The Use of NbC20Ni Hard Materials for Hot Rolling Applications

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Daniel Rodrigues[1], Eduardo Cannizza[2]

EHTCANNIZZA CONSULTORIA EM ENGENHARIA LTDA

BRATS SINTERED FILTERS SPECIAL METALIC POWDERS

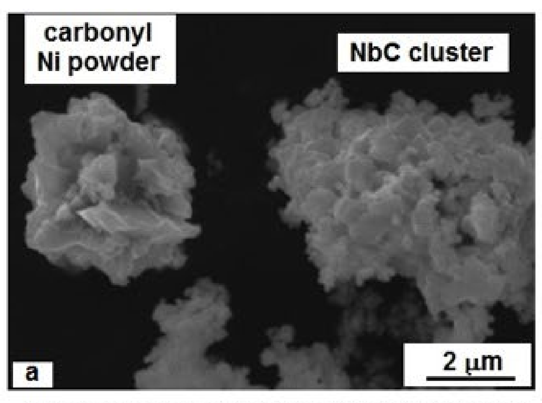
[1] BRATS Sintered Filters & Metallic Powders, São Paulo, Brazil
[2] EHTCANNIZZA – Consultoria em Engenharia, São Paulo, Brazil

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.

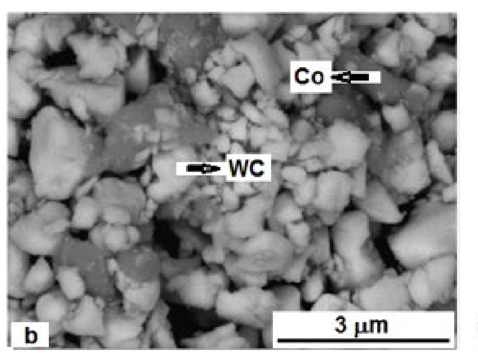
Introduction

The replacement of the Tungsten Carbide (WC) by Niobium Carbide (NbC) is not new, but the market has been dominated by WC since 1930. Currently, 80% of the world's Tungsten production, which is 100,000 tons per year, comes from China. It is estimated that 66% of the produced Tungsten is converted into carbides or hardmetals, 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%. 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. 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.

