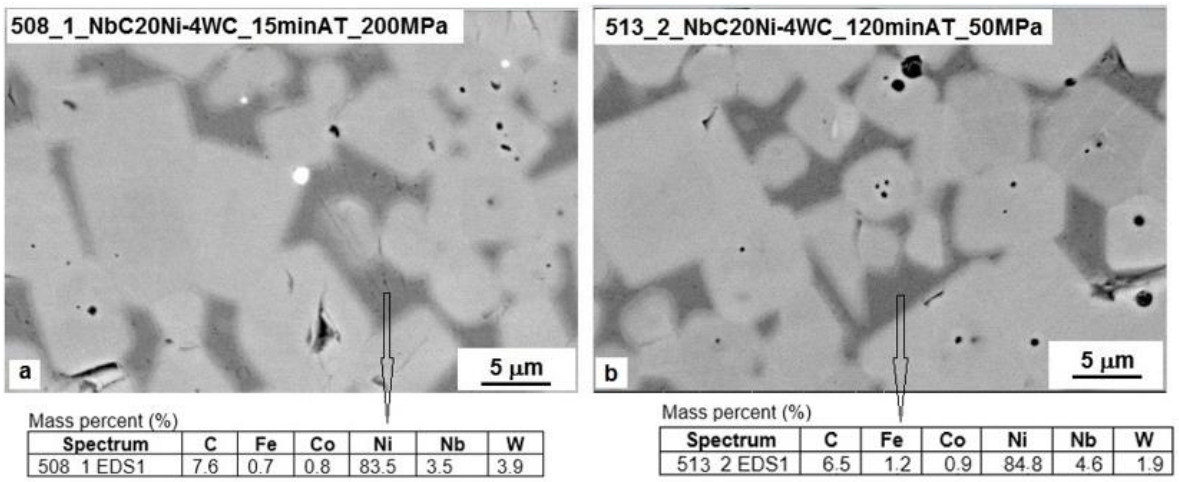


Figure 11 – Optical micrographs (etched) for samples sintered in a dilatometer (Figure 9).



Mass percent (%)

Spectrum	C	Fe	Co	Ni	Nb	W
508_1 EDS1	7.6	0.7	0.8	83.5	3.5	3.9

Mass percent (%)

Spectrum	C	Fe	Co	Ni	Nb	W
513_2 EDS1	6.5	1.2	0.9	84.8	4.6	1.9

Figure 12 – SEM imagens and EDS for 2 samples sintered in a dilatometer (Figure 9).

Higher attritor milling time (240 minutes) was also investigated. Figure 13 shows dilatometric curves for samples pressed at 30MPa. Shrinkage for sample sintered directly for 2 hours at 1390 ^{o}C was higher. It is possible to observe for all curves a swelling that should be related to liquid formation. Considering attritor milled for 15 or 120 minutes' batches, there is no significant differences considering hardness (Figure 13) and microstructure (Figure 14) with 240 minutes milling.

