Reprinted from the

INTERNATIONAL JOURNAL OF

Refractory & Hard Metals

The Official Organ of the International Plansee Society for Powder Metallurgy

Vol. 4, No. 3, September 1985

Correlating WC Grain Size Analysis Techniques with Attritor Mill Monitoring in Cemented Carbides

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With the evolution of faster, higher energy milling techniques and narrower property range requirements in final products, tight control over the milling process is needed. A model appropriate for the material/device relationship of WC and cobalt mixtures in the attritor was developed. A form of the Charles equation ($\bar{E}=A\ d^{-\alpha}_{Median,P}$) was found to give good correlation between specific energy input to the mill and milled WC grain size in WC-Co mixtures. Mill runs included three different conditions; high speed, control and 25% less balls. Specific energy input ($\bar{E}$ = watt-hours/kilogram) was monitored in the runs using a shaft-mounted torque and angular velocity transducer and a digital power and energy computer. Grain size analysis on milled and sintered samples was performed by sedimentation and image analysis. Hardness and coercivity of sintered parts were also measured.

The rate of energy input to the three types of mill runs varies because of the different milling conditions. Results show that using energy input as a process parameter instead of time provides excellent control over milling, independent of milling conditions. The effects of cobalt content and energy input on milled powder grain size and distribution are shown. Comparisons between ASTM B430-79 rod milled powder and attritor milled powder are noted.

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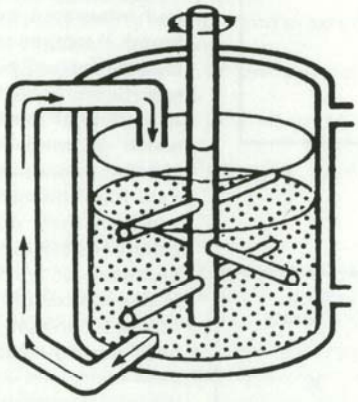


FIG.1 Union Process attritor grinding compartment

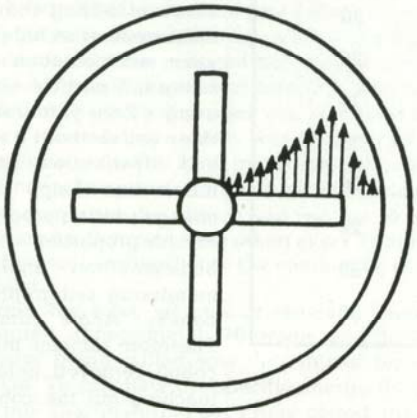


FIG.2 Ball velocity gradient across attritor mill

In a metallurgical system the mean grain size and distribution of grain sizes have an important effect on the properties and performance of the material. In the tungsten carbide-cobalt system, properties such as hardness and transverse rupture strength can be highly dependent on the tungsten carbide grain size distribution. (1,2) When cemented carbides are processed, the mix milling phase is considered to be one of the most important manufacturing steps. (3,4,5) During this stage of processing, WC agglomerates and polycrystalline particles are broken down and intimately mixed with cobalt. Small changes in the milling conditions during a run can produce differences in the WC mean grain size and distribution. These differences in the milled WC grain size and distribution can result in variations in cemented carbide properties and performance.

The attritor mill manufactured by Union Process Inc, is a very efficient device for mix-milling WC-Co. This equipment is approximately five times faster than the older rotating ball mill and is commonly used in the industry. The fact that milling action occurs so rapidly in the attritor dictates that special care be taken when milling. The attritor mill consists of a cylindrical water-jacketed vessel containing grinding media which are fluidised by a central, branched agitator shaft (see Fig 1). The processed material is trapped in the spaces between the balls, between the balls and the impeller shaft and, to a much smaller extent, between the balls and the chamber walls. During operation, a velocity gradient occurs across the vessel diameter. The ball velocity is low in the centre of the bowl near the shaft and increases with distance outward from the shaft, becoming a maximum at the arm tip. The velocity decreases rapidly beyond this point, as no energy is being transmitted directly from the shaft to the balls. Velocity is lower at the vessel wall, helping to reduce wear. (6)

In spite of the faster methods for milling WC that are available today, a reliable in-process method of predicting milling conditions and grinding behaviour has been lacking. A good mathematical model often used in the study of coarse grinding is the Charles equation. This equation relates energy input to some representative measure of particle size distribution. If the median of the size distribution is taken to represent the product size, the Charles equation takes the form:

$$\bar{E} = A\,(d^{-\alpha}_{Median,P} - d^{-\alpha}_{Median,F}) \qquad (1)$$

Where $\bar{E}$ = energy input to the mill

$$\frac{\text{Watt hours}}{\text{kilogram}}\ (\text{Wh}),\ \frac{\text{Joules}}{\text{kilogram}}\ (\text{J})\ \text{or}\ \frac{\text{Kilowatt hours}}{\text{ton}}\ (\text{kwh})$$

A = constant

$d_{Median,P}$ = median size of the product (microns)

$d_{Median,F}$ = median size of the feed (microns)

