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Development of a New Family of Cemented Carbides for Geothermal Drilling Final Report

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DEVELOPMENT OF A NEW FAMILY OF CEMENTED CARBIDES FOR GEOTHERMAL DRILLING

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ABSTRACT

The contractor fabricated samples of cemented carbides based on tantalum carbide and niobium carbide with cobalt and nickel binders. These materials were evaluated for use as rock-bit inserts in geothermal drilling. Carbon content in the niobium carbide (NbC_x) and the tantalum carbide (TaC_x) was varied (x is 0.83 to 1.0) and the effect of these changes on the carbides' mechanical properties was examined. Hardness, toughness, and abrasive wear resistance of the new materials were measured and compared to properties of tungsten carbide grades used in rock-bit inserts.

MAY 1983

FINAL REPORT

DEVELOPMENT OF A NEW FAMILY OF CEMENTED CARBIDES FOR GEOTHERMAL DRILLING

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Contract 74-4755
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SUMMARY

This project was a screening study to fabricate and evaluate a range of cemented carbides based on niobium carbide, NbC_x, and tantalum carbide, TaC_x, (where x is 0.83 to 1) with cobalt and nickel binders for use as rock-bit inserts in geothermal drilling. A major goal was to explore the influence of carbon content on selected mechanical properties of the cemented carbides. Most test materials were made by hot pressing, but exploratory work indicated that these cemented carbides could also be produced by cold pressing and sintering. Processing variables that were studied included milling conditions, hot pressing time, pressure, and temperature. The fabrication studies showed that the lowest porosities and most uniform microstructures were obtained in the NbC_x-Co System, and much of the study focused on these materials.

Hardness, fracture toughness, and abrasive wear resistance were measured and compared with data for cemented WC bit materials. For a given weight fraction of binder, stoichiometric NbC-Co was harder than the other experimental stoichiometric cemented carbides, and the substoichiometric material $NbC_{0.83}$-10Co was substantially harder than the equivalent stoichiometric alloy. The most significant toughness result was that, for a given hardness, the fracture toughness of $NbC_{0.83}$-Co was greater than that of stoichiometric NbC-Co. From these data, it was concluded that carbon content exerts a strong influence on the properties NbC_x-Co materials and that, by adjusting the carbon content of the carbide, it is possible to obtain simultaneous improvements in hardness and toughness in this system.

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 for rock cutting. Examination of wear surfaces indicated that both phases in $NbC_{0.83}$-10Co wear at a relatively even rate and that material is removed by a process primarily related to plastic flow, rather than microfracture.

RESEARCH CONTRIBUTORS

The principal investigator was David J. Rowcliffe. Sylvia M. Johnson and Ibrahim M. Allam contributed to the hardness and toughness evaluations. During this study we were fortunate to obtain significant input from individuals and organizations outside SRI. This was facilitated through the efforts of the project monitoring staff of the Geothermal Technology Division at Sandia National Laboratories. We would particularly like to acknowledge the contribution of Larry Pope of Sandia for his guidance in the fabrication studies. The wear tests were performed at the Security Division of Dresser Industries, Dallas, Texas and it is a pleasure to thank Jim Langford and Nelson Armitage for their extensive work. We also wish to thank Raymond Cutler at TerraTek, Salt Lake City who performed the short-rod fracture toughness tests and provided us with samples of WC-Co and detailed information on their properties.

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I INTRODUCTION

Rock-bit materials are subjected to very severe operating conditions in drilling geothermal wells. Typical rock formations such as granite and metamorphic sandstone are extremely hard and abrasive, and down-hole temperatures as high as 300°C can be reached with air-drilling. Corrosion is severe in hydrothermal systems at these temperatures because of the presence of hydrogen sulfide and sodium chloride. Although corrosion is less significant in dry steam wells, erosion can be severe because of the high velocity of the hard particles as well as the oxygen entrained in the superheated steam. The relative importance and contribution of chemical and mechanical effects on the wear properties of bit materials in geothermal wells are not well understood. The performance of conventional cemented tungsten carbide (WC-Co) inserts in roller-cone cutters is unacceptable.

A major cost in geothermal drilling is associated with the time spent in sinking the well. This cost depends mainly on the cutting rate of the rock-bit, its lifetime, the cost of bits, and the time taken to remove the drill string and replace a worn bit. Bit lifetimes of 25 hours at drilling rates of 10-15 feet/hour are typical for wells drilled between 5000 and 8000 feet in geyser formations, with loss of gauge as a primary cause of bit replacement.[1] Improved performance of rock bits could have a major impact on the economics of geothermal drilling. Higher cutting rates and increased bit life would shorten the drilling time, reduce the number of bits used, and reduce the total downtime for bit replacement. These improvements would also free the rigs earlier and allow them to be used for new wells.

To meet the need for improved bit materials, Sandia Laboratories funded a one-year program at SRI International to develop alternatives to WC-Co for use as inserts in roller-cone bits. The program was a screening study to fabricate and evaluate a range of cemented carbides based on niobium carbide, NbC_x, and tantalum carbide, TaC_x (where x is 0.83 to 1) with cobalt and nickel binders. The choice of these carbides was based on previous extensive studies of the deformation behavior of many transition metal carbides. The work described here represents an effort to apply the results of that fundamental research to the development of new cemented carbides for rock-bit inserts.

II BACKGROUND

Cemented WC-Co insert materials for three cone bits have been developed to withstand the severe mechanical conditions encountered in rock drilling. The cutting action of a three cone bit depends on its design, particularly the cone offset and the size and shape of the inserts. These features and the grade of carbide are determined by the type of formation being drilled. The cutting action varies from crushing and chipping in very hard formations to scraping and gouging in soft formations. In addition, the loading conditions are different for inserts in different parts of the bit.

The main parameters used to assess the suitability of a grade of carbide for a specific drilling application are toughness, hardness, and wear resistance. Although toughness can be measured using various fracture mechanics methods, there is also considerable advantage in using indentation techniques to obtain hardness and toughness data simultaneously. No wear test exists that is generally accepted by the carbide industry. Most bit manufacturers have their own proprietary test that involves abrading a cemented carbide on a controlled rock surface under known loading conditions and determining the volume worn off the carbide. In the development of new cemented carbides, measurements of hardness, toughness, and wear resistance together with microstructural characterization provide the information necessary to make comparisons with established grades of WC-Co.

In cemented carbide insert materials, it is generally accepted that the WC phase provides hardness and wear resistance while the cobalt contributes macroscopic toughness. However, the role of each phase is considerably more complex, and the properties also depend on the details of the microstructure. Further, it has been shown that the WC grains in cemented carbides can undergo considerable plastic deformation when subjected to high stresses.[2] The ability of WC grains to deform plastically probably makes a significant contribution to the fracture toughness of WC-Co.

The properties of WC-Co depend primarily on the cobalt content (8 to 16 wt%) and the WC grain size (0.5 to 5 μm). Commercial grades of WC-Co suitable for rock bit inserts have Vickers hardness in the range 10-17 GPa (~ 1000-1700 kg/mm^2) with a corresponding fracture toughness of 18-8 MPa m$^{1/2}$ and compressive strengths of 4000-7000 MPa.[3-7] Hardness and strength increase with both decreasing WC grain size and decreasing cobalt content.[3] For a given WC grain size, the fracture toughness of WC-Co increases with increasing cobalt and for a given Co content, coarse-grained WC-Co is tougher than fine-grained materials.[3,4]

The deformation behavior of transition metal carbides around room temperature has been studied mainly by indentation techniques. Indentation tests give information about elastic and plastic deformation of the material in a local region subjected to very high stresses. Under drilling conditions, loads are transmitted to the insert by point contact at asperities or with rock fragments; therefore, the microscopic yield and fracture properties of the cemented carbide should be important in determining the wear characteristics of the insert.

Indentation tests show certain similarities between WC, NbC, and TaC in the way that they deform. These stoichiometric carbides tend to deform plastically, whereas others such as TiC tend to crack. Tungsten carbide, differs significantly, from NbC_x and TaC_x in crystal structure and composition range with respect to carbon. Tungsten carbide has a hexagonal structure and is a stoichiometric compound; small decreases in carbon content cause the formation of W_2C or of other carbide phases containing cobalt. In contrast, the cubic carbides NbC_x and TaC_x maintain the same crystal structure over a wide range of carbon substoichiometry. The properties of these two carbides show a strong dependence on carbon content. For example, the hardness of single crystal TaC_x changes from 16 GPa for the stoichiometric compound to 38 GPa for the composition $TaC_{0.83}$.[8] The hardness of NbC_x shows a similar strong dependence on carbon content,[9] although the maximum achievable hardness is probably not as high as in TaC_x. The increase in hardness of both TaC_x and NbC_x is inevitably accompanied by a decrease in resistance to cracking although the extent of these effects has not been studied systematically. In both carbides, carbon substoichiometry is accommodated by ordering of the excess carbon vacancies. In TaC_x this is accomplished by the development of short range order (SRO). In NbC_x both SRO and long range order (LRO) are possible. Moreover, for a given composition of NbC_x, the LRO structure can be developed from the SRO structure by a heat treatment. This leads to a substantial increase in hardness, for example, from 18 GPa to 25 GPa.[9]

Limited studies have been made of cemented carbides based on TaC_x and NbC_x.[10,11] The way in which their properties change with binder content is qualitatively similar to that in WC-Co, and it can be expected that grain size and microstructure will exert the same sort of influence on properties in all these cemented carbides. However, the hardness of TaC_x and NbC_x can be varied over a wide range by control of the carbon content, and the hardness of a single composition of NbC_x can also be varied by heat treatment. This control of hardness available in TaC_x and NbC_x is not possible in WC because WC is a compound of fixed composition that does not undergo ordering. Control of the carbon content of the carbide in cemented NbC_x and TaC_x gives the possibility of a much greater range of properties than is available in WC-Co.

