WATERTOWN ARSENAL

RODMAN LABORATORY

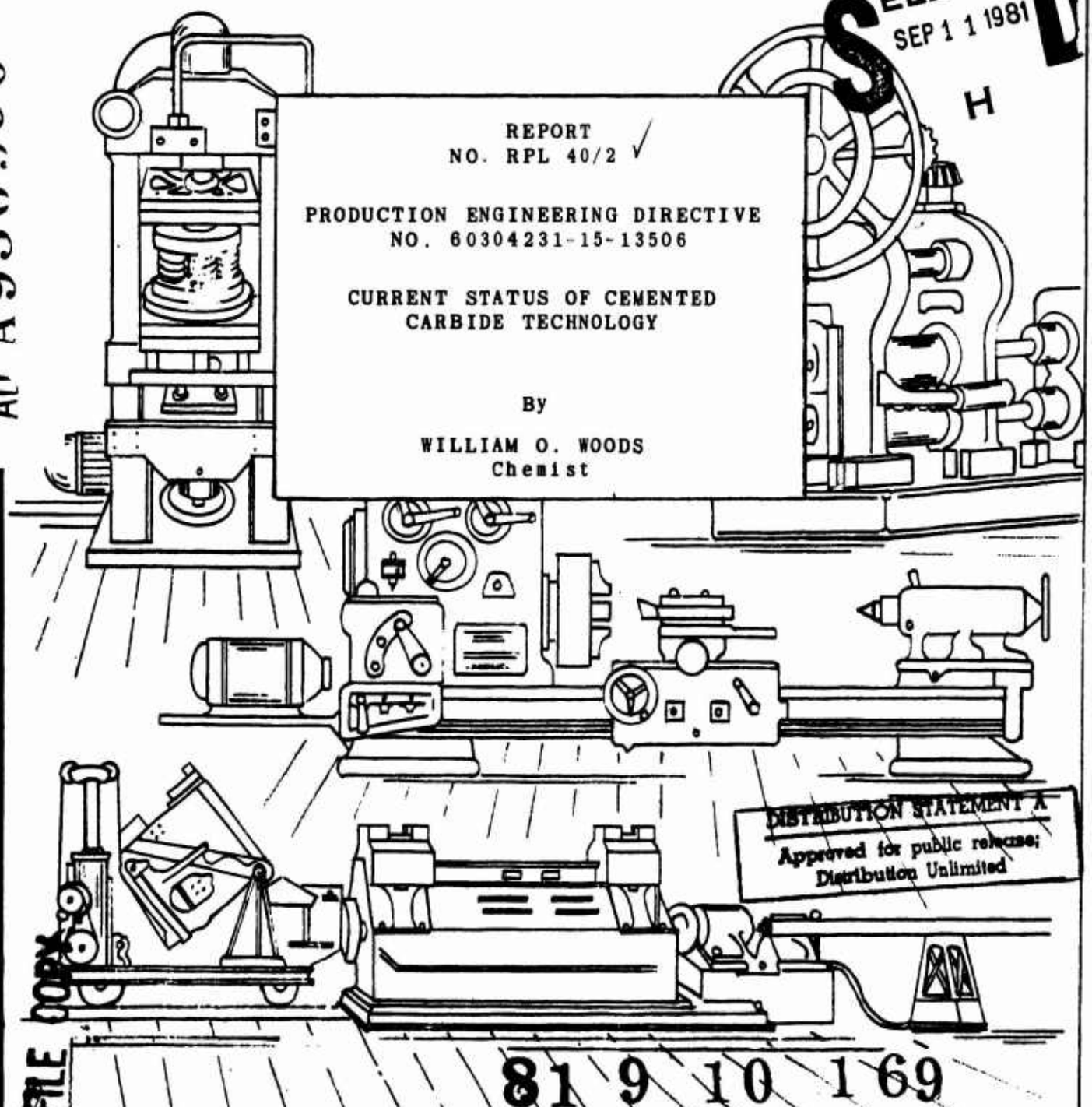
REPORT
NO. RPL 40/2

PRODUCTION ENGINEERING DIRECTIVE
NO. 60304231-15-13506

CURRENT STATUS OF CEMENTED CARBIDE TECHNOLOGY

By

WILLIAM O. WOODS
Chemist



DATE: JUNE 1958

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TITLE

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OBJECT

To determine the current status of cemented carbide technology, including fabrication, properties, and utilization, in order to provide a basis for the selection and classification of these materials for Ordnance application.

SUMMARY

The historical background, technological development, properties and applications of cemented carbides are presented in the body of this report. Recommended test methods for the determination of some of the physical properties, i.e., hardness, transverse rupture strength, and density, are included in the appendix to this report.

CONCLUSIONS

1. Techniques of manufacture and the use of cemented carbides have, in the last two decades, made extremely rapid progress; fundamental investigation, although not neglected, has lagged behind. The available technical literature is limited, although some commercial information is published by manufacturers.

2. The multiplicity of composition of carbide materials which can be used in the same area, emphasizes the need for correlation studies.

APPROVED:

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The material discussed in this report is presented in the following order:

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   Statement of Problem

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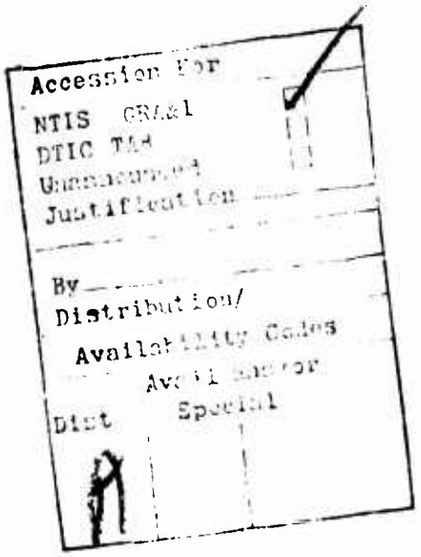


INTRODUCTION

In any industry, the approach to reduction of costs has been, for established processes, through the increase in rates of production attained by gradual development of the processing method with the application of improved materials and equipment. The history of the metal cutting industry exemplifies the benefits that can be derived by the use of improved materials. Increased output and reduction of cost has been realized with the substitution of cemented carbide for high speed tool steel and carbon tool steel cutting alloys. The major advantages of the changeovers, higher machining speeds and longer tool life, led to reduction of tool costs and increased productive time, as well as the productivity of equipment and manpower.

The period in which cemented carbides were brought to their present stage of development is quite short in comparison with the history of steel cutting tools. The relatively short time has introduced several areas in which the technical development and application has lagged while more fruitful developments have been exploited. Among these areas of retarded development is the proper designation of composition and process history for a carbide material which is to be used for a specific application. The absence of a satisfactory method for the selection of an optimum grade of carbide material for a service application often contributes to higher cost, lowered output, and inefficient utilization.

In view of the above considerations a program was initiated at the Watertown Arsenal to correlate the influence of chemical composition and processing conditions with the resulting physical and mechanical properties of tungsten carbide-based materials. The correlation will provide a basis for the establishment of satisfactory Government specifications and procurement by correlation of the properties with operational performance.

This report, undertaken as the initial activity under the program, summarizes the current status of cemented carbide technology. The summary is to be used to determine the most important areas of omission in the available technical literature as well as to broaden the dissemination of processing information and applications as presented by the carbide producers and the results of such application by the carbide consumers. The source material for this report includes metallurgical reviews, scientific journals, transactions of scientific societies, treatises and books both foreign and domestic.

HISTORICAL SUMMARY

The history of cemented carbides began in 1896 when H. Moissan[1] melted tungsten in the presence of carbon in an electric furnace. The resulting product, tungsten carbide, was accorded little interest beyond the curiosity given a very hard material, because its extreme brittleness prevented practical utilization.

The first attempts to fabricate the hard material were made in 1912 by Lohman(a*). He melted and cast tungsten carbide in an effort to use it as a die material for drawing dies. The brittle and non-uniform structure of the castings caused Lohman to employ powder metallurgical techniques in his next fabrication attempt. He sintered finely divided tungsten carbide powder at a temperature close to the melting point of the carbide, but the resulting product was still brittle. His work, although unsuccessful, formed the basis for modern cemented carbide production.

During the period from 1914-1925, the attempts to process this extremely hard material continued. Several patents were issued for tungsten carbide containing compositions which were less brittle; however, the reduced brittleness was accompanied by an undesirable reduction in hardness. Baumhauer (b) in 1922 attempted to improve the mechanical properties by infiltrating a sintered porous body of carbide powders with molten iron. He improved the mechanical properties but could not avoid a high residual porosity in the material.

The first successful method for utilization of tungsten carbide is the process developed by Schröter (c) of mixing, in powder form, tungsten carbide and up to 20% by weight of a metal of the iron group, i.e., cobalt, iron, and nickel. In the manufacturing process as subsequently developed in Germany, mixtures of 6-20% cobalt and 94-80% tungsten carbide powders were pressed into briquettes and sintered at high temperature in a reducing atmosphere. American rights under the original German patents were assigned in the United States to an industrial corporation in 1925 (d). This composition and processing method still is being used today. The cobalt cemented tungsten carbides were better than conventional materials in machining cast iron alloys and non-metallic materials. However, they were not suitable for machining steel alloys. Efforts continued to develop new hard metals to accomplish this. Attempts were made to replace partly or completely the tungsten carbide by the carbides of other materials such as titanium, tantalum, molybdenum, niobium, (columbium), and to modify the cobalt binder by iron, nickel and their alloys.

