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Coolant pH control for optimum ceramic grinding

Part II *Influence of the rebinder effect on the surface grinding of aluminum oxide*

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Variations in the grinding (machining) properties of aluminum oxide attributable to the Rebinder effect, an environment-caused variation in the hardness of rock, ceramic, or glass, were investigated using conventional surface grinding equipment. Systematic variation in normal force, tangential force, roughness average, waviness average, and post grinding flexural strength were attributable to the grinding condition (coarse or fine) and the pH of the coolant. Observations in this study are consistent with a ductile/brittle grinding transition for fine grinding, a brittle/brittle grinding transition for coarse grinding and pH control of plastic deformation.

1. Introduction

The Rebinder effect, an environment-caused variation in the hardness of rock, was discovered in 1928 by P. A. Rebinder [1, 2] who found an anomalous softening of rock associated with the environment to which it was exposed. Rebinder attributed this softening to an adsorption-caused reduction in the surface free energy of the material and attempted to use it to reduce the energy required to drill oil wells. While successful on a laboratory scale, Rebinder effect improvements in efficiency were not significant in field operations.

Interest in the Rebinder effect was revived in the 1960's and 70's by Westwood and others who extended the study of the Rebinder effect to include not only rock, but ceramics [3–6] and glasses [3, 7, 8] as well. This work demonstrated that the environment could cause an increase in hardness as well as a decrease and thus required an explanation other than Rebinder's because positive adsorption of a substance on a surface can cause only a reduction in surface free energy and, according to Rebinder's theory, a reduction in hardness [2]. Westwood did not appear to consider negative adsorption, i.e., near surface concentrations of species which are lower than the bulk concentration and would thereby cause an increase in surface free energy. Based on work with CaF [5, 9], MgO [4, 6, 9], and ZnO [10], Westwood proposed that the environment affects the charge at the surface of the material which, in turn, affects dislocation mobility and, therefore, hardness. It should be noted that Westwood's explanation for the Rebinder effect is not universally accepted. Alternate mechanisms involving hydrogen embrittlement [7], water content [11], coefficients of friction [12], and changes in the properties of the diamond indenter or drill bit rather than the substrate [13], have been proposed and are supported by specific data sets. Additional papers by Westwood [14, 15] and Macmillan [16] provide reviews and insights into the subject. Of particular relevance to this work is a study by Czernuszka and Page [17] which examines surface changes in aluminum oxide caused by n-alcohols of varying chain length.

It is the intent of this and subsequent works to develop techniques to study the Rebinder effect using conventional equipment to determine whether it can be effectively used to improve the quality of ground (machined) ceramic parts. Hainsworth and Page [18] have demonstrated the applicability of nanoindentation techniques to this topic; however, as has been indicated, this is inconsistent with our objectives.

A recent work [19] demonstrated the existence of the Rebinder effect in polycrystalline aluminum oxide using conventional hardness measurement equipment. The data therein are consistent with Westwood's mechanism for the Rebinder effect in that hardness varied with environment pH and, therefore, surface charge. Unlike Westwood's mechanism (surface charge affects dislocation mobility and, therefore, hardness) the data indicate that the surface charge may affect a non-time dependent plastic deformation mechanism, such as twinning, which in turn affects hardness.

The present work investigated whether variations in the hardness of aluminum oxide caused by the Rebinder effect can be used to improve the surface grinding of this material, i.e., reduce the time required for grinding and/or improve the material properties of the ground part, e.g., surface finish or flexural strength. Equipment

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and conditions of industrial significance were employed.

The basis for the present work is a proposed interaction between Rebinder effect-caused variations in substrate hardness and mechanistic transitions which occur, or are postulated, in the grinding of ceramics. Direct evidence exists for a brittle/brittle grinding transition, i.e., an intergranular fracture/transgranular fracture transition, for aluminum oxide substrates ground with diamonds of varying friability [20, 21]. In these works, where grinding was conducted under aggressive conditions, blocky, low friability, diamonds produced high impact energy collisions between diamonds and substrate asperities and produced a different fracture pattern and surface appearance when compared with high friability, lower collision energy, diamonds. Indirect evidence for a brittle/ductile grinding transition has been obtained for ultra-low expansion glass in environments of n-alcohols of varying chain length using high precision grinding equipment and undeformed chip thicknesses in the nanometer range [22]. This work indicated that the mechanism of grinding changed from brittle to ductile when the undeformed chip thickness was reduced below a critical level. The critical undeformed chip thickness is a function of substrate hardness. Based on the existence of these grinding transitions and their apparent dependence on hardness, it is proposed that for a given grinding condition (depth of cut, table speed etc.) variation in the hardness of the substrate caused by changes in the pH of the grinding coolant will affect grinding parameters such as normal and tangential force, and grinding results such as post grinding flexural strength and surface profiles. With proper selection of grinding conditions and coolant pH, it should be possible to produce “better” ground ceramic parts more rapidly than current practice permits.

