THE MANUFACTURING PROCESS FOR

CEMENTED TUNGSTEN CARBIDES

BY:

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Metals & Compounds Primarily Used in Manufacturing Tungsten Carbide

        a)   Tungsten Carbide

        b)   Titanium Carbide

        c)   Tantalum Carbide

        d)   Cobalt

Other Metals & Compounds Used in Carbides
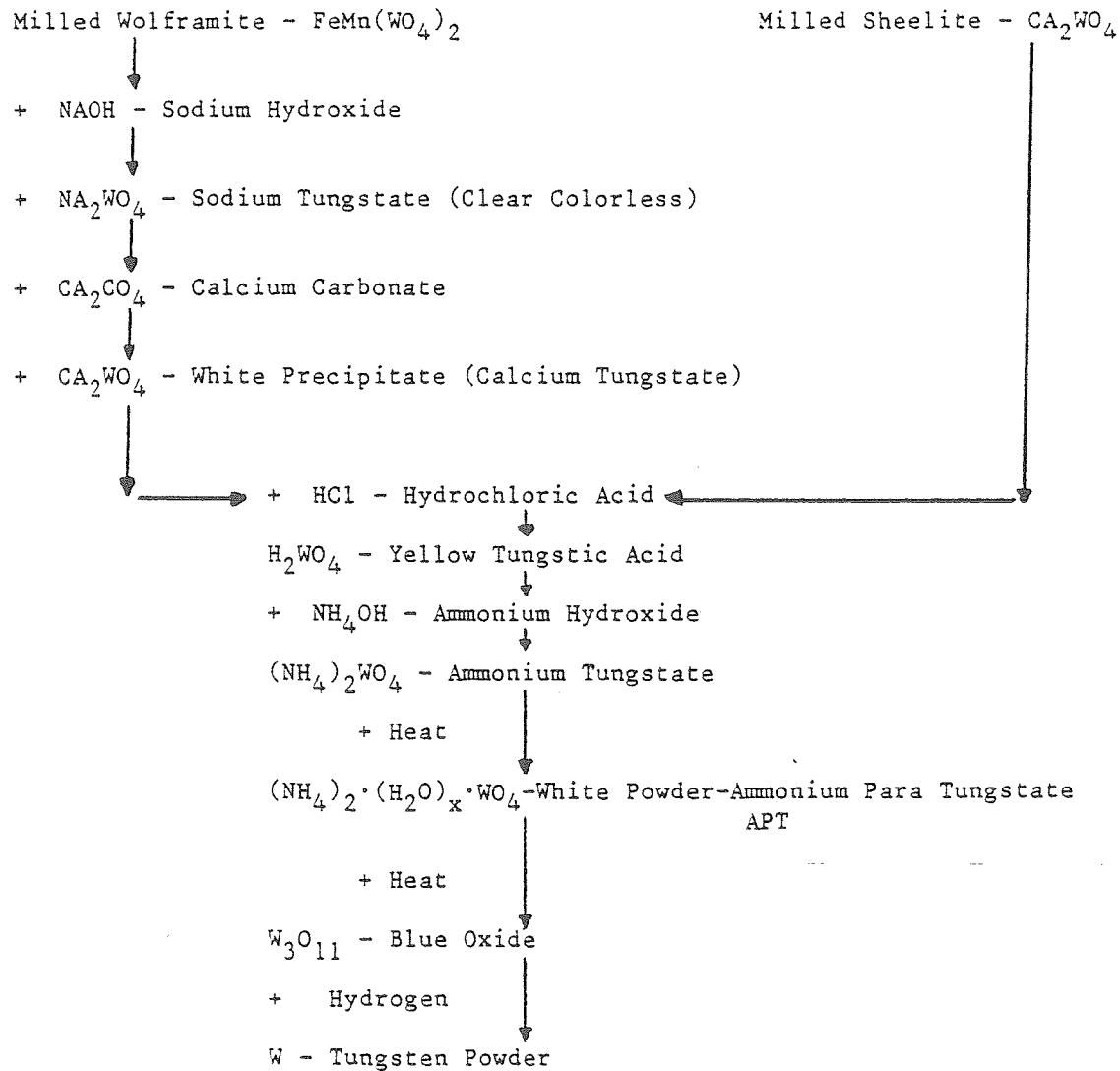
        a)   Vanadium Carbide

        b)   Columbium Carbide

        c)   Chromium Carbides

        d)   Nickel

        e)   Molybdenum Carbide

What is Tungsten Carbide? Tungsten Carbide is a compound formed by the reaction of tungsten metal powder and carbon powder (carbon black) at temperatures of 2600° - 2700° F.

Tungsten has a chemical symbol "W" which comes from the name "Wolfram" and that is how it is known in Europe. There are a total of thirteen tungsten bearing ores of which four (4) types are the most plentiful. These are:

ORE TYPE	CHEMICAL FORMULA
a) Wolframite	$FeMn(WO_4)_2$
b) Scheelite	$CAWO_3$
c) Ferberite	$FeWO_4$
d) Hubnerite	$MnWO_4$

CHEMICAL PROCESS FOR TUNGSTEN ORES

Milled Wolframite - $FeMn(WO_4)_2$ Milled Sheelite - CA_2WO_4

+ NAOH - Sodium Hydroxide

+ NA_2WO_4 - Sodium Tungstate (Clear Colorless)

+ CA_2CO_4 - Calcium Carbonate

+ CA_2WO_4 - White Precipitate (Calcium Tungstate)

+ HCl - Hydrochloric Acid

H_2WO_4 - Yellow Tungstic Acid

+ NH_4OH - Ammonium Hydroxide

$(NH_4)_2WO_4$ - Ammonium Tungstate

    + Heat

$(NH_4)_2 \cdot (H_2O)_x \cdot WO_4$ - White Powder - Ammonium Para Tungstate
                                                                    APT