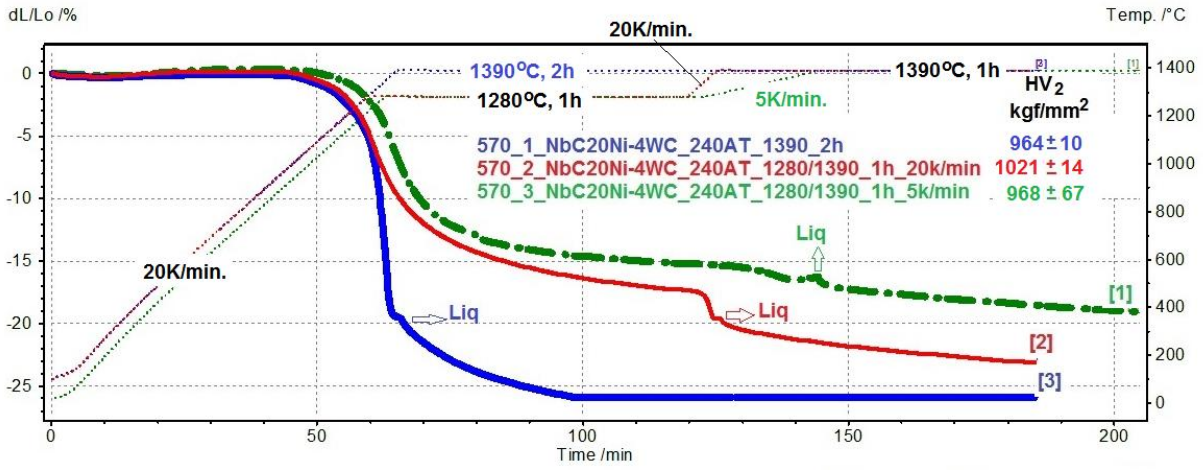


Figure 13 - Dilatometric measurements for 570_1, 570_2 and 570_3 samples. Thermal cycle can be achieved at temperature versus time curves. Densities and hardness are also presented in the figure. Samples were pressed at 30MPa.

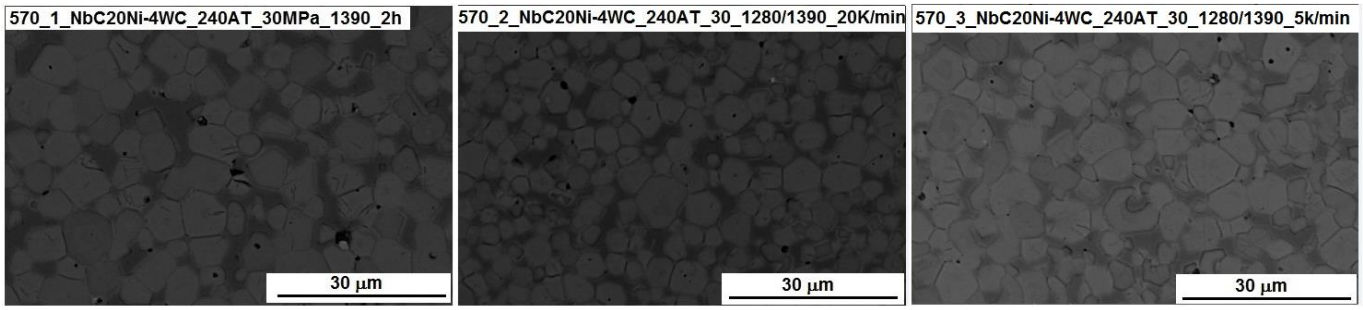


Figure 14 – SEM imagens for 3 samples sintered in a dilatometer (Figure 12).

To get even higher hardness, a NbC18Ni-6WC (lower Ni and higher WC content) batch was produced by ball milling (15h). Figure 15 shows DSC curve for a two-stage sintering. Previously the sample (pressed at 200MPa) was heated up at 1280ºC for one hour and at 1200ºC for more one hour, and then cooled. DSC curve for Figure 15(a) was plotted after that cycle, and a sintering step at 1420ºC for 30 minutes was carried out. It is possible to observe melting during heating (endothermic peak) that started at 1360-1370ºC, and solidification (exothermic peak) at 1370ºC. Figure 14(c) shows final microstructure. The obtained hardness (HV_2) was 1166±28.

