CEMENTED NbC-Co FOR GEOTHERMAL DRILLING APPLICATIONS

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Final Report

May 1987

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Materials Research Laboratory

Prepared for:
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SUMMARY

Sintering and hot isostatic pressing were explored to produce a range of NbC-Co materials. Stoichiometric NbC-10Co and NbC-20Co were sintered close to the theoretical density relatively easily. Cemented $NbC_{0.83}$-10Co and $NbC_{0.83}$-20Co were more difficult to process. Some dense materials were prepared by a combination of sintering and hot isostatic pressing at 1420° to 1450°C. The carbide in these samples appeared to have the composition $NbC_{0.9}$. Hardness, toughness, and wear tests showed that the properties of these $NbC_{0.9}$-10Co samples were inferior to those of $NbC_{0.83}$-10Co materials produced previously by hot pressing. We concluded that contamination from WC milling balls and excessive processing times were the main causes of the difficulty in controlling the composition and properties of substoichiometric cemented niobium carbide.

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I INTRODUCTION

Cemented WC-Co is extensively used for both geothermal and oil drilling. These applications demand a range of cutting insert materials in which different combinations of hardness, toughness, and strength permit effective drilling in a variety of rock formations. Of the many cemented carbides that have been developed commercially, only the unalloyed WC-Co grades are suitable for rock cutting. Additions of TiC or other cubic carbides improve the performance of WC-Co in metal cutting applications, but these multicomponent grades and other cemented carbides based on TiC are less effective as rock-bit inserts. By experience, rock-bit manufacturers are able to specify grades of WC-Co that are appropriate for different drilling conditions, but a fundamental understanding of the importance and interplay of materials properties is lacking.

In WC-Co, the cobalt content and the WC grain size are the main parameters that are used to vary the mechanical properties. Commercial rock cutting grades contain 8 to 16 wt% Co and the WC grain size can be from 0.5 to 5 μm. These materials have Vickers hardness of 10-17 GPa, compressive strengths of 4000-7000 MPa, and fracture toughnesses of 18-8 MPa $m^{1/2}$. Hardness and strength increase with both decreasing WC grain size and decreasing Co content. For a given WC grain size, the fracture toughness of WC-Co increases with increasing Co, and for a given Co content, coarse-grained WC-Co is tougher than fine-grained materials.

Within limits, higher hardness and resistance to abrasive wear can thus be developed at the expense of toughness. However, as the hardness and brittleness increase, the wear mechanisms change from those in which plastic deformation is important to others that are dominated by elastic micro- and macrofracture. One approach to improving the performance of bit-inserts is to look for systems in which the hardness of the composite is not so closely tied to the fracture toughness, as is the case for WC-

Co. Cemented niobium carbide NbC_x (where x is approximately 0.6 to 0.96), offers such a possibility. The hardness of NbC_x depends strongly on carbon content with a maximum hardness close to $NbC_{0.83}$. In contrast, WC is a stoichiometric compound and loss of carbon causes the formation of W_2C. Thus, in cemented NbC_x the factors controlling properties are cobalt content, carbide grain size, and carbon content of the carbide.

In a previous study, a range of cemented carbides based on NbC_x and TaC_x (tantalum carbide) with Co and Ni binders was fabricated and evaluated.[1] Hardness, fracture toughness, and abrasive wear resistance were measured for hot-pressed materials and compared with data for cemented WC-Co bit materials. The NbC_x-Co materials showed the best combination of properties. It was found that, for compositions with the same hardness, the fracture toughness of $NbC_{0.83}$-Co was greater than that of stoichiometric NbC-Co. In addition, abrasive wear tests showed that the wear-resistance of NbC_x-Co lies within the range of wear resistance of grades of WC-Co commonly used in rock-cutting. From these results it was concluded that by adjusting the carbon content of the carbide it is possible to obtain simultaneous improvements in hardness and toughness in this system.

In the previous project, all materials were prepared by hot pressing and some nonuniformity of microstructure and evidence for residual stresses were thought to be associated with the processing technique. The goals of the present project were to establish a sintering route for NbC_x-Co materials, to evaluate their properties, and to produce samples suitable for rock drilling tests.

[1] D. J. Rowcliffe "Development of a New Family of Cemented Carbides for Geothermal Drilling," SRI Final Report on Sandia Contract 74-4755 (May 1983).

II EXPERIMENTAL PROCEDURES

Fabrication Methods

Table 1 lists powder sources and particle sizes. The substoichiometric $NbC_{0.83}$ was specially prepared at Wah Chang by reacting the appropriate amount of Nb powder with stoichiometric NbC powder. The manufacturers analysis is given in Table 2. The carbon contents of several NbC_x powders were determined by combustion,* and the oxygen contents were measured by fast neutron activation.† These data, which are given in Table 3, show good agreement with the data of Table 2. In addition, lattice parameters of NbC_x samples were measured by x-ray diffraction and compared with published data on the dependence of lattice constants on carbon content.[2] The agreement between the measured carbon contents and those estimated from the lattice parameter was within 2% for carbides of nominal composition $NbC_{0.83}$. The lattice parameter of the nominally stoichiometric NbC was 4.4709 Å, as expected. However, the carbon analysis shown in Table 3 for this material corresponds to $NbC_{0.95}$. This discrepancy is related to the high oxygen content (0.63%) of the fine stoichiometric powder. A calculation of the composition gave a metal/nonmetal molar ratio of unity, indicating that oxygen had substituted for an equivalent quantity of carbon in the NbC lattice.