In addition to exploring the practical connection between variations in substrate hardness and surface grinding, the present work qualitatively considers the kinetics of the Rebinder effect. Although it has not been a central issue in most investigations of the Rebinder effect, there appears to have been a presumption in these investigations that the effect requires some time to develop because the processes studied, e.g., indentation and drilling, are slow speed operations. Presumably this predisposition toward slow speeds came from Westwood’s work demonstrating the increase in size of dislocation etch pit rosettes over a period of hundreds of seconds [3]. This work will consider surface grinding, a high speed operation in which the time between exposure of the substrate to the environment and its removal are extremely short and where the depth of material removal is significantly greater than the depth to which the Rebinder effect is thought to act. The observance of the Rebinder effect in a surface grinding operation will indicate that the time constant for the effect is far shorter than has apparently been assumed in the past.

2. Materials and equipment

The substrate investigated was polycrystalline α aluminum oxide (fully dense, 0.998 aluminum oxide, 30–50 μm grain size) supplied by Vesuvius McDanel (Beaver Falls, PA). This material was selected based on its commercial importance and past work using a similar material [24].

The environmental factor under consideration is pH, which has been shown by Parks and deBruyn to be potential-determining for oxides [25]. Variations in the pH of the grinding coolant were achieved through the use of distilled water, and NaOH.

Two bronze bonded diamond grinding wheels, 120 and 400 grit, (D1A1 D 120N 100 M 1/8 and D1A1 D 400N 100 M 1/8) supplied by United States Diamond Wheel (Oswego, IL) were used in this investigation. Bronze bonded wheels were selected to minimize changes in sharpness with time [23].

Grinding was conducted on a Brown and Sharp Micromaster 618 surface grinder, a typical 15.24 × 45.72 cm (6 × 18 inch) industrial surface grinder. This machine had manual table and depth of cut controls. Depth of cut was controllable to 2.54 μm (0.0001 in). (Measurements made on this machine were in English units; metric equivalents should be regarded as approximate). A variable speed DC gear motor was added to the grinder to control longitudinal table motion.

Flexural strength and surface profilometry measurements were carried out in accordance with ASTM standard C 1161-94 and ANSI standard B46.1 using equipment from Instron (Canton, MA) and Federal Products (model 5000 Surfanalyzer (Providence, RI)).

Force measurements were obtained using a three axis piezoelectric dynamometer (Kistler model 9257B transducer and model 5804 amplifier (Amherst, NY)) and computerized data acquisition equipment (Keithly model 500A (Taunton, MA)).

3. Procedures

Samples were prepared so that their final dimensions would be in accordance with ASTM standard C 1161-94 for four point bending, size B (45 mm × 4 mm, 3 mm). During initial preparation, the thickness dimension was left oversize by 203 μm (0.008 in). This material was removed during the experiment, i.e., the specimens were ground to 3.00 mm thickness using the experimental procedures described below.

Two grinding procedures, coarse and fine, were used in this investigation. In both cases samples were ground in groups of 10 in a direction perpendicular to the long axis of the sample. Cracks formed during grinding in this orientation are perpendicular to the stress applied in four point bending, maximizing the effect of crack size on flexural strength. Since the gauge length of the sample, 40 mm, is considerably wider than the width of the wheel, 13 mm (1/2 in), several passes were required to complete each grinding operation. Grinding was always performed in the “up” grinding mode. Each grinding pass was followed by a sparkout pass in which the wheel was returned to its original position. The wheel was then indexed laterally approximately 10 mm to prepare for a new grinding/sparkout pass. This procedure was repeated until the entire sample was ground. Parameters for coarse grinding were: 120 grit wheel, 127 μm (0.005 in) wheel depth of cut, and 0.18 m/s (35.4 ft/min) table speed. Parameters for fine grinding were 400 grit wheel, 2.54 μm (0.0001 in) wheel depth of cut, and 0.00153 m/s (0.301 ft/min) table speed.