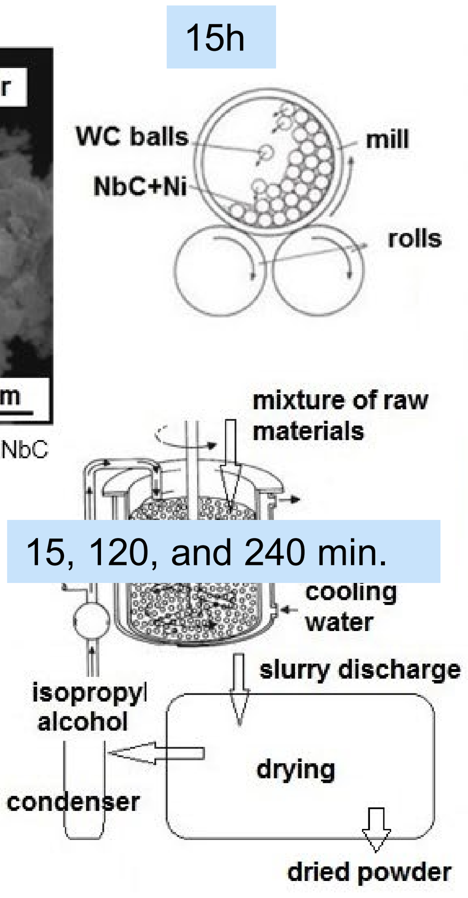
Experimental Procedures

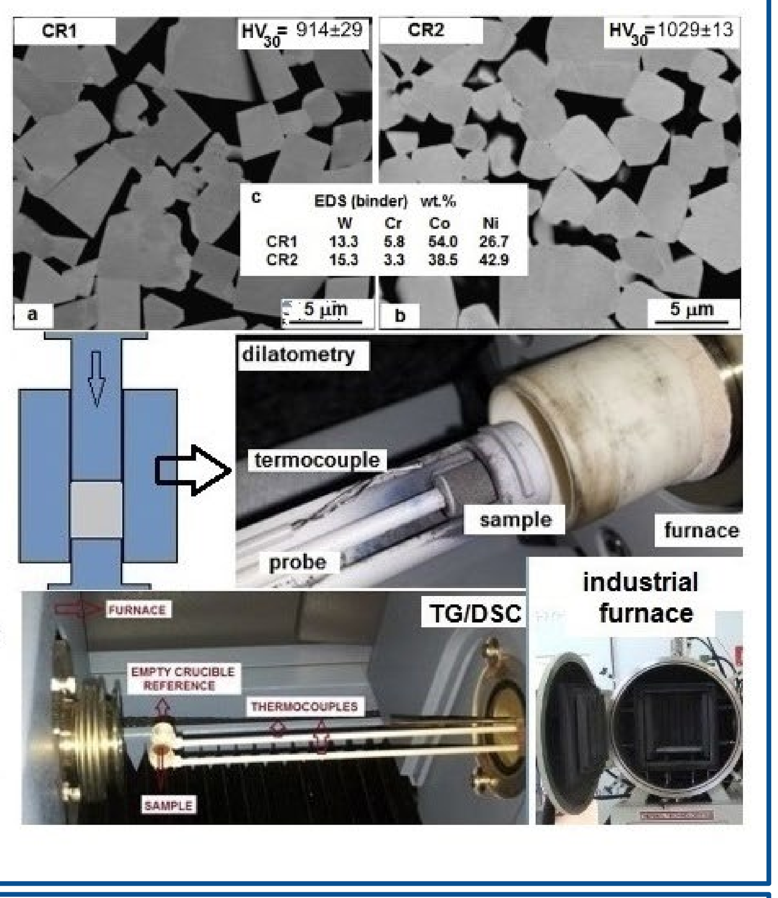


SEM for raw materials: (a) carbonyl Ni and NbC



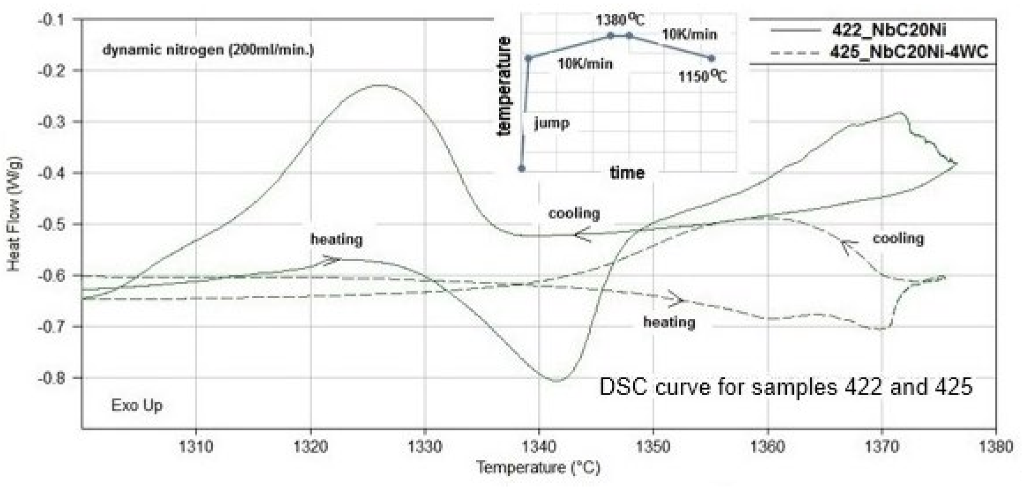
WC carrier, a commercial ready-to-press WC6Co.





