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Energy Input Monitoring During Attritor Milling

R Goodson, F Larson, L Sheehan (Sii Tungsten Carbide Mfg., Division of Smith International Inc., Tustin, California, USA)

One of the most critical steps in hardmetal production is the milling of the carbide and binder powders. Significant changes in the particle size and grain size of the carbide and in the distribution of the binder occur during milling. These changes strongly influence the microstructure and properties of the sintered product. A model appropriate for the material-device relationship of WC and cobalt mixtures in the attritor was sought. A form of the Charles equation ($\bar{E}=A\ d^{-\alpha}_{Median,P}$) was found to give good correlation between specific energy and product particle size for WC. Tests included 6 and 12 weight percent cobalt mixtures under 3 different milling 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-angular velocity pickup and a digital power and energy computer. Properties of the sintered carbide had maximum spreads of up to 9 times greater in hardness and 5 times greater in coercivity when evaluated on a time basis rather than on an energy basis. It was shown that it is possible to predict sintered carbide properties within a narrow band, independent of milling conditions or time.

Energy Input Monitoring During Attritor Milling

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The mix-milling process is considered to be one of the most important steps in the manufacture of hardmetal components (1,2,3). Properties such as hardness, coercivity, and transverse rupture strength, which determine the performance of a cemented carbide product, are strongly related to the milling conditions used (4).

The attritor mill manufactured by Union Process Inc., is a most efficient device for carrying out this mix-milling and is commonly used in the industry. The attritor mill consists of a cylindrical water-jacket vessel containing grinding media which is fluidised by a central, branched agitator shaft (see Fig. 1). The processed material, trapped in the space between the balls, is subjected to a combination of rubbing impingement action 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 lowest at the vessel wall, helping to reduce wear (Fig. 2).