The coolant for all grinding tests was distilled water adjusted for pH with NaOH. Due to absorption of CO_2 from the air, it was necessary to continuously monitor and adjust the pH of the coolant. Approximately 20 liters of coolant were prepared for each pH value studied. This coolant was recycled during each test and reused from test to test; the coolant always contained sufficient grinding swarf so as to be saturated with aluminum oxide.

Surface profiles were measured in accordance with ANSI standard B46.1. The instrument was operated in the "5 cutoff length" mode using a cutoff length of 2.5 mm (0.100 in). The surface values reported are the averages of 5 or 6 measurements at different points on the sample. Roughness average (R_a), waviness average (W_a), and roughness skew (R_{sk}) were measured. Roughness skew is a measure of the shape of a surface. Zero skew indicates a saw tooth surface while a negative skew indicates a surface with long flat "peaks" and sharp narrow valleys.

Forces generated during grinding were measured using a three axis, piezoelectric dynamometer with computer controlled data acquisition. Data were collected at 100 Hz. Due to the small magnitude of the forces generated, forces were only measured for the coarse grinding condition. Interpretation of the normal force measurements was complicated by the superposition of vibrational forces on the mean grinding forces.

Flexural strength was measured in four point bending in accordance with ASTM C 1161-94. Ten samples were tested for each pH value. To avoid data bias caused by variations in room temperature and humidity, the first sample from each pH value was tested prior to the second sample from any pH value.

4. Results

As previously described [19] and shown in Fig. 1, the zeta potential and hardness of the aluminum oxide material used in this study varied with pH; a maximum in hardness and the zero of the zeta potential occurred at pH 9.5 when the environment consisted of distilled water adjusted for pH using NaOH. Figs 2–6 demonstrate that the pH of zero zeta potential is also important to the process and results of surface grinding.

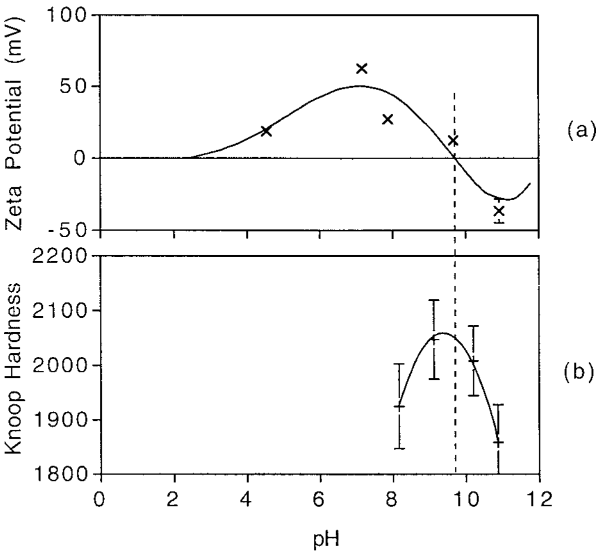

Figure 1 Variation in hardness with indenter load. Polycrystalline aluminum oxide in pH controlled distilled water. Error bars represent 90% confidence for the mean.

Figs 2 and 3 demonstrate that both the normal and tangential forces are functions of pH for the coarse grinding condition. The normal force exhibits a maximum and tangential force exhibits a minimum at the pH of zero zeta potential and maximum hardness, 9.5.

The relationship between surface profiles, grinding aggressiveness and pH is shown in Figs 4 and 5. Fig. 4 shows that for the coarse grinding condition, the

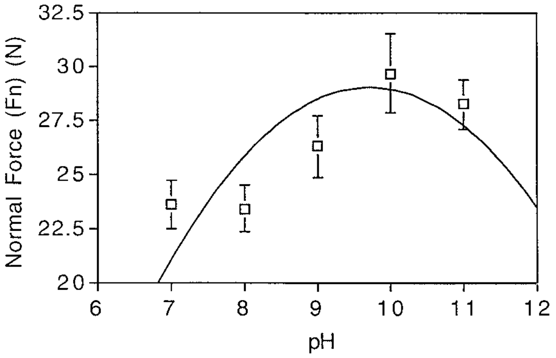

Figure 2 Variation in normal force with environment pH (coarse grinding conditions). Polycrystalline aluminum oxide in pH controlled distilled water. Error bars represent 90% confidence for the mean.