    + Heat

W_3O_{11} - Blue Oxide

+ Hydrogen

W - Tungsten Powder

The thirteen tungsten bearing ores are in combinations with eight elements. These are iron, manganese, calcium, aluminum, copper, lead, zinc and sulphur.
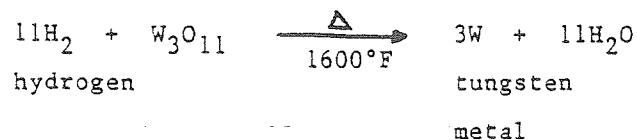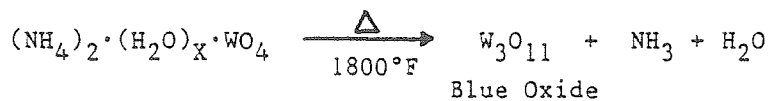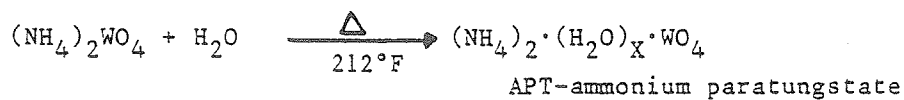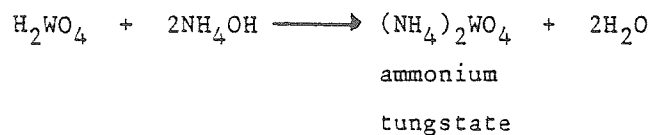
The two most plentiful and widely used ores are Wolframite and Scheelite. In processing Wolframite the tungsten contained is first converted to the Scheelite (CA_2WO_4) form by reacting with Sodium Hydroxide (NAOH), Sodium Carbonate, (NA_2CO_3) or Sodium Bi-Carbonate (NA_2HCO_3) usually under heat and pressure. The sodium tungstate liquid is clear and colorless. The liquid is filtered from the residue and collected in large vats where calcium carbonate (CA_2CO_4) is added precipitating Calcium Tungstate (CA_2WO_4) which is then filtered and dumped into a digester containing hydrochloric acid (HCl) where with heat added tungstic acid (H_2WO_4) is formed. After filtering, the cake is dumped into a slurry tank containing ammonium hydroxide (NH_4OH). At this point clear colorless ammonium tungstate is formed $(NH_4)_2WO_4$. After filtration the rich "W" containing liquid is pumped to a crystallizer. Steam heat evaporates the water and precipitates a white chemical called Ammonium Paratungstate or APT--$(NH_4)_2 \cdot (H_2O)_X \cdot WO_4$.

Applying high heat in a calciner reduces the compound to blue oxide which is approximately WO_3O_{11}. Pure tungsten oxide is WO_3 and yellow. Further heat under a hydrogen atmosphere in high nickel boats reduces the oxide to tungsten metal powder "W". In the reduction operation the grain size of the tungsten metal powder is closely controlled by controlling these variables:

Main Factors Controlling Particle Size

1. Depth Of Powder In The Reduction Boat

2. Flow Of Hydrogen

3. Dew Point Of Hydrogen

4. Temperature

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Chemical Formulae From Scheelite Ore to Tungsten Carbide

$$CA_2WO_4 \; + \; 2HCL \; \xrightarrow[180°F]{\triangle} \; 2CA(OH)_2 \; + \; H_2WO_4$$

Scheelite   tungstic acid

$$H_2WO_4 \; + \; 2NH_4OH \longrightarrow (NH_4)_2WO_4 \; + \; 2H_2O$$

ammonium

tungstate

$$(NH_4)_2WO_4 + H_2O \; \xrightarrow[212°F]{\triangle} \; (NH_4)_2 \cdot (H_2O)_X \cdot WO_4$$

APT-ammonium paratungstate

$$(NH_4)_2 \cdot (H_2O)_X \cdot WO_4 \; \xrightarrow[1800°F]{\triangle} \; W_3O_{11} \; + \; NH_3 + H_2O$$

Blue Oxide

$$11H_2 \; + \; W_3O_{11} \; \xrightarrow[1600°F]{\triangle} \; 3W \; + \; 11H_2O$$

hydrogen   tungsten

metal

$$W \; + \; C \; \xrightarrow[2700°F]{\triangle} \; WC$$

lampblack   Tungsten Carbide

After the proper tungsten particle size has been established, it is mixed with carbon black, packed into carbon boats or pots and heated to approximately 2700° F. There is some grain growth when going from W to WC. Low sulphur carbon black is necessary to produce the finer micron sizes required for the high hardness carbide grades.

The carburized cake is relatively soft and has the consistency of regular blackboard chalk. It is crushed and either ball milled or hammer milled to below 200 mesh. It is now ready for the production of tungsten carbide grades as you know them.

Cobalt is mined in only a few countries and is generally associated with copper and/or nickel mining. The major metal being mined is either nickel or copper. Cobalt is primarly imported and no cobalt powder is made in the USA from domestic concentrates. There is one cobalt powder plant operating in the USA and it is in North Carolina. During the cobalt crisis when fine grain cobalt powder reached $55/lb on the black market, there was no powder plant in the USA. The shortage arose as a result of a raid on the major cobalt mine in Zaire (Katanga Province) by Angolan rebels. The only railroad to the sea was also severed at the same time.

Major Free World Deposits of Cobalt

1. Zaire   * – Zaire and Zambia account for
                                 70% of the world production

2. Zambia

3. Finland

4. Morocco

5. Canada

The U.S. does have one cobalt deposit of some consequence and it is in the "Wilderness Area" of Idaho. The environmentalists are against opening this area to industry for fear that the natural beauty would be destroyed.

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Titanium Carbide   is made from titanium dioxide that is found in beach sands and is plentiful in nature. The white in paint pigments is titanium dioxide (TiO_2); the most common forms are rutile, illmenite and anatase. The cost of (TiO_2) is very low and when combined with carbon at approximately 3800° F in graphite boats forms TiC. TiC is seldom used in the production of tungsten carbide as such. It is added as a solid solution of tungsten carbide and titanium carbide that is formed by heating a mixture of both compounds to 3800° F. The most common solid solution contains 50 weight percent of each compound.

Tantalum Carbide   is made from the carburization of TA_2O_5 (tantalum pentoxide). This reaction occurs at 2750°F and the reaction is:

$$2TA_2O_5 + 9C \longrightarrow 5CO_2\uparrow + 4TAC$$

Tantalum is usually obtained as a by-product of tin smelting. Tantalum is found in nature in association with columbium. The separation of tantalum from columbium is difficult and expensive. Tantalite ores contain up to 30 percent columbium and columbite ores contain an equal amount of tantalum.

During the tantalum shortage that occurred a few years ago, the price of tantalum carbide rose to $200.00 per pound. American carbide producers were faced with a dilemma and as a result some decided to use tantalum carbide/columbium carbide mixtures as their chemistry occurred in nature without the costly separation step. European producers have always used combinations of columbium (niobium) and tantalum carbides. This substitution pertains only to the manufacturers of cutting tool carbides and not die grades. It was reported by these producers that the substitution did not reduce performance. Some of die grade producers reduced the tantalum carbide percentages or eliminated its use completely.