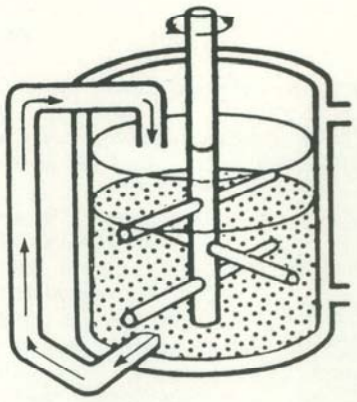

FIG.1 Union Process attritor grinding compartment

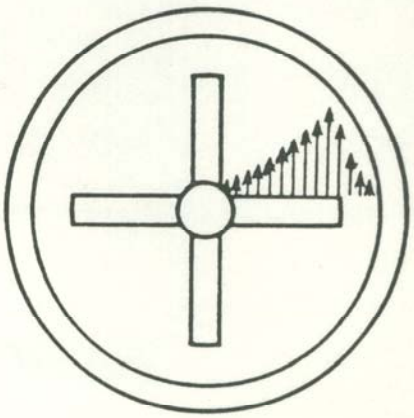

FIG.2 Ball velocity gradient across attritor mill

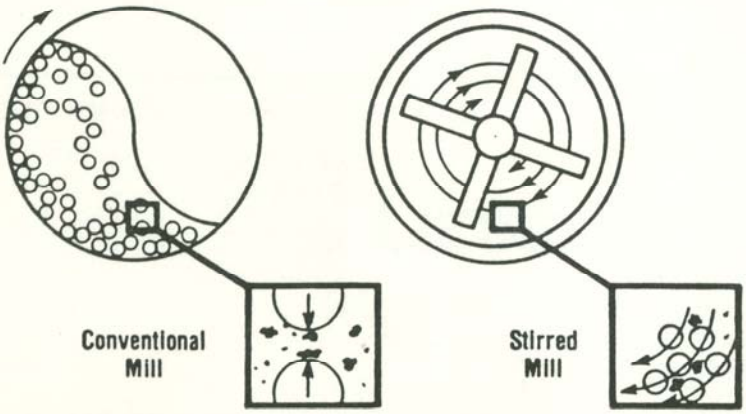

FIG.3 Comparison of the grinding action in conventional and stirred ball mills

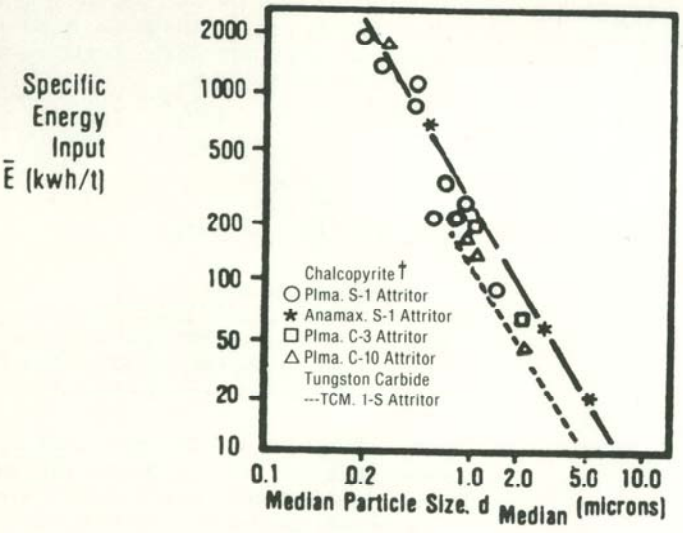

FIG.4 Energy-size reduction relationship for chalcopyrite atttrition milling in water

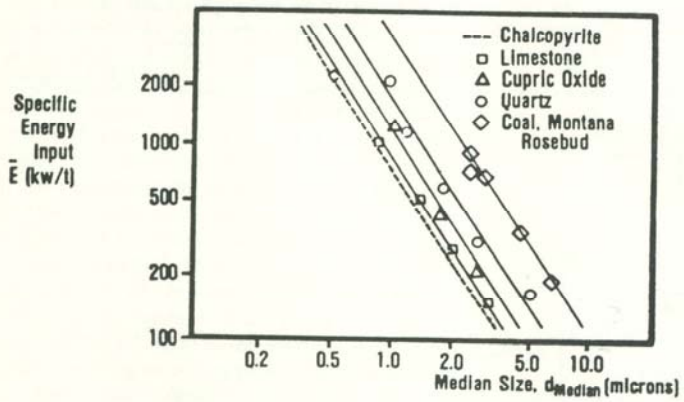

FIG.5 Energy-size reduction relationship for various minerals attrition milling in water, S-1 attritor

The forces applied to particles within the ball mass leading to fracture are believed to be intense shear and normal forces. There is also a small mean free path between the balls, providing for capture of small particles and milling progression into the submicron range (5,6). Small particles become more difficult to fracture because, as they are reduced in size, larger flaws are eliminated and the resulting smaller particles have an increased critical strength (7). According to stress analysis and rock mechanics the combined action of compressive and torsional stresses may result in an increased principal stress (8) which can lead to fracture (5,6). This combination of stresses is very important when fracturing particles in the one micron size range and has been shown in experimental observations by Schönert et al (5,6). When considering equipment for fine grinding, the standard ball mill, in which particle loading is predominantly compressive, appears inferior to the attritor mill for breakage of small (submicron) particles because of the combination of stresses which the latter provides (see Fig. 3).

A problem that has hindered manufacturing in the milling of cemented carbide is lack of product consistency. A reliable in-process method of predicting mill conditions and grinding behaviour has been lacking in the industry. If a good mathematical model relating energy input to product size could be found, it would help with scale-up relationships and consistency of product. An empirical relationship that is often used in the study of coarse grinding is the Charles equation.

This equation related energy input to some representative measure of particle size distribution (5,9). If the median of the size distribution is taken to represent the produce 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

$$\left(\frac{\text{kilowatt hours}}{\text{ton}} \text{ or } \frac{\text{watt hours}}{\text{kilogram}}\right)$$

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

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

This form of the Charles equation is easy to check for possible 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.

This relationship was tested in several studies at the University of Utah. Shown in Fig. 4 is such a plot for the grinding of chalcopyrite in water (5,6). This plot includes data for two different concentrates, three attritors (3.8, 11.4 and 37.8 litre capacity), stirring speeds from 100 rpm to 400 rpm, solids content from 30% to 70%, and grinding media diameters between 2.38 and 6.35 millimetres. It was found that linear regression for all of the data shown yields the equation:

$$\bar{E} = 460\,d^{-1.79}_{Median,P}$$

with a correlation coefficient of 0.95.

In the University of Utah study, the fact that all the data from the various mills and conditions falls in a straight line is highly significant. This indicates that, no matter what size mill or milling conditions are used, the product size can be accurately predicted for a given energy input. Further testing was done on various minerals and Fig. 5 shows these results. The straight lines in this figure show that equation (2) describes the milling action for these minerals. The lines are also almost parallel to each other which suggests that the exponent, α, in equation (2) has a constant value of 1.8 for stirred ball milling in water.