α = constant

When the products are much finer than the feed, equation (1) can be approximated by:

$$\bar{E} = A\,d^{-\alpha}_{Median,P} \qquad (2)$$

A logarithmic transformation of equation (2) yields

$$\log \bar{E} = \log A - \alpha \log (d_{Median,P}) \qquad (3)$$

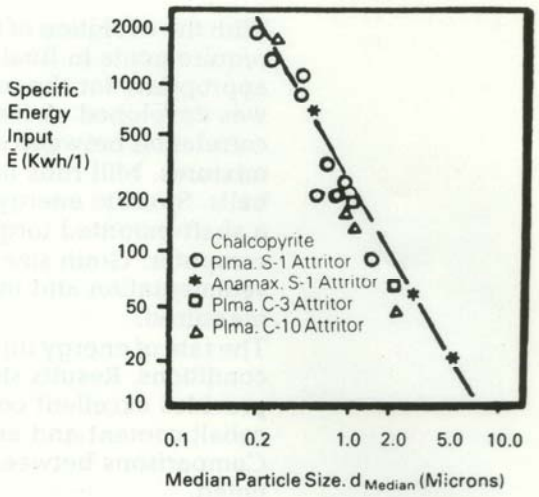


FIG.3 Energy size reduction relationship for chalcopyrite attrition milling in water (Herbst & Sepulveoa)

This form of the Charles equation is easy to check for posible application to a system, as a plot of log $\bar{E}$ vs log ($d_{Median,P}$) should result in a straight line of slope ($-\alpha$) if the grinding behaviour of the material-device combination is described by the model. (8,9)

For our system the mechanical energy that was being input to the charge in the attritor had to be obtained. Mechanical energy transmitted through a shaft can be calculated in the following way:

Power = K·Torque·angular velocity

A strain gauge and angular velocity (rpm) pickup mounted on the agitator shaft can be used to sense changes in shaft torque and rpm. If this data is entered into a computer, multiplied together to obtain power and integrated over time, total energy input can be found. If total energy input is divided by the amount of material actually in the mill for each period of time, specific energy will result, $\bar{E}$.

In a study at the University of Utah this equation was tested in three different size attritors under several operating conditions (see Fig 3). It was found that all the data from the various mills fell in a straight line. This suggests that, no matter what size mill or milling conditions are used, the product size can be accurately predicted for a given energy input.

In any system of milling the total energy input will be dissipated in many ways. Some energy will go to noise, heat, mixing or plastic collisions. In this study we will view energy on a macroscopic basis and consider only the total energy input to the mill. Work in our laboratory reported earlier showed good correlation between total energy input and cemented carbide properties. (10)

In order to get good quantitative evaluations of the effects of milling and sintering, two particle/grain size measurement techniques were used. These techniques were sedimentation analysis using a Micromeritics sedigraph particle size analyser and image analysis using a Zeiss video-plan image analysis unit. By using these two methods it was possible to evaluate grain size and distribution at all processing steps. This information helps determine what the effects of changes during processing have on the final cemented carbide properties.

Sedimentation analysis using an X-ray beam monitoring sedigraph can only be used on constant density, single component non-emitting powders. Therefore samples milled with cobalt had to have the cobalt removed before analysis. This was done by leaching out the cobalt with an acid that would not dissolve the WC particles. Nitric acid was used for this purpose. The Micromeritics sedigraph measures the

Powder	As received Mean Particle size, Fisher (µm)	Rod Milled Mean Particle size, Fisher (µm)
Tungsten Carbide SC 170-218FB	36	4.1
Cobalt Extra-fine SC 277	1.3	---

TABLE 1 Raw material characteristics

Type Run	Cobalt Wt%	Mill Speed RPM	Run Time, Hr	Run Temp C
High Speed	std	200	2	32
High Speed	std	200	2	32
Control	std	125	2	28
Control	std	125	2	29
Control	std	125	2	28
Control	std	125	2	28
Less Balls	25% Less	125	2	28
Less Balls	25% Less	125	2	28
Less Balls	25% Less	125	2	28
Less Balls	25% Less	125	2	28
WC Only	std	125	2	28

TABLE 2 Milling parameters

time dependence of transmission of an X-ray beam through a cell containing a liquid suspension of the particles being measured. The settling rate is determined by Stokes law, assuming spherical particles in a given viscosity liquid. Results are in equivalent spherical particle diameter versus cumulative weight percent and must be converted to number percent if they are to be compared to image analysis results.

A Zeiss videoplan quantitative image analysis unit was also used to measure particle sizes. This is a versatile system designed to quantify geometric characteristics of images and evaluate the measured data according to user requirements. The videoplan uses operator/instrument interaction to achieve pattern recognition, and combines this with modern computer technology. Image analysis was performed on copper infiltrated powders and sintered WC-Co samples. Tungsten carbide and copper have very limited solubility in each other, with widely divergent melting points. (11) Grains were traced from photos of a polished plane through the structure. No correction was made for particle shape of a three dimensional grain represented in two dimensions. The assumption was made that a random plane was taken through a random structure. If this is done and a large enough sample taken, the results in two dimensions will yield a representative size distribution. (12,13)

The grain sizes used in this study are in the form of Dcircle. Dcircle is the equivalent diameter of a circle with an area based on the actual traced grain. This method gives results that are independent of orientation, and easy to visualise. Data from the Zeiss unit had a normal distribution when plotted on a semi-log axis and could be represented by a Gaussian curve. Geometric means and standard deviations are used in this paper. In this study no attempt is made to correlate sedigraph and image analysis results.