Approximately 25 batches of NbC_x-Co powders were prepared by either ball milling or planetary milling using WC milling balls in polyethylene containers. Batches of approximately 80 g were milled with 2 wt% polyethylene glycol (Carbowax 4000) dissolved in deoxidized, deionized water or methanol. Both evaporative drying and spray drying were used to remove the solvent. Several 100 g batches and an additional 3 kg batch of $NbC_{0.83}$-10 Co was prepared using paraffin wax in a solvent of hexane.

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* Stanford University, Stanford, CA.

† IRT Corp, San Diego, CA.

[2] E. K. Storms, The Refractory Carbide (Academic Press, 1967), p. 67.

Table 1

POWDER SOURCES AND SIZES

Powder	Source	Size
Stoichiometric NbC	Herman Starck	2 μm
$NbC_{0.83}$	Wah Chang	-325 mesh, FSSS 16 μm
Co	Herman Starck	2 μm
Co	African Metals	2 μm

Table 2

ANALYSIS OF $NbC_{0.83}$

Element	Results (ppm)
O	160
N	170
Fe	<50
Al	22
Si	<50
Ta	1390
Ti	<55
Zr	<100
Hf	560
B	4
Cd	<5
Co	<10
Cr	20
Cu	<40
Mg	<20
Mn	<20
Mo	<50
Ni	<20
Pb	<20
Sn	<10
V	20
W	180
Zn	<10
C	9.75%, 9.77%
Free C	0.05%

Table 3

OXYGEN AND CARBON ANALYSES

Material Material	Carbon (wt%)	Oxygen (wt%)	Corresponding Carbide Compositon
SRI NbC$_{0.83}$	9.43	--	NbC$_{0.81}$
Starck NbC	10.93	0.63	NbC$_{0.95}$
Wah Chang NbC$_{0.83}$[a]			
No. 1	9.62	0.031	NbC$_{0.82}$
No. 2	9.76	0.031	NbC$_{0.84}$
Starck Co	--	1.2	--

---

[a] No. 1 and No. 2 were separate samples from the main batch.

Initially, cylindrical rods approximately 10 mm long by 12.5 mm in diameter were cold pressed with a range of pressures to define the pressures and corresponding green sizes that would sinter to full density. Based on the shrinkage data from these experiments, a die was machined to fabricate rods that would sinter to the dimensions of short-rod fracture toughness and wear test specimens (19 mm by 12.7 mm in diameter), and most samples prepared during the project were of this size.

Pressed cylinders were dewaxed in a horizontal tube furnace equipped with a programmable controller and facilities to control the environment. All samples were dewaxed in hydrogen. A typical dewaxing cycle was as follows: 25° to 250°C at 2° to 3°C/per minute, hold at 250°C for 10 minutes, 250° to 400°C at 2°C/minute, 400° to 600°C at 5°/minute, hold up to 2 hours at 600°C.

Dewaxed samples were stored under hydrogen until they were needed for further processing. Some samples were sintered in a carbon resistance furnace under pressures of argon up to 20 atm at temperatures between 1400° and 1550°C. Other samples were sintered under 1 atm of argon in a hot isostatic press. After sufficient time to close most pores (1/2 to 1 hour), the system was pressurized in an effort to reach full density. Several experimental samples were processed at Progressive Carbide by a similar sinter-HIP process, using a final pressure of 225 psi. Other samples were hot isostatically pressed at Reed Rock Bit.

Evaluation Techniques

Weight losses and dimensional changes were determined after dewaxing and after sintering or hot isostatic pressing. Densities of sintered samples were measured by weighing in air and in alcohol. Metallographic samples were prepared by conventional diamond polishing, finishing with 1-μm paste. Some samples were etched in Nital or Murakami's reagent.

Hardness and indentation toughness measurements were made on polished surfaces using either a standard Vickers machine with loads up to 100 kg or a Leitz microhardness system with loads up to 2 kg. Some fracture toughness measurements were made at Terratek using the short-rod technique. Wear tests were performed at the Security Division of Dresser Industries, using a proprietary method that determines the volume of material lost from a test piece that has been drawn across a rock slab under controlled conditions. Wear surfaces, fracture surfaces, and metallographic specimens were examined by scanning electron microscopy (SEM) using energy dispersive x-ray analysis to identify elements.

III. RESULTS AND DISCUSSION

Fabrication Studies

The fabrication of cemented carbides by sintering involves several steps, each with its own set of parameters. In developing a fabrication route for NbC_x-Co materials, we followed the steps generally used to fabricate WC-Co. The goal was to develop a route that could easily be scaled up or adapted to commercial processing of insert materials.

Discussions were held with Mr. John Fisher, Progressive Carbide, Cypress, California, concerning details of their process. On the basis of these discussions, we initially used Carbowax 4000 as a binder and ball milled powders in deoxidized, deionized water for 48 hours, and followed a pressing, dewaxing, and sintering schedule that was similar to that used at Progressive. When difficulties were encountered in processing, other powders were prepared using methanol instead of water. Some powders were milled in a planetary ball mill, and some were spray dried rather than evaporatively dried. No consistent differences were found between these powders, and planetary milling was adopted because it could be performed in a much shorter time. We did not find any evidence that any oxidation caused by milling in water was significant probably because the subsequent heat treatment of pressed bodies in hydrogen to remove the wax binder also reduced any oxides.