In any system of milling the total energy input will be dissipated in many different ways:

$$E_T = \Sigma E = E_N + E_H + E_M + E_{P.C} + E_S \ldots$$

E_N = energy to noise
E_H = energy to heat
E_M = energy to mixing
$E_{P.C.}$ = energy to plastic collisions
E_S = energy to form new surfaces

On a micro energy scale it is unknown how much energy is being used in each segment but it is believed that, in many cases, E_N, and E_H, the energy being diverted, is a constant amount. Although the Charles equation was developed using one component systems, where no energy would be consumed in the mixing of two components, it is believed that the relationships

Powder	Mean Particle Size, Fisher (μm)	Rod Milled Particle 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 %	Ball Charge	Mill Speed RPM	Run Time, Hr	Run Temp° C	Run Number
High Speed	6	std	200	2	32	837
High Speed	12	std	200	2	32	836
Control	6	std	125	2	28	830
Control	6	std	125	2	29	831
Control	12	std	125	2	28	828
Control	12	std	125	2	28	829
Less Balls	6	25% Less	125	2	28	833
Less Balls	6	25% Less	125	2	28	834
Less Balls	12	25% Less	125	2	28	835
Less Balls	12	25% Less	125	2	28	836
Cobalt Only	100	std	125	2	28	838
WC Only		std	125	2	28	839

TABLE 2 Milling parameters

Type Run	Run # & Sample	Time Min	Ē wh/kg	H_C Oe	Hardness R_A
High Speed	837-4	45	99	102	89.2
Control	830-4	45	64	87	88.7
Less Balls	832-4	45	42	82	88.4
High Speed	837-3	30	68	89	88.7
Control	830-4	45	64	87	88.7
Less Balls	832-6	105	63	92	88.8
High Speed	837-9	120	269	136	90.1
Control	830-9	120	141	115	89.7
Less Balls	832-9	120	100	109	89.3
High Speed	837-4	45	99	102	89.2
Control	830-6	90	96	99	89.1
Less Balls	832-9	120	100	109	89.3

TABLE 3 Properties of sintered samples 6% cobalt

will remain valid for the WC-Co system. In this study we view energy on a macroscopic level and consider only the total energy input to the mill. No attempts are made to separate the various energies into their groups or to classify them into constant or variable forms.

Mechanical energy transmitted through a shaft can be calculated in the following way:

$$\text{Power} = K \cdot \text{Torque} \cdot \text{angular velocity}$$

$$E = \int_{t_0}^{t} P(t)dt$$

A strange gauge and angular velocity (rpm) pickup mounted on the agitator shaft can be used to sense changes in shaft torque and rpm. If these data are 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,

$$\bar{E} = \frac{\text{watt hours}}{\text{kilogram}}$$

EXPERIMENTAL PROCEDURE

Milled Powder Preparation

Two compositions of milled powders were used in the testing; WC-6wt% Co and WC-12wt% Co. Commercial SYL-CARB® WC powder, type SC170 (GTE Sylvania), and commercial extra-fine cobalt were used (See Table 1).

The mix milling of all WC-Co powders was done in a laboratory size 1-ST mill, 5.7 litre capacity made by Union Process of Akron, Ohio. The runs were made using a constant ball charge except for the reduced ball charges which used 25% less balls. An organic milling fluid was used with 7.5% additional added approximately halfway through the run to account for evaporation. For the high speed runs, larger amounts were added (15%) because of a greater loss at the higher temperature and rpm. A mill speed of 125 rpm was used for all runs except the high speed milling, for which 200 rpm was used. All charges were initially run for 10 minutes at 250 rpm to ensure complete wetting of the powders before the peristaltic recirculation pump was turned on. Samples of approximately 70 grams were taken using a disposable pipet every 10 minutes for the first half-hour and every 15 minutes for the next 1½ hours. Total run time for all charges was 2 hours. An S. Himmelstein and Company 'System 6' digital power-energy computer and a strip chart recorder were coupled to a Himmelstein MCRT 9-02T torquemetre for information gathering and energy computation during the mill run. A printout was used to record instantaneous torque, speed, power, energy and time throughout the test. Specific energy was calculated for each segment of each run to account for the reduction in powder charge as samples were being withdrawn. Twelve milled powder batches were made. The parameters for each run are shown in Table 2.

Hardmetal Preparation

One 20 gram portion of each sample taken during each WC-Co run, (9 samples/run) was pressed into a 1.3cm diameter by 1cm high cylinder. All 90 cylinders from the 10WC-Co mill runs were vacuum sintered in the same furnace run for 1 hour at 1420C. Density, coercivity, specific magnetic saturation and hardness were measured on each cylinder. Metallographic samples were mounted in bakelite, polished according to ASTM Method B657, used to rate porosity and etched in Murakami's reagent for observation of microstructure.