PROCEDURES

In this study, four main methods were used for information gathering, they were:

(1) The recording of energy input to an attritor mill by means of sending equipment.

(2) Sedigraphic analysis of the powder in the as-received, and milled stages.

(3) Image analysis of the powder in the as-received, milled and sintered stages.

(4) Cemented carbide property evaluations on sintered samples.

Mill Sensing Equipment

A torque speed sensor manufactured by S Himmelstein and Company was mounted on the agitator shaft of a 1-ST attritor built by Union Press Inc Information from this sensor was input to a S Himmelstein System 6® controller with calculations being performed to produce speed (rpm), torque (lbs), power (watts) and energy (Kwatt hrs). Several runs were made using two cobalt contents (6 and 12 wt%). Commercial Syl-carb® WC powder, type SC170 (GTE Sylvania), and commercial extra-fine cobalt were used (see Table 1). In each of the WC-Co runs three different milling conditions were used; control runs, reduced ball charge runs in which 25% of the ball charge was removed, and high speed runs during which the speed was increased by 62%. A slurry recirculation system was used on all runs and samples were taken at 10 minute intervals for the first half-hour. The peristaltic slurry recirculation pump was turned on after the attritor had run for 10 minutes at high speed. Samples were taken every 15 minutes from 30 minutes of milling until the completion of the run at 2 hours.

During the runs, weights of removed samples were recorded, approximately 70 grams, and the amount of powder being milled was determined for each time period. To calculate the specific energy (Ē) going into the mill charge during each time period, the energy in watt hours was divided by the weight of the charge in the mill during that period.

An organic milling fluid was used during milling with 7.5% additional added approximately halfway through the run to account for evaporation. In the high speed runs, larger amounts were added (15%) because of greater losses. Twelve milled powder batches were made. The parameters for each run are shown in Table 2.

Particle Size Analysis by Sedimentation

Sedimentation analysis was performed using a Micromeritics sedigraph. This equipment evaluates X-ray beam intensity changes over time through a glass cell. The cell is filled with liquid and a powder sample. By determining the settling rate of constant density particles in a given viscosity liquid at a certain temperature, particle size can be determined. In order to do this in a mix-milled WC-Co powder the cobalt must be removed. This was done by leaching the cobalt away with nitric acid. During the leaching, the sample was repeatedly rinsed with 50% nitric and water until no colour changes were evident. The powder was then rinsed with sodium hydroxide and water to neutralise and remove the acid.

Grain Size Analysis by Image Analysis

To perform image analysis on the milled powder, a method to hold the samples and provide a contrasting background was needed. Copper sheet was rolled into a cylinder and filled with powder samples. These were