The binder phase in cemented carbides is extremely important in the fabrication process and in determining the macroscopic properties of the composite. Densification of the powder compacts occurs through liquid phase sintering, and this process is successful because WC is readily soluble in Co and because Co wets WC. Cobalt also fulfills three of the other requirements of a good binder phase. First, it has a high solid solubility for W and C, which provides increased strength and toughness to the composite. Second, Co is a weaker carbide former than WC, and third, Co is relatively refractory and resistant to corrosion.

The characteristics of the interaction between WC and Co can be used to select likely suitable binder phases for cemented carbides based on pure NbC_x and TaC_x. Sintered cemented NbC has been produced using Fe, Ni, and Co binders [11] and available information on phase equilibria[12] indicates that these metals will also promote liquid phase sintering of TaC_x. Pure Fe is probably the least suitable binder because of its low corrosion resistance and because the pseudo-binary eutectics with TaC_x and NbC_x contain less liquid phase than those with Co and Ni. For these reasons, Co and Ni were selected as binders in the current program.

III EXPERIMENTAL PROCEDURES

Compositions and Fabrication

Table 1 shows the range of compositions of cemented carbides studied in this program. Many of the possible 36 compositions were prepared in the initial screening study, and specific compositions were chosen so that properties could be compared between systems (for example, TaC-Ni and TaC-Co) and trends could be established within individual systems (for example, the effect of binder content on the properties of $NbC_{0.83}$-Co).

Table 1

COMPOSITIONS OF CEMENTED CARBIDES

Carbides	TaC, NbC
Carbon/metal ratio	1, 0.9, 0.83
Binders	Co, Ni
Binder content	5, 10, 20 weight percent

Table 2 shows the powder sources and particle sizes. Substoichiometric carbides were prepared by reacting appropriate mixtures of the carbide powder and the parent metal at 1700°C under deoxidized argon. The reaction products were crushed and milled to -325 mesh, then examined by x-ray diffraction. Reaction times of 1 hour were required to remove all x-ray peaks due to the parent metal. The measured lattice parameters of the substoichiometric carbide were compared with published data [13] on the dependence of lattice constants on carbon content, to confirm the composition. The agreement between the calculated composition and that estimated from the lattice parameter was within 2%.

Table 2

POWDER SOURCES AND SIZES

NbC:	Herman Starck	2 μm
TaC:	Wah Chang	3 μm
Ni:	International Nickel, Type INCO 123	3-7 μm
Co:	Herman Starck	2 μm
Nb:	A. D. Mackey	-325 mesh

All test materials were hot pressed because of the large number of compositions and relatively small numbers of samples of each that were required, but the feasibility of cold pressing and sintering was also investigated. For both processing routes, weighed powders were ball-milled in 100g lots in polyethylene bottles using cemented WC balls and cyclohexane, for times up to 96 hours. After milling, the cyclohexane was evaporated in air.

Discs (9.5mm diameter by 6.4mm thick), or short-rods (12.7mm diameter by 19mm long) were hot pressed under vacuum in graphite dies coated with a boron nitride wash. Pressing time, temperature and pressure were varied to obtain uniform pore-free microstructures.

The use of cold pressing and sintering was explored for NbC-20% Ni and TaC-10% Co to establish whether this was a feasible route for preparing cemented NbC_x or TaC_x. The powders were prepared for sintering by adding paraffin wax dissolved in cyclohexane to the milled dried powder previously prepared for hot pressing. The cyclohexane was evaporated on a hot plate with rapid stirring to ensure a uniform distribution of the wax. Cylinders (13mm by 13mm) were cold pressed in a steel die, and the wax was removed by heating in hydrogen at 300°C until the samples achieved a constant weight. The cylinders were sintered in a graphite tube furnace in deoxidized argon at 1370°C, which is 50°C above the reported pseudo-binary eutectic temperature.[12] Densities were up to 95% of the theoretical value, calculated according to a rule of mixtures. Metallographic observation of polished cross-sections showed a relatively uniform distribution of roughly circular pores. Observation of etched surfaces indicated that liquid phase sintering had taken place, but was incomplete locally, probably because of a non-ideal distribution of the binder phase. No effort was made to optimize the process because all the test materials for the project were made by hot pressing. However, these results show that densification can occur by liquid phase sintering without external pressure and suggests that a process equivalent to that used commercially for WC-Co could be developed.

Evaluation Techniques

Densities of hot pressed samples were determined by weighing in air and in carbon tetrachloride. Metallographic samples were prepared by conventional diamond polishing, finishing with 1-μm paste. Some samples were polished further using an alumina slurry to which was added a few drops of alkaline potassium ferricyanide.

Hardness and indentation toughness were measured on polished surfaces using a standard Vickers machine with loads up to 100 kg. Some fracture toughnesses were measured at TerraTek using the short-rod technique.

Initial wear tests were performed using the Riley-Stoker test according to ASME-AINSI. However, the level of reproducibility of the results was unacceptable, so wear tests were then performed at the Security Division of Dresser Industries, using a proprietary method. This method determines the volume of material lost from a cemented carbide after it 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 and wavelength x-ray techniques to identify the distribution of elements.

IV RESULTS AND DISCUSSION

Fabrication

The goal of the fabrication studies was to establish the conditions for producing pore-free materials with uniform microstructures. The main pressing variables were the milling time for the powders and the hot pressing temperature, time, and pressure. Most studies were made on a single composition, NbC-10Co, and the parameters for other compositions were developed from these data. For a fixed hot pressing cycle, milling times of 16 and 24 hours were found to be insufficient to obtain a uniform distribution of the binder phase. In this case "lakes" of cobalt, approximately three times the carbide grain size, were formed. Milling for 36, 48, or 96 hours removed this problem, and 48 hours was adopted as the standard milling time. The formation of lakes was more common for binder contents of 20% of either Co or Ni.

The initial selection of hot pressing temperatures was based on available phase diagram information in the literature.[12] Table 3 shows the compositions and melting points of the relevant pseudo-binary eutectics. Fixed pressures were selected between 1000 and 4000 psi and applied through the heating cycle to the maximum temperature.

Comparison of the hot pressing cycles for many samples showed that significant compaction of the powder began at approximately 1150°C, with a change to more rapid consolidation around 1280°C, as estimated from the motion of the pressing rams. Around the pseudo-binary eutectic temperature (1380°C), the consolidation rate became very low. High pressures and temperatures at or above 1380°C caused extrusion of the binder phase and local porosity within 1/2 mm of the specimen surfaces. This effect was most pronounced at the highest binder content (20%). Extending the pressing time after the consolidation rate had slowed also caused segregation of binder to the surface of the specimen. To avoid this effect the exact amount of powder required for a specimen of a certain size was pressed until the ram had reached a predetermined distance that corresponded to the length of a fully dense specimen. When this condition had been achieved, the rate of ram travel became very low, as expected. Representative data illustrating the effect of varying the processing conditions are given in Table 4.

Table 3

COMPOSITIONS AND MELTING POINTS OF PSEUDO-BINARY EUTECTICS

System	Composition (Mole % C)	Melting Point (°C)
NbC-Co	5	1380
NbC-Ni	5	1320
TaC-Co	3	1370
TaC-Ni	3	1370

Table 4

EFFECT OF PROCESSING CONDITIONS ON THE CONSOLIDATION OF NbC-10Co

Pressing Temperature (°C)	Pressing Pressure (psi)	Pressing Time (min)	% Theoretical Density
1145	4000	29	70*
1285	1000	30	90*
1285	4000	17	97
1285	4000	21	98
1285	4000	30	99
1375	1000	2	98
1375	1000	0.5	97
1375	4000	1	--†

*Pressing stopped before reaching required size because of low consolidation rate.
†Density not measured because of extrusion of cobalt.

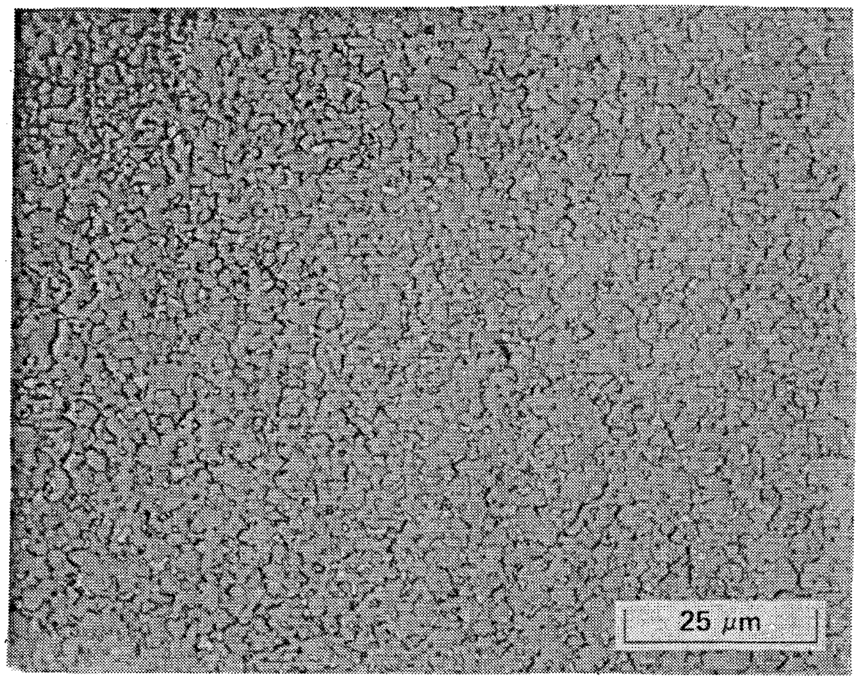
Similar sets of hot pressing runs were made for other compositions and Table 5 shows the hot pressing conditions that were adopted for each material. Hardness measurements were made on most samples produced during the process optimization study, so that an idea of the relative properties of the different cemented carbides could be obtained as early as possible. As it became evident that the NbC-Co materials showed the most promise, more effort was placed on optimizing the conditions to process these materials, and this is reflected in the more specific conditions shown in Table 5 for those NbC-Co compositions. Using the conditions of Table 5, the densities of both stoichiometric and substoichiometric cemented carbides were consistently between 98.5 and 100% of the theoretical density. Metallographic examination of polished surfaces showed that pores were present in a narrow surface region in the samples whose densities lay below the theoretical value. This surface porosity occurred if any of the pressing conditions was exceeded.