The successful conclusion of these many attempts came when Schwarzkopf[2](e) initiated the method of combining tungsten carbide with titanium carbide in a single phase solid solution. Since 1929 cemented carbides consisting of solid solutions of WC-TiC, Mo_2C-TiC, WC-Mo_2C-TiC, and WC-TiC-TaC bonded with metals of the iron group, especially nickel and cobalt or their alloys have given outstanding performance as tool materials in the high-speed machining of steels and other materials which form long continuous chips.

Parenthetical letters refer to patents of historical interest on page 28.

McKenna[3] claims that superior products are obtained by synthesizing a compound $W_2Ti_2C_4$ and using the compound instead of a solid solution of WC-TiC. However, X-ray[4] and other evidence has not confirmed the existence of a compound having the claimed composition.

TECHNOLOGICAL DEVELOPMENTS

Cemented carbides or hard metals are sintered products consisting of carbides of metals of the fourth, fifth and sixth group of the Periodic Table of Elements and a metal of the iron group as a binder. Those metals having properties of particular interest to the hard metal industry are, in order of importance, the carbide formers: tungsten(W), titanium(Ti), tantalum(Ta), molybdenum(Mo), vanadium(V), chromium(Cr), niobium(Nb), zirconium(Zr), and hafnium(Hf) and the binder metals - cobalt(Co), nickel(Ni) and iron(Fe).

The carbides of these materials exhibit properties which are normally considered of metallic character. Their melting point is very high ranging from 5000 to 7000°F; their electrical and heat conductivity is within the range encountered in metals; their hardness and strength at normal and elevated temperatures are extremely high; their resistivity against chemical attack is good; and their mutual solubility is good. The property of major importance to the hard metal industry is their capability of forming, to a limited extent, alloys with metals of the iron group.

TABLE I

KIEFFER AND KÖLBL[30]

CHARACTERISTICS OF METAL CARBIDES

CARBIDE	CARBON CONTENT WT%	LATTICE TYPE	DENSITY gm/cc	ROCKWELL HARDNESS, "A"	MELTING POINT C°	MELTING POINT F°
TiC	20.04	Cubic	4.7	92-93.5	3250	5880
ZrC	11.70	Cubic	6.7	90-92	3250	5880
VC	19.00	Cubic	5.3	90-91	2800	5070
NbC	11.40	Cubic	7.7	90-91	3800	6870
TaC	6.20	Cubic	14.0	87-88	3800	6870
Cr_3C_2	13.33	Ortho-rhombohedric	5.6	85	2000	3630
Mo_2C	5.88	Hexag. close-packed	8.8	88-90	2500	4530
WC	6.12	Hexag.	15.6	92	2900*	5250*
W_2C	3.16	Rhombohedric	16.5	93	2700	4890

On account of decomposition, the melting point values are only of limited significance.

The cemented carbides owe their existence to the discovery of the manner in which the bond metal can be incorporated in order to impart strength and maintain hardness in the final product. The metals of the iron group, in particular cobalt, are especially suitable for this purpose. The effect of the cobalt is essentially a cementing action, hence the name cemented carbides. It is now realized that cobalt owes its superiority as a binder to its ability to wet the carbide at high temperatures[31]. Table II lists some physical properties of the bond materials used in the manufacture of cemented carbides.

TABLE II

PHYSICAL PROPERTIES OF BOND METALS[28]

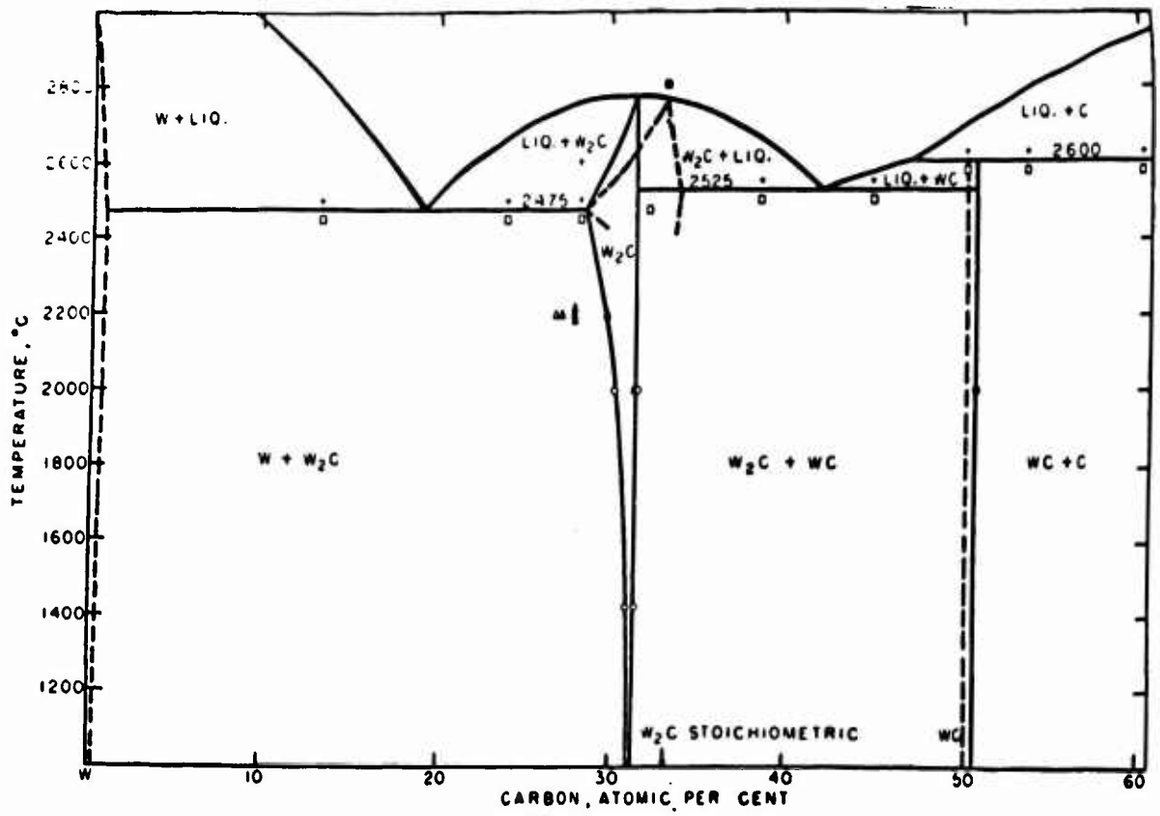
METAL	DENSITY gm/cc	MELTING POINT (°C)	ANNEALED HARDNESS (Rx)	MOD. OF ELAST. (psi IN TENSION)	COEFF. OF THERMAL EXPANSION (20°C)
Cobalt	8.90	1495 ± 1	60.0 - 63.0 R_A	30 x 10^6	12.3
Iron	7.86	1535 ± 1	39.0 - 55.0 R_B	28.5 x 10^6	11.7
Nickel	8.90	1455 ± 1	60.0 - 75.0 R_B	30 x 10^6	13.3

The first systematic study of the tungsten-carbon system was made by Ruff and Wunsch[5] in 1914. Their equilibrium diagram required considerable modification in the light of later investigations. In 1926 Westgren and Phragmen[6] reported that their X-ray examination of the tungsten carbon system revealed no carbides other than those of WC and W_2C. Investigation of the W_2C composition led them to the conclusion that the carbide was a solid solution of carbon in tungsten. However, in 1927 Becker and Holbling[7] demonstrated that WC and W_2C are chemical compounds and not solid solutions.

The corrected equilibrium diagram for the W-C system was made by Sykes[8]. The diagram is based upon chemical analysis, microscopic examination, melting point determinations, and X-ray data. The diagram reproduced in Figure 1 shows that the first eutectic, consisting of W - W_2C and containing 1.5% carbon, appears at 2475°C and the second consisting of W_2C and WC, contains 4.5% carbon, and appears at 2525°C. The WC phase decomposes at approximately 2600°C to a tungsten rich liquid and graphite.

FIGURE 1

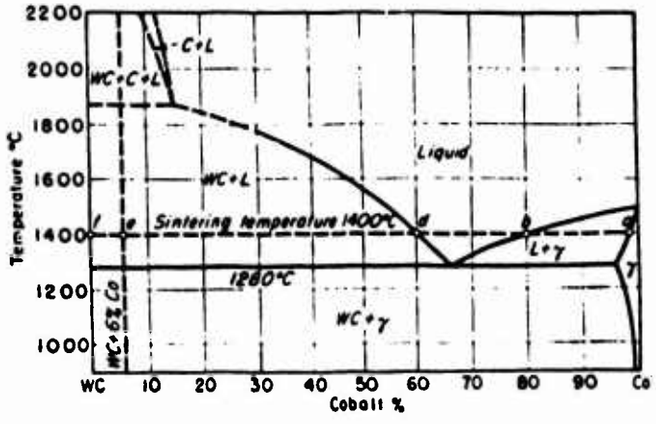
BINARY DIAGRAM OF W-C SYSTEM (Sykes[8])



Takeda[9], and more recently Brownlee[10], expanding the work of Sykes, investigated the ternary system W-C-Co. The sintering or cementing mechanism of a typical carbide containing 6% cobalt was established by Takeda on the basis of the diagram of the pseudo-binary alloy WC-Co, which is the region of the ternary system of greatest practical interest.

