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Surface hardening of ruby and sapphire

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A simple surface treatment is found to improve mechanical strength of corundum crystals. The surface treatment is as follows: the titanium mono-oxide layer, 0.1 μm, thick is deposited onto the polished surface of the corundum crystals and the crystals are then fired at 1200 to 1300° C for a few hours in air. The treatment improves the mechanical strength of the corundum crystal surface. The surface microhardness increases by nearly × 2 and the mean wear resistance against the iron plate increases by several times. The surface hardening mechanism is discussed in relation to the diffusion of titanium ion into the corundum crystals.

1. Introduction

Corundum crystals, ruby and sapphire, are widely used as machinery jewel parts in fine instruments since these crystals are synthetically manufactured and are polished precisely into various form of the machinery jewel parts. Since the mechanical strength of the corundum depends strongly on the crystal orientation [1], suitable crystal orientation should be selected during the polishing process in order that a long service life is attained in the machinery jewel parts. For the machinery jewel parts of a complex structure, each of the rubbing surfaces exhibits different wear resistance owing to the orientation dependence of wear. Thus, it is difficult to ensure that all rubbing surfaces are polished to a crystal plane having a high wear resistance. This difficulty reduces their effective service lives.

Recently we have succeeded in hardening a surface layer of polished corundum crystals. It is found that the service life of the surface-strengthened corundum phono-styli is about twenty times longer than that of conventional corundum phono-styli [2]. This paper describes the mechanical properties of the surface-strengthened corundum crystals.

2. Experimental procedures

Synthetic corundum crystals, ruby and white sapphire, were used for the surface hardening test. The surface treatment for the hardening purpose was carried out by the following steps: first, a titanium mono-oxide (TiO) layer, 0.1 μm thick, was vacuum deposited on to the mechanically polished surface of the corundum crystals. During the vacuum deposition the crystals were maintained at 200° C. The corundum crystals were then fired in air at 1100 to 1600° C for a few hours and were then quenched in air.

The mechanical properties of the processed corundum crystals were studied by measuring surface microhardness and wear resistance. The microhardness was evaluated for the corundum plate by pressing a pyramid-shaped diamond indentor used in the Vickers test and measuring the diagonals of the square indentation. The load used for the surface microhardness was 25 to 50 g, and the loading time was 30 sec. At least five indentations were measured on each specimen. The cyclical wear resistance was evaluated for the corundum styli against a pure iron surface (carbon, 0.035%) at sliding speed of 0.5 m sec^{-1} and load of 3 g. The wear apparatus is shown schematically in Fig. 1. All tests were conducted in air at room temperature. Surface structure and the wear scar

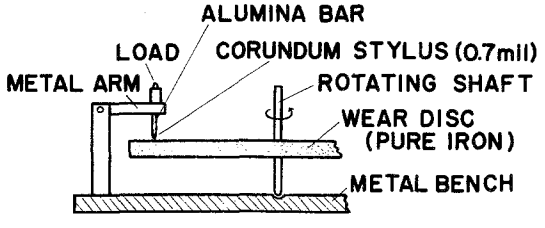

Figure 1 Cyclical wear apparatus.

of the processed corundum crystals were measured using a scanning electron microscope.

3. Results and discussion

3.1. Hardness variation with firing conditions

Fig. 2a and b show the variations of the surface microhardness with firing temperature and firing time, respectively, for the $(1\,0\,\bar{1}\,0)$ sapphire crystal plates. The original hardness of the sapphire plates was $1900\,kg\,mm^{-2}$. It is noted

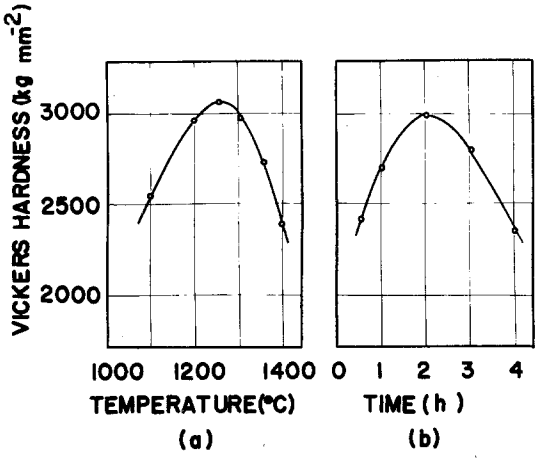

Figure 2 Variation of surface hardness of the $(1\,0\,\bar{1}\,0)$ sapphire plate with firing temperature and firing time measured at an indentor load of 25 g; (a) fired for 2 h in air under various firing temperature; (b) fired at 1300° C in air for various firing times.

that an optimum hardening condition exists in the firing temperature and the firing time. Firing at 1200 to 1300° C for 2 h is the optimum condition for which the hardness is $3100\,kg\,mm^{-2}$. Similar results were also observed for the ruby crystals.