Table 5

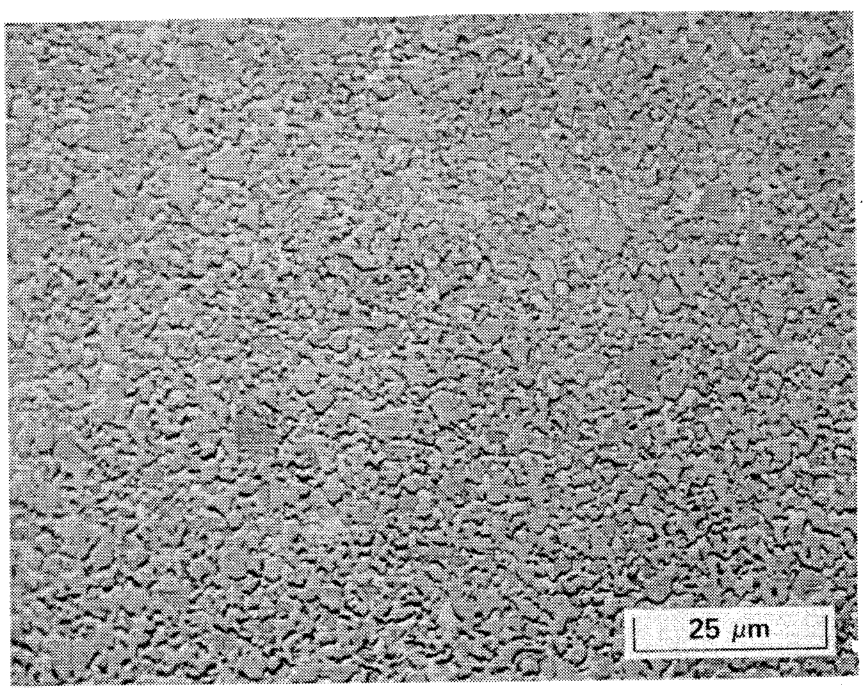
PRESSING CONDITIONS TO PRODUCE DENSE CEMENTED CARBIDES

Composition	Temperature (°C)	Pressure (psi)
NbC-5Co	1320	4000
NbC-10Co	1285	4000
NbC-20Co	1235	2000
NbC 5-20Ni	1225	2000
TaC 5-20Co	1370	2000
TaC 5-20Ni	1370	2000

Figures 1 through 3 illustrate the range of microstructures made during the processing studies. Figure 1 shows the relatively uniform distribution of NbC_x and Co that was generally achieved in these cemented carbides. The carbide grains are equiaxed and the size is about 3 μm. The microstructures of cemented NbC_x with a fixed Co content but different carbon contents were indistinguishable.

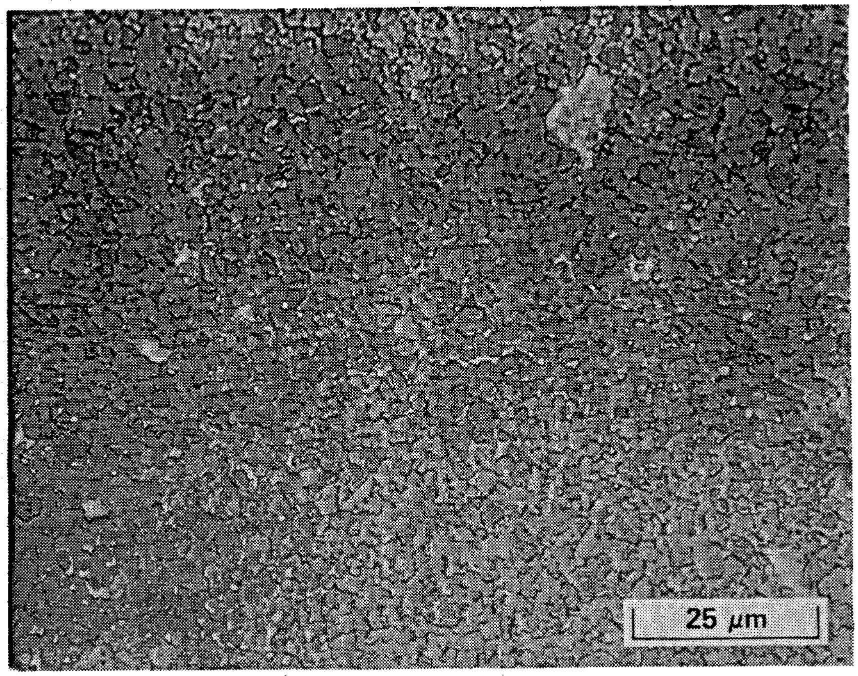


H.P. 56 NbC-10 Co DENSITY 7.92 (100.2% T.D.)

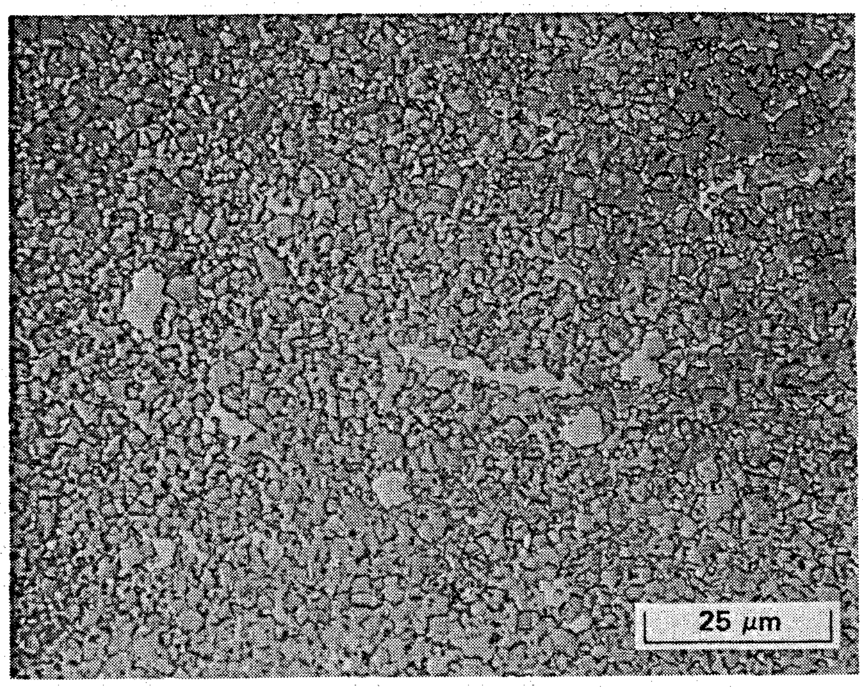


H.P. 26 NbC-20 Co DENSITY 7.87 (98.3% T.D.)

Figure 1. Microstructures of Hot Pressed NbC-Co

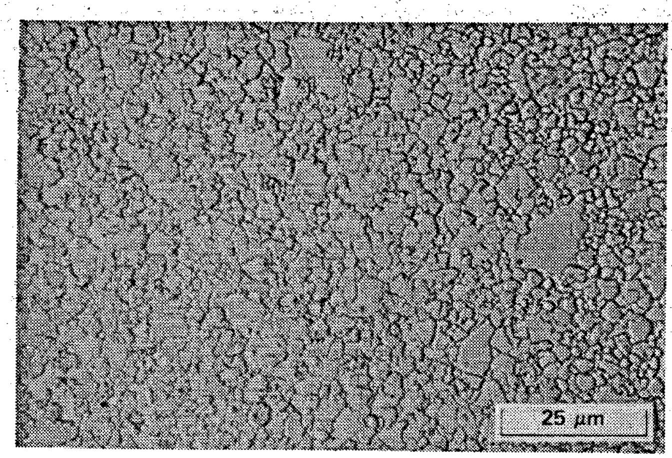


H.P. 45 NbC-10 Ni DENSITY 7.94 (100.5% T.D.)

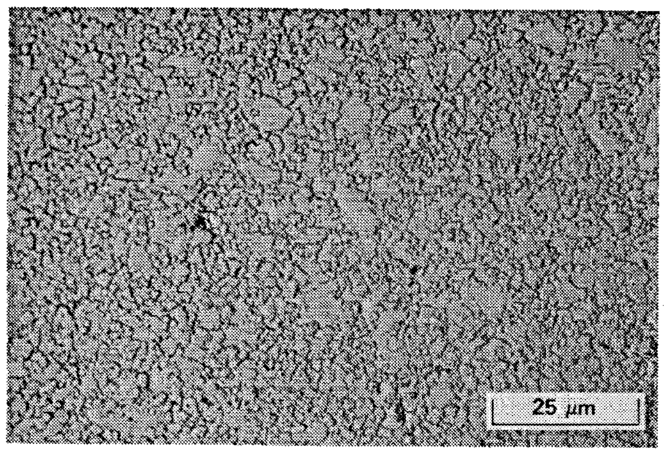


H.P. 47 NbC-10 Ni DENSITY 7.6 (96% T.D.)