FIGURE 2

PSEUDO-BINARY DIAGRAM OF WC-Co SYSTEM (Takeda[9])



During the cementing of carbide materials it is necessary that there be a liquid phase. The common sintering temperature, 1400°C, is 90° below the melting point of the pure cobalt metal, 1490°C . Hence there is no liquid phase of pure binder metal during sintering. Sintering however does occur at this temperature indicating interdiffusion at the particle interfaces in the solid state. As a consequence of the solid solubility, the melting point of the binder is lowered sufficiently for melting to ensue. At the time melting occurs, as shown in Figure 2, about 1.5% WC has been dissolved forming the γ solid solution. With increased sintering time, the WC continues to dissolve in the liquid binder phase, displacing the com position gradually from point *a* to point *b*. At point *b* (composition 81% cobalt, 19% WC, temperature 1400°C), the binder metal is completely molten. The liquid phase continues to dissolve more carbide until equilibrium is established between WC and the melt. The liquid phase wets the carbides and penetrates into the pores and capillaries of the carbide crystal agglomerates. At first this process could be considered " soldering" of the primary crystals but at higher temperatures the cobalt is built into the lattice of recrystallizing WC. With moderate or slow rates of cooling from point *d*, WC is reprecipitated at the residual WC particles, resulting in grain growth. Kieffer[11] reporting on the structure of cemented carbides, states, " The structure of WC-Co cemented carbide consists of a more or less developed skeleton of α_1 and α_2 solid solutions which have formed from *a* crystals the pores of which are filled with cobalt solid solution."

This almost total reprecipitation of WC from solid solution with the cobalt explains the advantage of cobalt over iron and nickel as a binder metal for WC. The cobalt after sintering, is for all practical purposes as pure and consequently as ductile as it was initially.

Iron and nickel, on the other hand, retain carbide to a much greater extent (see Table III) forming an undue amount of comparatively brittle binder. Brownlee[12], reporting on the effect of carbon in this system, states that very slight variations in the carbon content of tungsten carbide-cobalt hard metals have a marked effect on their structual and mechanical properties. This can be seen by a study of his ternary diagram and table relating hardness and carbon content.

TABLE III

SMITHELLS[31]

SOLUBILITY OF CARBIDES IN BOND METALS

	NICKEL		COBALT		IRON	
CARBIDE	LIMIT OF SOLID SOLUBILITY	EUTECTIC	LIMIT OF SOLID SOLUBILITY	EUTECTIC	LIMIT OF SOLID SOLUBILITY	EUTECTIC
WC	25%	-	1%	35%	5%	30%
Mo_2C	12%	30%	6%	30%	2%	0%
TaC	20%	40%	6%	35%	-	-
TiC	Insol.	-	2 phases 5-90% TiC	-	-	-
Cr_3C_2	.8%	30%	8%	35%	-	-

The mechanism of the cementing of mixed carbides during sintering is basically no different than that discussed for the single carbide systems. Several investigations[13,14,15,16,17,18] have been made into the complexities of the sintering mechanism of the mixed carbides, however, a detailed discussion of them is beyond the scope of this report. It should be mentioned, however, that cobalt, due to its properties, is the only satisfactory binder metal for combinations containing tungsten carbide.

The physical properties of tungsten carbide-cobalt hard metals are decidedly influenced by the amount of cobalt binder metal. This is apparent from Figure 3 and also from Table IV which are representative of Engle's[23] findings. Hardness decreases steadily from 91-93R_A for compositions of 3% Co to 85R_A for 20% Co. The transverse rupture strength increases with rising cobalt content to a maximum of nearly 400,000 psi for 20% Co. Other noteworthy properties include an extremely high modulus of elasticity of nearly 1×10^8 psi and a high compressive strength of nearly 1×10^6 psi. The fatigue strength is comparable to that of hardened tool steel, $85 - 105 \times 10^3$ psi. The impact strength of carbides is low but increases somewhat with increased cobalt content from 0.73 ft-lbs for 6% Co to 1.75 ft-lbs for 20% Co on specimens of 1/4 inch square section.

As is indicated by Figure 3, the transverse rupture strength is a function of the amount of binder. An experimental study[27] of the variation of transverse rupture strength with composition and grain size has shown that the strength reaches a maximum for values of the mean free path between carbide particles of 0.3 - 0.6 microns. The study also indicates that the fracture originates in and proceeds through the carbide grains; hence, the strength is limited only by the susceptibility to fracture of the grain. The ideal structure for high strength cemented carbides is accordingly, one of small carbide grains separated by the thinnest possible binder layer. The strength (transverse rupture) of cemented carbides is maintained well at elevated temperatures. The following figures are cited by Hoyt[33] for a carbide containing 13% cobalt:

TEMPERATURE °C	MODULUS OF RUPTURE	
20	174 Kg/mm^2	237.5×10^3 psi
800	137 Kg/mm^2	194.9×10^3 psi
850	127 Kg/mm^2	180.6×10^3 psi
900	105 Kg/mm^2	149.3×10^3 psi

PROCESSING AND TESTING METHODS

The common commercially available cemented carbides consist of various compositions of tungsten carbide and cobalt with additions, for specific applications, of carbides of other metals of the fourth, fifth, or sixth groups of the Periodic Table of the Elements. The carbide or carbides, in powder form, are mixed with the binder metal, usually cobalt or an alloy of the iron group, and molded to shape under pressure. The compact thus formed

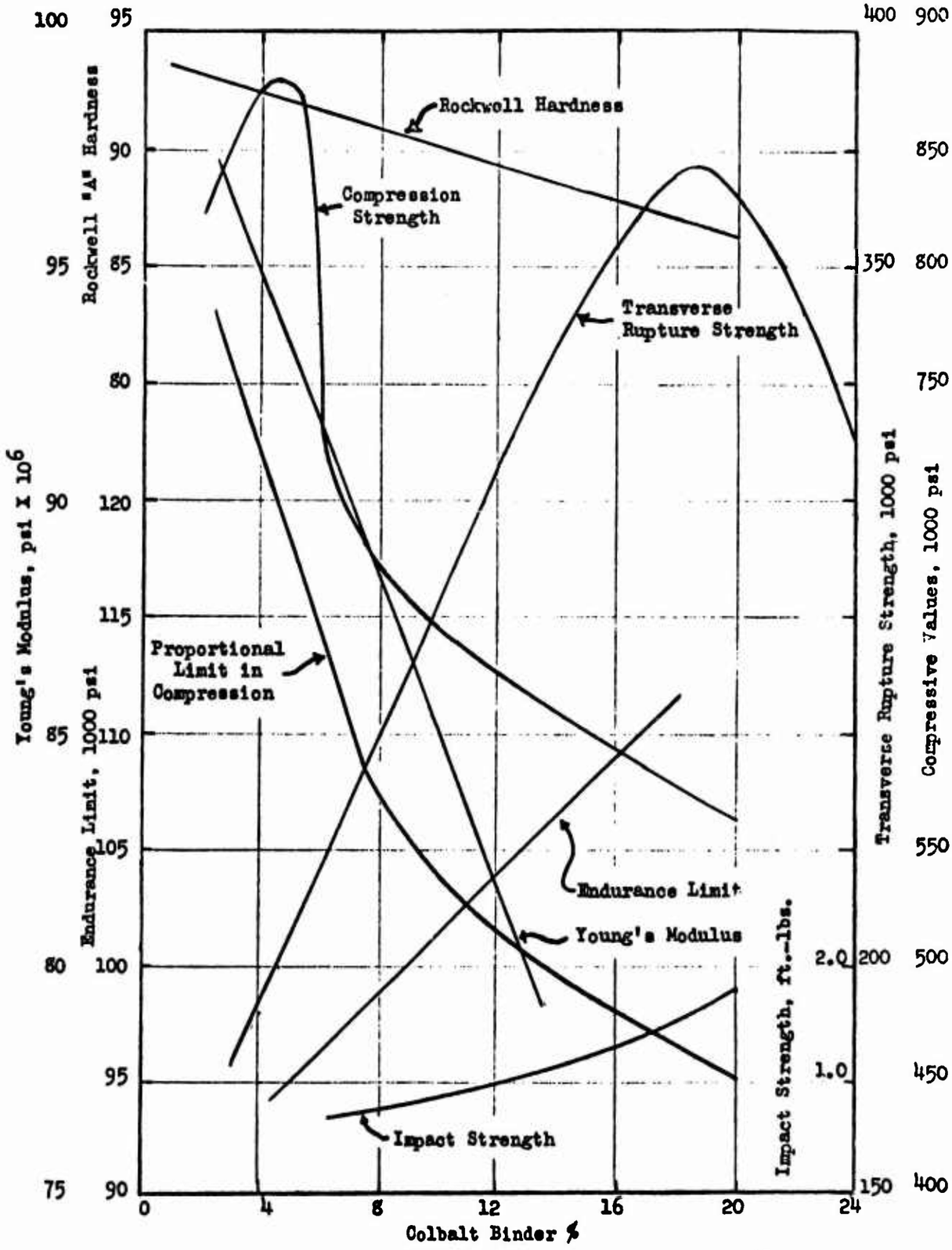


FIGURE 3 PHYSICAL PROPERTIES Vs. COBALT % (Engle[23])

TABLE IV

PHYSICAL PROPERTIES OF SOME COMMERCIAL CEMENTED CARBIDE COMPOSITIONS (ENGLE[23])

COMPOSITION	DENSITY gm/cc	HARDNESS ROCKWELL "A"	TRANS. RUPT. STRENGTH psi	COMPRESS. STRENGTH psi(b)	IMPACT STRENGTH ft-lb (c)	COEFFICIENT OF THERMAL EXPANSION (d)
97% WC, 3% Co	15.25	92.7	170,000	815,000	-	-
95.5% WC, 4.5% Co	15.05	92.3	200,000	890,000	-	-
94% WC, 6% Co	14.85	90.0 - 92.0	225,000	750,000	0.73	5.0×10^{-6}
91% WC, 9% Co	14.60	89.5 - 91.5	275,000	685,000	-	-
87% WC, 13% Co.....	14.15	87.5 - 90.0	300,000	625,000	1.10	5.9×10^{-6}
80% WC, 20% Co	13.55	85.0 - 87.0	350,000	550,000	1.75	-
Predominantly WC with TaC and 13% Co	13.90	87.0 - 88.0	275,000	610,000	-	7.25×10^{-6}
Predominantly WC with TaC and 6% Co	14.70	91.0 - 92.0	220,000	752,000	0.65	-
Predominantly WC with TiC and 6% Co	11.20	92.0 - 93.0	160,000	700,000	0.40	6.8×10^{-6}
Predominantly WC with less TiC than above 8% Co.....	12.80	91.5 - 92.5	250,000	570,000	0.60	-
Predominantly WC, larger amount TiC, 7% Co	9.00	92.0 - 93.0	150,000	725,000	-	7.0×10^{-6}
Predominantly WC with TaC and TiC 8% Co	11.70	91.5 - 92.5	165,000	720,000	-	6.75×10^{-6}
Predominantly WC with TaC and TiC 11% Co	11.60	90.5 - 91.5	175,000	680,000	0.60	6.0×10^{-6}
Predominantly WC with TaC and TiC 15% Co	11.40	89.5 - 90.5	190,000	670,000	9.92	7.5×10^{-6}

(a) The above values represent properties obtained in production, not maximum or minimum values.