Table 4 lists the batches of powders prepared during the project, with the details of binder, solvent, and milling procedure. Table 5 shows the fabrication data for one series of runs for the four cemented carbide compositions, all sintered at 1450°C.

Table 4

PREPARATION CONDITIONS FOR NbC-Co POWDERS

Powder	Composition	Additive (wt%)	Additive Solvent	Milling Method[a] and Time (hr)
A	NbC-10Co	2 Paraffin	Cyclohexane	BM/48
B	$NbC_{0.83}$-10Co	2 Paraffin	Cyclohexane	BM/48
C	NbC-10Co	2 Carbowax	Cyclohexane	BM/48
D	NbC-10Co	4 Carbowax	Cyclohexane	BM/48
E	NbC-10Co	2 Carbowax	Water	BM/48
F	$NbC_{0.83}$-10Co	2 Carbowax	Water	BM/48
G	NbC-20Co	2 Carbowax	Water	BM/48
H	$NbC_{0.83}$-20Co	2 Carbowax	Water	PM/12
H_1	$NbC_{0.83}$-20Co	2 Carbowax	Water	PM/12
H_2[b]	$NbC_{0.83}$-20Co	2 Carbowax	Water	PM/12
F_1[b]	$NbC_{0.83}$-10Co	2 Carbowax	Water	PM/12
H_3[b]	$NbC_{0.83}$-10Co	2 Carbowax	Methanol	PM/12
I[b]	NbC-20Co	2 Carbowax	Methanol	PM/12
J[b]	$NbC_{0.83}$-10Co	2 Carbowax	Methanol	PM/12
K	NbC-10Co	2 Carbowax	Methanol	PM/12
M	NbC-10Co	2 Carbowax	Methanol	PM/6
W	NbC-10Co	--	Water	PM/4
X	$NbC_{0.83}$-10Co	--	Water	PM/4
Y	$NbC_{0.83}$-10Co	2 Carbowax	Water	PM/4
Z	$NbC_{0.83}$-20Co	--	Water	PM/4

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[a] BM = ball mill; PM = planetary mill.

[b] All powders were evaporatively dried except H_2, F_1, H_3, I, and J.

Table 5

FABRICATION DATA FOR CEMENTED NIOBIUM CARBIDES SINTERED AT THE SAME TEMPERATURE

Sample	Powder	Composition	Pressing psi	Grn. Density g/cm^3	Wt. Loss Dewax (%)	Sintering Pressure (psi)	Temp. °C	Wt. Loss Sinter (%)	Diam. Chg. (%)	Height Chg. (%)	Sintered Density g/cm^3	Density (%) Theoretical
4.1	F	NbC.83-10Co	8,700	4.472	2.2	225	1,450	4.1	18.3	17.4	7.854	100.1
4.2	F	NbC.83-10Co	12,800	4.568	2.5	225	1,450	3.6	17.8	17.6	7.859	100.1
4.3	F	NbC.83-10Co	25,500	4.785	2.5	225	1,450	3.6	15.2	14.8	7.518	95.8
4.4	F	NbC.83-10Co	47,400	4.983	2.5	225	1,450	3.6	14.6	13.9	7.641	97.3
5.1	G	NbC-20Co	11,200	4.118	3.7	225	1,450	5.8	21.3	20.3	8.022	100.1
5.2	G	NbC-20Co	17,800	4.265	3.7	225	1,450	5.7	20.3	19.6	8.021	100.1
5.3	G	NbC-20Co	22,900	4.418	3.6	225	1,450	5.6	19.4	18.4	8.019	100.1
5.4	G	NbC-20Co	42,300	4.678	3.7	225	1,450	5.6	18.2	17.0	7.940	99.1
6.1	E	NbC-10Co	11,700	4.485	2.3	225	1,450	4.1	18.3	17.1	7.934	100.4
6.2	E	NbC-10Co	14,800	4.614	2.2	225	1,450	4.1	17.5	15.8	7.932	100.4
6.3	E	NbC-10Co	36,000	4.870	2.3	225	1,450	4.1	16.1	15.0	7.929	100.4
6.4	E	NbC-10Co	56,000	5.069	2.3	225	1,450	4.0	15.0	14.2	7.928	100.3
7.1	H	NbC.83-20Co	12,200	4.657	7.7	225	1,450	9.7	12.1	12.5	7.458	93.6
7.2	H	NbC.83-20Co	15,300	4.706	7.5	225	1,450	9.6	11.7	12.1	7.436	93.4
7.3	H	NbC.83-20Co	20,400	4.849	7.4	225	1,450	9.6	10.8	11.7	7.383	92.1
7.4	H	NbC.83-20Co	33,100	4.973	7.2	225	1,450	9.0	10.1	11.0	7.305	91.7
8.1	H1	NbC.83-20Co	10,200	4.247	3.4	225	1,450	4.6	20.1	19.7	8.074	101.4
8.2	H1	NbC.83-20Co	17,900	4.393	3.4	225	1,450	4.6	19.3	19.1	8.037	100.9
8.3	H1	NbC.83-20Co	23,000	4.518	3.3	225	1,450	4.6	18.6	18.2	8.029	100.8
8.4	H1	NbC.83-20Co	38,300	4.725	3.3	225	1,450	4.7	17.3	17.1	8.007	100.5
8.5	H	NbC.83-20Co	30,600	4.698	3.2	225	1,450	4.7	11.6	10.7	7.304	91.7