Tantalum carbide powder is usually added as such by USA manufacturers. European producers prefer adding double and triple carbides such as WC·TAC or WC·TiC·TAC.

Basically we have touched on Tungsten Carbide, Cobalt, Tantalum Carbide and Titanium Carbide. The other metals in Slide #1 are used as grain growth inhibitors as is the case with Vanadium Carbide and substitution for tantalum carbide as is the case with columbium carbide. Chromium Carbide is the base material in the few grades of chromium carbides made; the binder is nickel. Nickel is also the binder for titanium carbide base grades and a few tungsten carbide grades as well where corrosion is a problem.

Carbide Grade Production

We are now ready to begin the manufacture of carbide grades. The sequence is as follows:

1. Weighing

2. Ball Milling
   a) Cascading Mills
   b) Attritors

3. Screening

4. Drying
   a) Vacuum Dryers
   b) Spray Dryers

5. Lubricant Addition
   a) Paraffin
   b) Camphor
   c) Wax
   d) Methylene Glycol

6. Homogenizing or Delumping

7. Pressing
   a) Isostatic
   b) Hydraulic
   c) Mechanical

8. Pre-Sintering
   a) Vacuum
   b) Hydrogen

9. Preforming

10. Sintering
    a) Hydrogen
    b) Hydrogen Combination Half-sinter & Final
    c) Combination Vacuum Pre-Sintering & Sintering
    d) Vacuum Sintering
    e) Combination Vac & Hot Isostatic

11. Hot Isostatic Pressing

All grades follow the same sequence thru item six.

1. <u>WEIGHING</u>-

Process Engineering or the Technical Department usually calculates the exact weights of all materials to be used in each grade. Finite calculations are required to control the ultimate carbon content so as not to produce carbon deficient or carbon excess carbide lots. The finer the powders, more absorbed oxygen will be present and in vacuum sintering only carbon will remove the oxide present. In hydrogen, most of the oxides in combination with tungsten and cobalt will be reduced therefore not robbing the carbon from the mix.

2. <u>BALL MILLING</u> -

In the past, most carbide companies employed regular horizontal ball mills - most were stainless steel and stainless balls were used as the milling media. Evolution saw liners of carbide and carbide balls being used to reduce contamination and improve quality. The speed of the ball mills is usually set at 80% of critical speed. Critical speed is the rotational speed at which point centrifugal force is equal to the gravitational forces; also at this point, the balls and powder will not cascade but cling to the mill walls. Milling is always done in an organic solvent such as acetone, heptane, hexane and solvent naptha. · The solvents are used to keep the balls clean at all times so that they impact the maximum amount.

New techniques employ attrition mills that are vertical and there is constant collision of balls and powder. The agitator bars are carbide sleeved, the mill is lined with carbide and the balls are carbide. With this milling concept a C-2 grade can be milled in less than 8 hours as against 72 to 96 hours for the regular cascading mill.

3. <u>SCREENING</u> -

Some companies screen the powders as a liquid slurry thru -200 or -325 mesh screens to remove unmilled particles, contaminates, ball chips and other foreign particles. Other companies dry the powder first and screen dry. Newer techniques favor wet screening directly out of the attrition mills.

4. **DRYING** –

Older procedures employed open pans in vacuum dryers and the milling solvent was not recovered. Later, steam jacketed tumbling vacuum dryers were used; some used bread type mixers with an agitator but also under vacuum. These later techniques employed water cooled condensors to recover the solvent especially when the price rose to $1.30/gallon.

5. **LUBRICANT ADDITION** –

Materials, such as vacuum distilled paraffin, camphor, stearates etc., were used both as pressing aids and lubricants. Amounts of 0.5% to 2.0% by weight additions are used depending on the pressing technique. The lubricants mentioned above can be dissolved in most hydrocarbon solvents and this is a plus factor. When using vacuum dryers, the wax is added to the dryer either as a liquid, flakes or granules. The heat used during drying and the solvent itself will dissolve all the wax and disperse it evenly.

When "Spray Drying" is used, the wax is added in the milling cycle.

Acetone does not dissolve some of the more common lubricants and with the newer technology its use has probably been discontinued.

6. **HOMOGENIZING OR DELUMPING** –

After vacuum drying the powders are fed thru a series of high speed carbide tipped hammers and a -20 mesh screen, or it is forced thru a screen to break up any lumps. Any technique can be used including high energy mixing.

7. **PRESSING** –

All powders whether spray dried or conventionally dried are ready to be pressed. Pressing is either by isostatic, hydraulic or mechanical means.

Isostatic Pressing – This technique is where powders are placed in rubber bags, sealed and then inserted into a liquid such as water. The water is pumped to pressures of approximately 30,000 psi. Some presses operate at 60,000 psi but there is very little advantage in using the higher pressure.

Solid pieces, hollow cylinders or pieces with nearly exact configurations can be pressed in this fashion. For high volume and continuous production such as spark plug ceramics, dry bag pressing is employed - this is where the rubber bag is an integral part of the press. The lubricant content of the carbide grades is approximately 0.5% when iso pressing is used.

Hydraulic Pressing - Before the advent of isostatic pressing, billets for preforms were pressed in either closed dies or collapsible dies. Shrinkage was more difficult to predict because of the variations in pressed density throughout the billet. Iso-pressing provides equal pressures in every direction and on every square inch of the billet thereby providing better size control.

Automatic Pressing - (Either Mechanical or Hydraulic) Parts can be made to exact sizes by using closed die techniques. The powder fill can be controlled easily when using closely controlled flowable granules. The parts being pressed are usually identical in size and weight. Minor adjustments can be made from time to time very readily.

8. **PRE-SINTERING** -

Parts that require further work prior to final sintering may or may not require presintering. Diamond wheels or plated wheels are not easily "loaded-up" when working with pieces that contain wax and they make a neat clean preform. Diamond boring bars, or diamond plated saw blades and diamond plated drills are also commonly used. They require no dressing and produce much more product than carbide tipped tools and regular drills.

Some of the more intricate shapes, thin sections, lower cobalt grades and titanium carbide containing grades are more difficult to work and may require presintering - either in a hydrogen atmosphere or in vacuum. Temperatures of between 1200° F and 1500° F are used for presintering.

9. **PREFORMING** -

Carbides that have been pre-sintered have the consistency of blackboard chalk; those that have not been pre-sintered are more fragile and require greater care.