(b) Values for compressive strengths are given through the courtesy of P. W. Bridgman of Harvard.

(c) Impact values are from unnotched specimens approximately 1/4 inch square section.

(d) Average coefficient of expansion per ^{o}C for the range 20-700^{o}C (68 - 1290^{o}F).

is sintered in a furnace under an inert or reducing atmosphere, or in vacuo, at temperatures ranging from 1300 to 1550°C. The sintering process imparts to the compact the observed characteristics of cemented carbide.

The following methods of producing the basic metal carbides are reported in the literature: (1) production by fusion; (2) carburization of the metal or metal oxide by solid or powdered carbon; (3) carburization of pulverized metals or metal oxides by means of carbonaceous gases; (4) precipitation from a gaseous phase; (5) chemical separation from carburized ferro-alloys; and (6) precipitation from an inert molten menstruum.

Methods (1) and (4) are no longer in use; (6) is used only in the production of titanium and tungsten-titanium carbides. Method (2) is most often used for the production of carbide -- carburizing mixtures of the refractory metals or their oxides with solid or powdered carbon, below the melting point of the carbide. Details of the practices employed in preparing high-grade tungsten carbide powder are given by Brownlee, Geach, and Raine[19].

Lampblack is the most suitable form of carbon (see Table V). If the pure refractory metal is used, an excess of 10 to 15% of carbon above

TABLE V

KIEFFER AND HOTOP[32]

PRODUCTION METHODS FOR HARD METAL CARBIDES

SUBSTANCE	METHOD	TEMPERATURE	
CARBIDES		°C	°F
W_2C; WC	WO_3 - lampblack	1400-1600	2550-2910
	W powder - lampblack	1400-1600	2550-2910
	W powder - lampblack hydrocarbon gas	1200-1400	2190-2550
Mo_2C	MoO_3 - lampblack	1200-1400	2190-2550
	Mo powder - lampblack	1200-1400	2190-2550
	Mo powder - lampblack hydrocarbon gas	1100-1300	2010-2370
TiC	TiO_2 - lampblack	1700-1900	3090-3450
ZrC	ZrO_2 - lampblack	1800-2000	3270-3630
VC	V_2O_3 or V_2O_5 - lampblack	1100-1200	2010-2190
NbC	Nb_2O_5 or Nb powder - lampblack	1300-1400	2370-2550
TaC	Ta powder - lampblack	1300-1400	2370-2550
MULTICARBIDES*	Metal oxide A - Metal oxide B - lampblack	1500-1700	2730-3090
	Metal powder A - Metal powder B - lampblack	1500-1700	2730-3090
	Carbide powder A - Carbide powder B	1700-2000	3090-3630
	Chemical isolation of highly carburized ferro alloys by acid digestion	30-100	86-212

Solid solutions of two or more of the carbides above

theoretical requirement is added; if the oxide is used, an excess of 70 to 90% of carbon is added to allow for the formation of carbon dioxide. Non-stoichiometric amounts of carbon may cause undesirable compounds to be formed in the finished product. The mixing is conducted in a ball mill and the actual carburization is carried out in either a continuous muffle furnace or a batch type high frequency furnace at 1200 to 1900°C.

Tungsten carbide powder is usually produced by mixing tungsten powder, of a similar quality and purity level to that used in the production of ductile tungsten products, with between 6.9 and 7.2% lampblack. The mixture is heated about two hours at 1400 to 1500°C. Lower temperatures or shorter times cause the formation of W_2C instead of the desired WC. On the other hand, overheating for prolonged times results in free carbon formation and porosity in the final product.

Ideally 6.12% combined carbon is desired in the sintered cake or briquette. An acceptable analysis, for production, is between 6.05 and 6.20% carbon with not more than 0.2% free carbon present. In case of a deficiency in carbon content, reheating with additional carbon is possible; if too much free carbon is present, additional metal may be added and the batch reheated.

After the carburizing operation, the carbide is easily crushed and ball milled so that the maximum number of particles are on the order of two microns, with a maximum particle size of 20 microns. The particle size is very important because coarse particles can contribute to porosity in the finished product. The ball milling is accomplished in a cemented carbide-lined mill using cemented carbide balls. The use of iron or steel balls or mills is detrimental, due to the "pickup" of iron which acts as a contaminant. After the milling operation, the carbide powder is blended to attain proper particle size distribution.

The cobalt binder is usually prepared from its oxide by reduction with hydrogen at temperatures below 800°C, although the temperature must be high enough to insure complete reduction. Imperfectly reduced cobalt tends to cause laminations and fractures in the finished material.

The predetermined weight percentages of carbide and binder are roughly mixed prior to introduction into the mill. Two to three times the powder weight of hard metal balls, 1/2 to 1 inch in diameter are added to the mill. The general practice is to wet mill using a quantity of an inert volatile liquid 6 to 8 times the powder volume as a medium, although dry milling under a hydrogen atmosphere is preferred by some manufacturers. Dry milling in air is impracticable as the reduced cobalt has a great affinity for oxygen. The milling time may vary from one day to several days depending upon the composition and milling technique. The effects of variation of processing techniques on the constitution of the principal carbide and binder metal powders used in the fabrication of hard metals has been recently reported by Krainer[20]. A long milling time is necessitated to insure surface coverage of the carbide particles with the binder metal. In this manner the binder is equally distributed in the mixture. After milling, the slurry is removed from the mill and the liquid medium is eliminated by decantation and evaporation.

Due to the poor molding characteristics of the unlubricated carbide-cobalt mixture in die cavities, powders which are to be processed by the cold pressing (and sintering) method are usually mixed with a lubricant such as ethylene glycol, camphor, or paraffin. One or two percent by weight is generally sufficient to make the powder easily moldable. The lubricant is added to the powder as a solute in a solvent such as benzene or carbon-tetrachloride, and intensive mixing produces surface films around the individual powder particles. The solvent is allowed to evaporate and the powder is screened to break up agglomerates. Lubrication is not needed for processing by the hot press method.

The carbide-binder powder mixtures are generally cold (room temperature) pressed at pressures of 5 to 30 tsi in molds of hardened steel or cemented carbide. Either high-tonnage hydraulic, or quick acting mechanical presses are suitable equipment depending upon the size of the compact. It is necessary to insure uniform filling of the die cavity because of the poor flow characteristics of the powder under compression. The compression ratio of the powders is about 3:1, and multiple-level parts require split punches[21] that are individually activated to obtain the correct compression for each cross section.

In some cases, the powders are formed by extrusion at high pressures using appropriate equipment[22]. The process consists of mixing the powder with an organic binder, such as starch, sugar syrup, or cellulose dissolved in alcohol or ether, which acts as a plastic matrix for the hard particles. The plastic mixture is extruded through diamond or carbide dies to form the cross sections in extended lengths. The extruded lengths are then cut to size in preparation for sintering. The application of the extrusion process is of special value for the production of parts which are too long to permit uniform pressure transmission and powder distribution in the usual press compacting.

Cemented carbide compacts in the " green" or " as pressed" condition are weak structurally and handling must be limited. In order to give the compacts sufficient strength for extensive handling and further shaping, as required on complicated shapes, they may be presintered. Depending upon the amount of cobalt in the material, the presintering temperature for cemented carbides varies from 800 to 1000°C; the compacts that contain a large proportion of cobalt permit a lower presintering temperature. During the treatment the lubricant evaporates, but no important volume change occurs. The presintered compacts have a cohesive strength similar to that of chalk, which is sufficient for handling and careful machining.

In forming the presintered shapes, shrinkage during subsequent sintering must be taken into account. General practice, based on the average volume change, is to allow for 15 to 25% shrinkage during the final sintering operation.

The sintering operation, the mechanism of which involves partial fusion, solution, and reprecipitation, imparts to the cemented carbides their final physical characteristics. Temperatures for the sintering of cemented carbides vary from 1300 to 1550°C and times from one to two hours

at temperature. During the entire sintering operation and subsequent cooling, the charge must be protected against oxidation and decarburization by surrounding it with a neutral or reducing atmosphere, usually in the presence of carbon.