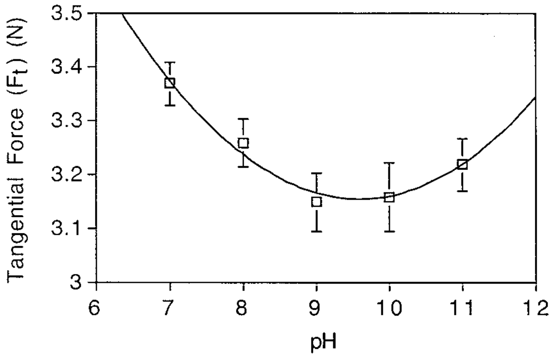

Figure 3 Variation in tangential force with environment pH (coarse grinding conditions). Polycrystalline aluminum oxide in pH controlled distilled water. Error bars represent 90% confidence for the mean.

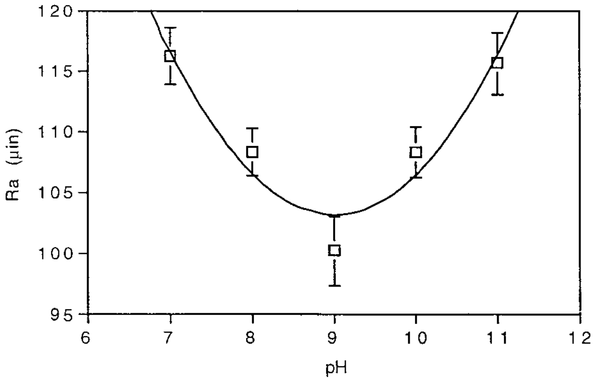

Figure 4 Variation in roughness average with environment pH (coarse grinding conditions). Polycrystalline aluminum oxide in pH controlled distilled water. Error bars represent 90% confidence for the mean.

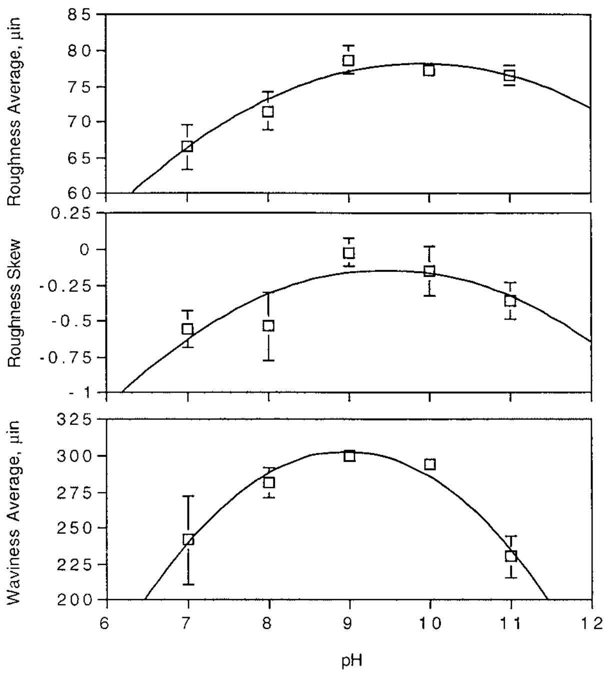

Figure 5 Variation in roughness average, roughness skew, and waviness average with environment pH (fine grinding conditions). Polycrystalline aluminum oxide in pH controlled distilled water. Error bars represent 90% confidence for the mean.

roughness average is smallest at the pH of maximum hardness and zero zeta potential. Fig. 5 shows that, for fine grinding conditions, the roughness average, waviness average, and the roughness skew are all pH sensitive and exhibit a maximum near the pH of maximum hardness and zero zeta potential.

Flexural strength values are shown in Fig. 6. The flexural strength for samples ground using fine grinding conditions is higher than the flexural strength for samples ground under coarse conditions for all values of pH tested. Samples ground using fine conditions exhibit a minimum in flexural strength near the pH of zero zeta potential and maximum hardness while samples ground using coarse conditions exhibit a distinct maximum in flexural strength at that pH value.