RESULTS

When the three types of mill runs, control, less balls, and high speed, are viewed in an energy input-milling time relationship as in Fig. 6 and Fig. 7, some interesting comparisons can be made. These graphs show that the energy input to the three types of runs is different and that this difference increases as the milling time progresses. The greatest amount of energy is put into the high speed run and the least into the run with 25% less balls, while the control run falls between the two. It is evident that, with the exception of the ten minute run-in-time, the three charges have received different

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Type Run	Run # & Sample	Time Min	$\bar{E}$	H_C Oe	R_A
Control	828-5	60	88	61	87.0
Less Balls	834-5	60	52	58	86.6
H.S.	836-5	60	133	73	87.4
Less Balls	834-5	60	52	58	86.6
Control	828-3	30	53	53	86.3
H.S.	836-2	20	48	56	86.3
Less Balls	834-9	120	99	70	87.3
Control	828-9	120	164	75	87.5
H.S.	836-9	120	280	88	87.8
Less Balls	834-9	120	99	70	87.3
Control	828-6	75	105	66	87.0
H.S.	836-4	45	99	68	87.1

TABLE 4 Properties of sintered samples 12% cobalt

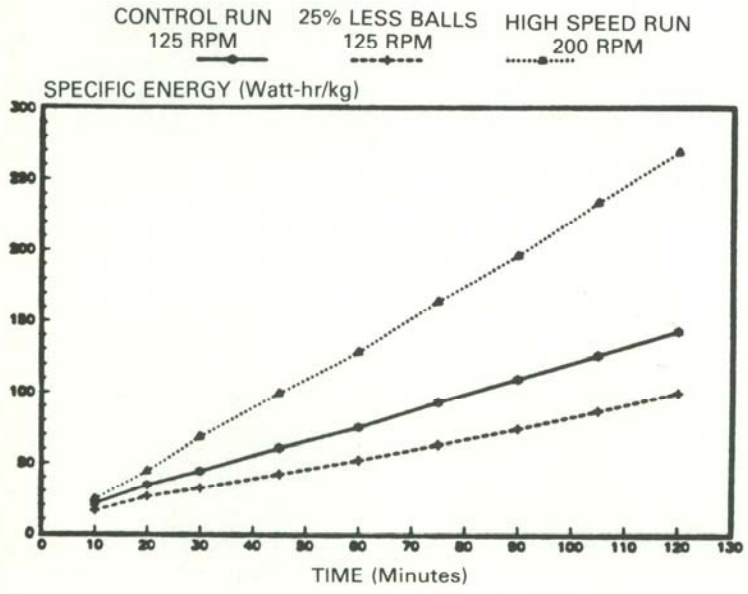


FIG.6 Energy vs time (6% Co)

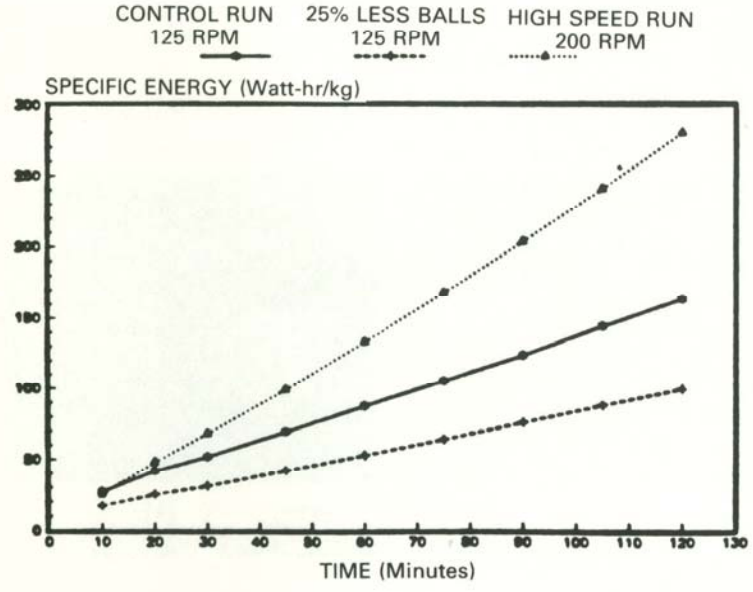


FIG.7 Energy vs time (12% Co)

amounts of energy input and the material in the mill will be in a different condition for each run. In traditional cemented carbide milling, charges are run on a time basis. It is very difficult to adjust for changes in milling conditions due to factors such as shaft wear, ball charge, and scale-up, except on a trial-and-error basis. If, on the other hand, milling were done on a specific energy input basis, many of these factors could be ignored and the consistency of the milled WC-Co powder should be greatly improved.

In this study, milling conditions are compared with finished cemented carbide properties. Since all the samples were sintered at the same time, it is assumed that sintering effects were approximately equal in the samples, and that differences in the final properties were caused by milling changes. This makes it possible to compare the end point differences of milling conditions with final properties. In future studies, the intermediate steps of milled particle size and sintering effects, as well as final properties, will be examined.