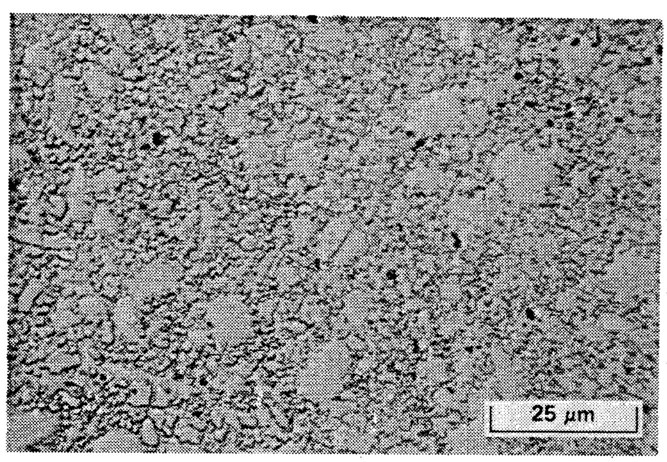
Figure 2. Microstructures of Hot Pressed NbC-Ni



H.P. 28 TaC-5 Ni DENSITY 13.91 (98% T.D.)



H.P. 50 TaC-10 Ni DENSITY 13.59 (97.5% T.D.)



H.P. 30 TaC-20 Ni DENSITY 12.66 (95% T.D.)

Figure 3. Microstructures of Hot Pressed TaC-Ni

The effects of insufficient milling can be seen in Figure 2 for NbC-Ni milled for 24 hours. This figure also illustrates the consistency of microstructure in samples made in different hot-pressing runs for the same nominal processing conditions. Although the carbide grain size is uniformly small, occasional large lakes of Ni can be seen. It was found more difficult to obtain dense uniform microstructures with Ni binders than with Co, and the TaC_x-based systems were more difficult to consolidate than the NbC_x cemented carbides, as can be seen by comparing Figures 1 and 3. Cemented carbides based on NbC_x might be easier to fabricate than those containing TaC_x, because the phase diagrams indicate that a larger amount of liquid phase is present during hot pressing of NbC_x materials.

A number of samples were examined to determine whether differences in microstructure or properties existed between the center and the surfaces of hot pressed rods. Figure 4 shows a hardness trace made across a longitudinal section of a short-rod specimen. The small change in hardness with distance that occurs over most of the length is probably a real effect and could be caused by a small density gradient in the hot pressing direction. Within 1/2-mm of the top and bottom surfaces, the hardness is very high. Transverse sections also showed similar high hardness within a 1/2-mm peripheral zone, but the hardness across the rest of the section was constant. Scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) showed that these narrow regions of high hardness generally contained much less Co than the bulk. Some loss of cobalt by extrusion during hot processing is difficult to avoid.

Hardness and Toughness

The first part of this evaluation concentrated on establishing the influence of binder type and content on the hardness and crack resistance of cemented stoichiometric carbides. Figure 5 shows the hardness of various cemented carbides as a function of binder content. Each point represents the mean of five readings on each specimen; two or