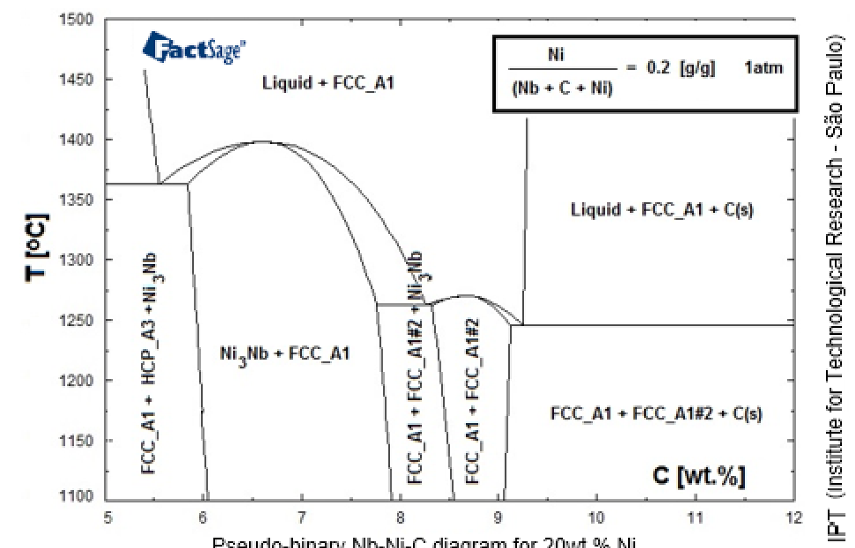
Results and Discussion

ball milling

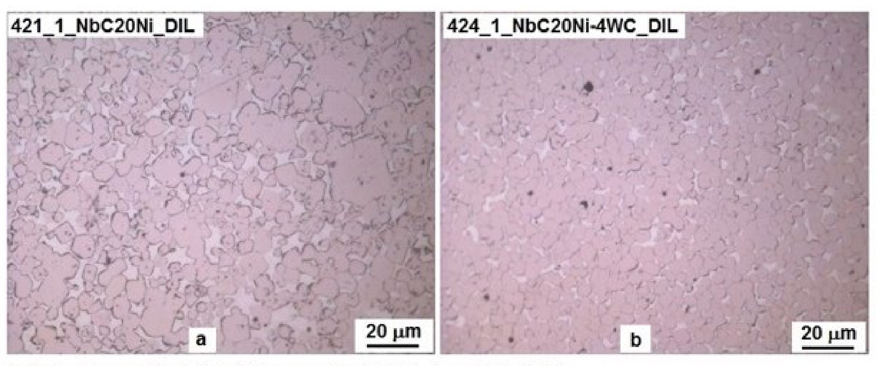


sample	d_g [g/cm³]	d_s [g/cm³]	HV_2 [kgf/mm²]
422_NbC20Ni_DSC	-	-	948±58
425_NbC20Ni-4W_DSC	-	-	1266±49

An endothermic peak ("binary" system) at ~1320°C, during heating (liquid formation). Solidification occurs at ~1340°C during cooling. WC addition changes profiles. Two small endothermic peaks (1360 and 1370°C) were observed during heating. No peaks were observed during cooling, so the formed liquid seems to be transient, in this case.