Depending upon the method of sintering, and the size, shape, and quantity of compacts, any of three types of furnace may be used: (1) Tube-type muffle furnaces with molybdenum resistor elements; (2) carbon-tube short-circuiting furnaces and (3) high-frequency induction furnaces. In the latter, the preformed compacts are placed on graphite disks that are properly spaced and supported on a central vertical trunk; the pieces are arranged so that they are equidistant from the susceptor walls and the trunk, insuring uniform heating by radiation from the heated wall. Radiation shields above and below prevent an undue temperature gradient in the longitudinal direction, and a tightly fitting graphite cover retains the hydrogen atmosphere in the crucible.

During sintering, marked shrinkage occurs and usually amounts to between 15 and 25% of the linear dimensions. The initial forming can compensate effectively for these dimensional changes because sound material is characterized by a uniform shrinkage. The presence of objectional impurities may cause surface or internal defects such as porous areas, large voids, pits, or cracks. Minute porosity, frequently encountered after cold pressing, is attributed to solid or gaseous impurities in the powder, improper mixing and milling practices, pressing technique limitations, improper heat treatment, improper furnace conditions[23] or a combination of any of the above. However, slight porosity is not too objectionable for many commercial applications.

The pressing, shaping and sintering described above can only be used in the case of articles of relatively small dimensions, because it is impractical to provide a sintering furnace with a uniform hot zone of sufficiently large dimension, controlled to the required limits of temperature. When large articles are to be made of cemented carbide, it is more convenient to use the technique known as hot pressing. In this method, the pressing and sintering operations are effected simultaneously. The molds are made of high-strength graphite to the exact dimensions of the finished article excepting allowances for lapping and polishing when required. The carbide mixture is packed into the mold and pressure is applied through graphite plungers.

Heat may be applied in one of three ways: (1) by direct passage of current through the powder, slightly compacted between graphite electrodes (the top and bottom plungers serve as electrodes); (2) by heating the graphite mold by a direct electric current or (3) by heating the mold in an induction furnace. The pressures used are only a fraction of those required for cold pressing and usually range from 750 to 2500 psi. The upper pressure limit is determined by the strength of the graphite mold and the tendency of the binder metal to extrude out of the compact. The pressure must be maintained at the sintering temperature, to prevent deformation of the compact through shrinkage and to ensure a material free

from pores. This method, through more efficient use of the binder metal often produces cemented carbide of superior quality than the cold press and sinter method[23]. An interesting aspect of the hot pressing method is that it is not necessary to prepare tungsten carbide prior to pressing. If necessary, the mold may be filled with a mixture of tungsten, cobalt and carbon powders, and if the powders are sufficiently fine, a material is obtained which is microscopically indistinguishable from the normal product[24]. A comparison of properties between sintered, hot pressed and cast carbides can be found in the following table.

TABLE VI

KIEFFER AND HOTOP[11]

PROPERTIES OF SINTERED, HOT PRESSED, AND CAST TUNGSTEN CARBIDE-COBALT

PROCESS	C CONTENT IN WC, WT%	Co ADDITION WT%	DENSITY gm/cc	ROCKWELL HARDNESS "A"	TRANS. RUPT STRENGTH psix10^3
Sintered	6.12	6.00	14.8-14.9	90-91	213-240
Hot-pressed	6.12	6.00	15-15.1	91-93	213-255
Cast	6.00	6.00	13.5-14.0 (porous)	70-88	14-28
Cast	4.30	6.00	16.2	91-92	57-70
Hot-pressed	6.00	0.50	15.5-15.6	92-94	70-100
Fuzed with 0.5% Fe	4.00	-	17.0-17.2	92-94	43-57

The physical properties of cemented carbides depend entirely on their composition and production conditions. Whether produced by hot pressing or by cold press and sinter, the material assumes its final physical characteristics at the conclusion of the heat treatment. The properties of the material must then conform to the requirements of the intended application. Chemical composition and physical properties (density, haraness and transverse rupture strength) are used to express these requirements.

Control of composition requires almost continuous analytical work. Loss of binder metal is as objectionable as undue increases of the free to combined carbon ratio and these effects are chiefly responsible for the deterioration of the physical properties[12]. Details of the methods of analysis of both single and mixed cemented carbide compositions have been published[25, 26].

Changes in density can often be used as a primary indication of possible composition changes because the density of sintered carbides is very close to the theoretical density as determined by the rule of mixed proportions. In many compositions, a value above the theoretical indicates loss of binder metal because metals of the iron group have a lower specific gravity than the carbides. If titanium carbide is involved, this conclusion does not

hold, for titanium is much lighter than either the other carbides or the binder metals. Density measurements also give an indication of internal porosity and, thus serve as a measure of the degree of shrinkage attained and of the completeness of sintering.

One of the most important and valuable properties of cemented carbide compositions is their very high hardness. The Rockwell hardness test with a diamond indenter is commonly used for this determination. For most grades, the "A" scale with a 60 kg. load is used (see Appendix I). For extremely hard grades, the Rockwell superficial tester with less load may be preferable. Hardnesses are generally in the range from 85 to 93 Rockwell "A" depending upon the composition of the material. The extremely high hardness is only slightly impaired by rising temperature until the point of rapid oxidation is reached. A hardness of 80-85R_A may be retained beyond 750°C[23]. The abrasive or scratch-hardness value is high, being of the order of 9, on Moh's scale. The combination of high indentation hardness at both normal and elevated temperatures with extremely high resistance to abrasion constitutes, basically, the most valuable property of carbides.

The physical characteristics of cemented carbides are difficult to determine by conventional strength tests. Due to the high indentation hardness and high abrasive resistance, standard sample shapes can be prepared only with extreme difficulty. There have, however, been laboratory tests run reporting figures of several compositions of cemented carbides for Young's modulus, compressive strength, endurance limits and impact strength[23]. More generally, tests of the strength of cemented carbides have been limited to calculating the modulus of rupture or maximum stress in the outermost fibre by the transverse rupture test.

Recommended methods for the determination of density, hardness, and transverse rupture strength can be found in the appendix to this survey. Variations in the constitution of the ingredients of the carbide powder mixture and the cemented carbide products, such as those caused by changes in raw materials, additions, or the sintering cycle can be determined by sensitive laboratory test methods. X-ray diffraction [10], magnetic testing[20], dilatometry[8], and resistivity measurements[20] are effective in these determinations but these testing methods are not suitable for routine quality control work.

For close examination of the character of the porosity, a microscopic study of a ground and polished surface is necessary. The sample may be cut with a diamond cut-off wheel and rough ground on a boron carbide wheel. After rough grinding, metallographic lapping is accomplished with diamond dust on a metal lap with an oil, such as kerosene, used as a medium for holding the diamond dust. For rough and intermediate lapping boron carbide may be substituted, although the results are less satisfactory.

The examination of the character of the surface porosity and voids in the material is conducted under a low magnification of 200x on the as-polished surface. Figures 4a, 4b, and 4c are reproductions of porosity standards as seen in as-polished photomicrographs at 200x magnification.

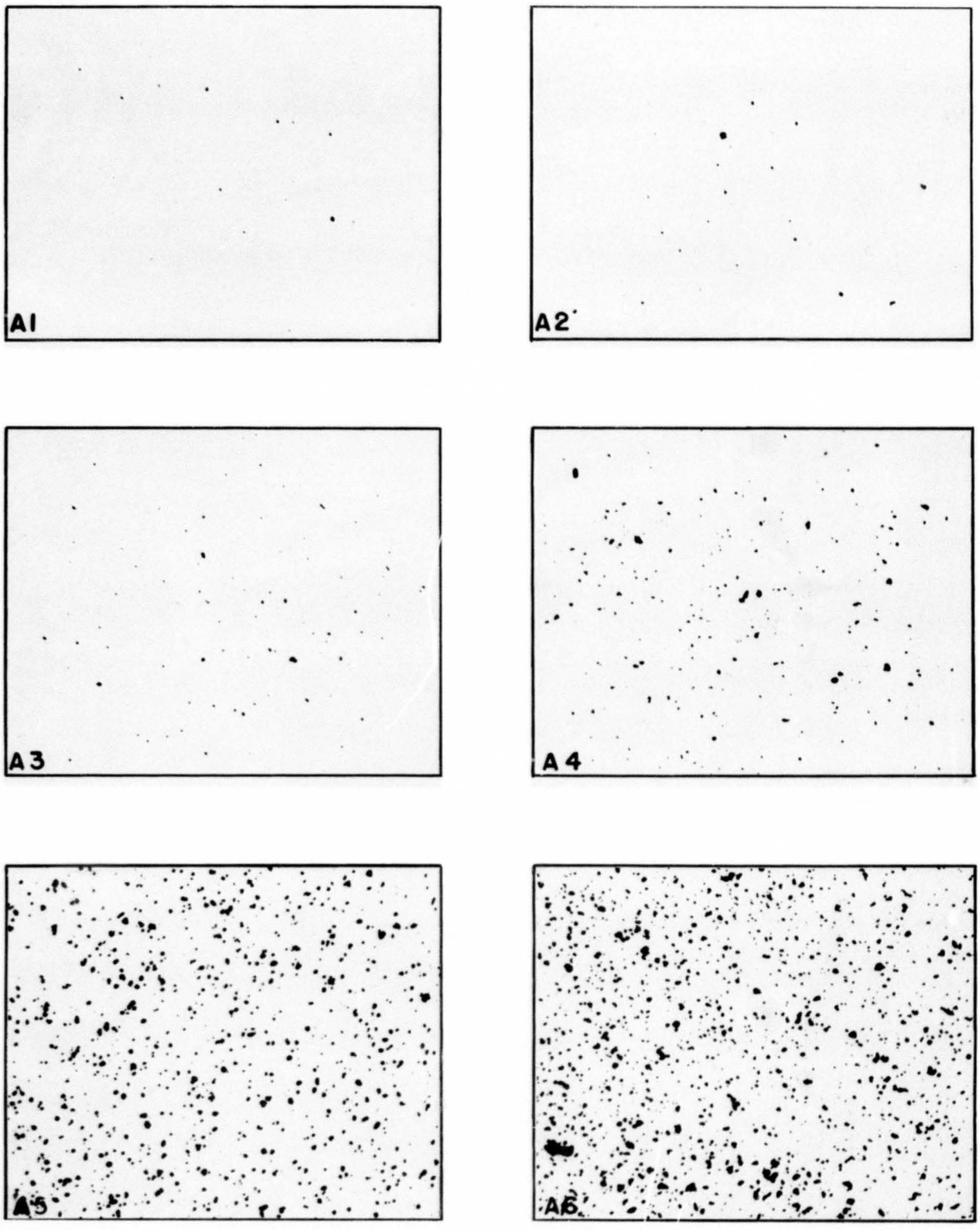


FIGURE 4a. POROSITY STANDARDS A1-A6 200X (ASTM CARBIDE RECOMMENDATION B-276-52T)