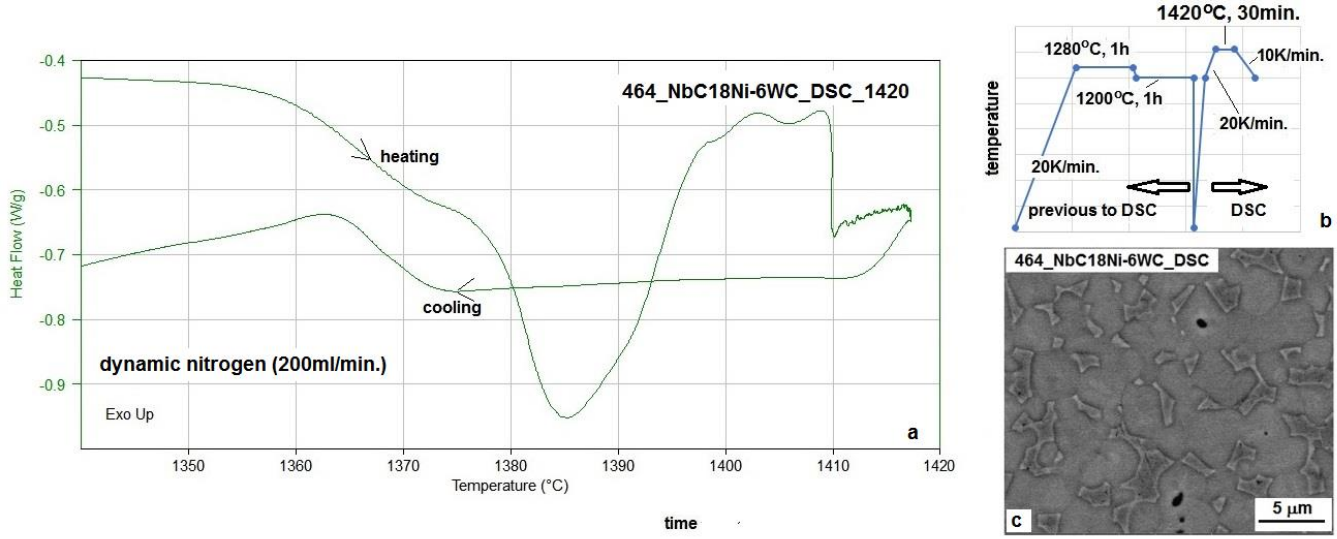


Figure 15 - (a) DSC curve for 464 sample, (b) thermal, and (c) SEM (etched) micrograph for this DSC sample.

Figure 16(a) shows dilatometric curve for the same batch. Figure 16(b) presents a SEM image and qualitative chemical analysis for this sample. Microstructure is similar to that previously presented. The hardness value (HV_2) was 1167±20.

Sintering in Industrial Conditions

Based on thermal analysis, some samples were sintered under vacuum (mechanical pump) in a high temperature cold wall furnace. Table II presents some data for these samples. Samples produced with

longer time powder attritor milled mixture presented higher hardness. The reduction of binder content associated with a higher WC content produced samples with higher hardness.

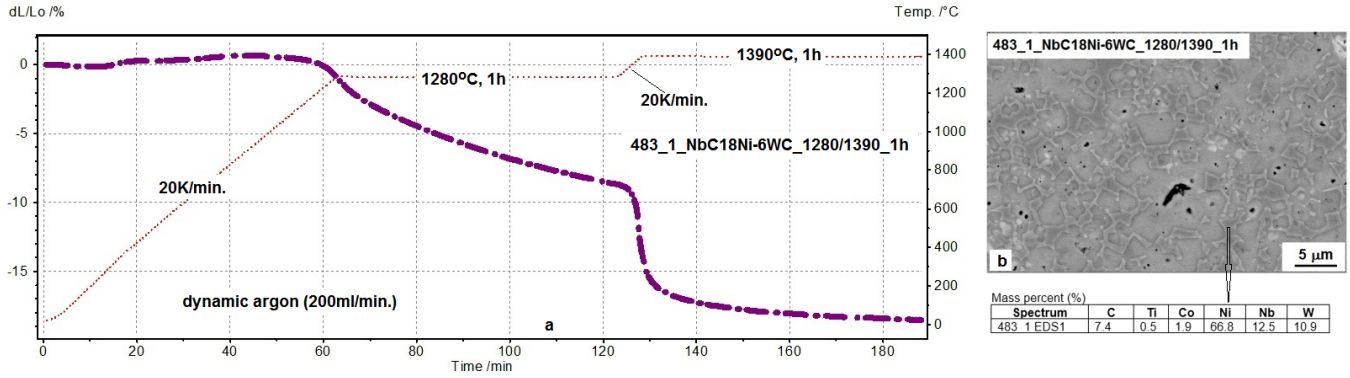


Figure 16 – Dilatometric measurements for 483_1 sample. Thermal cycle can be achieved at temperature versus time curves. Samples was pressed at 200 MPa.