Looking at several points during the three types of runs, at constant time and then at constant energy, it can be seen that very significant differences in properties of sintered carbides are obtained if a time base is used instead of an energy base (see Tables 3 and 4 and Figs. 8-11). At 45 minutes of milling with a 6% cobalt grade the maximum differences in sintered samples are 0.8 units Rockwell 'A' hardness and 30 Oe coercivity. Grain size differences can be seen in th micrographs. If an energy base is used there is a maximum difference of 0.1R_A and 5 Oe with mill times of 30 minutes, 45 minutes and 105 minutes (approximately equal energy input). Another check at 2 hours of milling shows maximum differences of hardness and coercivity to be 0.8 R_A and 27 Oe respectively. If energy is used as a base the differences are 0.2 R_A and 10 Oe with mill times of 45 minutes, 90 minutes and 120 minutes. Grain sizes are very similar and all three of these runs have a specific energy near 100 wh/kg. Similar trends can be seen in Table 4 where a 12% cobalt mixture was used. Hardness differences were 5 to 6 times larger and coercivity spreads 2 to 3 times greater when a time base was used, compared with the use of an energy relationship.

Another way of viewing the data is shown in Figs. 12 through 19: graphs of the cemented carbide hardness and coercivity versus milling time and specific energy input for 6% and 12% cobalt samples. In all cases when a time base is used the properties vary between the runs, with the high speed runs having the highest hardness and coercivity and the runs with 25% less balls having the lowest. There are a few instances in the first data points where crossovers occur but these are early in the test and could be due to experimental error. In all cases, though, an overall trend of three distinct levels of properties is clearly established. The graphs of properties versus specific energy input show a grouping of the data to a central curve, indicating that, for a given specific energy input, certain properties can be controlled within a narrow band independent of milling conditions or time.

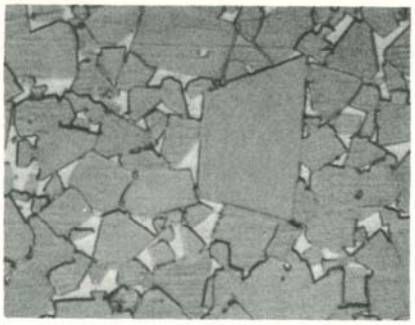
Data from a mill run of WC without cobalt were plotted on log-log axis to check conformance to the Charles equation. Linear regression analysis of the data resulted in a straight line with a correlation coefficient of 0.99, indicating excellent fit to the equation:

$$\bar{E} = A\, d_{Median,P}^{-\alpha}$$

$$\text{where } A = 186 \frac{\text{watt hours}}{\text{kilogram}} \text{ or } 169 \frac{\text{kilowatt hours}}{\text{ton}}$$

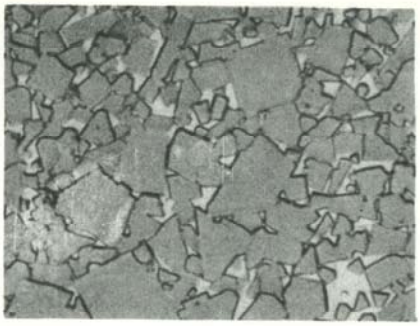
and $\alpha = 1.51$

Fig. 20 is a plot of the data with the calculated line included, showing the close fit. In Fig. 21, the WC data



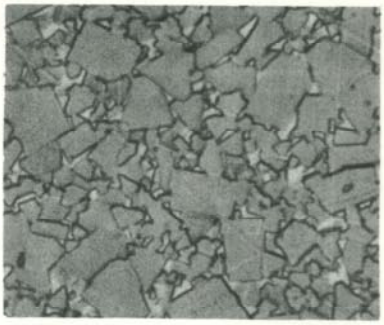
25% Less Balls
Time=120min
Hardness=R_A89.3

832-9
$\dot{E}$=100wh/kg
H_C=109 Oe



Control
Time=120min
Hardness=R_A89.7

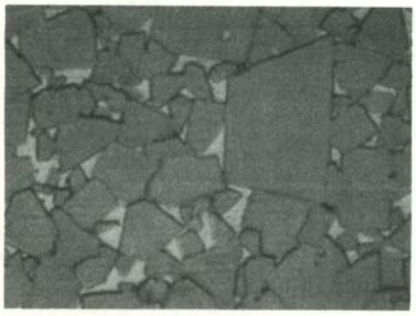
830-9
$\dot{E}$=141wh/kg
H_C=93 Oe



High Speed
Time=120min
Hardness=R_A90.1

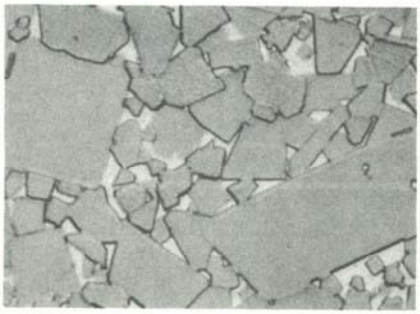
837-9
$\dot{E}$=269wh/kg
H_C=136 Oe

FIG.8 Comparison of microstructures at constant time (6% cobalt; 1600X; Murakami's Etch)