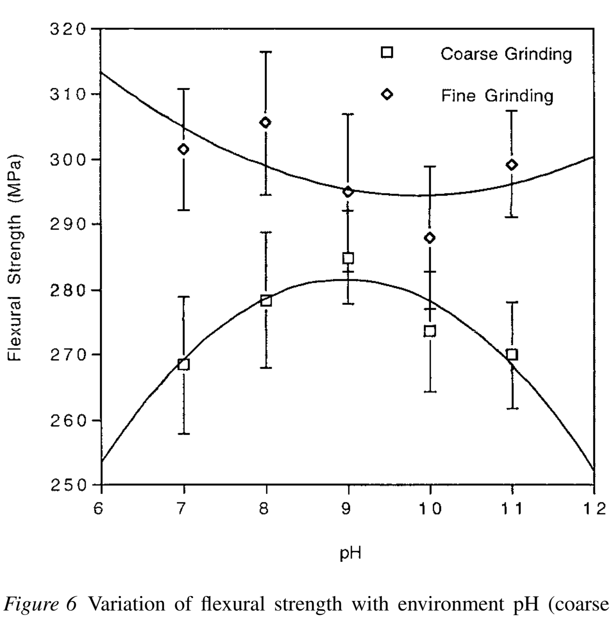

Figure 6 Variation of flexural strength with environment pH (coarse and fine grinding conditions). Polycrystalline aluminum oxide in pH controlled distilled water. Error bars represent 90% confidence for the mean.

TABLE I Correlations (R^2) between data and potential curve fitting functions for Figs 3–6. Perfect correlation, $R^2 = 1$, no correlation $R^2 = 0$

Figure number	Data set	R^2, Second order	R^2, Linear
3	Tangential force	0.976	0.502
4	Roughness avg.	0.907	0.001
5	Roughness avg.	0.939	0.661
5	Skew	0.664	0.271
5	Waviness avg.	0.964	0.002
6	Coarse	0.802	0.271
6	Fine	0.400	0.271

In Figs 1–6, error bars represent the 90% confidence interval for the mean as determined by the Student's T test. In each figure, there is a statistically significant difference (90% level) in the means of the data. Three forms of curve fitting were considered for each figure: second order polynomials, i.e., force, surface profiles, and bending strength vary in the same manner as hardness with respect to pH; first order polynomial, i.e. there is a linear variation in the measured property with pH; and a horizontal line, i.e. there is no variation in the measured property with pH. In each case the R^2 correlation of the data indicated that a second order polynomial better explained the variability of the measured property with pH. Although it is possible to draw a horizontal line through the error bars in Fig. 6, to do so would significantly reduce the quality of fit and ignore the statistically significant differences in the data. Although curves fit with higher order polynomials would improve the fit for the fine grinding portion of Fig. 6, such correlations were not employed for lack of theoretical basis. Table I shows the correlations (R^2) between the plotted data, 2nd order polynomials, linear, functions for each curve in Figs 3–6. For Fig. 2, correlations between the data and a second order curve fitting function and the data and a linear function are similar indicating that the data could be equally represented by either function. A second order function was chosen for Fig. 2 to be consistent with the other data represented.

5. Discussion

In Figs 2–6 it is seen that in surface grinding, normal and tangential forces, surface finish and post grinding flexural strength are dependent on the pH of the grinding coolant, exhibiting a maximum or minimum in the measured value at the pH of maximum hardness and zero zeta potential. The variation in hardness with pH of the workpiece, as shown in Fig. 1, in conjunction with the existence of a brittle/brittle grinding transition [20, 21] and the proposed existence of a brittle/ductile grinding transition [22], provides a comprehensive, qualitative explanation for the pattern of results provided by Figs 2–6.

The brittle/brittle grinding transition refers to a transition between intergranular and transgranular fracture. The existence of a brittle/brittle grinding transition for relatively coarse grinding conditions has been demonstrated by Caveney [21]. In this work, the friability of the diamonds in the wheel, which affects the impact energy between the diamonds and the substrate and is equivalent to modifying the hardness of the substrate, was varied and resulted in a transition between trans- and intergranular fracture. Although not reported in this investigation, it is reasonable to expect that a change in fracture mode would result in a change in surface finish of the substrate. A mathematical relationship to predict this transition was not presented by Caveney.