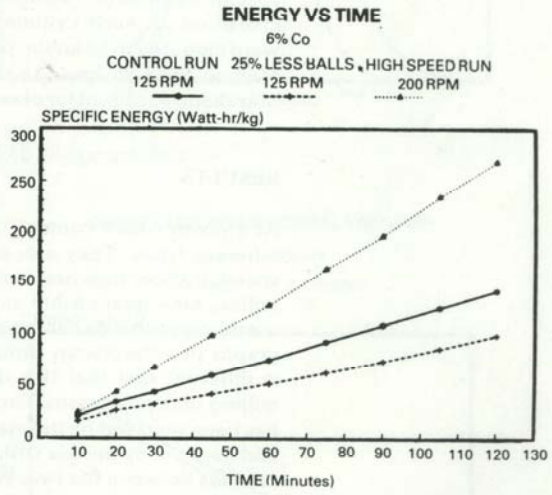


FIG.4a Energy vs time - 6% Co

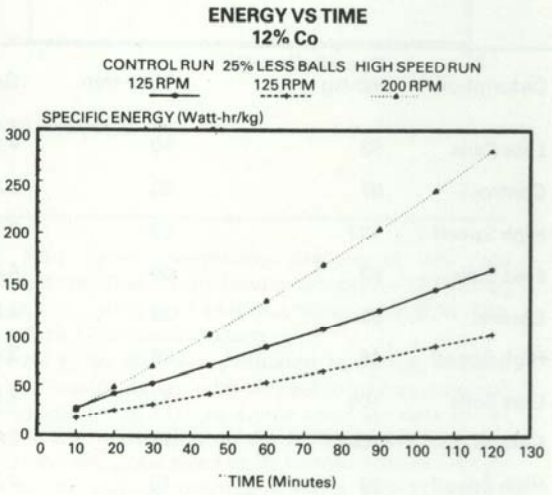


FIG.4b Energy vs time - 12% Co

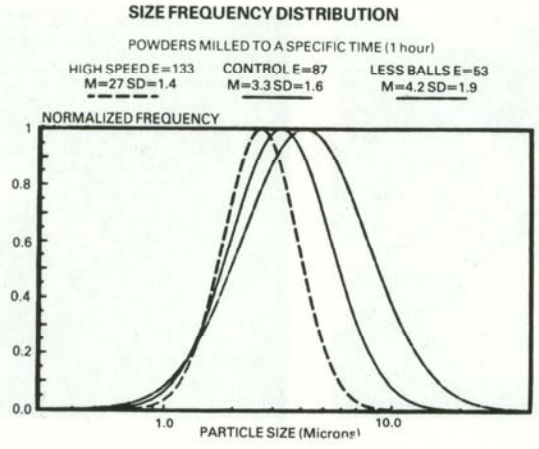


FIG.5a Sedigraph data

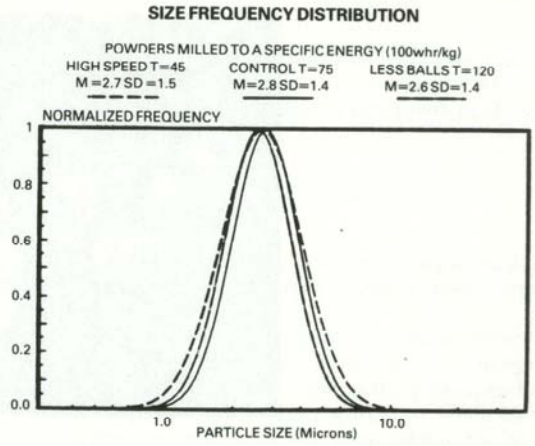


FIG.5b Sedigraph data

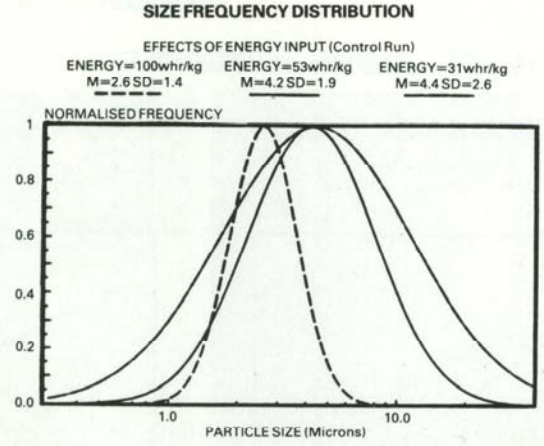


FIG.6a Sedigraph data

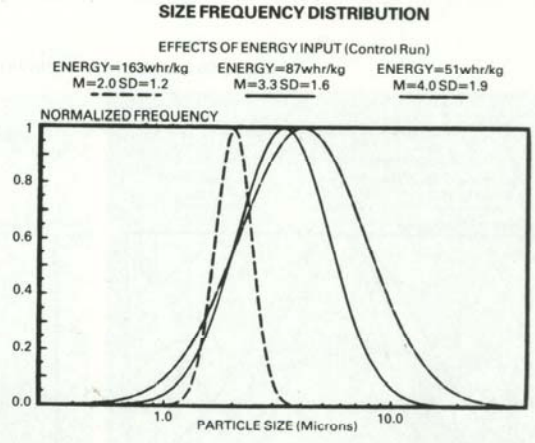


FIG.6b Sedigraph data

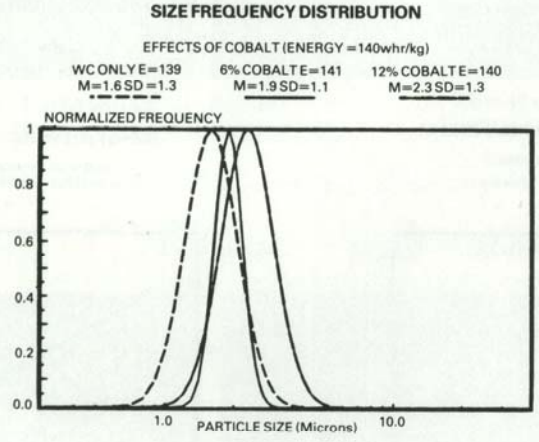


FIG.7a Sedigraph data

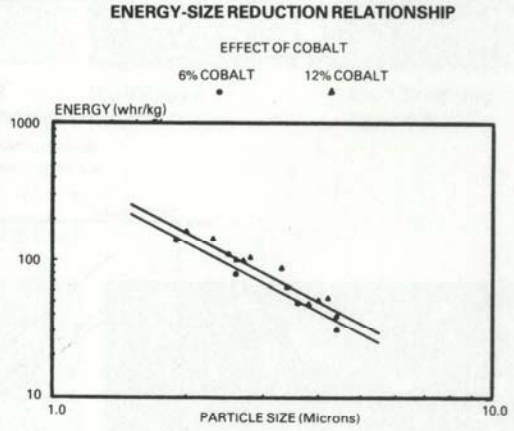
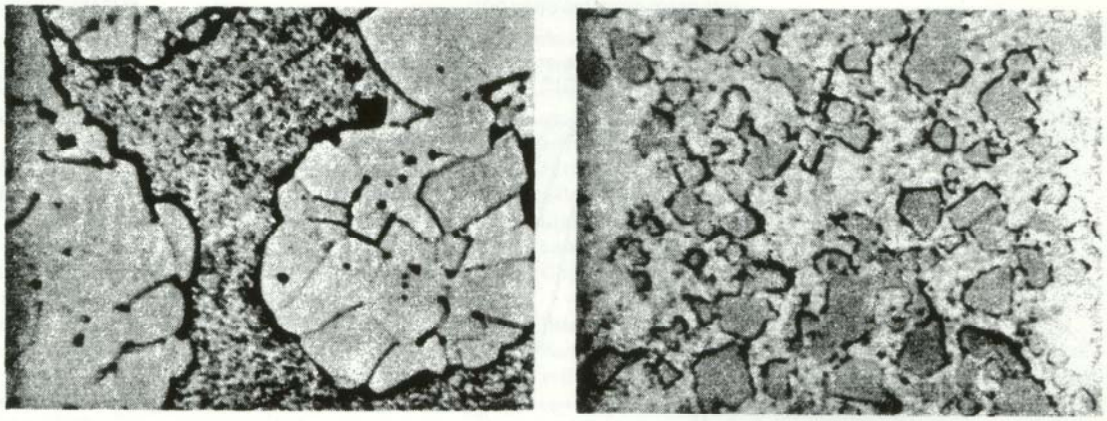


FIG.7b Sedigraph data

milling vary depending on the starting WC used. A comparison was made of the rod milled and attritor milled sedigraph results. They are similar at forty-five minutes of milling time with 6% cobalt and at one hour with 12% cobalt for this particular WC type and lot (see Fig 9).

If the effects of milling are plotted on time versus grain size and on energy versus grain size axes as in Fig 10, the following can be observed. In the time based graph, (Fig 10a) different milling conditions produce three distinct lines. This shows that breakage rate depends on the conditions in the mill and is relatively constant for a given constant condition. When energy is used as a milling base the data can be represented by a single line (Fig 10b). Linear regression analysis of this data produces the Charles equation constants A=505 Wh/kg and α = 1.7 with a correlation coefficient of 0.95. This line is for a 12% cobalt mixture.

Sintered grain size was evaluated by image analysis and the results plotted with respect to milling time and energy input (Fig 11). On a time basis the data shows three trends depending on the milling conditions (Fig 11a). Sintered grain size can be represented as a single line for all milling conditions when plotted against energy (Fig 11b). Linear regression analysis gives the Charles equation constants A = 520 Wh/kg and α = 1.8 with a correlation coefficient of 0.97, similar to those for the milled powder.