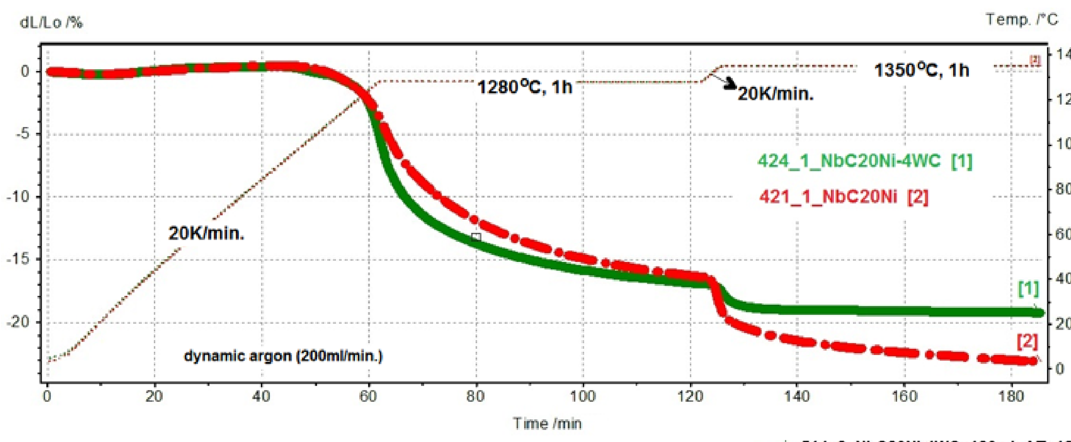


Pseudo-binary Nb-Ni-C diagram for 20wt.% Ni.



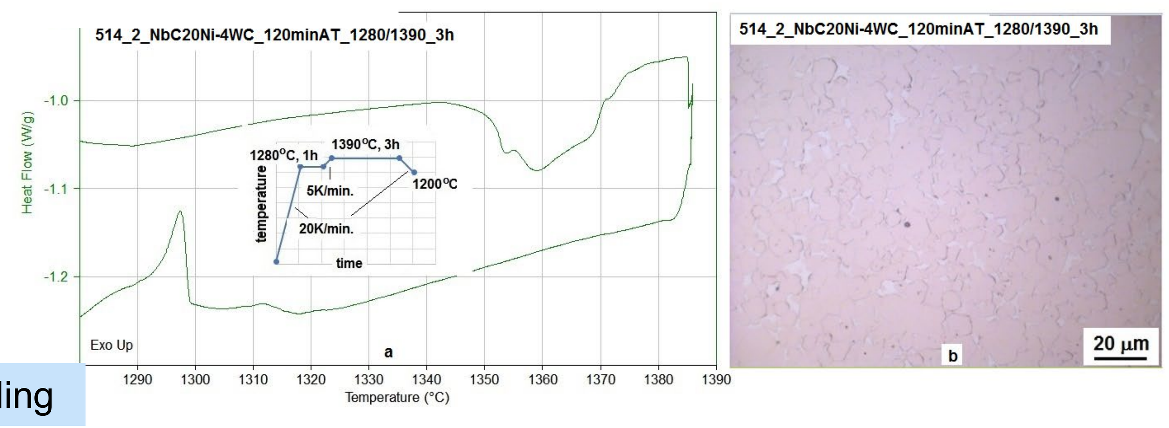
Optical micrographs (etched) for samples: (a) 421_1, and (b) 424_1

sample	d_g [g/cm³]	d_s [g/cm³]	HV_2 [kgf/mm²]
421_1_NbC20Ni_DIL	4.00	7.32	1019±133
424_1_NbC20Ni-4WC_DIL	4.54	7.98	1176±109



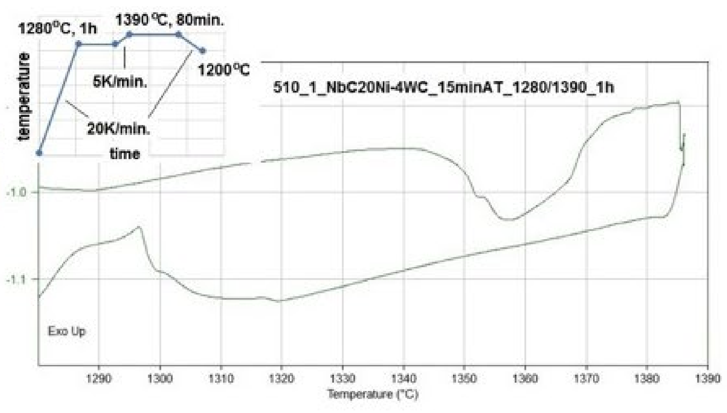
Shrinkage starts at around 1100°C (with and without WC). WC reduces the total linear shrinkage. At 1350°C, and with the addition of WC, there is no liquid to the rearrange the NbC particles.