3.2. Wear resistance

Without selecting the direction of the crystal orientation, the sapphires were shaped into cylinders of 0.5 mm diameter and sharpened to 0.7 mil (18 μm) radius of curvature. When the sapphire styli were worn by using the wear apparatus shown in Fig. 1, a circular wear scar was observed at the top of the stylus tips. By measuring the diameter of the scar, the volume of the worn-off cap could easily be calculated. Since the wear resistance depends strongly on crystal orientation of the sapphire styli, numerous sapphire styli should be tested in order to eliminate possible error due to the orientation dependence of the

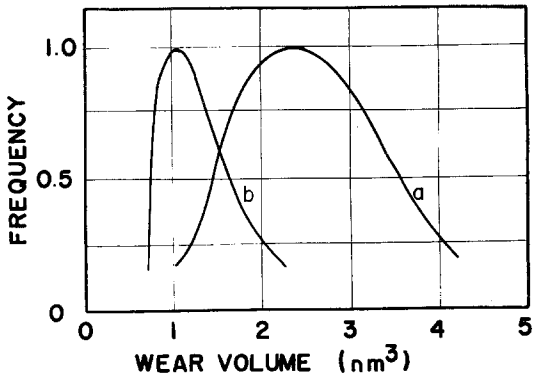

Figure 3 Wear volume distribution of 0.7 mil sapphire styli (18 μm in radius of curvature); (a) conventional raw sapphire; (b) processed sapphire. Wear tests were conducted at a sliding speed of $0.5\,m\,sec^{-1}$, a load of 3 g and a wear distance of 300 m against a pure iron plate.

wear resistance. Fig. 3 shows the wear volume distribution at a constant sliding distance measured for each hundred raw and processed sapphire styli. It is seen that the wear volume of the raw sapphire styli is more widely spread than that of the processed styli. The broadness of the wear volume distribution results from the different

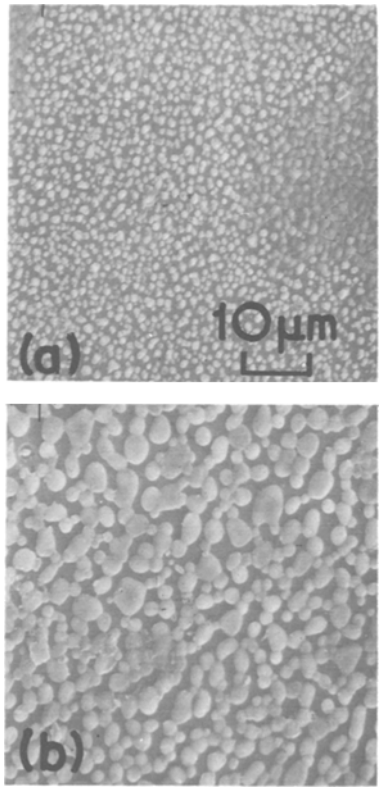

Figure 4 Surface microstructure of the processed sapphire; (a) fired at 1300° C for 2 h; (b) fired at 1600° C for 2 h.

orientations of the test specimens. The narrow distribution of the processed styli shows that the orientation dependence of the wear is clearly reduced by the treatment. It is also noted that the mean wear volume is reduced by a few tenths by this treatment.

3.3. Surface structure

Fig. 4 shows the surface microstructure of the processed sapphire for different firing temperatures, taken using the scanning electron microscope (SEM). The sapphire plate shown in the figure was mechanically polished and then treated by the optimum hardening conditions. The distribution of titanium in the sapphire plate was detected by electron probe microscopic analysis (EPMA). It is seen that the titanium clusters are spread over the surface and that the clusters grow with increase in firing temperature. The electron diffraction analysis suggested that the titanium was in the form of titanium dioxide. The diffusion depth of the titanium in the processed sapphire was studied by EPMA using an angle lapped specimen. Fig. 5 shows the typical results obtained for the processed sapphire fired at different firing temperatures. The titanium was found to diffuse into the specimen. The diffusion depth was 2 μm for a firing temperature of 1300° C and 30 μm for 1600° C. From the figure, the titanium intensity, I, except that near the surface, was found to obey the exponential relationship $I \propto \exp(-Ad^2)$, where d is the diffusion depth and A is a function of firing temperature and firing time. From the exponential relationship the diffusion

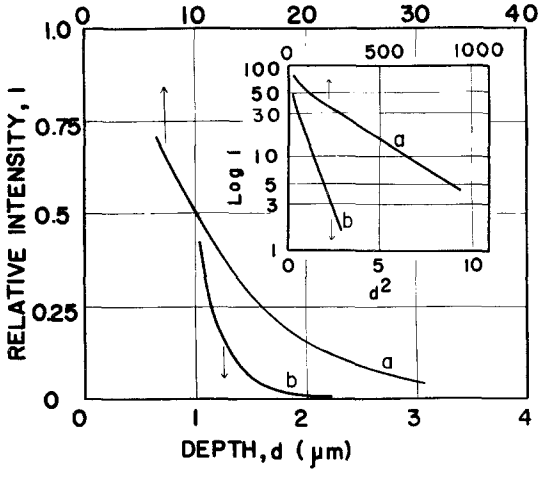

Figure 5 Diffused Ti intensity as a function of diffusion depth in the (1 0 $\bar{1}$ 0) surface of sapphire; (a) fired at 1600° C for 1 h; (b) fired at 1300° C for 2 h.