WTN. 639-10,801

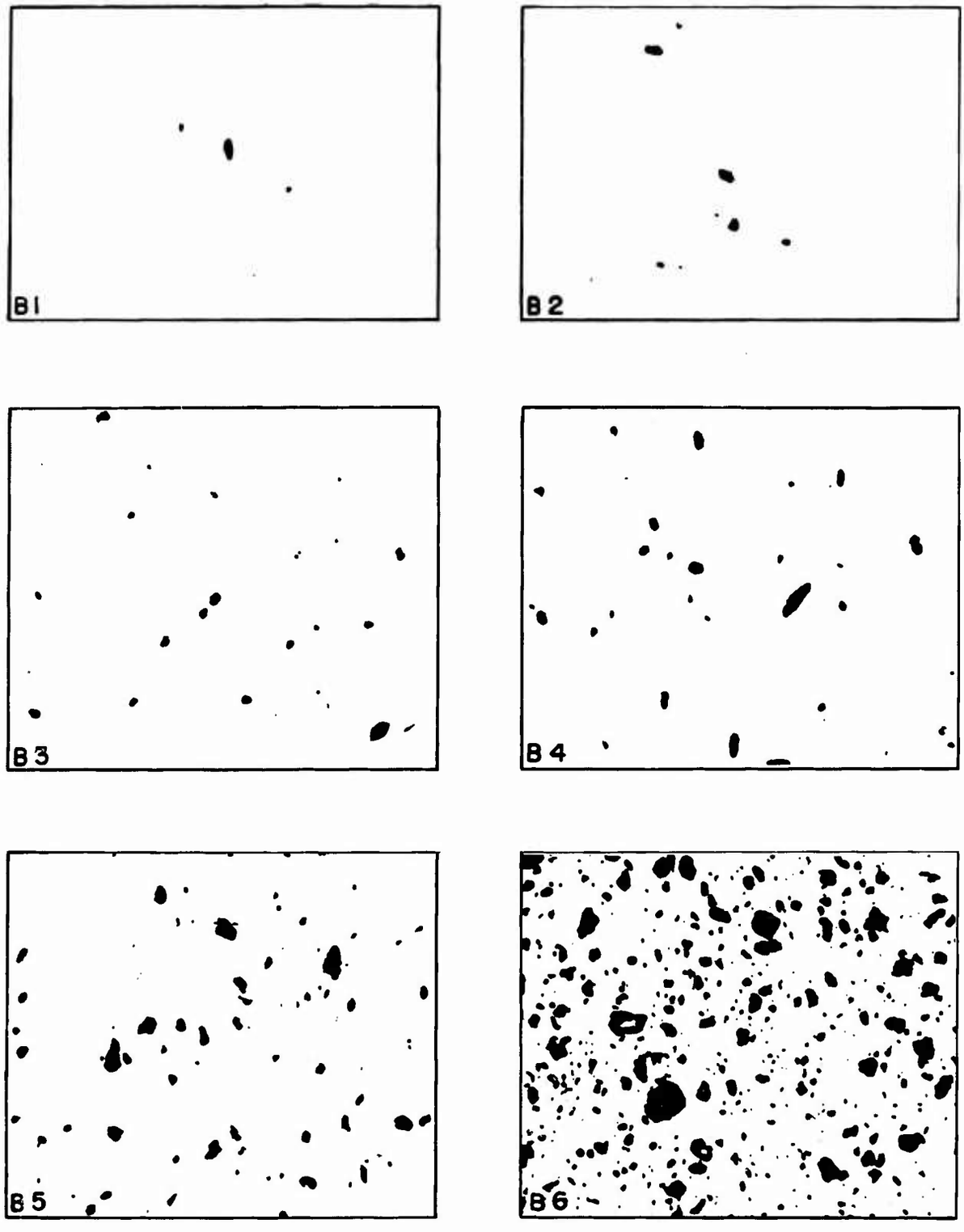


FIGURE 4b. POROSITY STANDARDS B1-B6 200X (ASTM CARBIDE RECOMMENDATION B-276-52T)

WTN. 639-10,800

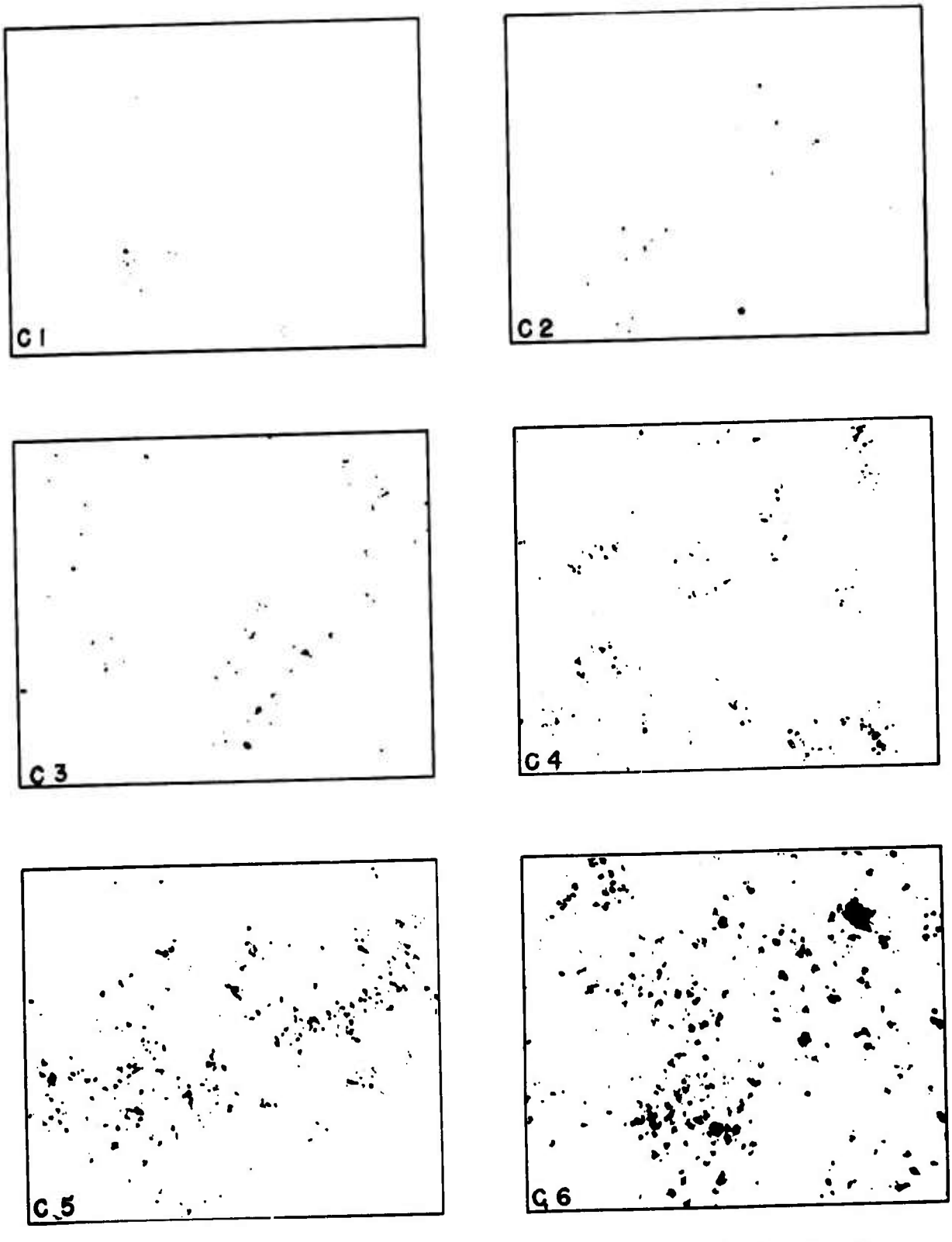


FIGURE 4c. POROSITY STANDARDS C1-C6 200X (ASTM CARBIDE RECOMMENDATION B-276-52T)

WTN. 639-10,799

W	C	Co
88.25	5.75	6.0

Grain Size — 3 - Microns
Etching Reagent — Alk. $K_3Fe(CN)_6$

X 1500

W	C	Co
81.68	5.32	13.0

Grain Size — 3 - 4 Microns
Etching Reagent — Alk. $K_3Fe(CN)_6$

X 1500

W	C	Co
75.10	4.90	20.0

Grain Size — 2 - 4 Microns
Etching Reagent — Alk. $K_3Fe(CN)_6$

X 1500

FIGURE 5. TYPICAL MICROSTRUCTURE OF WC-Co CEMENTED CARBIDES

Wtn. 639-16,046

The photos are marked with porosity ratings in accordance with ASTM Recommended Practice, B-276-52T. The porosity rating takes into account the amount, size, shape and distribution of the surface porosity in a cemented carbide. The rating groups A, B, and C pertain to the distribution, shape and size of the pores, while the numbers 1-6 in each group are associated with the degree of porosity. As the number increases from 1-6, the degree of porosity is accordingly more severe. A porosity rating of A-1 indicates an essentially porosity free surface with few minute scattered pores; the poorest porosity rating C-6 is characterized by large closely grouped pores.