The purpose of this series was primarily to explore the dewaxing procedure and the effect of cold pressing pressure on dimensions and density during processing. In this series, samples were processed at different pressures between 8000 and 60,000 psi. Green densities were determined from weight and dimensions. Weight losses were monitored after dewaxing in hydrogen and after sintering, and dimensional changes and densities were measured after sintering at 1450°C. As expected, the green density increased with pressing pressure, but after sintering the materials with lowest green density showed the largest decrease in dimensions and reached the highest densities. The weight loss after dewaxing was usually between 2.2 and 2.5% for both NbC_x-10Co materials and between 3.3 and 3.7% for the NbC_x-20Co materials. The weight loss was due to removal of wax and any other volatile material produced by the thermal treatment in hydrogen. The weight loss above the 2 wt% of wax binder is thought to be due to removal of oxygen, primarily from the cobalt, which would account for the larger weight losses in the samples containing 20% cobalt.

Powder H behaved differently in that in Run 7 the weight loss on dewaxing was about 7.5% and the sintered bodies were very porous. Run 7 was repeated in Run 8, with a new powder (H_1), with one extra sample prepared from powder H (8.5). Samples prepared from powder H_1 showed similar weight losses and sintering characteristics to those of Run 5. Although the weight loss for sample 8.5 was similar to that of the samples made from powder H_1 in Run 8, the linear shrinkage and the sintered density were again low and similar to those of Run 7. The reason for the poor sintering characteristics of powder H was not found and this powder was abandoned.

Microstructural Studies

Figure 1 shows optical micrographs illustrating the main features of samples listed in Table 5. Sample 4.1 [Figure 1(a)] had a uniform microstructure with no evidence of pores, in agreement with the measured density. The microstructure is characterized by relatively continuous,

