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Coolant pH control for optimum ceramic grinding. I. rebinder effect in polycrystalline aluminum oxide

DAVID W. ALLEY*†, OWEN F. DEVEREUX
Department of Metallurgy and Materials Engineering, University of Connecticut, Storrs CT 06269, USA

The Rebinder effect, an environment-caused variation in the hardness of rock, ceramic, or glass, was investigated in polycrystalline aluminum oxide using conventional microhardness and electrochemical techniques. For an environment of pH-adjusted distilled water, both hardness and zeta potential were found to vary with pH. Maximum hardness and zero zeta potential were found to occur at pH 9.5. Observations in this study are consistent with a mechanism for the Rebinder effect in which changes in surface charge influence near-surface plastic deformation of surfaces and, thereby, hardness.

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1. Introduction

The Rebinder effect 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 only cause 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 explanations 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], Macmillan [16], and Czernuszka and Page [17] provide reviews and insights into the subject.

Not withstanding the findings of Hainsworth and Page [18] regarding the desirability of using nanoindentation techniques for studies of this nature due to the small magnitude of the effect being measured as well as the reduced potential for operator bias, this study will utilize conventional microhardness measurement instruments. This choice is based on our intent to demonstrate, in this and subsequent works, that the Rebinder effect can be a useful tool in improving the process of machining ceramic components using equipment consistent with current manufacturing technology. Great care has been taken to minimize the potential problem of operator bias.

2. Experimental procedure

2.1. Material investigated and sample preparation

The material investigated was polycrystalline Al_2O_3 (fully dense, 0.998 aluminum oxide, 30–50 μm grain size) supplied by Vesuvius McDanel (Beaver Falls, PA).

Samples were hot mounted and metallographically polished to a finish resulting from 1 μm diamond slurry. Following each polishing step, samples were ultrasonically cleaned in distilled water to ensure that no material other than water was entrapped in the sample or chemically or physically adsorbed on its surface.

2.2. Hardness measurements

Hardness measurements (Knoop) were made using a Leco (St. Joseph MI) DM-400FT microhardness tester.

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*Author to whom all correspondence should be addressed.
†*Present address*: UOP LLC, Des Plaines IL 60017, USA

Dwell time was automatically controlled on this instrument and was adjustable from 5 to 53 seconds. Indent measurement was accomplished through digital photography and image analysis software. Each image was photographed using a Nikon Metaphot microscope and digital video system.

Images were enhanced and analyzed using Micro-GOP 2000/S v 2.52 image analysis software. Fixed uncertainties in the optical system include spherical aberration (NA of the objective lens = 0.85) of between 0.2 and 0.4 μm depending on the light frequency sensitivity of the digital camera and pixelation (pixel size = 0.07 μm). Image enhancement was limited to contrast improvement via gray scale expansion. Procedures and settings for photography and enhancement were kept constant throughout this work to avoid the introduction of systematic error. The adoption of this measurement technique significantly reduced operator fatigue and improved the repeatability (repeated measurement of the same indent) of measurements from 1–2% of the indent size to essentially ± 1 pixel. All the uncertainties shown in the figures are the result of a statistical analysis (Student's T test) and give the 90% probability range for the mean. This uncertainty includes the fixed uncertainties of the optical system as well as the uncertainties introduced by the operator and the actual variability of the hardness of the material.

Exceptional care was required in this work to ensure that optimal conditions were used for hardness testing as the variability in hardness due to the Rebinder effect among the conditions tested was expected to be relatively small in comparison to the hardness of the aluminum oxide material. Several test series were undertaken to optimize indenter load and dwell time. The load and dwell time parameters were varied from 50 to 1000 g and from 5 to 53 seconds respectively in these studies. For each study approximately 25 indents were made in a grid pattern with sufficient space between each indent to ensure that the stress fields created by the indentation process did not overlap, i.e., to ensure the independence of each indent. All the indents in each test series were made before any were measured. In some tests indents were made "dry," i.e., exposed only to the moisture in the air. In other series the indents were made "wet," i.e., the indents were made through 3–4 drops of distilled water.

The use of the "make all before measure/fixed grid spacing" indentation technique, which was absolutely necessary for "wet" indents, created one significant problem; it was not possible to position indents to avoid the numerous small surface flaws (grain pullouts and sintering voids) present in the sample. This, in conjunction with cracking and crushing around some indents, required that, for some tests, indents be classified as "good" or "bad." Most "bad" classifications were due to interactions between the indent and surface defects. While this type of culling procedure introduces the possibility of operator bias, it was not judged to be a problem in this work as the differences between "good" and "bad" indents were very apparent.