The structural details of grain size, grain boundaries and binder are resolved at a magnification of 1000 - 2000 diameters after etching the polished surface. Etching can be accomplished chemically or electrolytically[28] with any of the following solutions:

1. A 1:1 mixture of 10% KOH and 10% $K_3Fe(CN)_6$ @ 68°F;
2. A 10% solution of NaOH (electrolytic etch);
3. A mixture of 3 parts HF and 1 part HNO_3;
4. H_3PO_4 with a small amount of HNO_3.

The best results are obtained chemically with the basic $K_3Fe(CN)_6$ (cold). The etchant attacks the carbide and the carbide particles are grey in appearance. Figure 5 shows typical photomicrographs of cemented carbides. The composition, predominant grain size, magnification and etching reagent are as indicated.

APPLICATIONS OF CEMENTED CARBIDES

Cemented carbides are used commercially for many applications. In general, utilization falls into four major catagories: (1) cutting tool materials; (2) die materials; (3) wear and corrosion-resistant materials and (4) high temperature structural materials. Until recently fully 80% of all cemented carbide produced was being used for cutting tool and die applications, with the balance divided among all others.

In the field of metal cutting, cemented carbides have proven most valuable. Their hardness, strength, and abrasion resistance combine to enable them to perform cutting operations more efficiently than is possible with other common tool materials. The majority of industrially employed grades are of the single carbide type, although such compositions can be used with advantage only on materials which machine with short chips. For machining steels and materials giving long continuous chips, multiple carbide compositions are used. Recent developments in the carbide tool industry have approached an "all purpose" multiple carbide type cutting tool which is able to machine a wide range of materials which include cast iron, non-metallics, the entire range of steel alloys, and non-ferrous materials.

Cemented carbides have been found to be equally adaptable in other cutting operations. The mining and rock drilling fields are using cemented

carbide tipped drills; and stone masonry tools, again tipped with cemented carbide, have been found to have doubled their wear life potential, when compared with forged steel tools.

Initially cemented carbides were brazed to supporting steel shanks when used in cutting operations. More recently, mechanical fastening of cemented carbide inserts to steel supports is becoming general. This allows dull, or chipped tools to be changed with a minimum of time loss to the operation.

The following Table VII lists some commercial compositions giving their hardness, specific gravity and some general information as to potential usage.

Next in importance to the tool applications of cemented carbides is their use as a die material. Cemented carbide, in die applications, is usually used in the form of nibs or liners; the carbide being solidly surrounded by a supporting material such as forged steel. As can be seen in Table VII, carbides of WC-Co composition are entirely satisfactory for die applications. Wear life increases in excess of fifty fold can be expected when compared to hardened steel dies in wire drawing applications. The production of very large dies for deep drawing is a recent development. In one instance, a nib has been produced with an internal diameter of 13.5 inches weighing over 100 pounds. The present size and weight limitations are only determined by the equipment available and it is believed that when necessary the range can be extended.

The wear and corrosion resistance of tungsten carbide has become an important factor in the expanding use of the material. Cemented carbide materials are being used in applications where local wear or corrosion is a problem. The following list of current applications will give an idea of the extent to which carbide can be used as an engineering material: centers for lathes and grinders; rests for lathe work; rests for centerless grinder work; roll mills for sheet and cladding applications; grinder fingers, profiles, and cams; gages, micrometers, and indicator points; coiling guides and arbors; guides of all kinds, including thread, etc.; valves, valve stems and seats for hydraulic systems and pumps; mold liners for pharmaceutical, ceramic, and powder metallurgy industries; grinder parts for pulverizing most materials; precision balls for testing machines; and an almost limitless assortment of grooving tools, gripping devices, and chuck jaws.

Special compositions of cemented carbides have been developed to endure temperatures at which conventional carbide compositions are rapidly destroyed due to oxidation. The basic component is TiC, which is highly oxidation and heat-resistant, bonded with cobalt or nickel. The material is characterized by its light weight, high thermal conductivity, high thermal shock resistance, and high strength and corrosion resistance at elevated temperatures. Among the specific applications to which these materials can be put are: support pins in porcelain furnaces, exhaust valve seats for internal combustion engines; furnace parts that are subjected to high temperatures and oxidizing or corrosive conditions, roll guides for hot-rolling mills, and other high temperature structures. Superior performance of cemented

TABLE VII

LI AND WANG[34]

APPLICATIONS OF SOME COMMERCIAL CARBIDE COMPOSITIONS

COMPOSITION	HARDNESS R_A	SPECIFIC GRAVITY
WC - 3% Co	92.5 - 93.0	15.1 - 15.3
Use: Tool material for light, low stress machining - Hardest cemented carbide - More brittle than higher binder materials.		
WC - 6% Co	90.0 - 92.0	14.8 - 14.9
Use: Tool material for finish cuts on cast iron, nonferrous metals, and nonmetals such as plastics - less hard than above.		
WC - 6 TO 9% Co	89.5 - 91.5	14.6 - 14.85
Use: Cutting material for noncontinuous chip and noncutting operations not subject to shock - Roughing cuts.		
WC - 9 TO 12% Co	87.5 - 90.0	14.2 - 14.6
Use: Heavy roughing cuts in cast iron - Noncutting operations involving limited shock - Limited shock resistance.		
WC - 20% Co	85.0 - 87.0	13.5 - 13.6
Use: Noncutting applications, as dies, rolls - Shock resistant.		
WC - 10% TaC - 6% Co	91.9 - 92.0	14.7 - 14.8
Use: Finishing cuts on tough materials - steels - TaC% can vary.		
WC - 10% TiC - 6% Co	92.0 - 93.0	11.2 - 11.3
Use: Finishing cuts on tough materials giving long chip.		
WC - UP TO 20% TiC - 7% Co	92.0 - 93.0	9.0 - 9.10
Use: Special applications requiring abrasion resistance where shock does not figure.		
WC - 10% TaC-10% TiC-8% Co	91.5 - 92.5	11.7 - 11.8
WC - TaC - TiC-12% Co	90.5 - 91.5	11.6 - 11.7
WC - TaC - TiC-15% Co	89.5 - 90.5	11.4 - 11.5
Use: As general cutting tool material for machining steels.		

carbide in service as turbine buckets or blades over those made from conventional alloys has been reported[21].

Another interesting application is the use of cemented carbides for contact materials or relays and transmitters in telegraphic systems. In this application WC-Co and WC-Os compositions have a life of over two years and meet the requirements for polar relays in every respect.

Military usage of cemented carbides has been generally restricted to ballistic applications, in addition to instances of ordnance manufacture where normal industrial practice is followed. Ballistic applications of cemented carbide, involving its use as cores in high velocity armor piercing ammunition, were first employed by the German Army during the tank warfare of the North African campaign of WW II.

Tungsten carbide is twice as dense and much harder than the hardened steel formerly used in armor piercing applications. These factors more than offset its relatively low shock resistance. Bullet cores of tungsten carbide proved highly effective at the extremely high pressures and temperatures produced in penetrating armor plate. Recent attempts to substitute other hard materials in the role of core material has proven the superiority of cemented carbides.

In a comparison of ballistic limit ratio made at Watertown Arsenal Laboratories[29] among tungsten carbide, steel and aluminum oxide core materials, the following data was obtained:

TABLE VIII

ABBOTT[29]

THEORETICAL AND ACTUAL BALLISTIC LIMIT RATIOS

TARGET	STANDARD CORE	CARBIDE CORE RATIO TO STAND.		STEEL CORE RATIO TO STAND.		ALUM. OXIDE CORE RATIO TO STAND.	
		THEO.	ACTUAL	THEO.	ACTUAL	THEO.	ACTUAL
1" Armor @ 0°	1	1	1	1.46	2.46	1.95	>>2.0
1" Armor @ 30°	1	1	1	1.46	1.79	1.95	>>2.0
1" Armor @ 45°	1	1	1	1.46	1.74	1.95	>>>2.0

As is indicated, the calculated ballistic limit ratio for steel and aluminum oxide should be 1.46 and 1.95 respectively. The actual ratio indicates clearly that both are inferior to the carbide.

CONCLUSIONS

The survey of the published literature pertaining to cemented carbide materials shows that there are several areas which can be served by a variety of compositions. The multiplicity of composition of carbides which can be used in the same area emphasizes the need for correlation studies. The need was further amplified by the realization that although manufacturing techniques and areas of utilization of carbide materials have expanded rapidly fundamental investigation has lagged. Proof of this fact is the limited availibility of modern technical literature compared with the volume of literature published by the carbide manufacturers.

ACKNOWLEDGEMENT

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PATENTS OF HISTORICAL IMPORTANCE

(a) German Patent - 286,184

(b) German Patent - 443,911; U.S. Patent - 1,512,191

(c) German Patents - 420,689; 434,527

(d) United States Patents - 1,549,615

(e) Austrian Patent - 138,284; German Patent - 720,502

United States Patents - 1,959,879; 2,122,157; 2,170,433; 2,246,287; 2,356,009

United States Reissues - 22,073; 22,074; 22,166; 22,207

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APPENDIX I

RODMAN LABORATORY
RECOMMENDED PRACTICE FOR DETERMINATION OF HARDNESS OF CEMENTED CARBIDES

1. Scope

This recommendation describes the method of determining hardness of cemented carbides using the Rockwell Hardness Tester.