A model for a brittle/ductile transition during grinding has been described by Bifano [22] and others. This model is supported by a significant body of indirect evidence but lacks direct evidence such as observation of curved chips or twins. The transition between brittle and ductile grinding occurs at the critical undeformed chip thickness, t_c^*, given by

$$t_c^* = 0.15\left(\frac{E}{H}\right)\left(\frac{K_{cs}^2}{H^2}\right) \tag{1}$$

where: E = Elastic modulus
H = Hardness
K_{cs} = Surface fracture toughness

In general, the undeformed chip thickness, t_c, is related to process parameters by

$$t_c = \sqrt{\frac{4v}{VCr}\sqrt{\frac{d}{D}}} \tag{2}$$

where: v = Table or work piece speed
V = Wheel speed
d = Wheel depth of cut
D = Wheel diameter
C = Cutting points per area of wheel
r = Ratio of mean width of cut to depth of cut

According to Bifano's model, a process producing chips of thickness t_c^* or smaller will produce a surface which appears ductile, i.e., a glass surface so ground will appear transparent and fracture free. We expect that light, low energy interactions between asperities will produce ductile effects, while the more energetic interactions between asperities which interact with greater interference will produce brittle effects. Since, in any grinding process, there will be a spectrum of interactions occurring simultaneously, we may expect that there will be some ductile character to the grinding process even at chip thicknesses greater than that predicted by Equation 1. As the undeformed chip thickness increases from the transitional value of Equation 1, the fraction of ductile interactions between asperities will decrease from 100% to a value approaching zero under more aggressive conditions.

Although somewhat less intuitive, rather than adjusting the undeformed chip thickness as a means to influence the amount of ductile character present in a grinding operation, adjusting the hardness of the substrate will, within limits, accomplish the same purpose. As may be seen from Equation 1, decreasing the hardness of the substrate increases the critical undeformed chip thickness. For any relatively fine grinding condition the actual undeformed chip thickness will be closer to the critical undeformed chip thickness when the substrate is soft. This will result in an increase in the ductile character in the grinding process for softer materials. This trend may be observed for all data obtained using fine grinding conditions. Surfaces are smoother and asperities are more flat topped when the material is soft. Flexural strength is expected, and observed, to be greatest for the softest material because a higher percentage of ductile interactions should produce fewer and smaller surface cracks which will result in higher strength.

Tangential force measurements for the coarse grinding condition, Fig. 2, are also consistent with a gradual transition from ductile to brittle wheel/substrate interactions. Given that the tangential force needed to grind the substrate is related to required grinding power and that the specific energy required to remove material in a brittle manner is much lower than for ductile removal, it is reasonable to expect that tangential force will be higher for softer material even when the percentage of ductile interactions is quite low and the appearance and character of the surface is controlled by brittle fracture.

Normal force, roughness average, and flexural strength results for the coarse grinding conditions (Figs 1, 2 and 6) are not consistent with a ductile/brittle grinding transition. Trends in the normal force appear to indicate that a hard substrate resists vertical penetration of the wheel and results in increased forces. The existence of a minimum in roughness average and a maximum in flexural strength at the pH of maximum hardness and zero zeta potential is consistent with the intergranular/transgranular fracture transition observed by Caveney [21]. Lacking this transition, no variation in flexural strength and surface profilometry is expected for the coarse grinding condition because the surface is dominated by brittle fracture at all pH values tested.

6. Conclusions

While previous works have demonstrated the existence of the Rebinder effect for static or slow speed operations such as hardness testing or drilling, this work extends the applicability of the Rebinder effect to the high speed operation of grinding. It has been shown that grinding forces, surface profiles, and post grinding flexural strength are all affected by the pH of the grinding fluid. In each case, the pH at which the sample demonstrates maximum hardness and zero zeta potential corresponds to a maximum or minimum in the measured property. The results obtained are consistent with an explanation for the Rebinder effect based on surface charge and its effect on plastic deformation. For fine grinding, the results obtained may be explained by a combination of the Rebinder effect and a proposed ductile/brittle grinding transition. For coarse grinding conditions, the results obtained are consistent with the Rebinder effect in combination with a brittle/brittle grinding transition. Despite the fact that the above explanations for the observed results must be considered proposals rather than conclusions as they do not eliminate alternative explanations, the results indicate that the Rebinder effect may be used to simultaneously improve part quality and rates of production in the grinding of ceramics.