The selection of the conditions under which the test indents, i.e., those designed to study the Rebinder effect, were made required a compromise between light loads which minimized cracking but were prone to significant measurement uncertainty and heavier loads which cracked more frequently but, if "bad" indents were discarded, suffered from much lower measurement variability. All test indents were made "wet" using a load of 100 g and a dwell time of 10 seconds. "Good" indents were made, processed, and measured as previously described. "Bad" indents were not measured. The test fluids were distilled water adjusted to the desired pH with NaOH or commercial buffer solutions. Although unintended, the test fluids also contained CO_2 which was absorbed from the air. Although an attempt was made to correlate cracking with pH, the variability in the interactions between indents and surface flaws precluded any meaningful results from being obtained.

2.3. Electrochemical measurements

The electrochemical parameter of interest in this study of the Rebinder effect is surface charge, specifically the point at which the surface charge is zero. Surface charge is a function of both the material being studied and the environment to which it is exposed. Although the surface charge is not generally amenable to direct measurement, we made use of the streaming potential, an electrokinetic phenomenon, to calculate the zeta potential, which is commonly considered to represent the potential at a point within the diffuse portion of the electrical double layer that spontaneously forms at an interface involving an electrolyte. The streaming potential is the potential difference between electrodes placed upstream and downstream of a surface over which an electrolyte is flowing. The zeta potential, ζ, is related to the streaming potential by

$$\zeta = \frac{4\pi E\mu k}{PDD_0} \tag{1}$$

where: E = Measured streaming potential; μ = Viscosity; k = Conductivity of the electrolyte; P = Pressure drop; D = Relative dielectric constant of the electrolyte; D_0 = Dielectric constant of a vacuum ($1.112 \times 10^{-10}\ \mathrm{C^2/N\,m^2}$).

For a simple Gouy–Chapman double layer, the apparent surface charge, η, is related to the potential measured at any distance from the surface within the double layer by

$$\eta = \frac{DD_0\kappa\psi_x e^{\kappa x}}{4\pi} \tag{2}$$

where: η = Charge density, charge/unit area; D = Relative dielectric constant of the electrolyte; D_0 = Dielectric constant of a vacuum ($1.112 \times 10^{-10}\ \mathrm{C^2/N\,m^2}$); κ = Constant, $1/\kappa$ is half the thickness of the diffuse layer; X = Distance measured from the surface; ψ_x = Potential at a distance x from the surface.

The zeta potential may be substituted for ψ_x and used to calculate the surface charge provided the limitations for the Gouy–Chapman model, especially the requirement for a dilute solution, are met and the distance between the surface and the point corresponding to the zeta potential is known. Lack of knowledge of

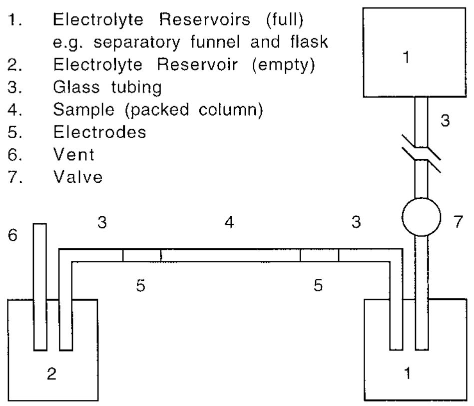

Figure 1 Schematic of streaming potential measurement apparatus.

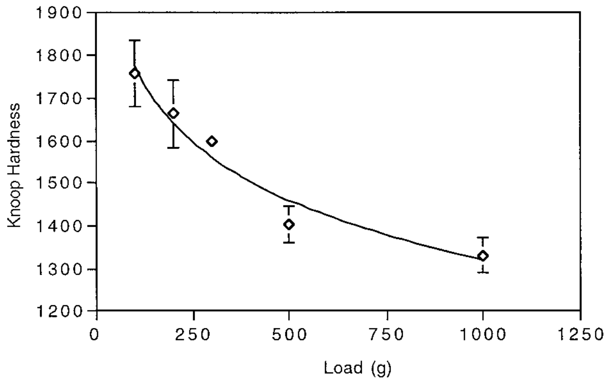

Figure 2 Variation in hardness with indenter load. Polycrystalline aluminum oxide in pH controlled distilled water. Error bar represents 90% confidence for the mean.