2. Size of Specimens

The area of the surface of the specimen depends on the skill of the operator. However, the thickness of the samples should be at least 10 times the depth of the indentation or not less than 1/16th of an inch.

3. Preparation of Specimens

The surface on which the indentation is to be made must be parallel to the surface adjacent to the anvil of the tester. This may be accomplished by grinding in a suitable jig with a diamond wheel.

4. Equipment for Testing

Testing will be conducted using a Rockwell Normal Hardness Tester with a 60 Kg load equipped with a 120° spheroconical diamond indenter ("Brale") with a spherical apex of 0.2-mm radius.

5. Method of Testing

a. The tester should be placed so that vibration does not seriously affect the readings of the dial gage.

b. For the minor load to be properly applied, the large needle on the dial gage should be at "set" within plus or minus five scale divisions. If the elevating operation results in the needle stopping within this range, but not on "set", no further adjustment should be made by means of the elevating screw, but the dial should be rotated to "set" under the needle.

c. On the normal tester, the dashpot, which controls the speed of application of the major load, should be adjusted so that the operating crank completes its travel in five seconds with no specimen on the machine, but with the machine set up to apply a major load of 100 Kg. In a similar manner the superficial tester is set for seven seconds with a major load of 30 Kg.

d. The machine should apply the major load, that is, the operator should avoid any manual pressure on the crank after releasing the lever system. The major load is allowed to act until either the pointer on the dial gage suddenly slows down or the weight arm is completely free from control of the dashpot; the latter is preferred, because it is a clean-cut end point. Within two seconds after either of these points is reached, the operating crank should be returned gently to its starting position; snapping the crank to the starting position may cause an error of several points in the dial indication.

e. The performance of the machine should be checked frequently against standard test blocks supplied by the manufacturer. If the hardness value obtained differs from that inscribed on the test block the machine should be adjusted according to the instructions supplied by the manufacturer.

f. Because the accuracy of the hardness determination depends on an accurate measurement of the depth of penetration, particular care must be taken to seat the indenter and anvil firmly. Any vertical movement at these points results in additional depth being registered on the gage and therefore, means a false number.

APPENDIX II

RODMAN LABORATORY
RECOMMENDED PRACTICE FOR DETERMINATION OF TRANSVERSE RUPTURE STRENGTH OF CEMENTED CARBIDES

1. Scope

This recommendation describes the method for determing the transverse rupture strength of cemented carbides.

2. Size of Specimens

The specimens shall be cemented carbide pieces of sufficient size so that they may be ground to the following dimensions:

0.200" ± 0.010" Thick
0.250" ± 0.010" Wide
0.875" Min. Length

3. Preparation of Specimens

a. Specimens shall be ground to a surface finish to 15 RMS max. on four sides, to the tolerance shown above, in such a manner that all grinding marks are parallel to the long (0.875) axis. Parallel ground faces shall be parallel and free of taper within 0.001". The two faces perpendicular to the long axis need not be ground. The grinding shall be done with diamond wheels and copious quantities of coolant shall be used. In the case of machine grinding, no pass shall exceed 0.005" in depth.

b. The four corners of the specimen representing the intersection of ground faces may be chamfered or honed to a maximum of 0.010" x 45°. Care should be taken that any grinding marks are parallel to the long axis of the specimen.

c. Each specimen shall be measured by micrometer or other suitable means to within 0.001" in both directions perpendicular to the long axis. Sufficient readings shall be taken at various points across each dimension to ensure compliance with the parallelism or taper tolerance.

d. Each specimen shall be visually inspected after grinding. Any specimen showing cracks, chips or obvious structural defects on ground surfaces shall be eliminated from the test.

4. Equipment Required for Testing

The test may be conducted using either a specially adapted machine for applying the load, or a special fixture suitable for use with a conventional load applying machine. In either case the apparatus

shall fulfill the following requirements:

It shall have two 0.125" diameter ground tungsten carbide cylinders at least 0.500" long rigidly mounted with their long axis parallel, and center to center spacing of 9/16" - .005". A movable member (free to move substantially only in a line perpendicular to the plane established by the axis of the two cylinders) containing a 10mm tungsten carbide ball rigidly attached and so positioned with respect to the two previously mentioned cylinders that movement of the member can cause the ball to contact a specimen placed on the two cylinders at the midpoint of the span. The apparatus shall be so constructed that application of sufficient load to the movable member to effect breaking of a specimen shall be capable of applying sufficient load to the specimen to cause breakage. The movable member shall have a rate of movement not to exceed 0.005" per min. in its approach to the point at which application of pressure on the specimen begins. The apparatus shall be capable of registering the load required to break the specimen within 1% of the load.

5. Method of Testing

a. The cylinders and ball in the fixture shall be visually examined for cracks, chips, deformation or misalignment and the movable member shall be tested for freedom of movement. Any defects appearing shall be corrected prior to use.

b. A properly prepared and measured specimen is placed on the two cylinders of the fixture with the 0.250" ± .010" dimensions parallel to the axis of the cylinders, and the moving member is moved until the ball contacts the specimen. Care should be taken to place the specimen so that the ball will contact at midpoint of the width of the specimen and contact shall be affected without substantial impact. A load shall be applied by the loading apparatus at a rate not to exceed 500 psi per second (equivalent to 60 lbs per second). Upon fracture of the specimen the number of pounds required to cause fracture shall be noted.

6. Calculations

The transverse rupture strength shall be calculated as follows:

$$S = \frac{3PL}{2bh^2}$$

Where S = transverse rupture strength in PSI
P = load in pounds required to fracture
b = specimen width (see 3 c.)
h = specimen thickness (see 3 c.)
L = length of span in thousandths

APPENDIX III

RODMAN LABORATORY
RECOMMENDED PRACTICE FOR DETERMINATION OF DENSITY OF CEMENTED CARBIDES

1. Scope

This specification prescribes the method for determining the density of cemented carbides.

2. Size of Specimens

Specimen size is limited by weight due to limit of accuracy of an analytical balance above 200g.

3. Preparation of Specimens

Specimens may be used in the " as sintered" condition providing loose scale is removed with a wire brush.

4. Equipment Required for Testing

a. Analytical Balance
Balance to be accurate to - 0.10mg.

b. Platform
Platform able to support liquid container and so constructed as not to interfere with balance operation.

c. Beaker
Beaker, or other transparent container large enough to allow insertion of sample and pan, so constructed as not to interfere with balance operation.

d. Pan
Small pan with holes in the bottom so constructed as to be able to support sample in solution.

e. Wire
Fine flexible wire, corrosion resistant, .004 inch in diameter.

5. Method of Testing

a. The specimen is tied with fine flexible, corrosion resistant, wire; Nichrome wire, .004 inches in diameter, is used because it satisfies these requirements. Only one strand of wire is allowed to pass through the surface of the water because surface tension has the effect of holding the wire and preventing motion of the balance under the influence of the final few milligrams of the weighing. For the same reason, the diameter of the wire is kept as small as

possible because the holding effect is greater with the larger diameters of wire. The weight of the wire used is determined in both air and as immersed in water so that the appropriate corrections can be made. A more convenient procedure than tieing with a fine wire is to construct a small pan with holes in the bottom to facilitate the passage of liquid. Such a pan is especially useful when there are a large number of density determinations to be made.

b. When immersing the specimen in the water, it is essential to eliminate all air bubbles, however small. The prevention and removal of air bubbles is made easier if a small amount of wetting agent is added to the water, but it is necessary to determine the density of the resulting solution because the usual effective concentration of a wetting agent, about .2%, is sufficient to affect the density in the fourth significant figure. What is actually done is to determine the specific gravity of the solution at one temperature on the assumption that there will be no significant change in specific gravity with temperature. The wetting agent also reduced the holding effect of the surface tension on the wire passing through the surface; this advantage alone is great enough to justify the use of the wetting agent.

c. In the absence of sufficient reason, there is no attempt made to control the temperature of the specimen or water; the room and water temperature are measure to .1°F; and the calculations based on the measured temperatures. In actual practice, the room temperature is neglected in the calculations, and it is assumed that the specimen is at the water temperature by the time the weighing is completed.

d. When the specimen is weighed in air, no correction for the buoyancy of the air is ordinarily made. This correction is small and appears in the fourth place to the right of the decimal point.

e. Weighings are made to the nearest tenth of a milligram; they are probably accurate to plus or minus two tenths of a milligram. The data are collected in this form:

1. Wt.specimen plus wire in air -
2. Wt. wire in air -
3. Wt.specimen in air -(1-2)

4. Wt.specimen plus wire in soln.@ °F -
5. Wt. wire in soln.
6. Wt.specimen in soln.@ °F -(4-5)

3. Wt.specimen in air -
6. Wt.specimen in soln. -
7. Wt.solution displaced - (3-6)

8. Density of water @ °F, g/cc - (Handbook)
9. Specific gravity of solution -
10. Density of solution @ °F, g/cc-

11. Volume of specimen, cc, 7 ÷ 10
12. Density of specimen @ °F, g/cc, 3 ÷ 11

If a correction for the buoyancy of the air is desired, the following additional steps are added:

13. Density of air @ °F, g/cc (Handbook)

14. Buoyancy correction, g., 11x13 - ADD
3. Wt. specimen in air -
15. Wt. specimen in vacuo -

16. Density (in vacuo) of specimen, g/cc @ °F

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