Figure 1

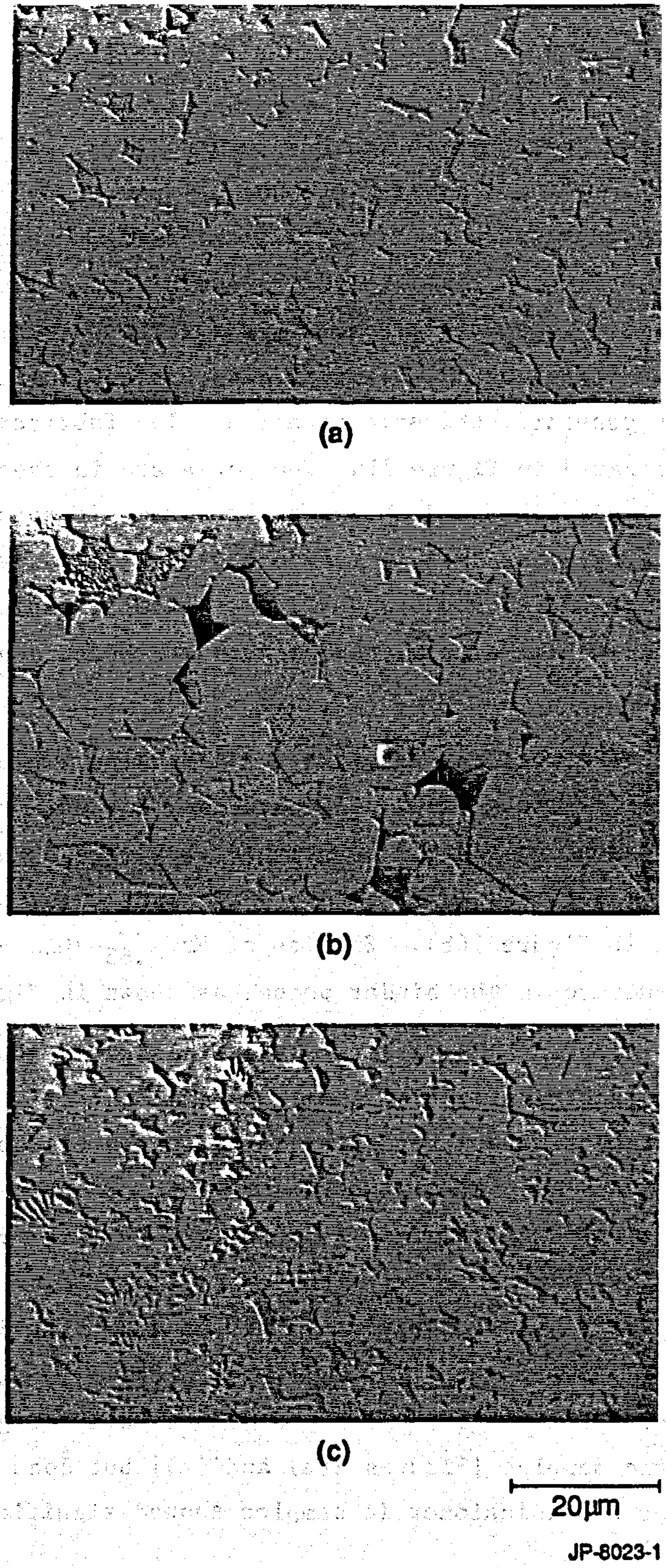

FIGURE 1 MICROSTRUCTURES NbC_x-Co MATERIALS SINTERED AT 1450°C
(a) $NbC_{0.83}$-10Co (b) NbC-20Co (c) $NbC_{0.83}$-20Co

interconnected carbide grains. Most carbide/cobalt boundaries are curved. The few planar boundaries are probably high symmetry planes [e.g, (100) NbC], which tend to form when single crystals are grown from dilute solution. The grain size is about 15 μm. In many examples three grains grew together, apparently totally excluding cobalt. This microstructure indicates that liquid phase sintering occurred relatively readily. However, some samples in this series and others in Table 5 contained pores that were extensive in some cases. The form of the porosity was generally the same in all samples fabricated on this project and is illustrated in Figure 1b. The pores are in the cobalt regions. The carbide grain sizes and shapes are the same in porous and in pore-free regions, suggesting that liquid cobalt binders was in the pores at least during part of the sintering. It was also possible that there was a local wetting problem or that the sintering temperature was not high enough.

A variety of structures were observed in the binder phase. In Figure 1(b) most of the binder is featureless, but some regions etched differently, suggesting a different composition or even a multiphase binder. Such binder structures were often associated with regions of porosity, as in Figure 1(b). Samples of $NbC_{0.83}$-20Co all showed a eutectic structure in the binder phase, as shown in Figure 1(c).

The next series of experiments was designed to evaluate the effect of sintering temperature on microstructure and density of sintered materials. Sets of samples were pressed and sintered at 1400°, 1450°, and 1500°C. The processing details are given in Table 6. Figure 2 shows micrographs of series 10 samples sintered at 1400°C and allows a direct comparison between the sintering characteristics of samples containing stoichiometric and substoichiometric NbC. It was consistently found that stoichiometric NbC-Co samples sintered more readily than $NbC_{0.83}$-Co under any conditions. The carbide grain size is clearly larger in the stoichiometric samples [Figures 2(a) and (c)] but does not depend on Co content. The substoichiometric samples showed significant porosity

Figure 2

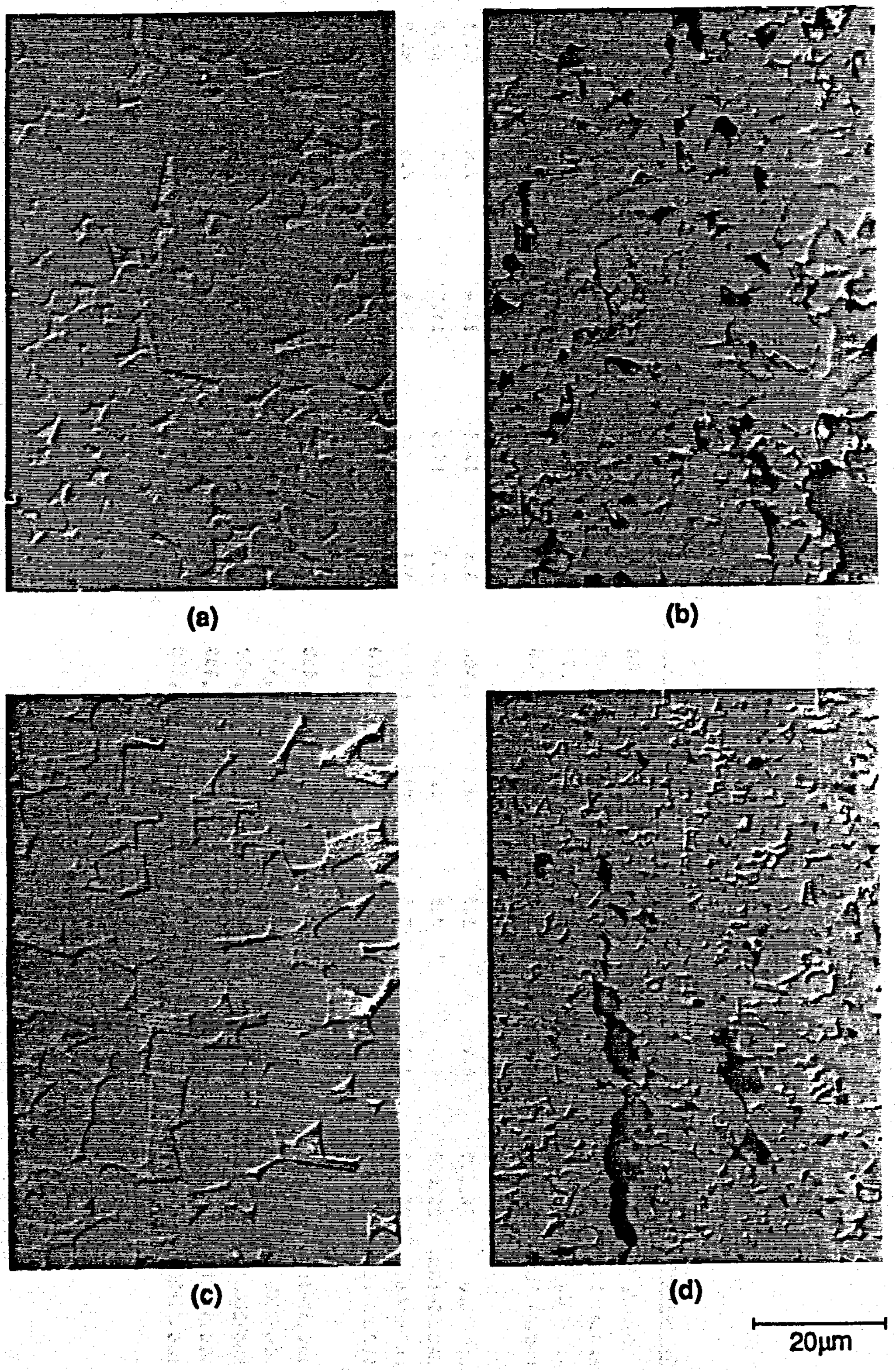

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FIGURE 2 MICROSTRUCTURES OF NbC_x-Co MATERIALS SINTERED AT 1400°C (a) $NbC_{0.83}$-10Co (b) $NbC_{0.83}$-20Co (c) NbC-10Co (d) NbC-20Co