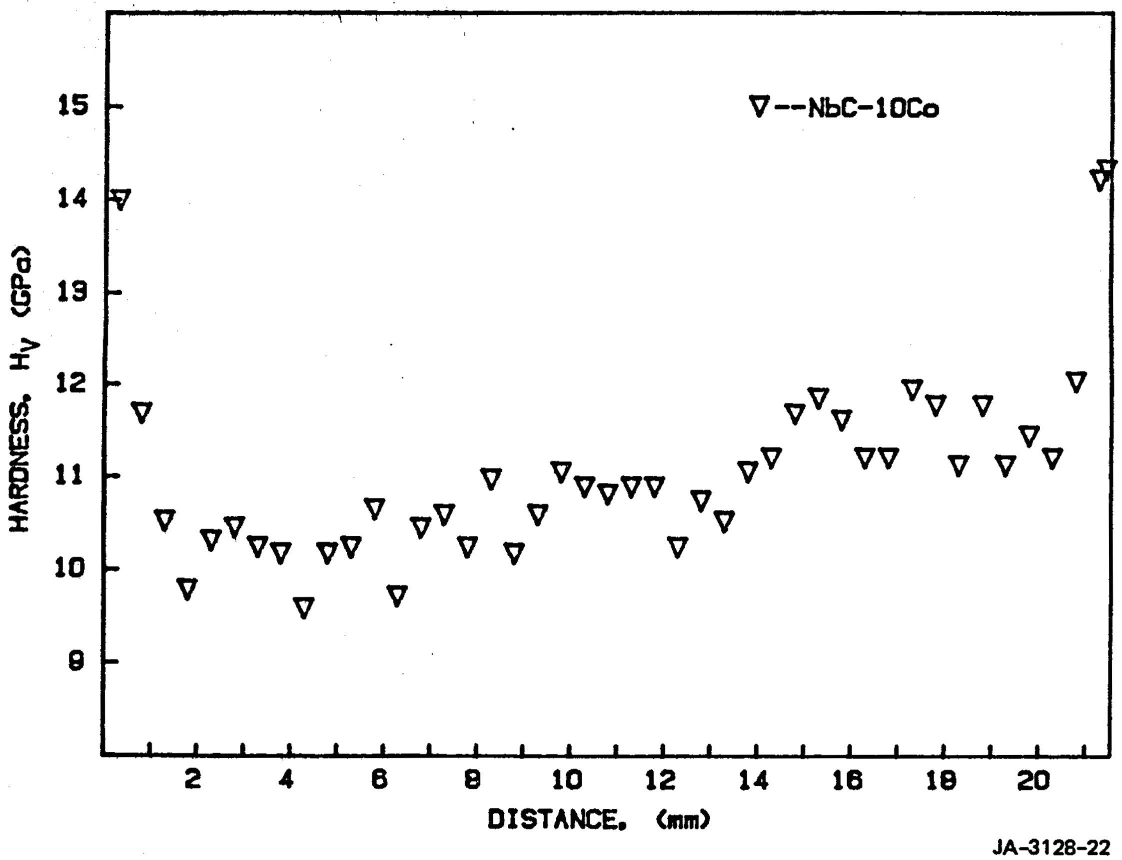


FIGURE 4 HARDNESS TRACE ACROSS A LONGITUDINAL SECTION OF A HOT PRESSED SHORT ROD SPECIMEN OF NbC-10Co

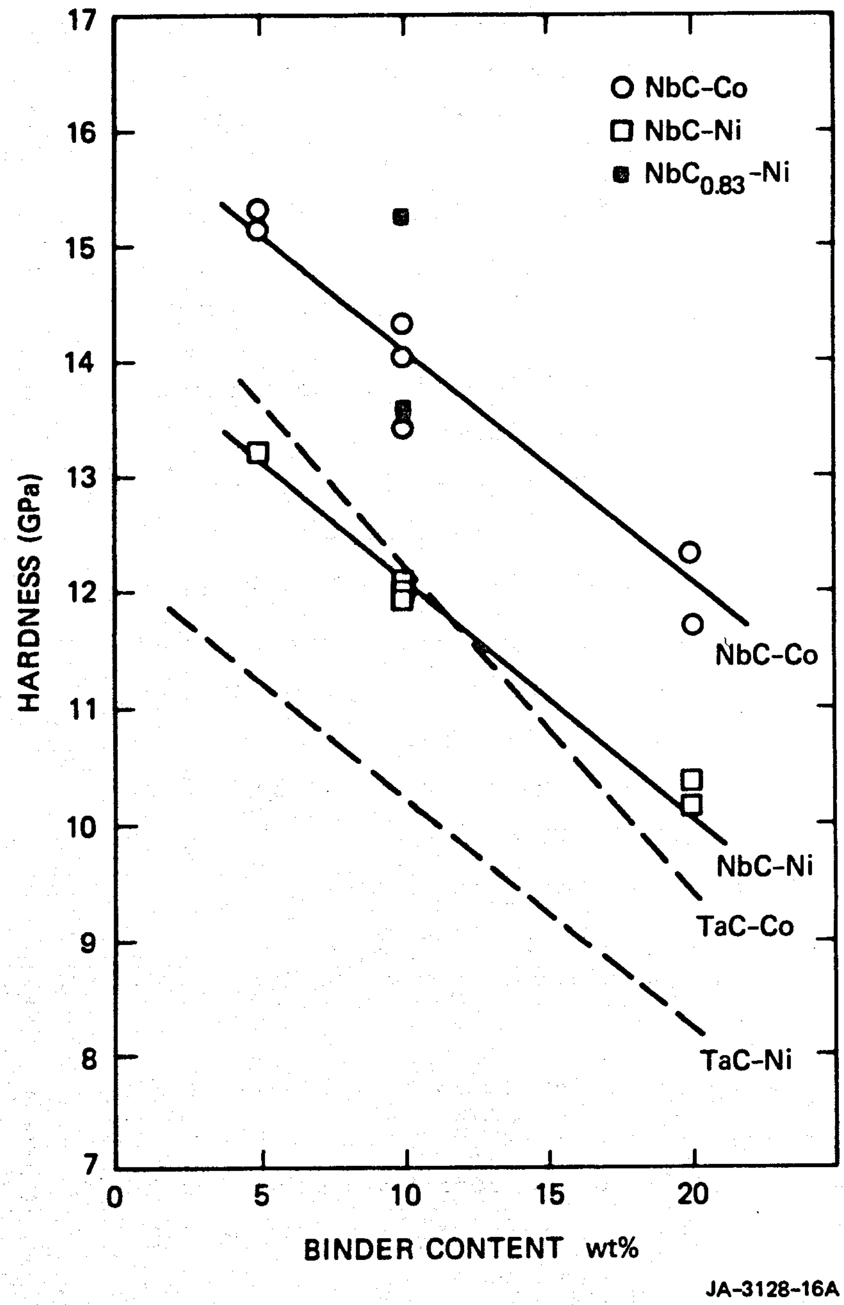


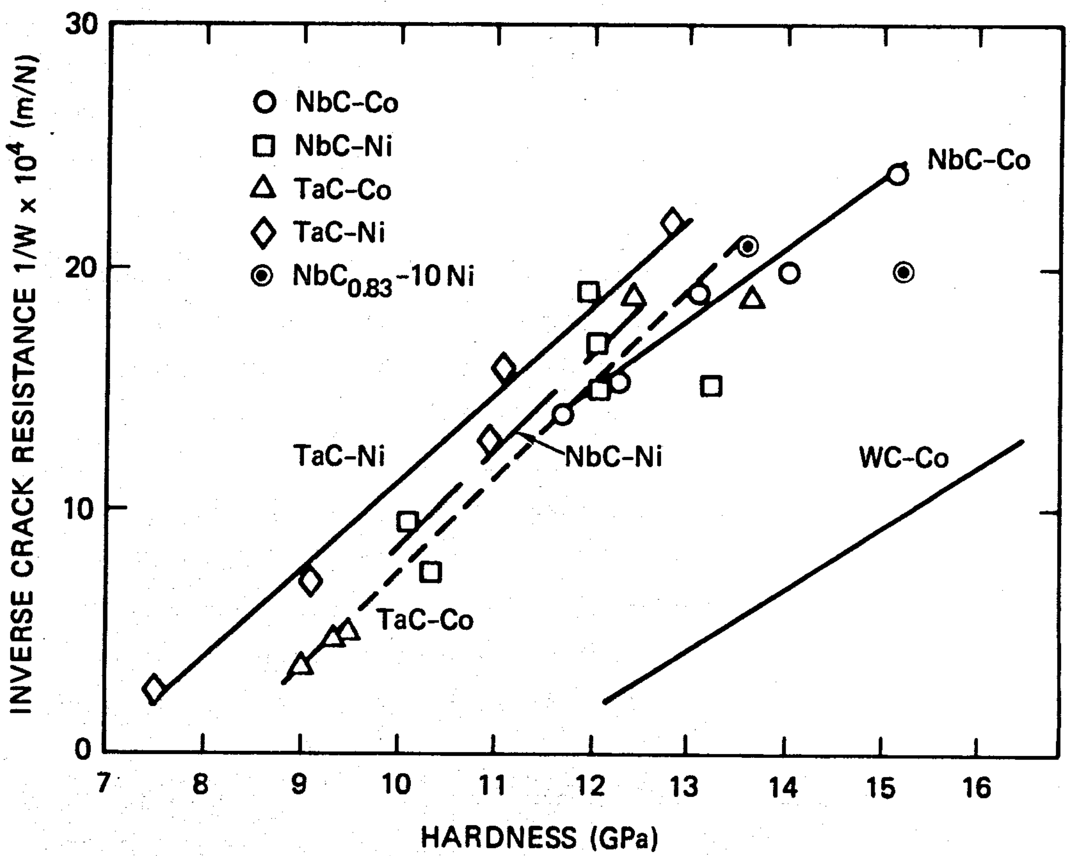
FIGURE 5 HARDNESS OF NbC AND TaC CEMENTED CARBIDES

three specimens of each composition were tested. Points for the TaC_x-based materials have been omitted for the sake of clarity but the scatter was the same as for NbC_x materials. For a given binder content, the hardness of NbC-Co is greater than that of any of the other systems and for both carbides Co produces a harder material than does Ni. Since Ni and Co have the same density, the quantitative differences in hardness between these systems is the same in terms of weight or volume fraction of binder. The density of TaC is approximately 1.7 times that of NbC, therefore, on a volume fraction basis the hardness of the TaC materials is closer to that of their NbC counterparts, but the hardnesses of the latter are still significantly higher.

The data for $NbC_{0.83}$-10Ni reflect the strong effect of the carbon content of the carbide on hardness. The difference between the hardness of the two samples of $NbC_{0.83}$-10Ni is probably associated with differences in density; the harder material was close to theoretical density, whereas the softer one had approximately 4% porosity.

The relative crack resistance[14] of these materials was determined from measurements of the lengths of cracks generated at the hardness impressions. In this test the total length of radially oriented cracks generated at the four corners of a Vickers hardness impression is measured for a specific load. A crack resistance parameter W is then defined as the load to produce a crack of unit length. This parameter provides a useful qualitative method of ranking the relative toughnesses of similar cemented carbides, without a detailed knowledge of other mechanical properties.

The data are shown in Figure 6 as a function of hardness. The location of the curve for commercial grades of WC-Co is shown for comparison. The NbC and TaC cemented carbides show qualitatively the same behavior as WC-Co in that the softer grades have the best crack resistance. Clearly, the crack resistance of the well-established grades of WC-Co is considerably higher than that of the experimental materials, but the same range of hardness can be achieved with stoichiometric NbC-Co and with $NbC_{0.83}$-Ni. For a given hardness, the



JA-3128-17A

FIGURE 6 RELATIVE CRACK RESISTANCE OF CEMENTED CARBIDES crack resistance of NbC-Co and possibly $NbC_{0.83}$-Ni is greater than that of any of the other experimental materials.

Based on these results and those of the microstructural studies, the properties of the NbC_x-Co alloys were investigated in more detail. Figure 7 shows the hardness of cemented carbides in this system. The curves tend to converge at high binder contents because of the greater influence of the larger quantity of cobalt. The curves diverge at low cobalt contents, reflecting the higher hardness of substoichiometric NbC. With 10 wt% Co, cemented $NbC_{0.83}$ is approximately 15% harder than cemented stoichiometric NbC, and for a given binder content, the hardness of cemented $NbC_{0.9}$ lies between that of the other two carbide compositions.

Figure 8 shows the hardness and toughness of all compositions of NbC_x-Co. The toughness values were measured by the indentation technique as described in the appendix. Comparative data, measured by the short-rod technique, are shown for WC-Co. For a given hardness, the substoichiometric cemented NbC is tougher than the stoichiometric material, which further illustrates the extra degree of control of properties that can be obtained in cemented NbC_x compared with cemented WC. The range of hardness of most of the compositions of NbC_x-Co (in Figure 8) includes that of typical rock-bit cemented WC as well as harder materials based mainly on substoichiometric NbC. Comparison of the data in Figure 8 shows that, for a given hardness, the toughness of NbC_x-Co is less than that of WC-Co and that the variation of hardness with toughness is much stronger in NbC_x-Co. The data for stoichiometric NbC show more scatter than those for $NbC_{0.83}$.

There is a large variation in hardness for stoichiometric materials with a toughness between about 5 and 6 MPa $m^{1/2}$. All these materials are NbC-10Co, made under different conditions in the process optimization studies. Figure 9 plots the hardness of these samples with respect to percentage of theoretical density. These data show that removal of the last 3% of porosity can increase the hardness by approximately 30%. The data in Figures 8 and 9 also indicate, however, that toughness is insensitive to this level of residual porosity.

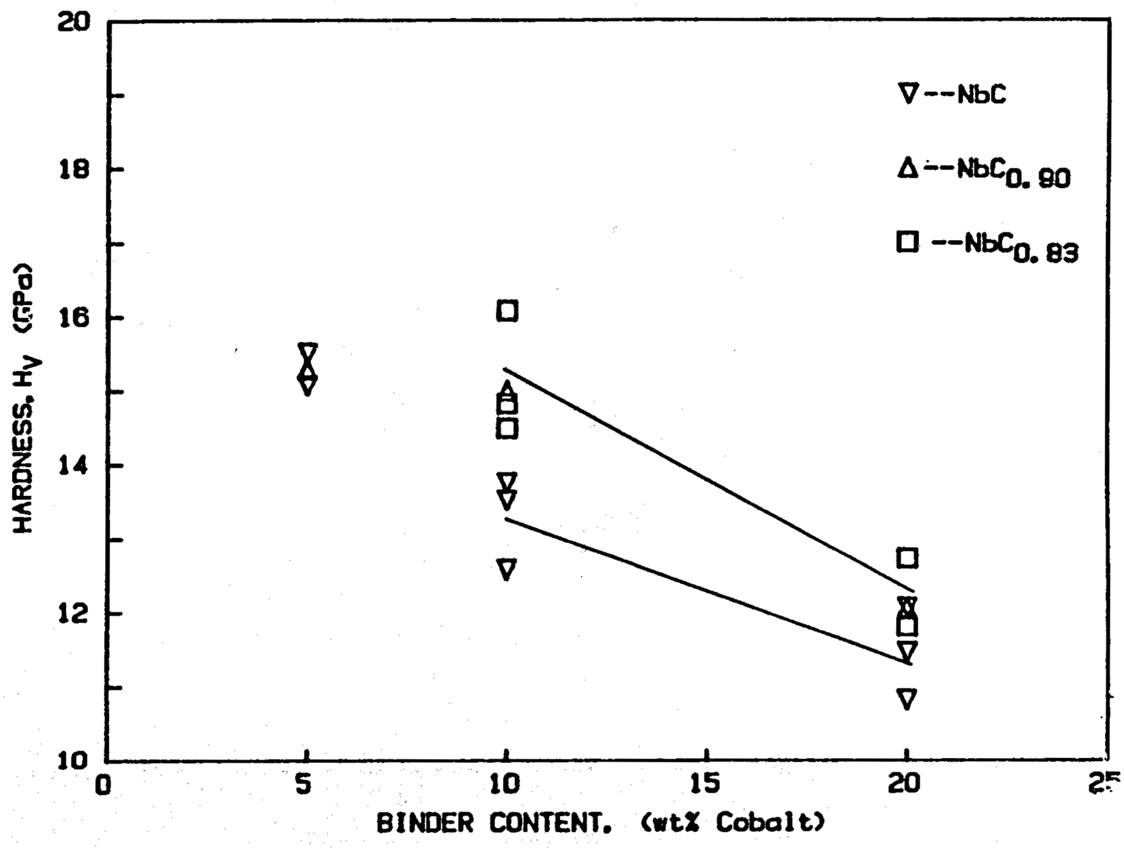


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FIGURE 7 EFFECT OF BINDER CONTENT AND CARBON CONTENT ON THE HARDNESS OF CEMENTED NIOBIUM CARBIDE.