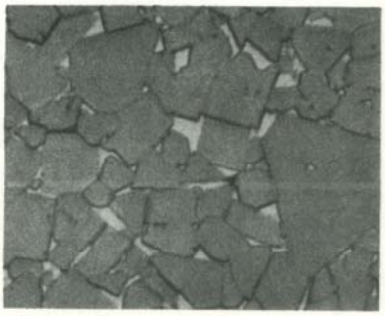
25% Less Balls
Time=120min
Hardness=R_A89.3

832-9
$\dot{E}$=100wh/kg
H_C=109 Oe



Control
Time=90min
Hardness=R_A89.1

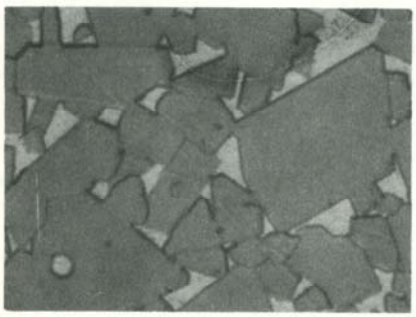
830.6
$\dot{E}$=96wh/kg
H_C=99 Oe



High Speed
Time=45min
Hardness=R_A89.2

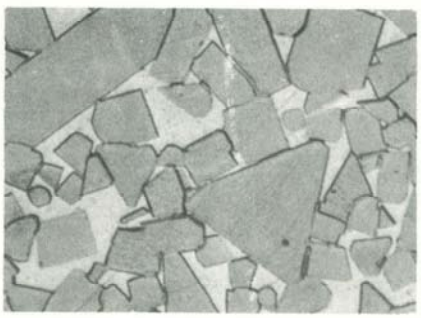
837.4
$\dot{E}$=99wh/kg
H_C=102 Oe

FIG.9 Comparison of microstructures at constant energy (6% cobalt; 1600X; Murakami's Etch)



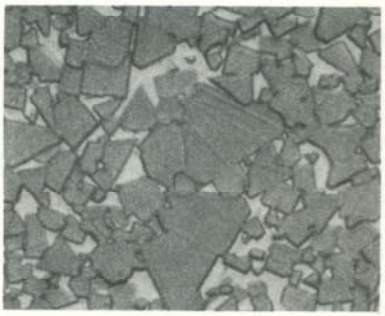
25% Less Balls
Time=60min
Hardness=R_A86.6

834-5
$\dot{E}$=52wh/kg
H_C=58 Oe



Control
Time=60min
Hardness=R_A87.0

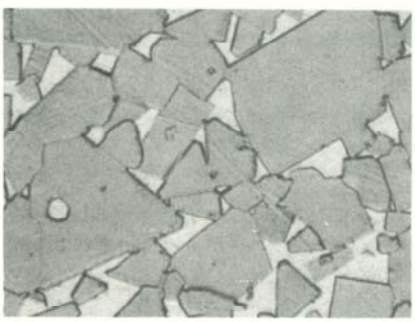
828-5
$\dot{E}$=88wh/kg
H_C=61Oe



High Speed
Time=60min
Hardness=R_A87.4

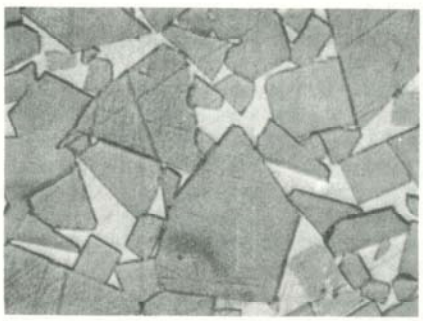
836-5
$\dot{E}$=133wh/kg
H_C=73 Oe

FIG.10 Comparison of microstructures at constant energy (12% cobalt; 1600X; Murakami's Etch)



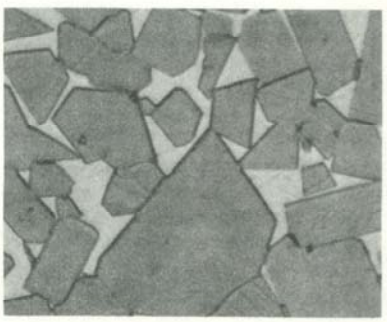
25% Less Balls
Time=60min
Hardness=R_A86.6