Table 6

FABRICATION DATA FOR CEMENTED NIOBIUM CARBIDES SINTERED AT VARIOUS TEMPERATURES

Sample	Powder	Composition	Pressing psi	Grn. Density g/cm^3	Wt. Loss Dewax (%)	Sintering Pressure (psi)	Temp. °C	Wt. Loss Sinter (%)	Diam. Chg. (%)	Height Chg. (%)	Sintered Density g/cm^3	Density (%) Theoretical
9.1	E	NbC-10Co	25,500	4.8	2.2	225	1,500	4.2	17.0	15.7	7.8	99.1
9.2	F	NbC.83-10Co	28,100	4.8	2.6	225	1,500	3.6	16.2	16.3	7.8	99.7
9.3	G	NbC-20Co	28,100	4.5	3.5	225	1,500	5.5	18.9	18.9	7.9	98.1
9.4	H1	NbC.83-20Co	25,500	4.6	3.4	225	1,500	4.9	18.5	18.8	7.9	98.5
10.1	E	NbC-10Co	26,500	4.7	2.2	225	1,400	3.9	17.1	15.6	7.8	99.1
10.2	F	NbC.83-10Co	26,000	4.7	2.5	225	1,400	3.3	14.6	14.3	7.3	92.8
10.3	G	NbC-20Co	25,500	4.4	3.4	225	1,400	5.1	19.6	18.6	7.9	98.5
10.4	H1	NbC.83-20Co	25,500	4.6	3.5	225	1,400	4.6	17.5	16.7	7.7	96.7
11.1	F	NbC.83-10Co	28,100	4.8	2.5	45	1,450	3.2	15.3	14.9	7.5	95.0
11.2	G	NbC-20Co	13,800	4.2	3.4	45	1,450	5.3	20.4	20.3	8.0	99.3
11.3	G	NbC-20Co	29,600	4.4	3.4	45	1,450	5.2	19.3	18.1	7.9	99.1
11.4	H1	NbC.83-20Co	11,200	4.2	3.6	45	1,450	4.7	20.0	19.5	7.9	98.6
11.5	H1	NbC.83-20Co	25,500	4.5	3.5	45	1,450	4.5	18.5	18.6	7.8	98.1

[Figures 2(b) and (d)], and again a eutectic structure was prominent in the binder phase of $NbC_{0.83}$-20Co [Figure 2(d)].

Similar features were observed in the series 9 samples sintered at 1500°C, except that the grain size was larger in the stoichiometric materials and the porosity was much less in the substoichiometric samples. These observations confirmed that the stoichiometric NbC-Co materials could be sintered relatively readily between 1400° and 1500°C. However, the substoichiometric materials, which were of primary interest, were difficult to densify at any temperature, and the appearance of the eutectic structure in $NbC_{0.83}$-20Co samples was an additional complication. In addition, comparison of series 10 and 11 suggested that the use of higher pressure in the second half of the sintering cycle had no discernable effect on microstructure or density of samples sintered at 1450°C. However, the high pressure cycle was continued in most subsequent runs because we expected that a similar procedure would be used for samples processed at Progressive Carbide.

Commercial Processing

Eight pressed samples and sufficient powder to prepare a further six samples were sent to Progressive Carbide for processing. The two sets of samples were dewaxed using Progressive's standard procedure for WC-Co pressed with Carbowax, and each set was sintered in separate runs at 1400°C with a standard production run of WC-Co specimens. It was estimated that the porosities of the six samples pressed and sintered at Progressive were about 10%, and the densities were therefore not measured. The eight samples pressed at SRI were better. Two samples of $NbC_{0.83}$-20Co apparently reached the theoretical density but had some areas of voids near the specimen surfaces. The remaining samples all had densities of about 96% of the theoretical value and correspondingly large areas of voids were visible in the microstructure. As expected, the propensity of small angular carbide grains suggested that little liquid phase sintering had occurred. Although the sintering temperature of 1400°C was somewhat low for the substoichiometric carbides, it was surprising that the stoichiometric materials did not sinter well.

The nonreproducibility in the sintered densities had several possible causes. The main ones considered were poor distribution of the wax binder and secondary reactions in liquid phase sintering that might affect solubility or wetting behavior. Three powders (W, X, and Z in Table 4) were milled without any binder. Samples of powders Z, Y, and H_3, all $NbC_{0.83}$-20Co, were pressed at the same pressure, heat treated in the dewaxing furnace under hydrogen, and sintered at 1450°C. The three samples all reached the theoretical density and their microstructures were indistinguishable. These results suggested that the problems of nonreproducibility were not related to the milling and green stage processing. In a further run of nine specimens, four did not contain the wax binder and so were not heat treated in hydrogen with the five wax-containing specimens. On sintering all samples together at 1450°C, no systematic differences in sintered density were found for powders that originally contained or did not contain the wax binder. Densities ranged from 96 to 100% of thereotical for the respective carbide-cobalt compositions.