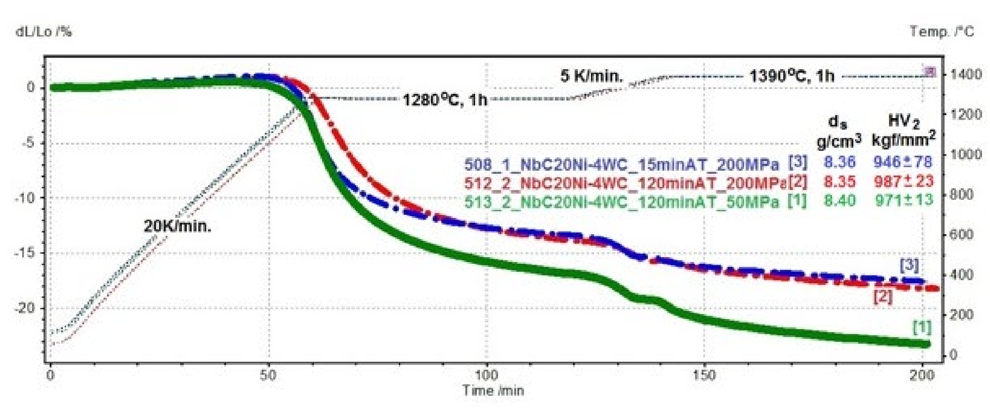
Endo peaks (liquid) were observed during heating. Two peaks were observed during cooling: close to 1310°C (Ni-C eutectic transformation ~1316°C); and a well-defined exo peak, bellow to 1300°C (Nb-Ni-C eutectic phase, 8.5 wt.% C).