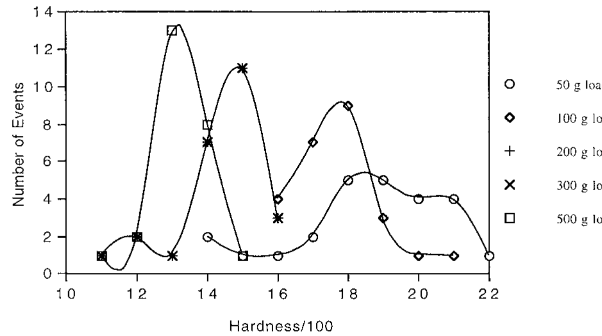

Figure 3 Frequency of occurrence of hardness values at various indenter loads. Note the large scatter in the hardness measurements for the 50 g indenter load when compared to higher loads.

this distance precludes calculation of the surface charge for most conditions, but it may be seen that the surface charge must be zero when the zeta potential is zero and that for other values of the zeta potential there is a monotonic relationship between the zeta potential and surface charge [19].

The charged surface in this case was a packed bed of crushed α-Al_2O_3, as described above. Maximum particle size was 1 mm; fines created by crushing were not removed. Streaming potentials were measured with the apparatus schematically represented in Fig. 1. The packed column was approximately 20 cm long by 6 mm diameter and the hydrostatic head was of the order of 3 m. Flow rates through the apparatus of approximately 3–5 drops per second produced stable and consistent streaming potential values. In this instance the packed bed and the tube containing it were similar materials, however, the use of an alternate material, e.g., Pyrex® for the tube should have a negligible effect on the streaming potential given the high surface area of the bed. The electrodes were lengths of type 316 stainless steel tubing loosely packed with stainless steel ribbon.

Streaming potential measurements were made by filling the test apparatus with a solution of the desired pH and allowing 100–200 ml to pass through the packed column to rinse it. The flow was stopped and an electrometer was then connected to the electrodes. The system was allowed to stabilize so that the drift in measured potential difference was less than 0.1 mV/s. The electrometer never stabilized at zero volts. The flow was re-initiated, producing a rapid change in potential difference followed, in a few seconds, by a period of markedly reduced change. The streaming potential was defined as the difference between the potential difference when the valve is opened and the potential difference when the rate of change of the potential difference slows [19–21].

3. Results

Fig. 2 shows the results of one of the preliminary tests investigating the effects of indenter load. Data points represent mean measured hardness values for the corresponding indenter load. Error bars represent the 90% confidence interval for the sample mean as determined by the Student's T test. All indents were made "dry" on a single aluminum oxide sample using a dwell time of 10 seconds. This figure illustrates an apparent softening of the material, known as the indentation size effect, as the depth (size) of the indent and the load on the indenter are increased. This effect is well known for ceramic materials and is attributed, among other reasons, to hardening of the surface material by ionic adsorption. The reader is referred to ample literature on this subject for additional description of the effect [11, 22–26]. The interpretation of this figure is complicated to some extent by cracking and spalling of some indents. All indents made at 500 and 1000 g loads were cracked and/or spalled. The hardness indicated by these indents is probably slightly understated when compared to lighter loads. Indents made with 300, 200, and 100 g loads reflect only "good" indents, those which were not cracked or spalled. Not shown in the figure is the fact that while uncertainty decreases with increasing load in the range of 100 to 300 g, the number of usable indents decreases sharply.

Fig. 3 illustrates the results of a second preliminary test investigating the effects of indenter load. This figure is essentially a histogram where the "number of events" are the number of measured hardness values falling within a band of 100 hardness units. All indents were made "dry" on a single aluminum oxide sample using a dwell time of 5 seconds. 25 indents were made for each load and measured irrespective of their quality. This figure illustrates the indentation size effect as shown in Fig. 1, but, more importantly, shows that the scatter (uncertainty) in the data is far greater for light loads, especially the 50 g load, than for heavier loads. Selection of an indenter load for the test indents must,

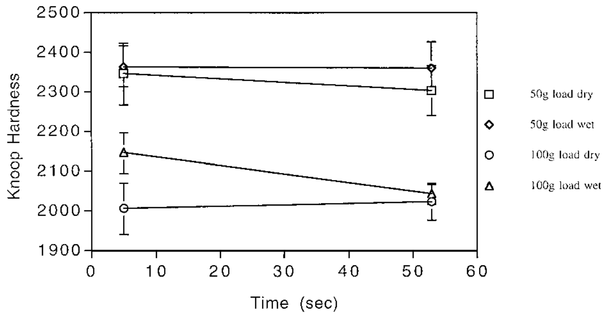

Figure 4 Variation in hardness with indenter dwell time. Polycrystalline aluminum oxide in pH controlled distilled water. Error bar represents 90% confidence for the mean.

therefore, be a compromise between cracking and uncertainty in the measurement of the indents.