SC170-218-FB As-Received SC170-218FB 12% Cobalt Milled 1 hour

FIG.8 Microstructure of powders - copper infiltrated 1600x Murakami's Etch

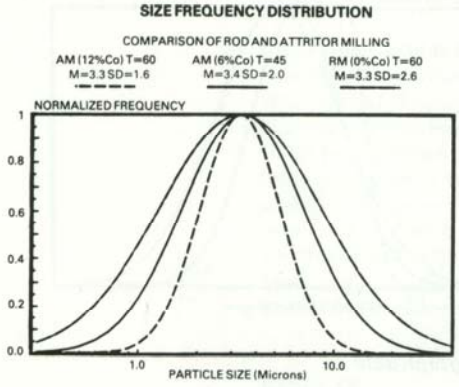


FIG.9 Sedigraph data

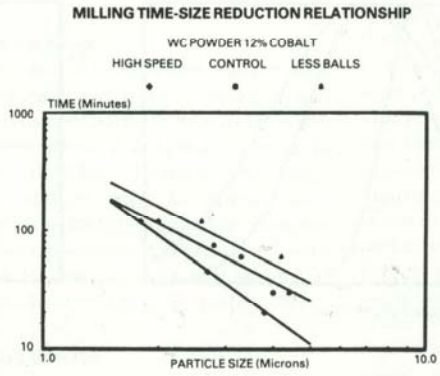


FIG.10a Sedigraph data

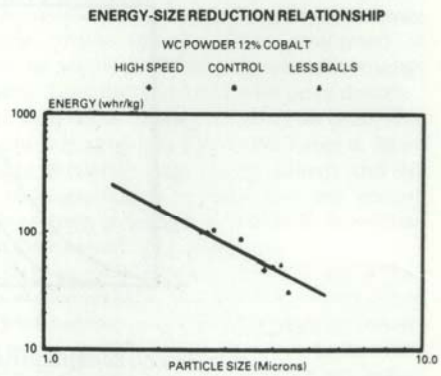


FIG.10b Sedigraph data

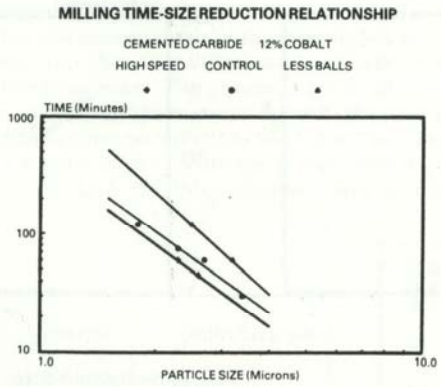


FIG.11a Sedigraph data

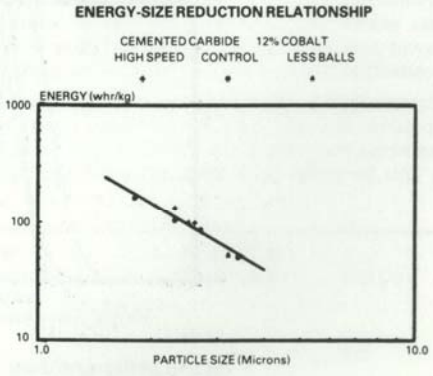


FIG.11b Sedigraph data

Image analysis results and microstructures of sintered samples appear in Table 5 and Figs 12 and 13. Here it can be seen that when a constant time base is used the sample mean grain sizes range between 3.2μm and 2.3μm, (a 0.9 μm spread) depending on the conditions used. If, on the other hand, samples at approximately 100 Wh/kg energy input are evaluated their mean grain sizes range between only 2.4μm and 2.6μm (a 0.2μm spread). Evaluating properties of these cemented carbide samples from the three types of runs reveals the consistency that can be obtained when using constant energy input. At sixty minutes of milling the maximum differences between properties of sintered samples were 0.9 unit Rockwell "A" hardness and 16 Oe coercive force. When samples at approximately the same energy level of 100 Wh/kg were tested, they had differences in hardness of only 0.1 unit R_A and 6 Oe coercive force.

Properties data from all the 12% cobalt runs are plotted against milling time and energy input in Figs 12-15. These graphs demonstrate the correlation obtainable with energy. Notice how the data points can be represented by one line instead of three separate lines

Descrip	Time (Min)	Energy (Wh/kg)	Grain (Size μm)		Hardness (R_A)	Coercivity (Oe)
			x	σ		
Constant Time						
Less Balls	30	31	3.2	1.6	86.5	61
Control	30	51	2.7	1.5	87.0	62
High Speed	30	68	2.3	1.7	87.4	77
Constant Energy						
Less Balls	120	100	2.5	1.5	87.2	74
Control	75	104	2.4	1.6	87.2	66
High Speed	45	99	2.6	1.6	87.1	72

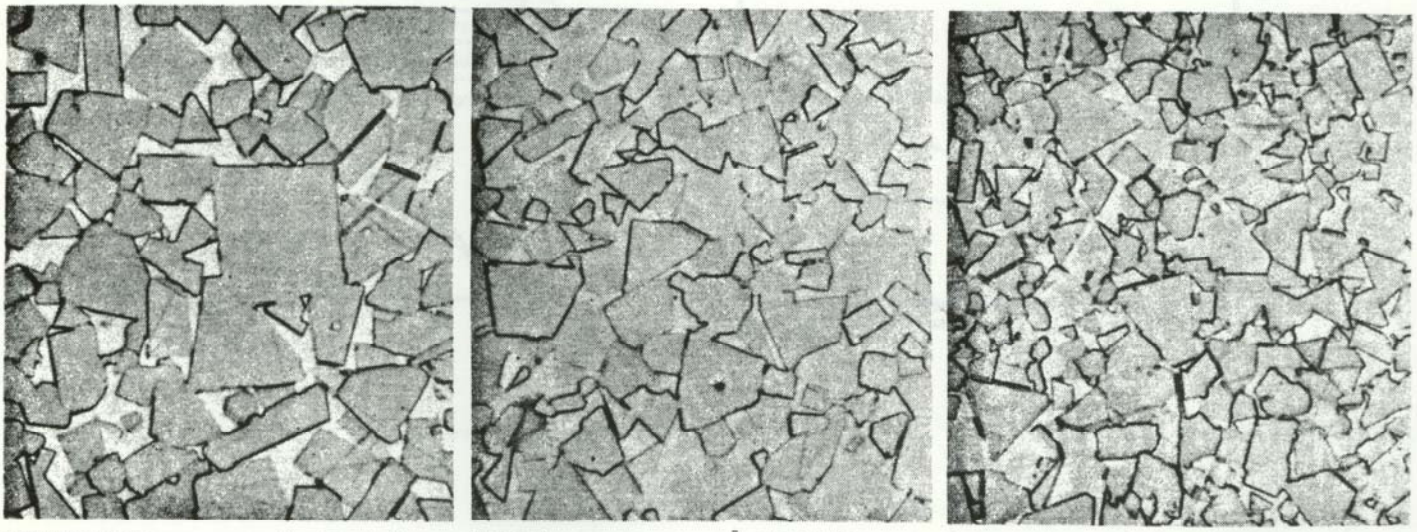
TABLE 5 Sintered grain size and properties

as in the time based graphs. This indicates that for a given specific energy input, certain properties can be controlled within a narrow band independent of milling conditions or time.