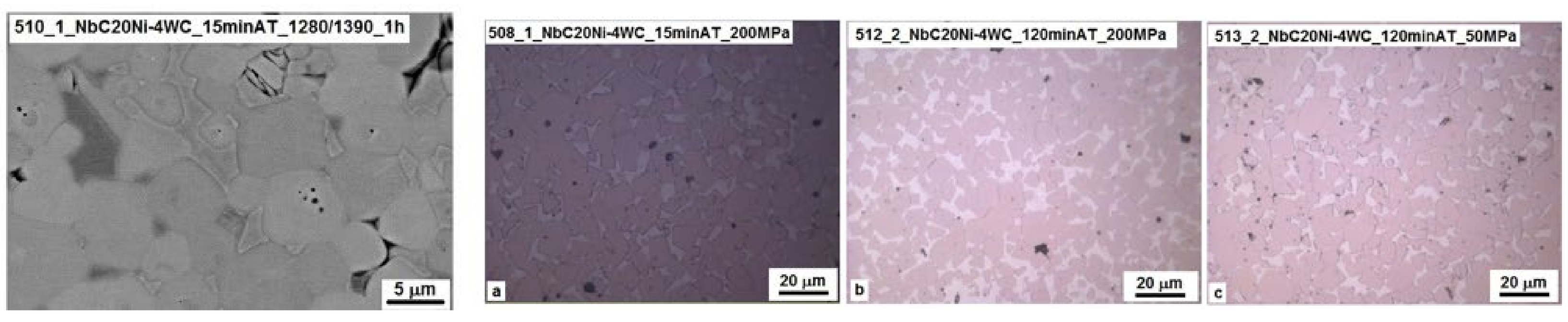


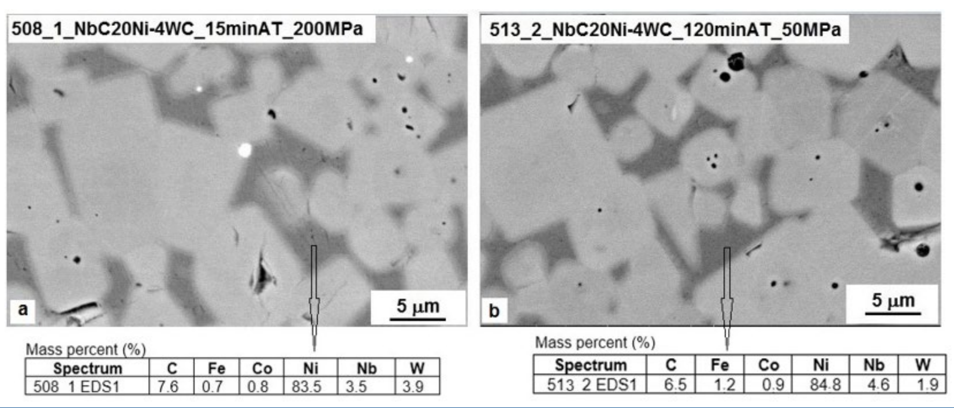
attritor milling

To anticipate the behaviour during typical industrial sintering cycles, thermal analysis (DSC and DIL) were carried out using two high temperature steps (1280°C/1390°C). 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.









Mass percent (%)

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

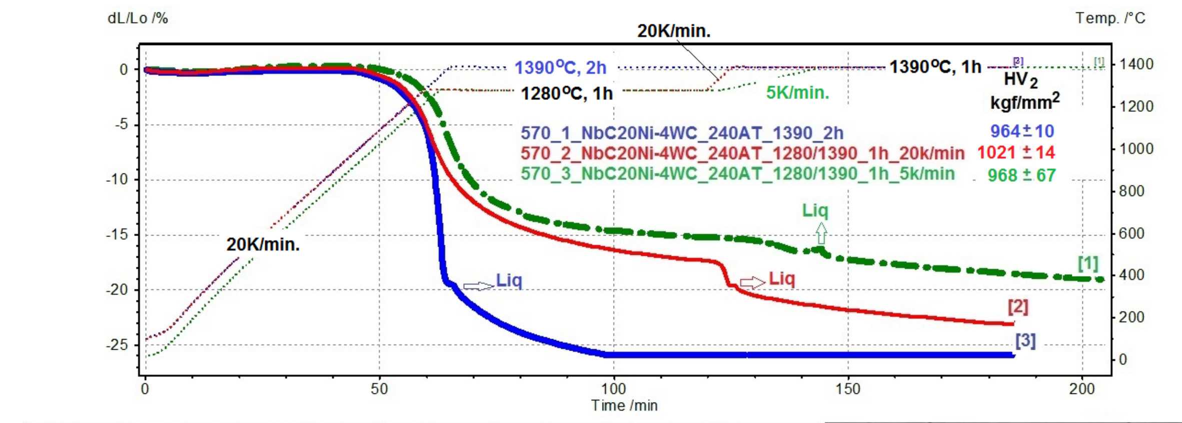
Mass percent (%)

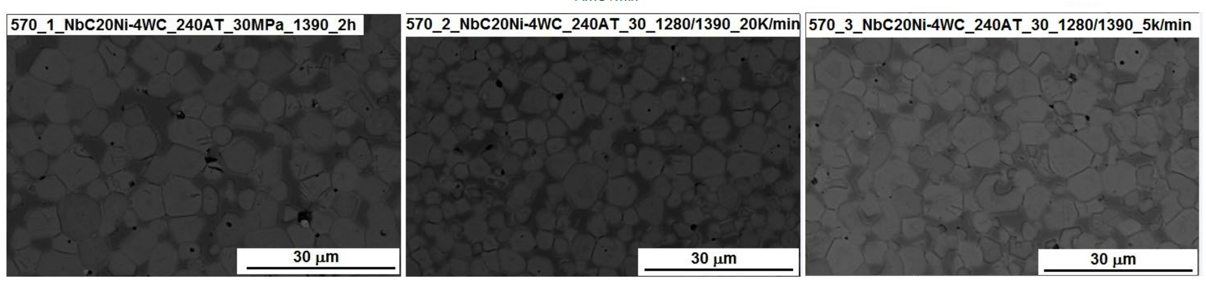
Spectrum	C	Fe	Co	Ni	Nb	W
513_2 EDS1	6.5	1.2	0.9	84.8	4.6	1.9