Conventional machine tools are used with the exception that some have been designed specifically for carbides and have less horsepower. Lathes, grinders and milling machines are used with diamond tools, wheels and drills. High efficiency dust control is a must so that all powder can be recovered and a dust free environment is maintained. Specially designed band saws, slicers and vertical lathes are used as common practice. Some companies use equipment with digital readouts. Some use tape controlled equipment and some use tracer equipment - either line tracers, template tracers or "copy" tracers.

For special radii and special shapes, either plated wheels are made to the exact form or green silicon carbide wheels are dressed to the required shape. Silicon carbide wheels "load up" readily and require constant dressing. Silicon carbide contamination is always a problem therefore the wheels are "dressed" in other areas far from the preforming departments.

10. **SINTERING** -

Sintering Methods Used in Carbide Manufacturing

    A. Hydrogen

    B. Hydrogen Combination Pre-Sintering and
       Final Sintering

    C. Combination Vacuum Pre-Sintering & Sintering

    D. Vacuum Sintering

    E. Combination Vacuum Sintering & Hot Iso-Pressing

A. **Hydrogen Sintering** - A hydrogen atmosphere protects the material from oxidation and reduces some oxides. The hydrogen flow is always in a direction opposite the direction of the material being sintered so as to "sweep" the impurities away. Graphite boats are required and temperatures of between 2500° F and 2750° F are used. All small parts are packed in alundum (AL_2O_3) grain.

B. **Hydrogen Combination Pre-Sintering & Final Sintering** - A pre-heat zone either "in-line" or an "off the side chamber" is used to remove the paraffin from the parts.

It is important to keep the paraffin vapors from back streaming into the hot zone where "cracking" could occur and carbon rich gases would be present to alter the carbon balance in the carbide grades. After the paraffin has been evolved, the boats are directed thru the hot zone for final sintering.

C. **Combination Vacuum Sintering** – Pre-sintering is done in vacuum or under inert gas at low temperatures until the paraffin has evolved; the gas is then pumped out and the temperature continually increased to the final temperature. Vacuum furnaces can either be vertical or horizontal. Vertical furnaces are round in shape and round graphite plates and/or trays are used to hold the parts to be sintered. A "wash" of aluminum dioxide, titanium carbide or other suitable material is painted on the graphite to prevent carbon pick-up. This "wash" is used in all sintering techniques if the carbides to be sintered are placed directly on the graphite plates.

Horizontal furnaces have rectangular cross sections and rectangular plates are stacked to get the proper height. Graphite spacers are used between trays. Graphite has the unique quality of maintaining both compressive strength and tensile strength at elevated temperatures.

D. **Direct Vacuum Sintering** – If there is no wax present in the parts to be sintered, the lower deparaffining step is omitted and the total time for the sintering cycle is reduced by 50%.

E. **Combination Vacuum Sintering and Hot-Iso Pressing** – Again new technology has emerged and furnaces are being made where vacuum is used to sinter the parts as previously discussed but after the cycle has been completed, the vacuum valves are closed and argon or other inert gases are pumped into the vessel to pressures of approximately 1000 psi and the furnace held at a temperature near the original sintering temperature for some period of time. This secondary consolidation is used to reduce porosity to a minimum and insure nearly defect free material.

The disadvantage over regular hot iso pressing decribed later on is that the furnace is not filled to nearly its capacity.

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Carbides as pressed have densities of 55% to 58% of theoretical. Shrinkage in sintering is approximately 50%. A normal furnace load uses only 50% of the volume available; if the parts shrink 50% by volume, then only 25% of the furnace is being utilized. The cost factors of this new method versus regular hot iso pressing are presently under study.

11. **HOT ISO PRESSING** –

After normal sintering is employed, the sintered parts can be subjected to a secondary consolidation which is now commonly called HIPing. In this process, the parts are stacked so as to utilize the entire furnace volume. The furnace is equipped with both vacuum pumps and inert gas compressors. Air is pumped from the furnace and inert gas is added as the pressure medium. The furnace contained in the hot iso unit is heated to about 100° F below the normal sintering temperature and the gas pressure is raised to 15,000 psi. The purpose is to take the binder phase (cobalt) to near plastic conditions and exert pressure on every square inch so as to "move" the carbide part sufficiently enough to fill any voids present.

A recent experiment on 100 samples -- 50 of which were HIPed and 50 not -- indicated that the average strength increased by 25,000 psi on the HIPed parts. There was approximately a 50,000 psi total variation in the "non-HIPed" parts and only 15,000 psi in the HIPed parts.

CARBIDE GRADE DEVELOPMENT

Key properties of some hard-metal carbides

	Microhardness	Melting point		Thermal density
	Kg/Sq mm	°F	°C	g/cm³
Tic	3200	5790	3200	4.94
VC	2950	5125	2830	5.71
HfC	2700	7030	3890	12.76
ZrC	2560	6380	3530	6.56
CbC	2400	6330	3500	7.80
Cr_3C_2	2280	3440	1895	6.66
WC	2080	4710	2600	15.67
Mo_2C	1950	4850	2400	9.18
TaC	1790	6835	3780	14.50

You will notice that tungsten carbide in this table is much lower in hardness than many other carbides. Addition of titanium carbide can significantly increase the hardness of tungsten carbide grades while the addition of tantalum carbide can slightly reduce the hardness.

Remember these points:

(1) The higher the hardness, the more brittle and more wear resistant the carbide.

(2) The higher the cobalt content, the carbide will be more ductile, it will be stronger, it will be lower in hardness and will have less wear resistance.

(3) The higher the tantalum carbide content, the carbide will be more crater resistant, it will have less tendency to gall and have slightly less strength.