CONCLUSIONS

(1) The Charles equation is an appropriate model for attritor milling of tungsten carbide and tungsten carbide cobalt mixtures.
(2) The high speed runs received the most energy per unit time and the runs with a reduced ball charge the least. The rate of energy input to the high speed runs was 76% greater than to the control run, while the rate of energy input to the run with reduced ball charge was 35% less than to the control run.
(3) Because of the differences in rate of energy input, time of milling did not correlate with grain size. Close

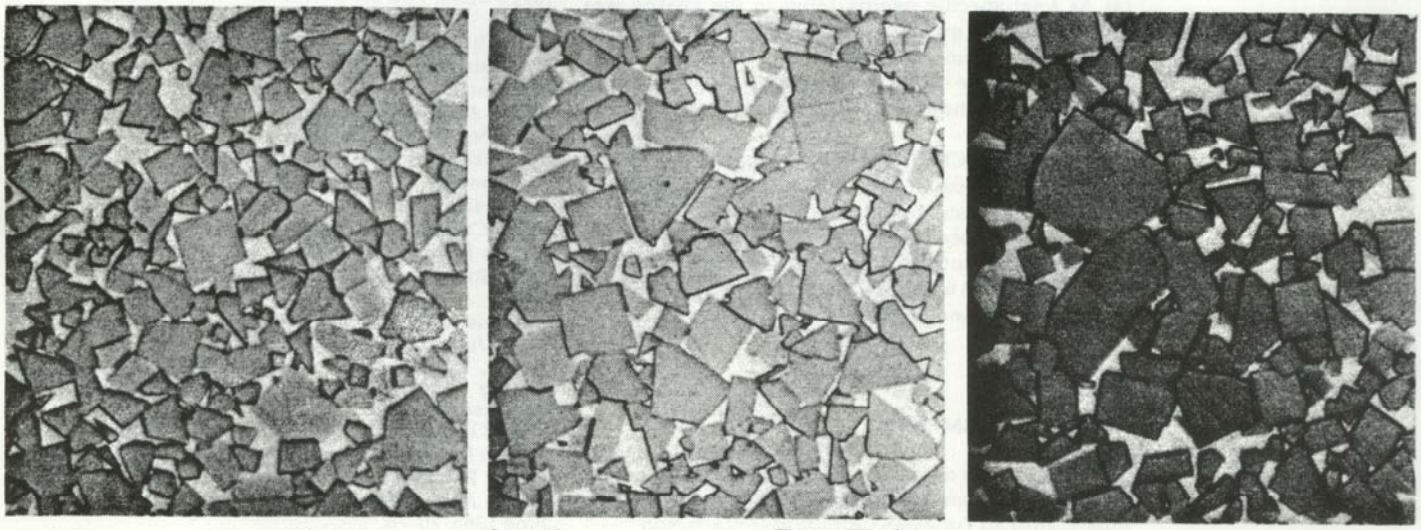
12% cobalt 1600x Murakami's Etch



25% Less Balls Mean = 3.2μm Ē = 53 whr/kg SD = 1.6 | Control Mean = 2.7μm Ē = 87 whr/kg SD = 1.5 | High Speed Mean = 2.3μm Ē = 133 whr/kg SD = 1.7

FIG.12 Comparison of microstructures at constant time (1 hour milling)

12% cobalt 1600x Murakami's Etch



Less Balls Mean = 2.5μm Time = 120 min SD = 1.5 | Control Mean = 2.4μm Time = 75 min SD = 1.6 | High Speed Mean = 2.6μm Time = 45 min SD = 1.6

FIG.13 Comparison of microstructures at constant energy E = 100 whr/kg.