Fig. 4 shows the results of preliminary dwell time testing. Data points represent mean measured hardness values for the corresponding dwell time. Error bars represent the 90% confidence interval for the sample mean as determined by the Student's T test. Two dwell times, 5 seconds and 53 seconds, which represent the minimum and maximum dwell times available on the instrument used, were considered. Four conditions were considered, 50 g load "dry" (exposed only to the moisture in the air), 50 g load "wet" (indents made through 3–4 drops of distilled water), 100 g load "dry," and 100 g load "wet." Fig. 3 shows a slight hardening with increased dwell time for one condition (100 g "dry"), no change for one condition (50 g "wet"), and softening for two conditions (50 g "dry" and 100 g "wet"). Due to the similarity of the changes in hardness and the uncertainties of the measurements, the data were analyzed using analysis of variance (ANOVA) techniques. Based on this analysis there is a 57% probability that the apparent softening observed in the 50 g "dry" case represents an actual softening in the material; there is a 2% probability that the apparent softening in the 50 g "wet" case represents an actual softening of the material; there is a 35% probability that apparent hardening in the 100 g "dry" case represents an actual hardening in the material; and there is a 98% probability that the apparent softening in the 100 g "wet" case represents an actual softening in the material. The typical criterion used for identifying statistically significant differences in populations is either 90 or 95%. Based on this criterion only one of the differences in hardness of the four cases investigated is statistically significant.

Fig. 5 illustrates the relationship of both hardness and zeta potential to environment pH. As previously stated, all indents were made through a few drops of distilled water adjusted for pH with NaOH. A dwell time of 10 seconds and a load of 100 g were used for each indent made. 25 indents were made for each condition; only "good" indents (as previously defined) were measured. The error bars in the figure represent the 90% confidence interval for the mean and include the uncertainties inherent in the system (spherical aberration, pixelation), operator uncertainties, and the actual variation in the hardness of the sample from one indent to the next. This figure shows that a maximum in the hardness of the sample occurs at the environmental pH which produces a zero zeta potential. Curve fitting for Fig. 5 was conducted using a typical spreadsheet program and maximizes the correlation (R^2) between the data and the mathematical function represented by the line on the graph. For section (a) of Fig. 5, R^2 for the correlation shown (5th order polynomial) is 0.876 (1 represents perfect correlation, 0 represents no correlation). A fifth order function was selected because this is the most simple function which can be used to represent the observed maximum and minimum and approximates the asymptotic approach of the zeta potential to zero as is required in concentrated electrolytes. When this correlation is replaced by a linear relationship, R^2 drops to 0.1547. When the slope of the linear function is forced to be 0, i.e., to represent the condition of no correlation between pH and zeta potential, R^2 drops to 0.03. The data included in the correlation are the points plotted and the fact that the zeta potential must be 0 at both high and low pH values. For section (b) of Fig. 5, R^2 as shown (second order polynomial) is 0.9974. Using a linear correlation function causes R^2 to drop to 0.0898. Use of a linear function with 0 slope, i.e., no correlation between pH and hardness, causes R^2 to drop to 0.0041.

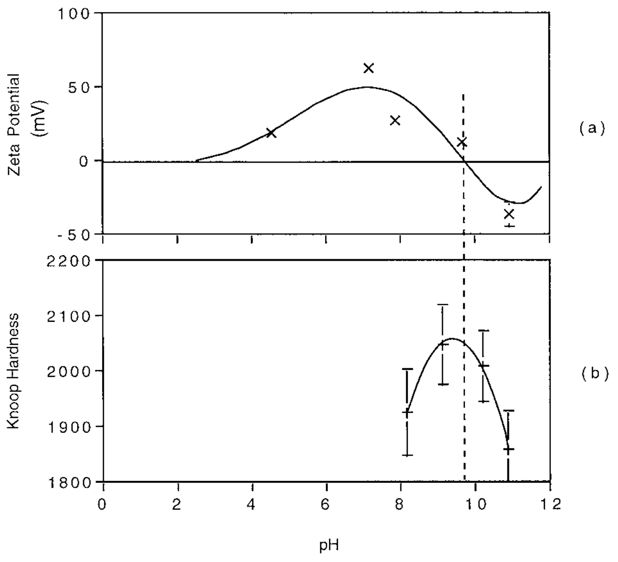

Figure 5 Variation of zeta potential (a) and Knoop hardness (b) with pH. Polycrystalline aluminum oxide in pH controlled distilled water. Error bar represents 90% confidence for the mean.