(4) The higher the titanium carbide content, the carbide will have better flank wear, be higher in hardness, have more abrasion resistance, be lower in specific gravity and be extremely more brittle.
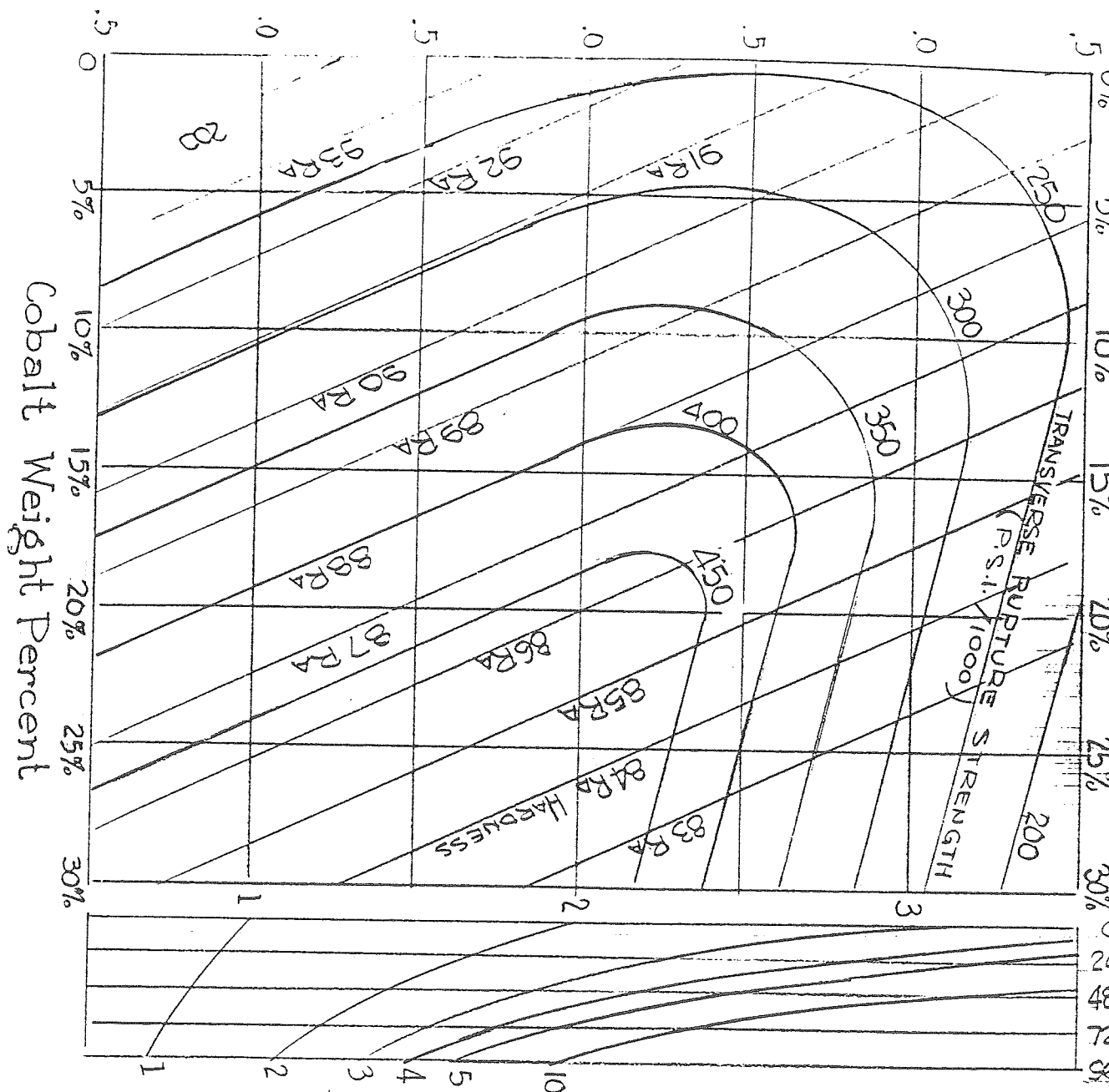
Cobalt Weight Percent

Cobalt Weight Percent

TRANSVERSE RUPTURE STRENGTH (P.S.I./1000)

RA HARDNESS

CHART OF WC-Co ALLOYS

EFFECTS OF % COBALT AND
POWDER PARTICLE SIZE
ON SINTERED HARDNESS
AND STRENGTH

STARTING WC PARTICLE
SIZE BEFORE BALL
MILLING

Transverse Rupture Strength (p.s.i./1000)

Rockwell 'A' Hardness

2 micron WC
3 micron WC
4 micron WC
5 micron WC
6 micron WC
1 micron WC

30% Co
25% Co
20% Co
15% Co
10% Co
5% Co

Volume Shrink Factor, VSF (Percent)

Cobalt Weight Percent, W%Co

Linear Shrink Factor, LSF (Percent)

Formula:
$$VSF = (1-\%WL) \ \frac{Vs}{Vp} = (LSF)^3$$

WCμ = 5.0μ

WCμ = 4.0μ
WCμ = 3.0μ

WCμ = 2.5μ

WCμ = 2.0μ

WCμ = 1.5μ

WCμ = 1.0μ

6.0μ

Co-WC System
SHRINK FACTOR
(VSF/W%Co/WCμ)