834-5
$\dot{E}$=52wh/kg
H_c=58Oe



Control
Time=30min
Hardness=R_A86.3

828-3
$\dot{E}$=53wh/kg
H_C=53 Oe



High Speed
Time=20min
Hardness=R_A86.3

836-2
$\dot{E}$=48wh/kg
H_C=56 Oe

FIG.11 Comparison of microstructures at constant energy (12% cobalt; 1600X; Murakami's Etch)

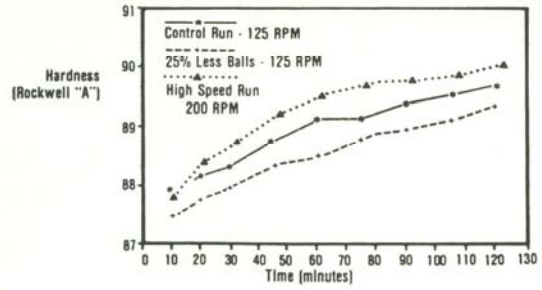


FIG.12 Hardness vs time (6% Co)

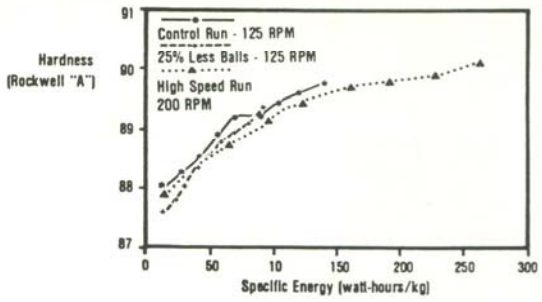


FIG.13 Hardness vs energy (6% Co)

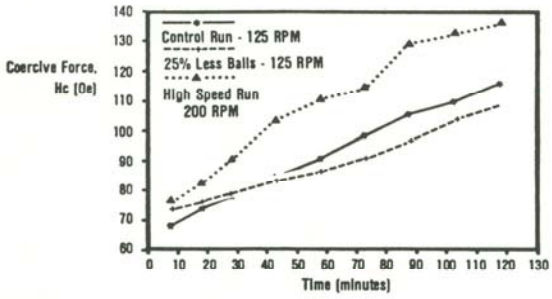


FIG.14 Coercive force vs time (6% Co)

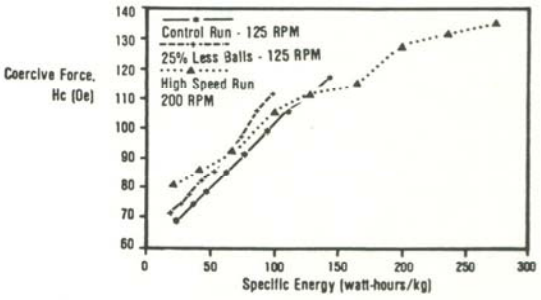


FIG.15 Coercive force vs energy (6% Co)

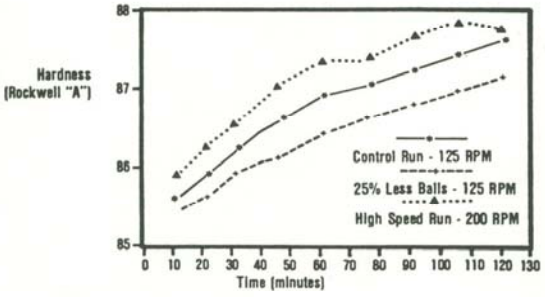


FIG.16 Hardness vs time (12% Co)

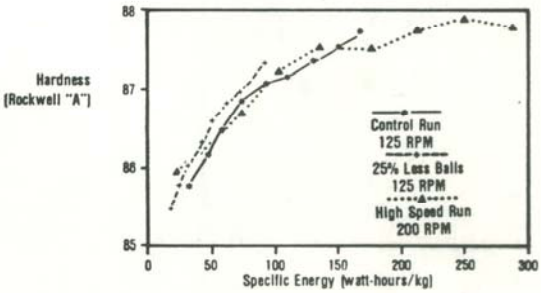


FIG.17 Hardness vs energy (12% Co)

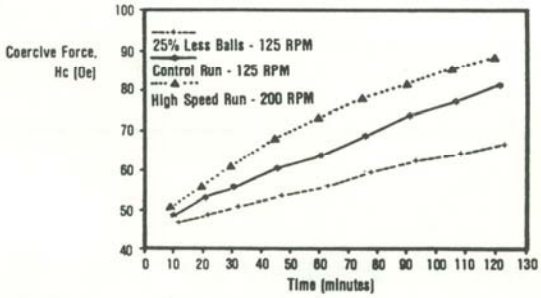


FIG.18 Coercive force vs time (12% Co)