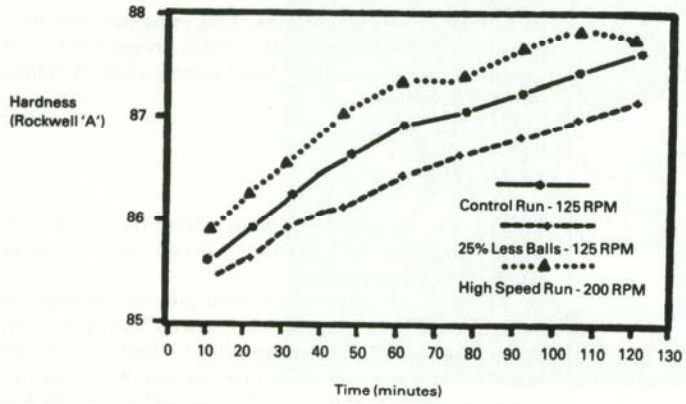


FIG.14 Hardness vs time, 12% Co

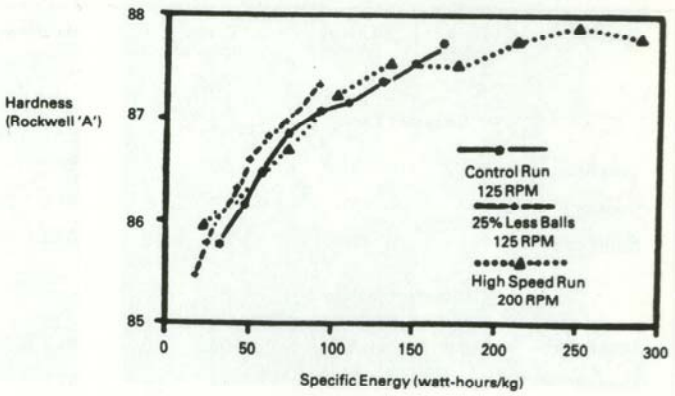


FIG.15 Hardness vs energy, 12% Co

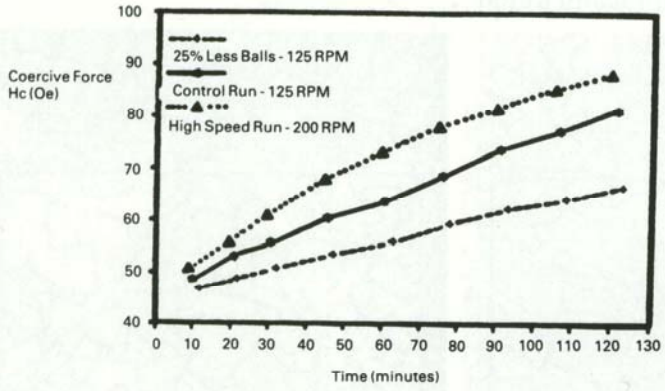


FIG.16 Coercive force vs time, 12% Co

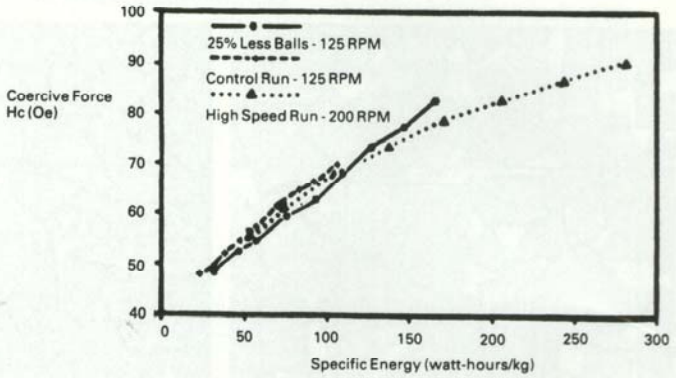


FIG.17 Coercive force vs energy, 12% Co

correlation between specific energy input and grain size was seen.

(4) As total specific energy input to the charge was increased, mean grain size decreased and the grain size distribution became narrower.

(5) Increasing the cobalt content of the WC-Co mixture being milled tended to slow down or dampen the breakage rate.

(6) Though the Charles equation was derived for as-milled particle size, it can be applied to sintered WC grain size for constant sintering conditions.

(7) For a given specific energy input, the milled particle size of WC and sintered properties of cemented carbide can be controlled within a narrow band, independent of milling time or conditions.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions and assistance of Ron White, Leticia Santos and Dave Milatz, all of Sii Tungsten Carbide Manufacturing.

REFERENCES

(1) P Schwarzkopf, R Kieffer, 'Cemented Carbides', 1960, The Macmillan Company, New York: 71, 140-155.

(2) W Dawihl, 'Handbook of Hard Metals', 1955: London, HM Stationery Office, 59.

(3) I Püpke, *Powder Metallurgy International*, 1971, 3, 94-96.

(4) Ed Bashkirov, 'Hard Metals Production Technology and Research in the USSR', 1964: Pergamon Press, Chapter 2.

(5) G J Rees, B Young, *South African Mechanical Engineer*, 1972, 22 (3), 81-87.

(6) A Szegvari, M Li, 'Attritor Grinding and Dispersion of Pigments and Resins in Fluid Media, Kent State University.

(7) R J Charles, *AIME Transactions*, 1957: 208, 80-88.

(8) J A Herbst, J L Sepulveda, 'Fundamentals of Fine and Ultrafine Grinding in a Stirred Ball Mill', United States Energy Research and Development Administration Contract No EY-77-S-02-2560, March 1979, University of Utah.

(9) J L Sepulveda, 'A Detailed Study of Stirred Ball Milling' Ph.D. Thesis, 1979: Metallurgy Dept., University of Utah.

(10) R Goodson, et al, 'Energy Input Monitoring During Attritor Milling', Advances in Hard Metal Production, A Metal Powder Report Conference, Nov 7-9, 1983. ***Intern Journal Refract & Hard Metals,*** Vol. 3, No. 2, June 1985, 70-76.

(11) American Society for Metals, 'Metallography, Structures and Phase Diagrams', 1973, Metals Handbook Vol 8, Metals Park, Ohio: 118.

(12) H Modin, S Modin, 'Metallurgical Microscopy', 1973, John Wiley and Sons, New York: 148-179.

(13) E E Underwood, 'Quantitative Stereology', 1970, Addison Wesley Publishing Company, Reading, Massachusetts: 133, 140, 185.