COBALT-WEIGHT PERCENT

0   5   10   15

10.00   11.00   12.00   13.00   14.00   15.00

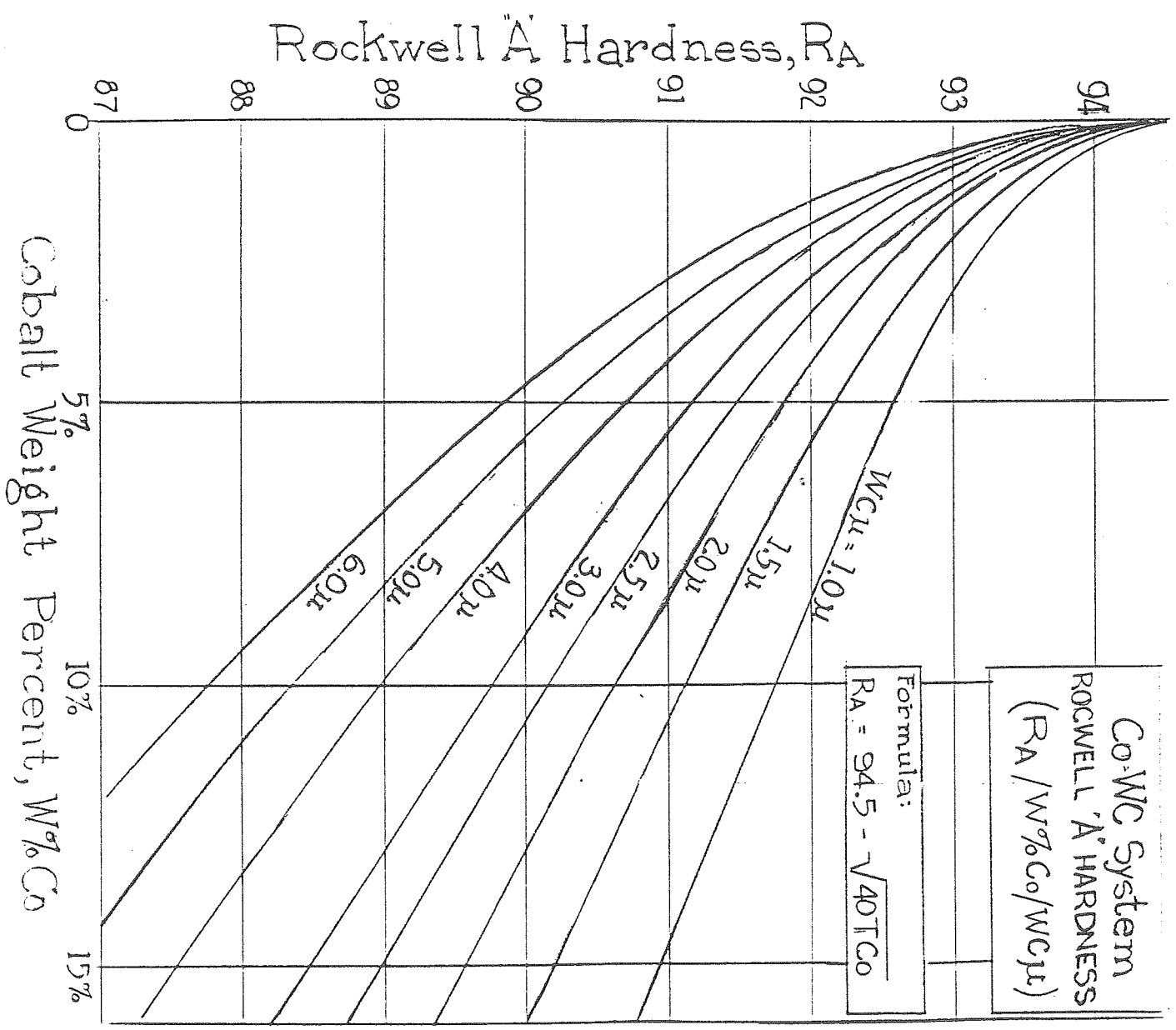10   11   12   13   14   15

25% TiC

20% TiC

15% TiC

10% TiC

5% TiC

0% TiC

DENSITY VS. COMPOSITION CHART
WC - Co - TiC Materials

Co-WC System
ROCWELL "A" HARDNESS
$(R_A/W\%Co/WC\mu)$

Formula:
$R_A = 94.5 - \sqrt{40TCo}$

WCμ=1.0μ
1.5μ
2.0μ
2.5μ
3.0μ
4.0μ
5.0μ