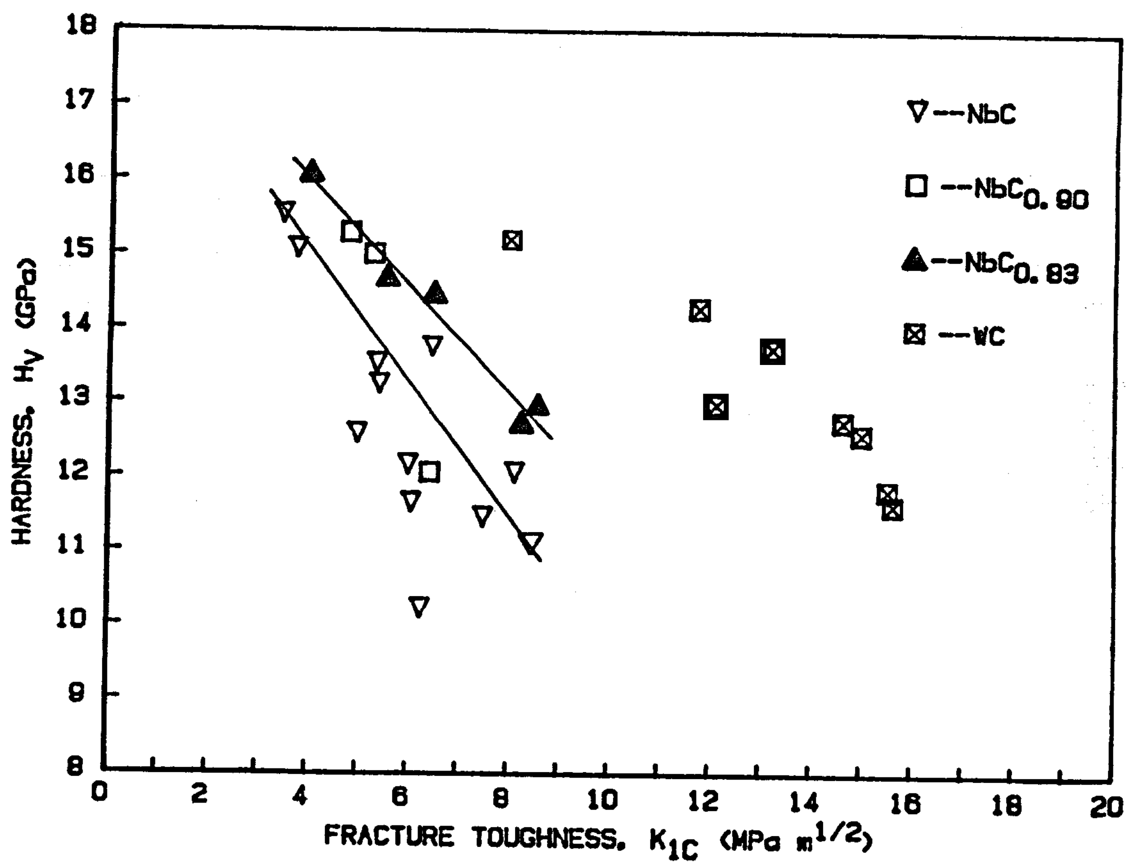

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FIGURE 8 HARDNESS AND FRACTURE TOUGHNESS OF CEMENTED CARBIDES.

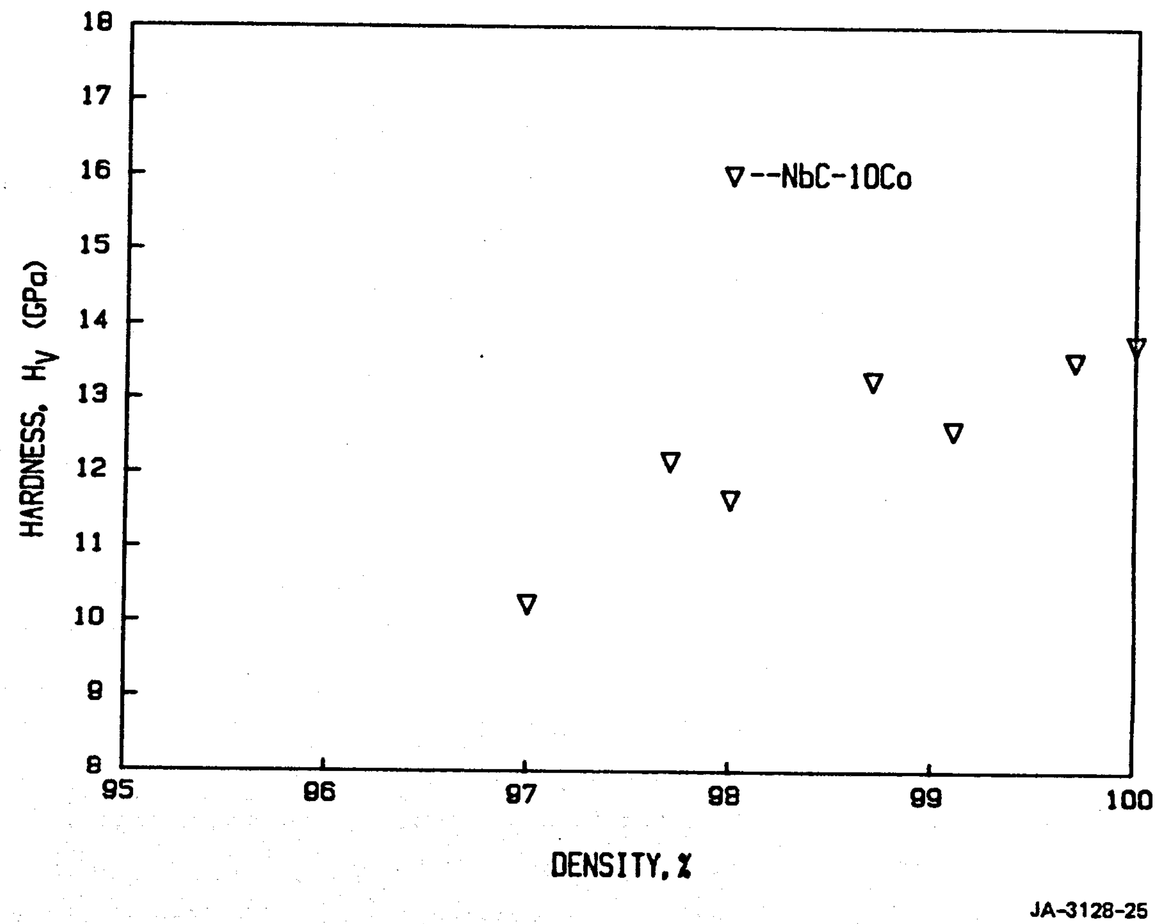


FIGURE 9 EFFECT OF DENSITY ON THE HARDNESS OF Nb-10Co

The factors that influence toughness include composition, details of microstructure, and the presence of residual stress. In this work it has been most convenient to express compositions in terms of weight fractions of carbide and binder. However, quantitative aspects of the microstructure such as the proportion of carbide grains with common boundaries (contiguity factor[15]) depend on the relative volumes of the phases. For a given weight fraction of cobalt, the volume fraction is much smaller in NbC_x-Co than in WC-Co because of the higher density of WC. Thus the contiguity factor will be considerably larger in NbC_x-Co; consequently, the toughness should be lower. Larger volume fractions of cobalt, comparable to those in current grades of WC-Co, can be expected to raise the toughness of NbC_x-Co, with some lowering of the hardness. For example in NbC-20 Co and WC-10 Co the volume fractions of cobalt are 17.6% and 16.3%, respectively. The hardness and toughness of NbC-20 Co is approximately 12 GPa and 8.5 MPa $m^{1/2}$ compared to 12 GPa and 14 MPa $m^{1/2}$ for an optimized commercial grade of WC-10 Co.

The presence of residual stress is expected to exert a strong influence on resistance to crack propagation. Residual tensile stresses normal to the plane of a crack assist its propagation and lower the apparent fracture toughness, whereas residual compressive stresses have the opposite effect. Residual stresses can arise during hot pressing, particularly as in the present case when the specimens are cooled rapidly at the end of the hot pressing cycle. On passing through the liquidus, the outside of the specimen becomes rigid while the center can still deform. When the whole specimen has cooled the outside will be in compression and the inside in tension. Depending on the rate of cooling, the exterior zone of compressive stress is likely to be relatively narrow and the stress gradient will be high. This type of macroscopic stress distribution is superimposed on the local stress pattern where the carbide grains are in compression with respect to the cobalt phase, because of the differential thermal expansion.

In the short-rod fracture toughness tests performed at TerraTek, negative displacement intercepts during cyclical loading indicated the presence of substantial macroscopic residual compressive stresses. These stresses were sufficient to raise the apparent fracture toughness, K_Q, by as much as 40% above the corrected value. On the other hand the fracture toughness values determined by indentation correlated reasonably well with the corrected values of K_{Ic}. This is expected because the indentation test only samples local stress fields, and the tests were made in the central regions of cross-sections. The presence of different levels of residual stressès is clearly a complicating factor in interpreting properties where fracture is involved. If macroscopic residual stresses originated as suggested here, then it should be possible to modify the stress fields and, to some extent, the fracture properties by heat-treatment.