Table II – Data for samples sintered in industrial condition. Compaction pressure was 50MPa.

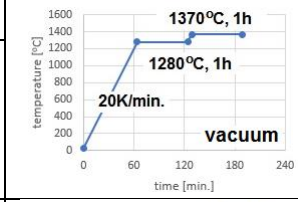
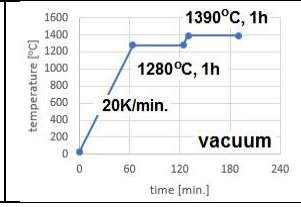
sample	milling time	dg [g/cm³]	ds [g/cm³]	HV2 [kgf/mm²]	sintering cycle industrial furnace
511_NbC20Ni-4WC	attritor: 15 min.	4.21±0.02	8.03±0.06	959±35	
515_NbC20Ni-4WC	attritor; 120 min.	4.19±0.07	8.08±0.06	1010±18	
517_1_NbC18Ni-6WC	ball: 15 hours	4.23±0.06	8.02±0.01	1232±44	

Figure 17 shows optical micrographs for these samples, compared with a micrograph for CR2. Grain size and binder distribution for 511, 515, and CR2 samples are quite close. Samples 517 presented a microstructure that explain the higher hardness (smaller grain size).

Two sets of guide rolls, as illustrated in Figure 17(a), were produced. Figure 17(b) compares microstructures of these guide rolls with that for commercial roll (CR1). Table III summarize some results. The NbC20Ni-4WC attritor milled 120 minutes mixture were pressed at 30 and 50 MPa. Rolls were sintered at 1370°C for 1 hour under vacuum. A previous 1280°C step (hour) was used. The hardness and microstructures of guide rolls are equivalent to that for commercial rolls.