References

1. P. A. REBINDER, Proc. 6th Physics Conf., Moscow, 1928.
2. P. A. REBINDER *et al.*, "Hardness Reducers in Rock Drilling," (C.S.I.R.O, Melbourne, Australia, 1948).
3. A. R. C. WESTWOOD and R. M. LATANISION, "The Science of Ceramic Machining and Surface Finishing," NBS Special Pub. 348 (U.S. Government Printing Office, Washington DC, 1972) p. 141.
4. P. J. BURNETT and T. F. PAGE, *J. Mater. Sci. Lett.* **4** (1985) 1364.
5. A. R. C. WESTWOOD and D. L. GOLDHEIM, *J. Appl. Phys.* **49**(7) (1968) 3401.
6. A. R. C. WESTWOOD, D. L. GOLDHEIM and R. G. LYE, *Phil. Mag.* **16** (1967) 505.
7. R. E. CUTHRELL, *J. Appl. Phys.* **49**(1) (1978) 432.
8. T. A. MICHALSKE and B. C. BUNKER, *Scientific American* (1987) p. 122.
9. A. R. C. WESTWOOD and D. L. GOLDHEIM, *J. Amer. Ceram. Soc.* **53**(3) (1970) 142.
10. J. S. AHEARN, J. J. MILLS and A. R. C. WESTWOOD, *Journal de Physique* **40**(c6) (1979) c6-173.
11. J. H. WESTBROOK and P. J. JORGENSEN, *Trans. AIME* **233**(2) (1965) 425.
12. R. E. HANNEMAN and J. H. WESTBROOK, *Phil. Mag.* **18** (1968) 73.
13. G. A. COOPER, "The Science of Ceramic Machining and Surface Finishing II," (NBS Special Pub. 562 (U.S. Government Printing Office, Washington DC, 1979) p. 115.
14. A. R. C. WESTWOOD, J. S. AHEARN and J. J. MILLS, *Colloids and Surfaces* **2** (1981) 1.
15. A. R. C. WESTWOOD and J. J. MILLS, in Proceedings of the NATO Advanced Study Institute on Surface Effects in Crystal Plasticity, Hohegeiss, Germany, Sept. 1975, edited by R. M. Latanision and J. T. Fourie (Noordhoff, Leyden, The Netherlands, 1977) p. 835.
16. N. H. MACMILLAN, in Proceedings of the NATO Advanced Study Institute on Surface Effects in Crystal Plasticity, Hohegeiss, Germany, Sept. 1975, edited by R. M. Latanision and J. T. Fourie (Noordhoff, Leyden, The Netherlands, 1977) p. 629.
17. J. T. CZERNUSZKA and T. F. PAGE, *J. Mater. Sci.* **22** (1987) 3917.
18. S. V. HAINSWORTH and T. F. PAGE, *ibid.* **29** (1994) 5529.
19. D. W. ALLEY and O. F. DEVEREUX, *ibid.* **37**(23) (2002) 5135.
20. D. M. BUSCH and J. F. PRINS, "The Science of Ceramic Machining and Surface Finishing," NBS Special Pub. 348 (U.S. Government Printing Office, Washington DC, 1972). p. 73.
21. R. J. CAVENEY and N. W. THIEL, "The Science of Ceramic Machining and Surface Finishing," NBS Special Pub. 348 (U.S. Government Printing Office, Washington DC, 1972). 99.
22. T. G. BIFANO, D. K. DEPIERO and D. GOLINI, *Precision Engineering* **15**(4) (1993) 238.
23. A. B. VAN GRONENOU, "The Science of Ceramic Machining and Surface Finishing II," NBS Special Pub. 562 (U.S. Government Printing Office, Washington DC, 1979) p. 147.
24. A. R. C. WESTWOOD, N. H. MACMILLAN and R. S. KALYONCU, *J. Amer. Ceram. Soc.* **56**(5) (1973) 258.
25. G. A. PARKS and P. L. deBRUYN, *J. Phys. Chem.* **66** (1962) 967.

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