Fig. 6 is identical to Fig. 5 except environmental pH values were obtained through the use of commercial buffer solutions which were diluted to 0.001 M. Buffer solution compositions are listed in Table 1. As in Fig. 5, there is an excellent correlation between the pH values of zero zeta potential and maximum hardness. Additionally, Fig. 6 shows a moderate correlation between the pH value of the absolute value of the zeta potential maximum and the hardness minimum.

4. Discussion

Prior to considering potential causes for the Rebinder effect as manifested under the conditions investigated, it may be beneficial to specifically exclude three sources of variation in hardness measurements from this discussion. They are, the presence or absence of environmental water, variation of indenter load, and variation in dwell time. It is well known that all of these variables

TABLE I Buffer solution compositions

pH	Component	Concentration (wt%)
pH 4	Potassium biphthalate	1.0
pH 5	Potassium biphthalate	1.0
	Sodium hydroxide	0.1
pH 6	Potassium phosphate monobasic	0.7
	Sodium hydroxide	0.02
ph 7	Potassium phosphate monobasic	0.7
	Sodium hydroxide	0.1
pH 9	Boric acid	0.3
	Potassium chloride	0.4
	Sodium hydroxide	0.1
pH 10	Potassium carbonate	0.6
	Potassium borate	0.2
	Potassium hydroxide	0.4

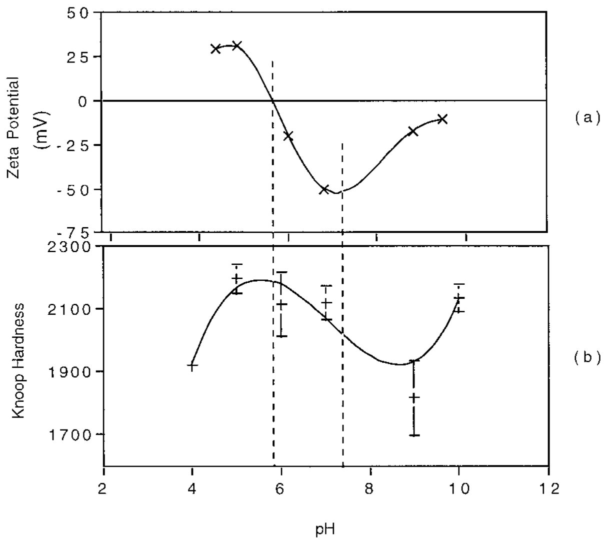

Figure 6 Variation of zeta potential and hardness of polycrystalline aluminum oxide with pH in commercial buffer solutions. Error bar represents 90% confidence for the mean. The error bar for the first data point in graph b is smaller than the symbol for that point and is, therefore, not visible.

do cause changes in measured hardness, but they are not germane to the present study.

Material hardness, including the hardness of single crystal aluminum oxide [11], under wet conditions, which include normal atmospheric conditions, differs from that under dry conditions (heated and kept under water-free toluene). The exact cause for this difference remains in doubt. Westwood [14] contends that the variation in hardness is due to a difference in surface charge between the conditions while Westbrook [11] contends that the difference is the result of the absence or presence of water. No attempt will be made here to resolve this issue as it is moot to the conditions investigated. In this investigation all measurements, including those labeled "dry" are in fact wet by Westbrook's definition. All hardness indents made for the purpose of studying the Rebinder effect, i.e., those made for Fig. 5 and 6, were made while the specimen was submerged in water. Therefore, environmental variations in the hardness of aluminum oxide under the conditions investigated are not due to the absence or presence of water, nor are they due to the amount of water which may be present.

The effect of indenter load on measured hardness, the indentation size effect, is well documented for a wide variety of materials. Fig. 2 and [11] show that aluminum oxide, in the polycrystalline and single crystal states respectively, exhibits an inverse correlation between measured hardness and indenter load. To eliminate any possibility that changes in hardness caused by the Rebinder effect may be confused with changes in measured hardness due to load, a single load of 100 g was selected for all test indents (those in Fig. 5 and 6 used for evaluating the Rebinder effect).