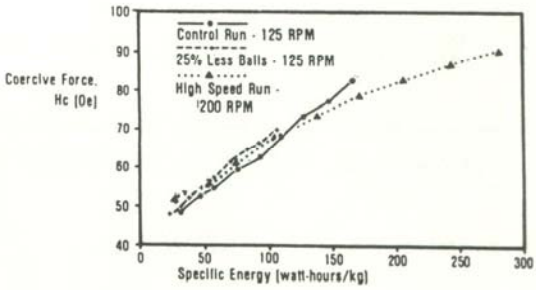


FIG.19 Coercive force vs energy (12% Co)

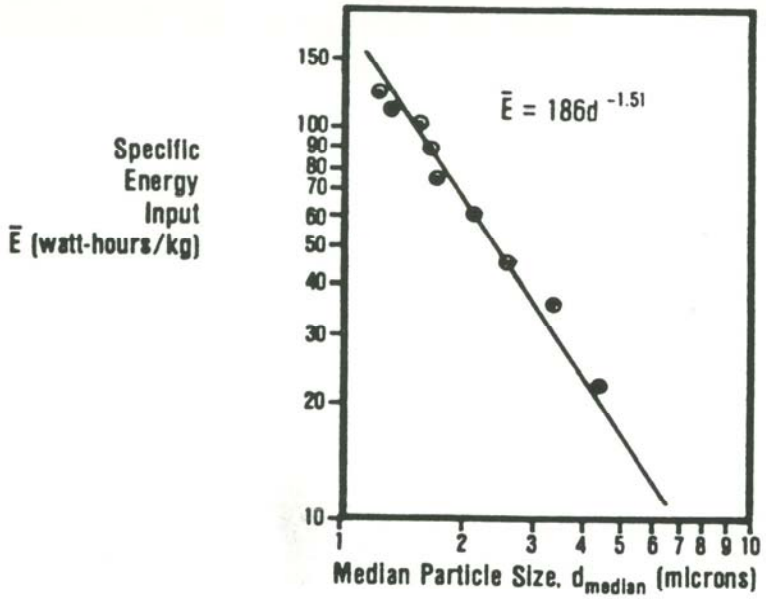


FIG.20 Energy-size reduction relationship for tungsten carbide

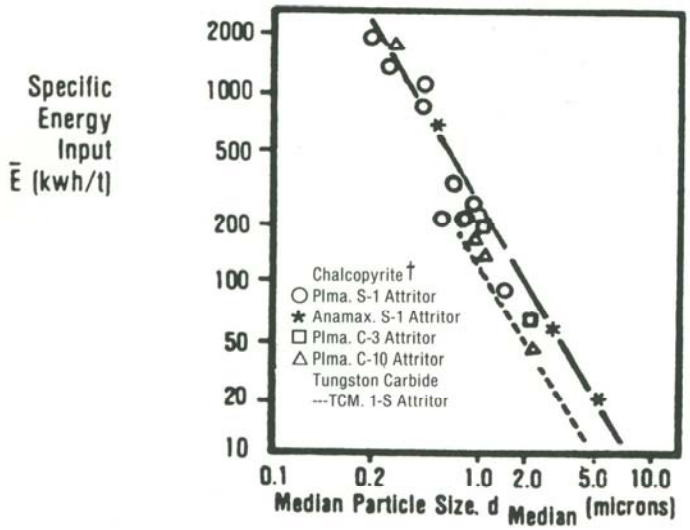


FIG.21 Comparison of energy-size reduction relationships for chalcopyrite and tungsten carbide

are compared with the chalcopyrite data shown earlier in Fig. 4, demonstrating the similarity of slope and position of the tungsten carbide line to those for chalcopyrite.

CONCLUSIONS

(1) The Charles equation is an appropriate model for attritor milling of tungsten carbide.
(2) Energy input to the three types of runs, high speed, control and 25% less balls, were different. The high speed runs received the most energy and the runs with less balls the least.
(3) At any given time in the runs, after the first ten minutes, the sintered carbide properties are different in three types of runs, following the same trends as energy input.
(4) For various points during the milling, the maximum properties differences were 8 to 9 times greater in hardness and 4 to 5 times greater in coercivity if constant time was used to compare results of different mill runs rather than constant energy.
(5) For a given specific energy input the sintered properties of WC-Co can be controlled within a narrow band, independent of milling time or conditions.

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