Wear Resistance

Table 6 shows the results of wear tests made at Security Dresser. The wear resistance number W reflects the volume of material lost from a standard 12.7 mm-diameter cylinder abraded on a rock surface under controlled conditions; the larger the value of W, the higher the wear resistance. The W values can be ranked approximately in order of increasing hardness and decreasing toughness. For a given cobalt content, the $NbC_{0.83}$ materials are generally harder, tougher, and considerably more wear-resistant than their stoichiometric counterparts. Examples of wear-resistance values for commonly-used rock cutting grades of WC-Co, determined by the same test, are given in Table 7. These examples show that the wear resistance of the NbC_x-based cemented carbides lies within the range of the grades of WC-Co commonly used in rock drilling. The high wear resistance values found in $NbC_{0.83}$-10 Co can be achieved in grades of WC-Co with a lower Co content. Such grades are not currently used for rock cutting because of their low fracture toughness. However, no wear resistance data on low Co grades of cemented WC were available for comparison.

Table 6

HARDNESS AND WEAR RESISTANCE OF CEMENTED CARBIDES

Composition	Hardness, Hv (GPa)	Fracture Toughness, K_{Ic} (MPa $m^{1/2}$)	Wear Resistance, W
NbC-10Co	12.70	-	784
NbC-10Co	-	-	669
NbC-10Co	12.16	5.98	1098
NbC-10Co	13.25	5.39	878
NbC-20Co	11.05	8.28	376
$NbC_{0.83}$-10Co	14.40	5.30	2065
$NbC_{0.83}$-10Co	14.28	6.47	1866
$NbC_{0.83}$-20Co	12.52	8.54	536

Table 7

EXAMPLES OF WEAR RESISTANCE VALUES FOR COMMONLY USED WC-CO

Wear Resistance, W	% Co
1076	10.35
872	12.35
803	12.35
611	10.35
581	10.35
565	10.35
448	10.35
267	16.51
258	15.13
236	16.51

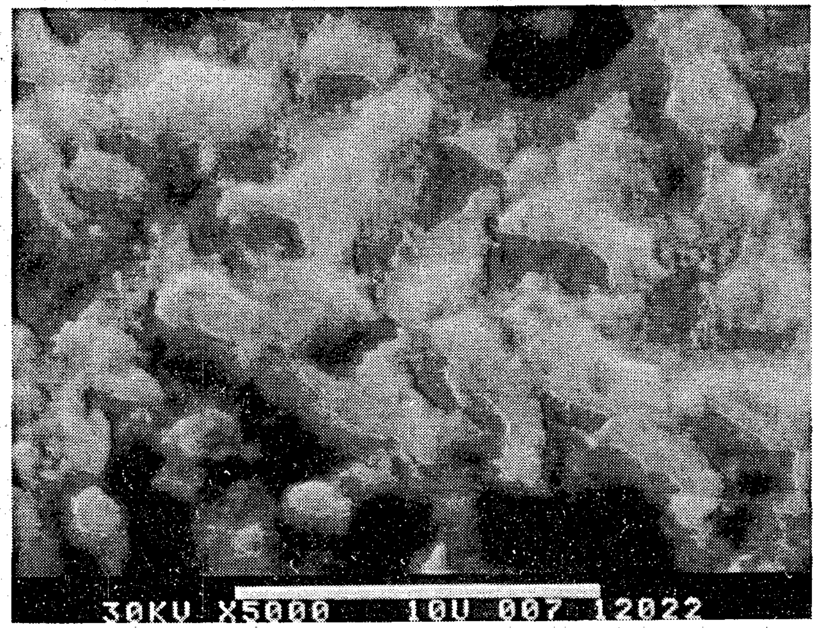
In comparing the properties of cemented carbides, it must be appreciated that hardness, toughness, and wear resistance are all considered when selecting a grade of carbide for a particular drilling application. It is clear that these experimental cemented carbides are extremely wear resistant, but the corresponding levels of toughness are below those that are usually required in WC-Co. The relative importance of hardness, toughness, and wear resistance in determining the drilling behavior of an insert might be different in WC-based and NbC-based materials, and drilling tests will be necessary before a valid comparison can be made.

Examination of Wear Surfaces

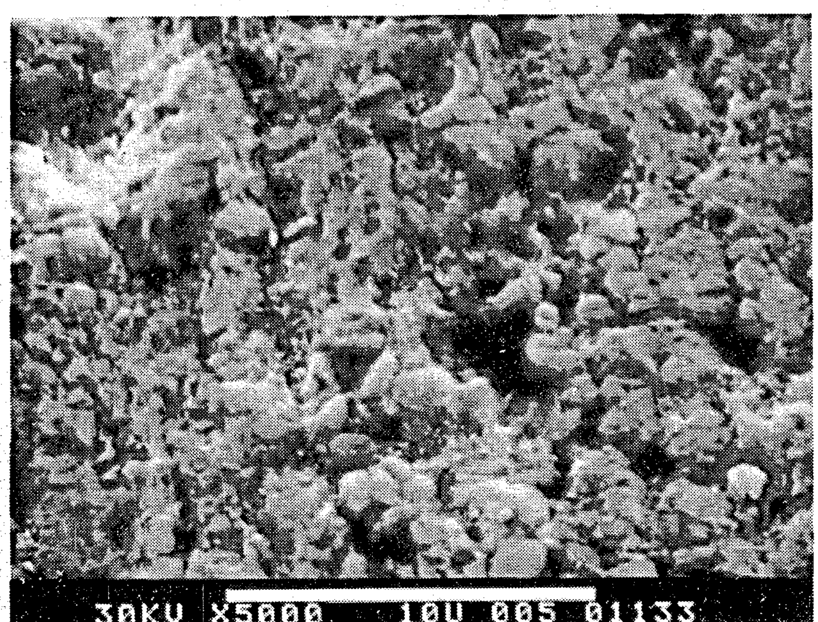
Several processes can occur separately or in combination that will cause loss of material in an abrasive wear test. If the cobalt is attrited away, the carbide grains can be pulled out; they can also fracture and fall out if they are unsupported by cobalt. This type of uneven wear can be expected if the cobalt regions are relatively large compared with the carbide grain size. This would arise either for large cobalt contents or in inhomogeneous microstructures. Alternatively, poorly bonded carbide grains might exist if the overall binder content is low or if local concentrations of cobalt exist due to inhomogeneities. In either case, loss of individual grains is expected to result in high wear rates. On the other hand, if the cobalt is lost gradually and the grains are well supported, the surface should wear more evenly. If the carbide has the right properties, it may wear by a process of plastic rounding rather than fracture. In this case, wear rates will be low. The wear mechanisms of individual cemented carbides are probably more complex than this description, and it is likely that several mechanisms of loss of material will contribute to the abrasive wear of specific grades of carbide.

Figure 10 shows examples of the abraded surfaces of materials showing the lowest wear resistance in the NbC_x series. In NbC-20Co, the cobalt is heavily attrited away, and some of it can be seen as approximately spherical debris. The relatively soft carbide grains show evidence of considerable rounding. There are no microfractures, but many grains have been pulled out. Consequently, the wear number is relatively low. In the example shown in Figure 10(b), the attrition of cobalt is probably very similar to that shown in Figure 10(a), but there is less loss of carbide by plastic rounding. Many grains have been pulled out and there is evidence for microfracture.

Figure 11(a) shows considerable microfracture and pull-out but little plastic rounding of the stoichiometric NbC grains. The materials shown in Figure 11 contain 10% Co so there is less binder to be lost by attrition. On the other hand, if insufficient cobalt is present, this can affect the degree of support given to the carbide grains. Figure 11(b) illustrates the wear surface of $NbC_{0.83}$-10 Co, the material with the highest W value. It shows many rounded carbide grains and some pull-out, but virtually no microfracture. This micrograph suggests that relatively uniform wear of both phases is occurring and that the main wear mechanisms is related to plastic flow. This could be an important observation because there is no evidence that the wear resistance is limited by the relatively low fracture toughness of $NbC_{0.83}$-Co compared with WC-Co.