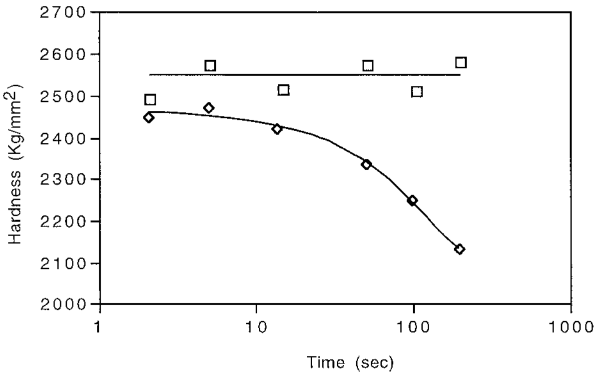

Figure 7 Variation of hardness of single crystal aluminum oxide with indenter dwell time (after [11]).

In single crystal materials such as CaF_2, MgO, and Al_2O_3 it has generally been found that increasing indenter dwell time causes a decrease in hardness under either all conditions tested [6, 9] or under wet conditions [11]. Fig. 7 illustrates this observation for single crystal alumina under atmospheric conditions. Although Fig. 4 indicates that the hardness of polycrystalline aluminum oxide may not be a function of indenter dwell time over the time interval of 5 to 53 seconds, a single dwell time of 10 seconds was adopted to ensure that environmental changes in hardness were not confused with the effects of dwell time.

It is now reasonable to evaluate the variations in hardness shown in Figs 5 and 6 from an environmental perspective other than the absence or presence of water. The statistically significant variation in hardness with pH demonstrates that the hardness of polycrystalline aluminum oxide is dependent upon environment. The very good correlation between the pH of zero zeta potential and the pH of maximum hardness (9.5 for the NaOH environment and 5.5 for the buffer solution environment) and the moderate correlation between the pH of maximum absolute value of zeta potential and minimum hardness suggest surface charge as a controlling factor for the near surface hardness of a material. These findings are in general agreement with those of Westwood [14] who has proposed that environment affects hardness because surface charge affects the ease with which dislocations move. When the surface charge is zero, dislocation motion is restricted and hardness is maximum. When surface charge is not zero, either positive or negative, dislocations move more readily and hardness is reduced. Works by Hainsworth and Page [18] and Mann and Pethica [27] are also relevant to changes in the interrelationship between surface properties, the environment, and dislocation nucleation and propagation.

The overall lack of dependence of hardness on indenter dwell time as shown in Fig. 4 raises some question as to the exact mechanism of the Rebinder effect as proposed by Westwood. If dislocation motion is responsible for variation in hardness, hardness should vary with dwell time as has been found to be the case with single crystals. The lack of correlation (or low degree of correlation) between hardness and dwell time shown in this study may be due to the polycrystalline nature of the aluminum oxide used, i.e., the distance dislocations can move is limited by grain boundaries, or to the limited difference between the shortest and longest possible indent times. While published data clearly indicate a dependence between time and hardness, it is not clear that the trend would be statistically significant if evaluated over only the time range possible in this work. Alternatively, twinning is known to be a mechanism for the deformation of polycrystalline aluminum oxide at room temperature. Since this is a non-time dependent mechanism, it provides an alternative mechanism for hardness variability with environment without necessitating a dependence of hardness on dwell time. This subject merits additional study.

One aspect of Fig. 6, at least to the authors, remains less than fully explained. Based on the similarity of the magnitudes of the zeta potentials and the shape of the fitted curves in Figs 5 and 6, it appears that the anions in the buffer solution caused the pH/zeta potential curve to shift. Despite the evidence provided in Fig. 6 which points toward this conclusion, it seems improbable that the wide variety of anions present in the buffer solutions used would each have the same effect in shifting the curve.

5. Conclusions

The Rebinder effect has been investigated in polycrystalline aluminum oxide employing conventional methods for measuring microhardness and zeta potential. When these methods were optimized, data scatter was reduced sufficiently to observe a statistically significant Rebinder effect for this material in environments of varying pH. The pH values for maximum hardness and for zero zeta potential were the same (9.5 in NaOH and 5.5 in buffer solutions). The Rebinder effect appears to be attributable to changes in plastic deformability caused by variations in surface charge. The exact mechanism for the plastic deformation remains unresolved.

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