To confirm these findings, we sent samples of several powders to Reed Rock Bit for processing, and a batch of $NbC_{0.83}$-10Co was milled at Reed using a paraffin wax binder and their standard milling procedure. At the same time further samples were processed at SRI by sintering and hot isostatic pressing to 2500 psi. Hot isostatic pressing is often used to close residual pores in batches of WC-Co that have not sintered satisfactorily. In some cases, the high pressure may overcome problems of insufficient local wetting. The first set of $NbC_{0.83}$-20Co samples hot isostatically pressed at SRI at 1500°C reached densities of 99.9, 100, and 93.5% of the theoretical value. Samples of $NbC_{0.83}$-10Co hot isostatically pressed at 1400°C reached densities of 96 to 100% of the theoretical value. Similar results were obtained at Reed using powders milled at SRI. The stoichiometric materials and the $NbC_{0.83}$-20Co reached densities >99% of the theoretical values, whereas the $NbC_{0.83}$-10Co reached about 96% on sintering and 98% after hot isosatic pressing.

Phase Composition Studies

These samples and others processed at SRI were examined metallographically and by SEM. The binder phase composition varied considerably between specimens and at different areas within a single specimen. Both W and Nb could be found in the predominantly Co binder phase. It was generally found that those specimens that sintered well contained very little W. Usually the Nb content was also low in such samples, but in some areas of one dense sample of $NbC_{0.83}$-20Co the Nb content was substantial, but the W was just detectable above the background. In all $NbC_{0.83}$-20Co samples the Co binder phase always appeared to have a eutectic structure. Selected porous samples were examined, and it was consistently found that the binder contained significant quantities of Nb and W as evidenced by strong EDX peaks. Figure 3 shows a porous region of a sample of $NbC_{0.83}$-10Co. Within the binder the Nb/W ratio varied from 1:1 to about 5:1. Tungsten probably arose from the WC balls used to mill the powders. In addition, measurements of the lattice parameter made on three substoichiometric dense specimens selected at random indicated that the carbon content of the NbC had changed during processing to a value corresponding to an approximate composition $NbC_{0.9}$.

Figure 3

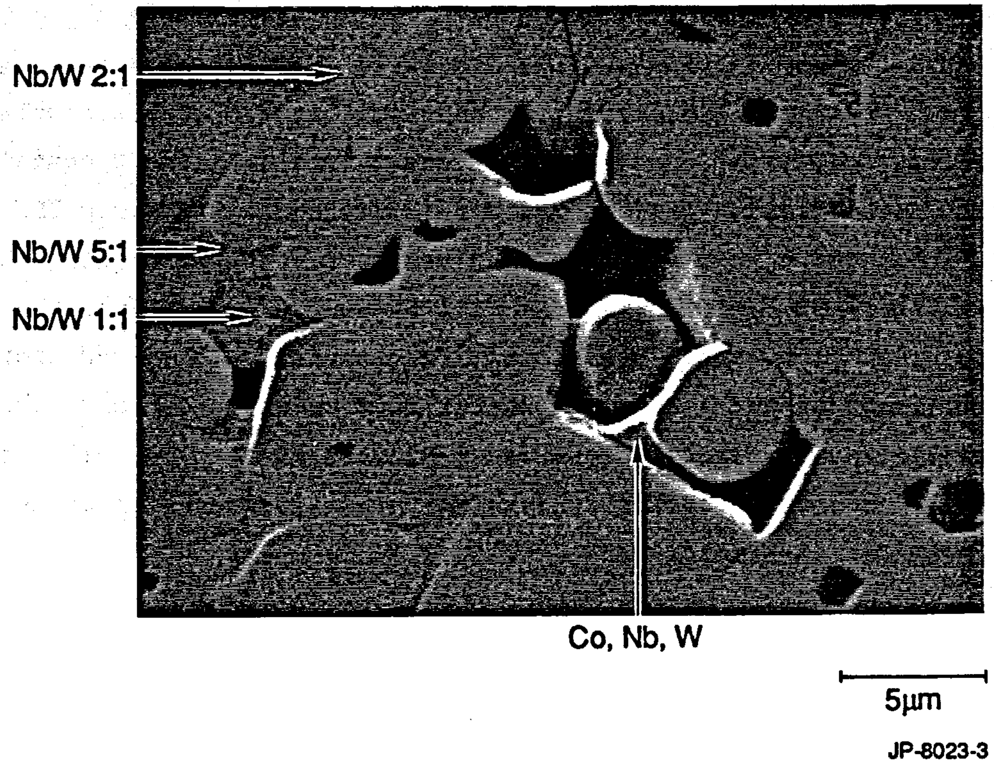

FIGURE 3 POROUS REGION IN $NbC_{0.83}$-10Co SINTERED AT 1450°C

Evaluation of Toughness, Hardness and Wear Resistance

Hot isostatic pressing (HIP) at pressures up to 2500 psi was generally beneficial in the processing of $NbC_{0.83}$-10Co. Approximately 15 HIP runs were performed to explore the temperature range 1375° to 1450°C, using a single batch of $NbC_{0.83}$-10Co containing 2 wt% paraffin wax, milled at Reed Rock Bit. Although some inconsistencies were evident, the majority of specimens had densities of 99% or greater for processing temperatures between 1420° and 1450°C. Four samples were sent to Terratek for short-rod fracture toughness tests, and four others were sent to Dresser Industries for wear testing.