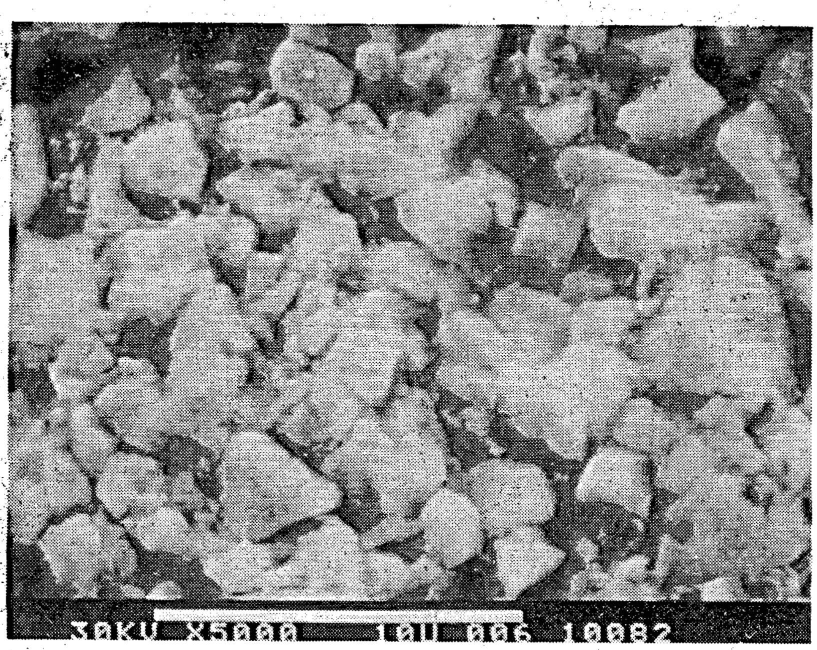


NbC-20Co W = 376

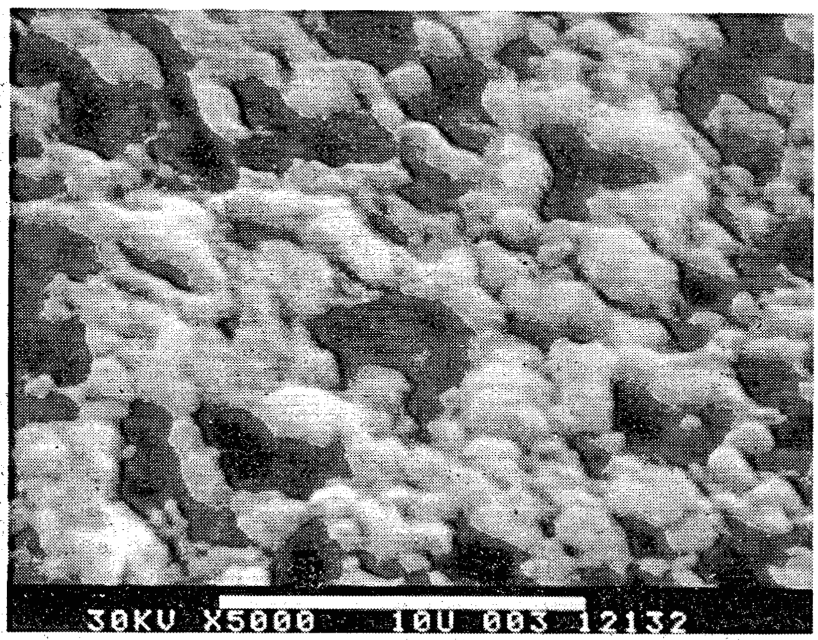


$NbC_{0.83}$-20 Co W = 536

Figure 10. Wear Surfaces of Cemented $NbC_{0.83}$



NbC-10Co W = 669



$NbC_{0.83}$-10 Co W = 2065

Figure 11. Wear Surfaces of Cemented Niobium Carbide

V CONCLUSIONS

The fabrication studies of cemented carbides based on NbC and TaC with cobalt and nickel binders showed that the lowest porosities and most uniform microstructures were obtained in the NbC-Co system, and much of the study focused on these materials.

The range of hardness that can be obtained in NbC_x-Co alloys is comparable to that found in rock cutting grades of WC-Co, and harder materials can be made using substoichiometric NbC. The fracture toughness of the experimental carbides was lower than that of WC-Co of the same hardness. The most significant toughness result was that, for a given hardness, the fracture toughness of $NbC_{0.83}$-Co was greater than that of stoichiometric NbC-Co. From these data it can be concluded that carbon content exerts a strong influence on the properties NbC_x-Co materials and that, by adjusting the carbon content of the carbide, it is possible to obtain simultaneous improvements in hardness and toughness in this system.

Observations made during toughness and wear tests suggest that residual stresses are present that might affect resistance to cracking. The presence of residual compressive stresses raises the apparent fracture toughness by as much as 40%. The residual stresses probably arise in hot pressing, and it is likely that such stresses could be controlled either by heat treatment or in a fabrication route based on cold pressing and sintering. The latter route would also eliminate microstructural and compositional inhomogeneities that arise if the cobalt phase is extruded at the surface during hot pressing.

Abrasive wear tests provided a valuable insight into the potential usefulness of cemented NbC_x. The abrasion resistance of the NbC_x-Co compositions is in the range of the WC-Co compositions that are currently in use for rock cutting and cemented carbides with higher wear resistance values can be made using $NbC_{0.83}$ cemented with Co.

Examination of wear surfaces indicated that both phases in $NbC_{0.83}$-10 Co wear at a relatively even rate and that material is removed by a process related to plastic flow, rather than microfracture. These observations suggest that the relative role of plastic flow and fracture in determining resistance to abrasive wear might be different in NbC_x-Co and WC-Co. Whereas the wear resistance results are encouraging, the fracture toughness levels are significantly below those used in current WC-Co insert grades. Thus the high levels of wear resistance that can be developed in NbC_x-Co might be difficult to utilize if the corresponding fracture toughnesses are insufficient to prevent macroscopic fracture during drilling.

Niobium carbide is also attractive because of its cost and relative abundance. The current price for NbC is $25/lb for 100-lb lots. Since the density of NbC is only about half that of WC, the cost of carbide per insert could be very low, depending on the composition. Further work that would focus on improved fracture toughness and on drilling tests is clearly required to establish the technical merits of NbC_x-Co for geothermal drilling applications.

VI RECOMMENDATIONS FOR FUTURE WORK

This program has established that cemented niobium carbides have some unique properties that make them an attractive alternative to conventional WC-Co rock bit materials. Further work is required to improve the fracture toughness and to evaluate performance in controlled rock drilling tests. A program containing the following tasks would accomplish these goals:

(1) Establish the conditions to produce $NbC_{0.83}$-10Co by cold pressing and sintering.

(2) Determine the fracture toughness, hardness, transverse rupture strength and abrasive wear resistance of sintered $NbC_{0.83}$-10Co

(3) Select a drilling system, conditions and insert design appropriate to the properties of $NbC_{0.83}$-10Co and fabricate the inserts.

(4) Perform drilling tests using a cutting structure containing inserts of $NbC_{0.83}$-10Co.

(5) Determine the wear mechanisms by examination of inserts after the drilling tests.

APPENDIX

Indentation techniques have been developed for measuring the fracture toughness of ceramics.[16,17]. These methods are potentially very valuable in materials development and in quality control because measurements can be made on a polished surface of any small sample. The use of indentation to measure the fracture toughness of cemented carbides was explored as a separate task on this project. The objective was to determine whether the indentation technique could give fracture toughness values for cemented carbides that are comparable with those obtained by other fracture mechanics methods.

When ceramics such as silicon nitride are indented with a diamond pyramid, radial cracks are generated from the corners of the plastic impression. These cracks are approximately semicircular and pass under the plastic impression. The driving force for the crack system is the residual stress that arises from the plastic deformation in the immediate vicinity of the impression. This configuration is described by the expression:

$$K_{Ic} = L(E/H)^{1/2} \; (P/C_o^{3/2})$$

where K_{Ic} is the fracture toughness, L is a material independent constant, E is the Young's modulus, H is the hardness, P is the applied load and C_o is the total crack length. In the original analysis,[17] L was determined by measuring the appropriate parameters at indentations made in a wide range of ceramics for which K_{Ic} was known from standard fracture mechanics measurements. Good agreement was obtained for ceramics with values of K_{Ic} between 1 and 5 Mpa $m^{1/2}$, for $L = 1.6 \times 10^{-2}$.

A series of well-characterized WC-Co materials with cobalt contents between 8 and 16% was obtained from Terratek. Indentation toughness measurements made using $L = 1.6 \times 10^{-2}$ yielded values of

K_{Ic} that were approximately one and a half times the short-rod fracture toughness values obtained at Terratek. Using the Terratek data, a new value of L of 1.06 x 10^{-2} was derived that gave reasonable agreement between the two techniques, as shown in Table 8. However, indentation tests made on WC-6 Co underestimated K_{Ic} substantially. Using the original value of L of 1.6 x 10^{-2} the value of K_{Ic} for WC-6 Co is 7.68 MPa $m^{1/2}$, which is reasonably close to the short rod value.

The other demands of the program did not allow us to investigate these discrepancies in detail. However, two factors that could affect the results are crack shape and relative size of the plastic zone compared to that of the crack. It is likely that the shape of the crack is controlled by the shape of the plastic zone in that the crack front forms at the plastic-elastic boundary and follows its contour. The free surface also influences the crack shape, because the crack will eventually run out at the surface.

Indentation in the cemented WC-Co materials with 8-16% Co forms Palmqvist cracks, which are short compared to the size of the plastic impression and extremely shallow. Palmqvist cracks could arise if the plastic zone is more or less spherical and extends relatively far into the material. On the other hand, cracks in ceramics and in WC-6Co, are approximately semicircular and connect under the indentation. In these materials the plastic zone is approximately hemispherical and it is very small compared to the crack. A transition from Palmqvist to the full semicircular radial cracks has been observed in ZnS[18] . Such a transition can be expected in WC-Co at high loads.

Indentations in the experimental cemented carbides based on NbC_x and TaC_x formed semicircular radial cracks similar to those seen in WC-6Co and in ceramics, and there was a linear relation between load P, and crack length $C_o^{3/2}$. Short-rods of NbC-10Co were tested at Terratek and indentation fracture toughness values were measured on the broken specimens using L = 1.6 x 10^{-2}. The results are shown in

Table 8

SHORT-ROD AND INDENTATION FRACTURE TOUGHNESS OF WC-Co

Composition % Co	Short Rod K_{Ic} MPa $m^{1/2}$	Indentation* K_{Ic} MPa $m^{1/2}$
16	15.5	16.9
11	13.2	11.3
10	14.6	16.2
10	15.6	16.9
9	11.8	11.0
8	12.1	12.6
8	15.0	17.5
6	8.0	4.8

*Mean of 3 readings with 50 kg load.

Table 9

SHORT-ROD AND INDENTATION FRACTURE TOUGHNESS OF NbC-10Co

Sample Number	Hardness* GPa	Indentation* K_{Ic} MPa $m^{1/2}$	Short-Rod K_{Ic} MPa $m^{1/2}$
HP 75	13.31	5.79	-
HP 78	13.03	6.24	5.32
HP 79	11.93	6.24	5.89
HP 80	13.14	6.20	5.04

*Mean of 3 readings with 50 kg load.

Table 9. The agreement was sufficiently good to permit this analysis to be used to determine the fracture toughness of the other experimental materials made in this program.

These results indicate that the currently available fracture mechanics analysis derived for indentation fracture in ceramics can only be used for cemented carbides with toughnesses below 10 MPa $m^{1/2}$. Indentation in tougher cemented carbides produces Palmqvist cracks. In this case, the crack and the plastic zone are of similar dimensions and the analysis becomes invalid. Further work is required to extend the analysis so that a reliable indentation method can be developed for materials with fracture toughnesses in the range 10 to 20 MPa $m^{1/2}$.

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