SEM images for two samples sintered in the dilatometer. The qualitative chemical analysis (EDS) shows high concentrations of Nb and W in the binder

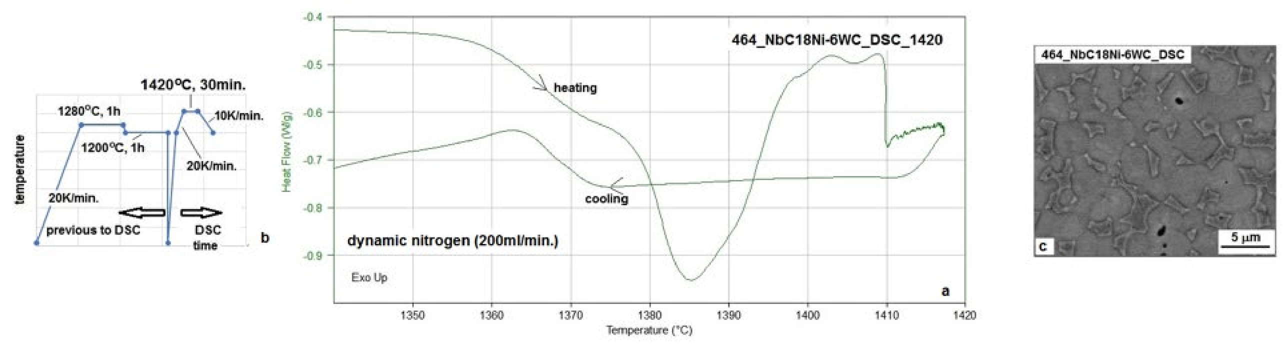
Results and Discussion

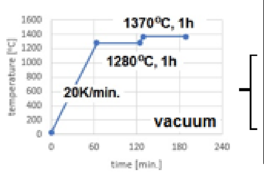
Higher attritor milling time (240 minutes) was investigated. Shrinkage for sample sintered directly for 2 hours at 1390 °C was higher. A swelling (liquid formation) was observed. Hardness and microstructure are similar considering milling time.



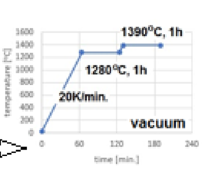


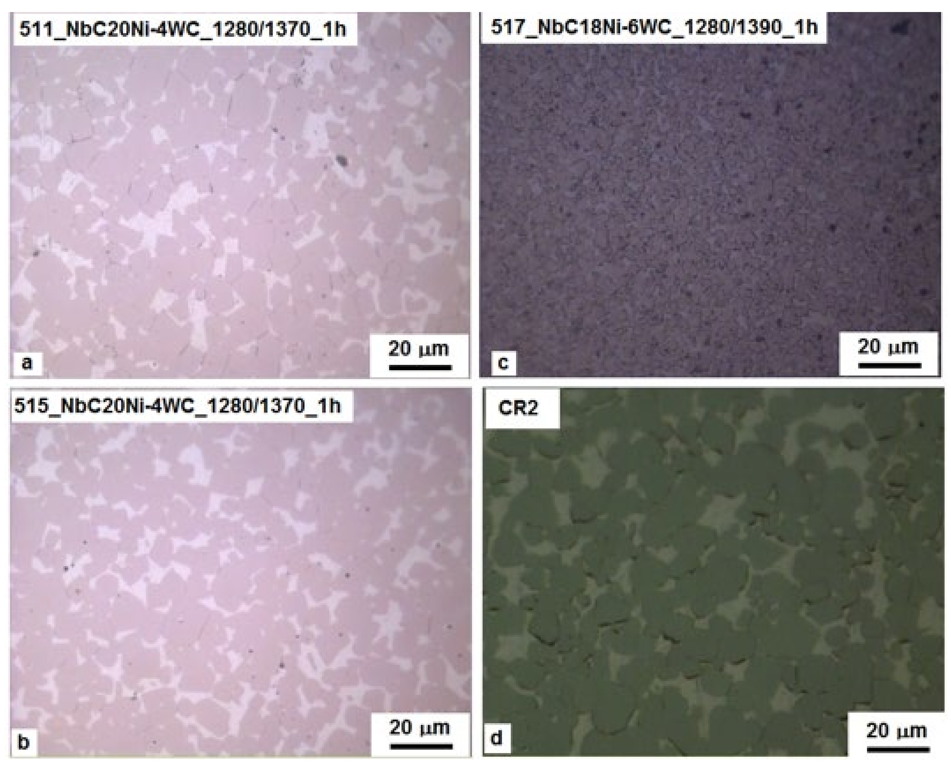
To get even higher hardness, a NbC18Ni-6WC (lower Ni and higher WC content) batch was produced by ball milling (15h). DSC curve (final cycle) for a two-stage sintering for sample pressed at 200MPa. It is possible to observe melting during heating (endothermic peak) that started at 1360-1370°C, and solidification (exothermic peak) at 1370°C. The obtained hardness (HV_2) was 1166±28.