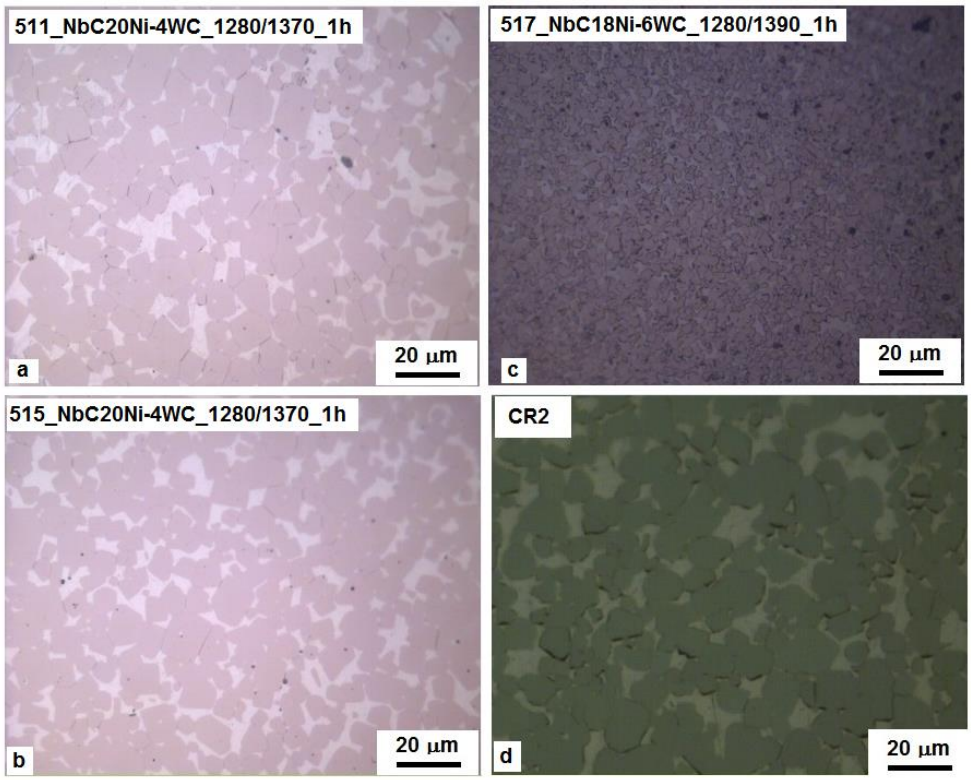
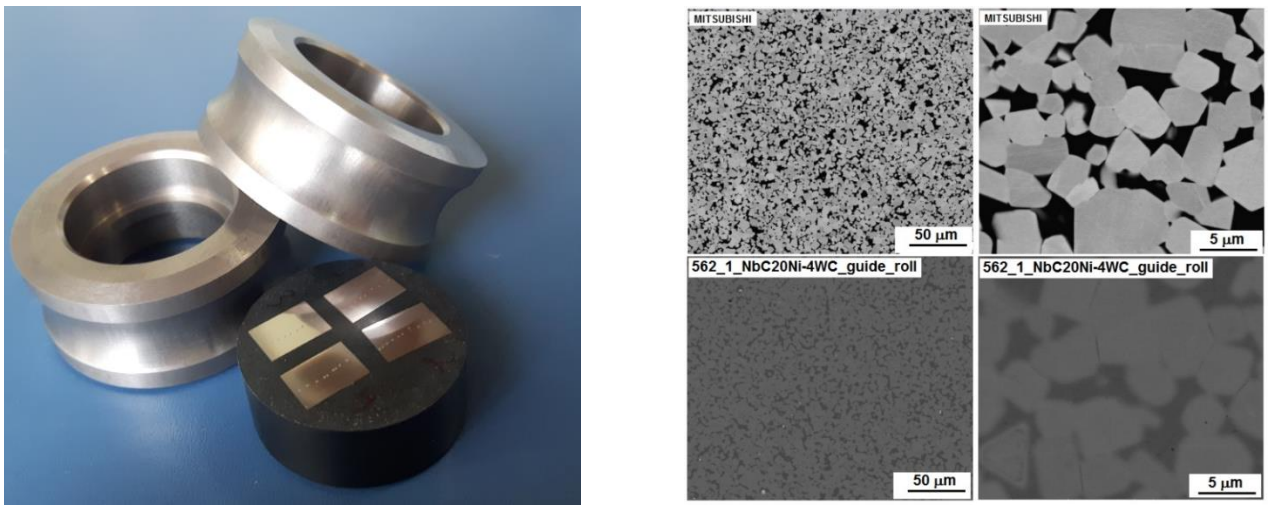


Figure 17 – Optical micrographs (etched) for samples sintered in industrial conditions (table II) compared with microstructure for a commercial roll (CR2).

Table III – Guide rolls sintered at 1370 ^{o}C for 1 hour under vacuum (previous step at 1280 ^{o}C/1h).

sample	P_{compac} [MPa]	d_g [g/cm^3]	d_s [g/cm^3]	HV_2 [kgf/mm^2]
561_3_NbC20Ni-4WC	30	4.35±0.05	8.07±0.30	1051±17
562_2_NbC20Ni-4WC	50	4,32±0.04	8,06±0.24	



a b

Figure 17 – (a) view of guide rolls produced here, and (b) comparison of microstructures (SEM) of guide rolls and commercial roll (CR1).

Conclusions

- Higher hardness values were obtained for NbC20Ni samples with WC, that acts a grain growth inhibitor.
- DSC measurement detected liquid formation during heating, for all samples, at temperatures higher than 1300^{o}C. The identification of a liquidus during cooling depends of the thermal cycle, and binders' carbon content. Higher liquidus were determined for samples with tungsten;
- Cooling DSC curves for samples "over-sintered", i.e., close to thermodynamic equilibrium, showed exothermic peaks at temperatures lower than 1300 ^{o}C, and should be related to high carbon Nb-Ni-C eutectic phase;
- Linear shrinkage measured by dilatometry was around 20%. The presence o tungsten reduces shrinkage. Depending of the thermal cycle, it is possible so observe swelling related to liquid formation;
- The hardness and microstructures of NbC20Ni-4WC guide rolls sintered in a high temperature vacuum furnace are equivalent to that for observed for WC-Co commercial rolls.

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