6.0μ

Rockwell "A" Hardness, R$_A$

94
93
92
91
90
89
88
87

Cobalt Weight Percent, W%Co

0
5%
10%
15%

Co-WC System
HARDNESS vs. SINTERED DENSITY
Ra / ds / W% Co / WC μ
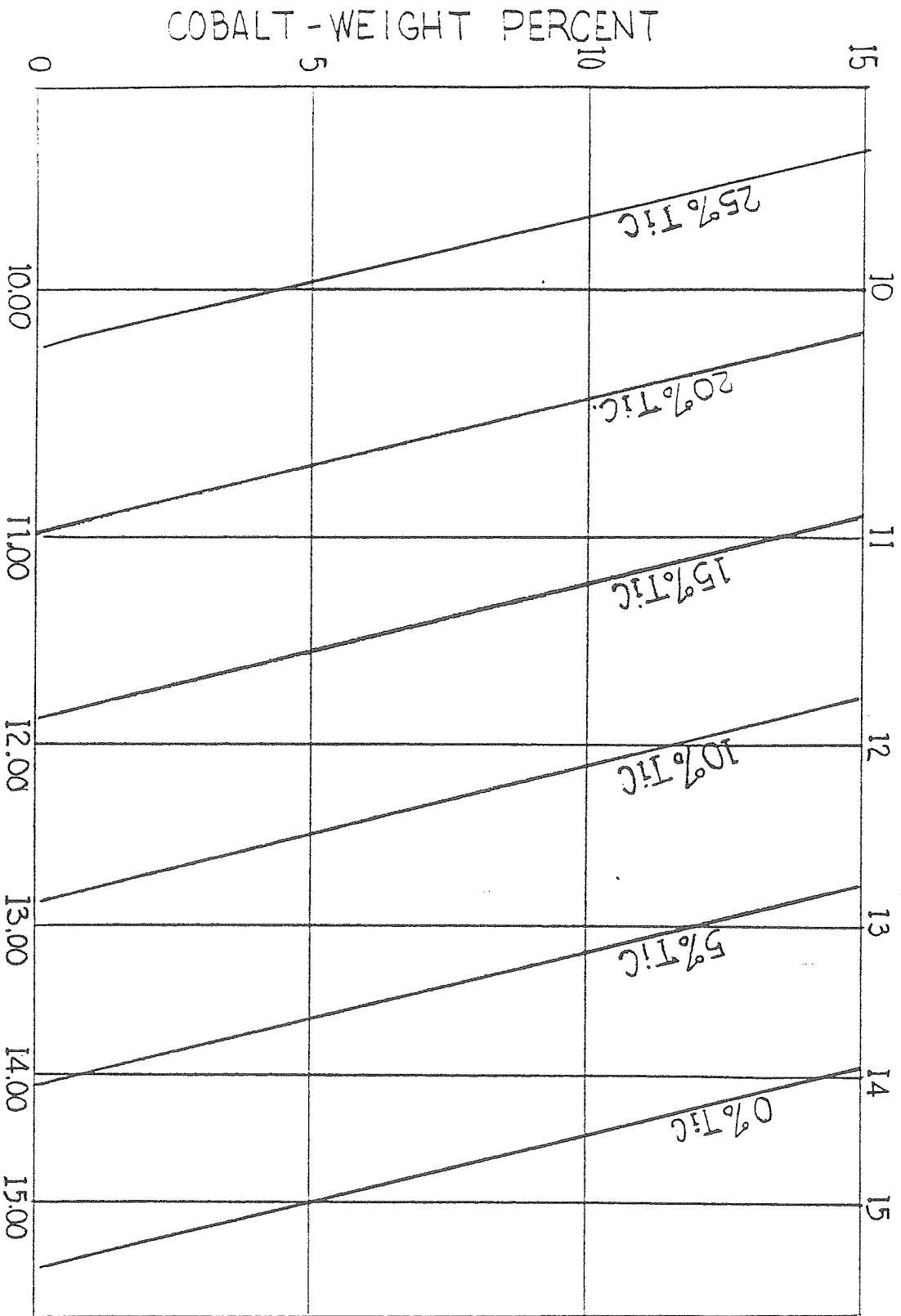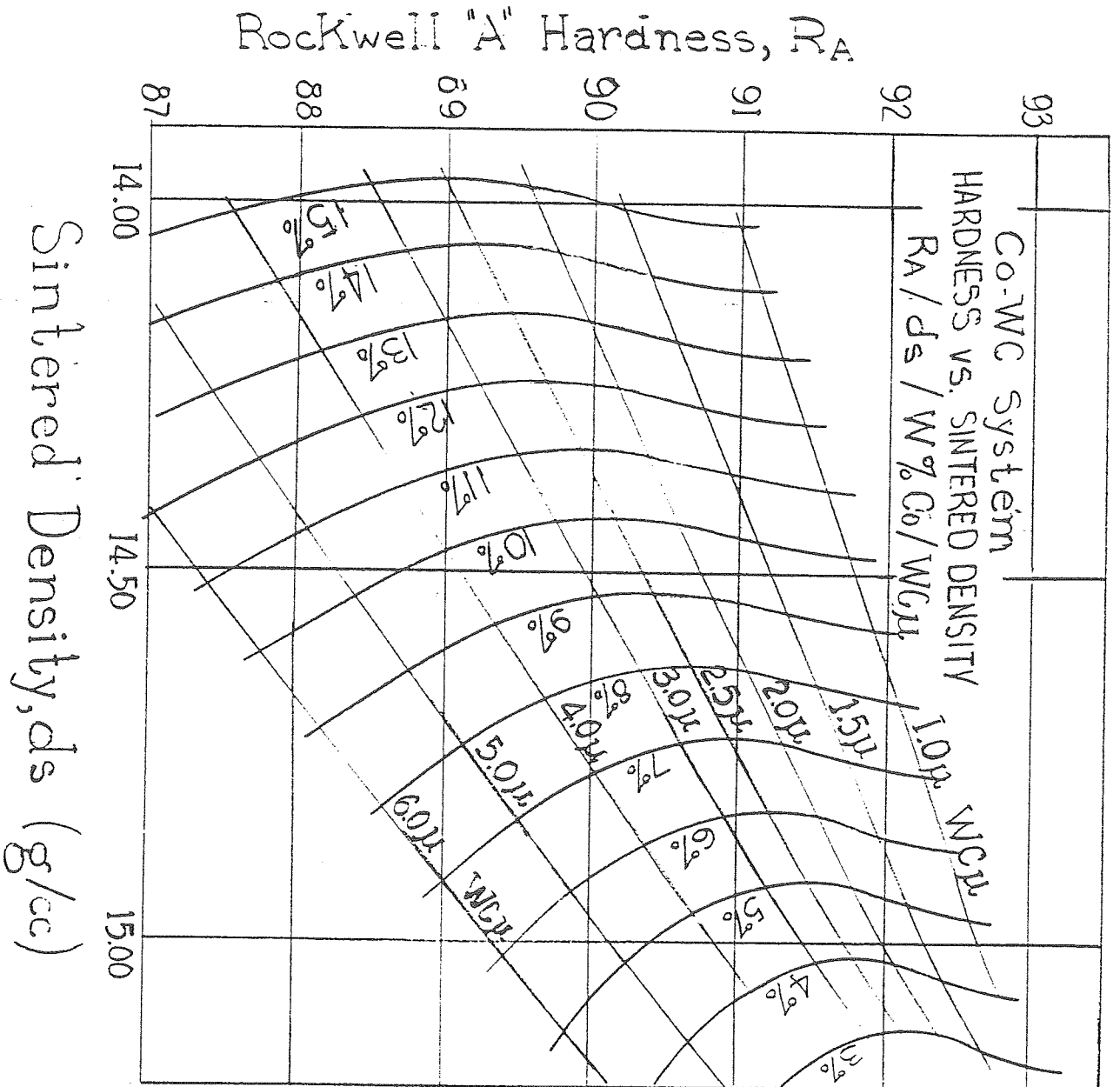
Co-WC System
TRANSVERSE RUPTURE STRENGTH
(TRS / W% Co /WC μ)
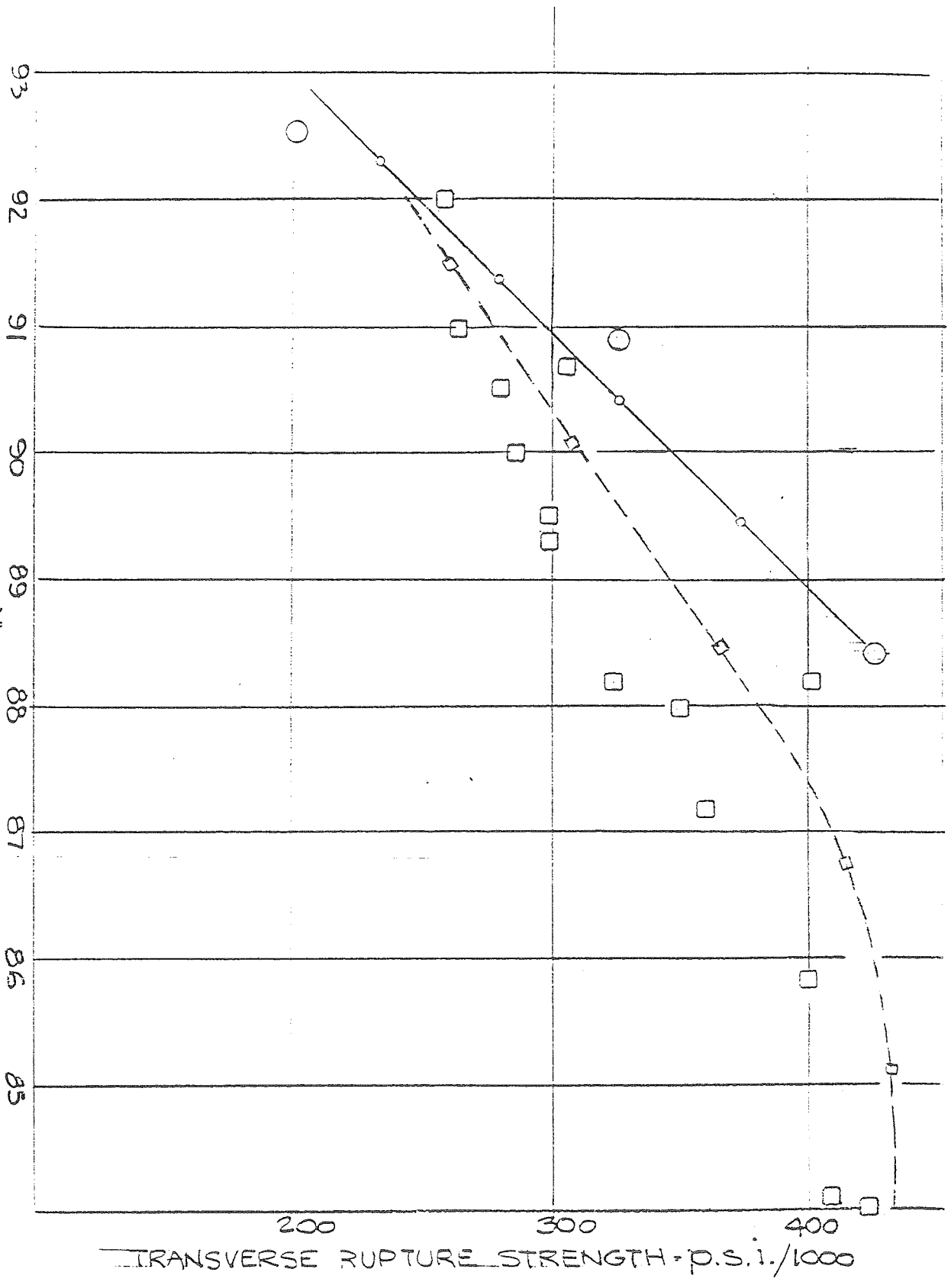
Transverse Rupture Strenth, TRS (psi/1000)