The short-rod fracture toughness values for $NbC_{0.83}$-10Co samples were 6.00, 6.33, 6.23, 5.45 MPa $m^{1/2}$. The longitudinal fracture faces were polished and longitudinal and diametral hardness traces were made. No significant changes in hardness were observed across the samples. In the previous project, hot-pressed samples showed high hardness near the surface and a tendency to longitudinal hardness gradients that was ascribed to corresponding density gradients. Mean hardness values were 13.3, 13.0, 13.1, and 13.4 GPa for the four short-rod samples. These values were considerably lower than those found for hot-pressed $NbC_{0.83}$-10Co samples prepared in the previous project although the toughness values were similar.

Table 7 shows the wear test results obtained at Dresser Industries, together with data on hot-pressed samples. The data that are averages of six runs per sample are consistent for the four sintered/hot isostatically pressed $NbC_{0.83}$-10Co samples. However, the wear resistances of these samples are disappointingly low compared with the hot-pressed samples of nominally the same composition, tested previously. An examination of wear surfaces by SEM showed preferential loss of the binder phase and microfracture of the carbide grains. In the previous study uneven wear of the phases and microfracture were thought to be associated with lower wear resistance, whereas the most wear resistant materials showed relatively even wear features and limited microfracture.

Table 7

WEAR RESISTANCE OF CEMENTED CARBIDES

Specimen No.	Nominal Composition	Wear Resistance Number
29.2	$NbC_{0.83}$-10Co	428
30.2	$NbC_{0.83}$-10Co	445
30.3	$NbC_{0.83}$-10Co	431
30.4	$NbC_{0.83}$-10Co	468
HP85	$NbC_{0.83}$-10Co	2065
HP86/87	$NbC_{0.83}$-10Co	1866
HP84	NbC-20Co	376
HP89	$NbC_{0.83}$-20Co	536

General Discussion

The low values of wear resistance are consistent with the lower hardness levels noted above. The difference in behavior between the sinter/hot isostatically pressed materials and the hot-pressed materials of the previous work is probably due to a difference in composition of the carbide. As noted above in the studies of binder phase composition, the lattice parameter of dense substoichiometric NbC-Co corresponded to a composition $NbC_{0.9}$, which is softer than the expected material $NbC_{0.83}$.

It is likely that the compositions of the carbide and the cobalt binder phase were very sensitive to the conditions during sintering. Both NbC_x and WC impurities can dissolve in the cobalt. Also, the carbon content of the binder depends on carbon arising from the furnace environment and that available in the form of WC, $NbC_{0.83}$, or NbC. Although WC is soluble in Co and in NbC, the EDX analyses suggested that W remained in the binder phase. The distribution of carbon in the sintered $NbC_{0.83}$-Co could not be determined, but it is possible that NbC_x

produced by solution and precipitation could be stoichiometric, whereas the grain cores could be $NbC_{0.83}$. It was observed that stoichiometric NbC-Co sintered relatively easily. Thus successful sintering of $NbC_{0.83}$-10Co might depend on the growth of a layer of stoichiometric NbC so that the wetting or transport kinetics become favorable. Other elements dissolved in the cobalt binder phase will also affect its wetting properties. If the concentration of elements in the binder phase changes appreciably during the sintering period, it is possible that the liquid phase sintering process could be inhibited. It was beyond the resources and scope of the project to investigate these effects in any depth. However, we suggest that sintering of the substoichiometric materials was difficult because the carbon content could not be controlled well enough. The problem is worse in $NbC_{0.83}$-10Co because the concentration of elements in the binder phase could be twice as high as in materials containing 20% Co. Time at the sintering temperature is probably critical and should be kept to a minimum.

IV CONCLUSIONS

A series of NbC_x-Co materials was prepared by sintering and hot isostatic pressing. The stoichiometric NbC-10Co and NbC-20Co were sintered to high density relatively easily, whereas materials based on $NbC_{0.83}$ were difficult to sinter. This difficulty is related to control of carbon content during processing. The carbon content of dense samples prepared from $NbC_{0.83}$ and Co increased to an average composition of approximately $NbC_{0.9}$ during processing. This higher carbon-content carbide is softer and less wear resistant than $NbC_{0.83}$, which was confirmed by the mechanical tests. Contamination from the WC milling balls complicated the processing further. On the other hand, the microstructures were uniform throughout all the dense samples that were examined.

Dense homogeneous materials in the system $NbC_{0.83}$-Co can probably be produced by more careful control of the processing conditions. In particular, powders should be milled with NbC-Co milling balls to avoid W contamination of the binder and excess C in the $NbC_{0.83}$. In addition, the processing time at temperature should be kept to a minimum to avoid excessive solution of Nb in the Co and increase of C in the $NbC_{0.83}$. Sintering for 5 minutes at 1420° to 1450°C followed by hot isostatic pressing for the same time in this temperature range should produce acceptable materials. In this case the hardness and wear resistance values are expected to reach those obtained previously on samples prepared by hot pressing.

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