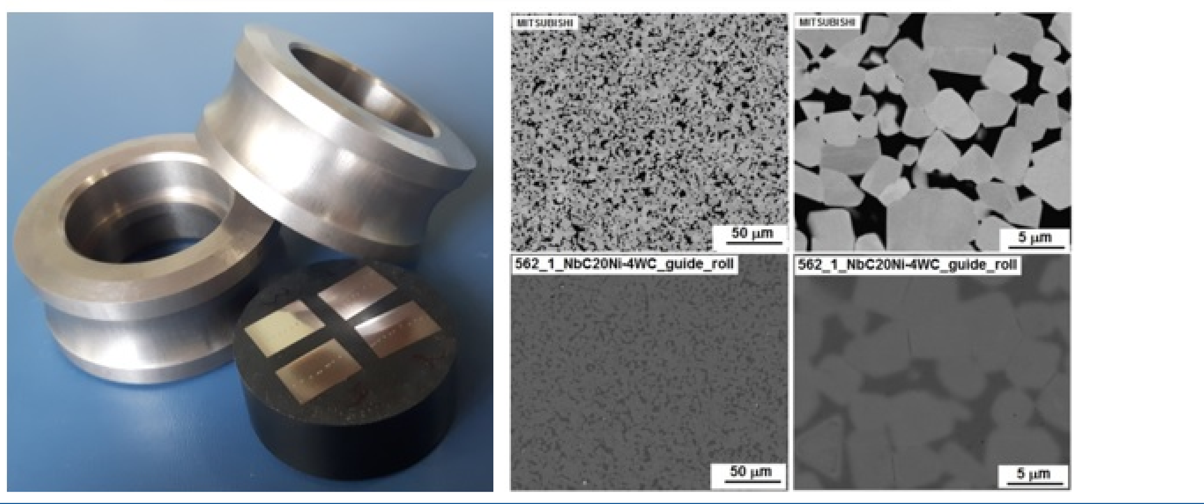
sample	milling	dg [g/cm³]	ds [g/cm³]	HV2 [kgf/mm²]
511_NbC20Ni-4WC	attritor: 15 min.	4.21±0.02	8.03±0.06	959±35
515_NbC20Ni-4WC	attritor; 120 min.	4.19±0.07	8.08±0.06	1010±18
517_1_NbC18Ni-6WC	ball: 15 hours	4.23±0.06	8.02±0.01	1232±44





Guide rolls sintered at 1370 °C for 1 hour under vacuum (previous step at 1280 °C/1

sample	P_{compac} [MPa]	d_g [g/cm³]	d_s [g/cm³]	HV_2 [kgf/mm²]
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	



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°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 °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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