Cobalt Weight Percent, W%Co

Formula:
TRS= 575-150 (1.40-T$_{Co}$)^2 -29WC$_μ$

WC$_μ$=1μ

1μ 2μ 3μ 4μ 5μ 6μ

2μ 3μ 4μ 5μ 6μ

200 300 400 500

5% 10% 15%
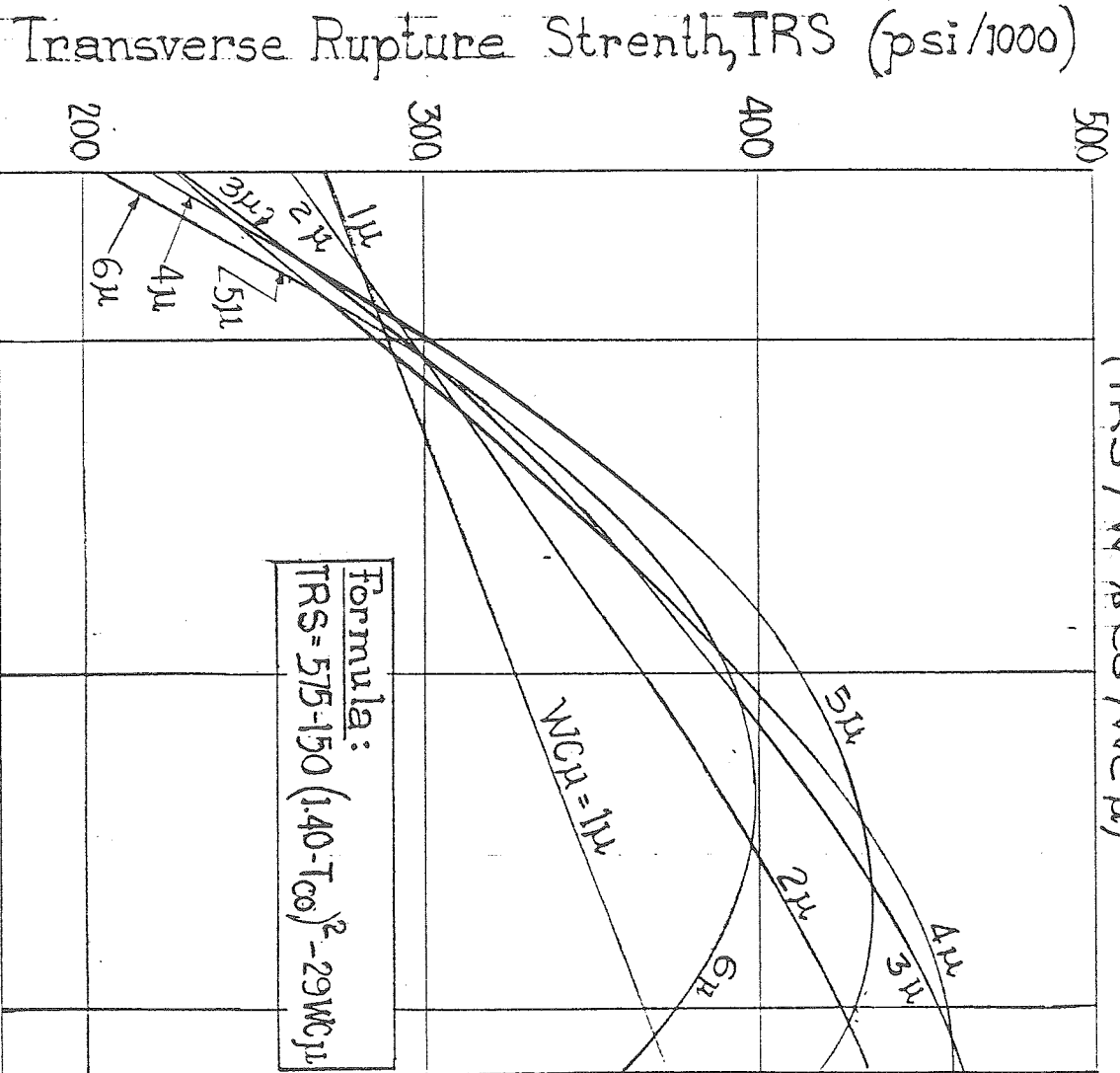
CHART OF HARDNESS VS. STRENGTH FOR WC-Co GRADE CARBIDES

POINTS IDENTIFIED BY COBALT WEIGHT PERCENT

ROCKWELL "A" HARDNESS

TRANSVERSE RUPTURE STRENGTH - p.s.i./1000

Rockwell 'A' Hardness

PROPERTIES OF WC·Co SINTERED MATERIALS

Cobalt -- Weight %

1.2 micron apt.

1.4 micron apt.

1.6 micron apt.

Density (g./c.c.)

Transverse Rupture Strength p.s.r./1000