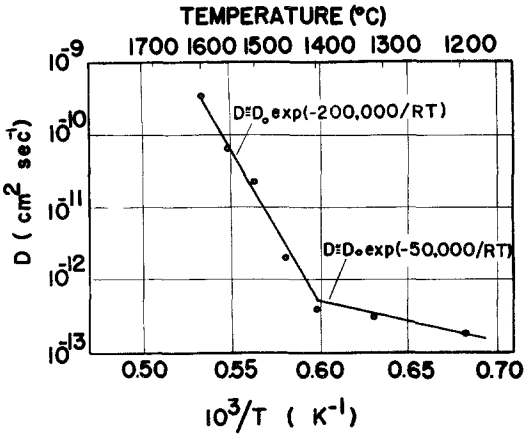

Figure 6 Diffusion coefficient of Ti in the (1 0 $\bar{1}$ 0) surface of sapphire as a function of absolute temperature.

constant can be evaluated under the assumption that A is represented by the following relation: $A = 1/4Dt$. The diffusion constant evaluated from this relation is shown in Fig. 6. It is noted that the diffusion constant, D, varies with temperature, T, as $D \propto \exp(-H/RT)$, where H is the activation energy and R the gas constant, and that there are two different diffusion processes in this temperature range. The first is about 50 kcal mol^{-1} of the activation energy below 1400° C, and the other is about 200 kcal mol^{-1} above 1400° C. The small activation energy observed below 1400° C suggests that a rapid diffusion process, such as surface or defect diffusion, prevails at a firing temperature below 1400° C. The relatively high activation energy observed above 1400° C indicates that bulk diffusion may prevail at a firing temperature above 1400° C [3]. From these results, it is considered that the optimum hardening condition, firing at 1200 to 1300° C for 2 h, is related to the generation of rapid diffusion of titanium on the polished surface layer of corundum crystals.

3.4. Hardening mechanism

It is reported that the mean resolved shear stress for the corundum bulk crystal is about 40 kg mm^{-2} at room temperature [4]. However, mechanical polishing reduces the shear stress to about 10 kg mm^{-2}. The small value for the polished surface is attributed to the fact that submicrocracks are formed on the surface during the polishing process. In the present optimum hardening condition the titanium diffuses along the dislocations or submicrocracks on the polished surface. This causes an increase in mechanical strength at the surface. The wear resistance will

increase due to a reduction of brittle rupture which takes place at the dislocations or sub-microcracks on the crystal surface.

The observed titanium diffusion depths suggest that the thickness of the hardening layer for the corundum treated at the optimum hardening condition is considered to be 1 to 3 μm. This is supported by the fact that the surface micro-hardness approaches the hardness of raw corundum when the indentor is thrust more than 2 μm deep as shown in Fig. 7.

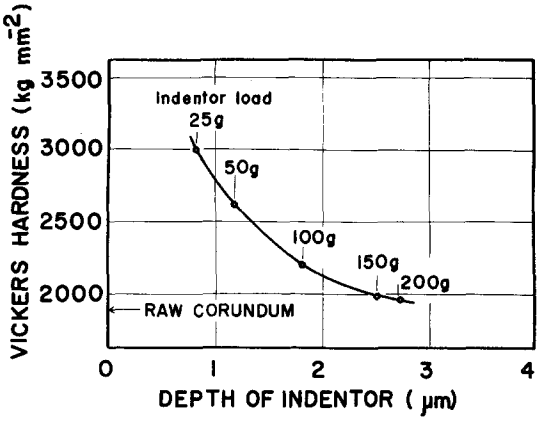

Figure 7 Variation of Vickers hardness with indentation depth for the (1 0 $\bar{1}$ 0) surface of processed sapphire.

The reasons for the existence of optimum hardening conditions are believed to be as follows:

(1) At high firing temperatures and long firing times, complete oxidization occurs and a solid-solution of TiO_2–Al_2O_3 may be formed on the surface through bulk diffusion process. This results in the softening of the corundum, which is similar to the softening of Al_2O_3 by a solid-solution of MgO–TiO_2 [5].

(2) At low firing temperatures and short firing times, the titanium may be not trapped by the surface microcracks or the dislocations. The firing temperature should be higher than 900° C where dislocation motion occurs freely and the titanium is easily trapped by the dislocations [6].

4. Conclusion

The corundum surface is strengthened by titanium along the surface microcracks or dislocations of the corundum crystal surface. Table I summarizes the mechanical properties of the surface-strengthened corundum.

TABLE I Physical properties of corundum*

	Conventional raw corundum	Surface-hardened corundum
Crystal surface	(1 0 $\bar{1}$ 0)	(1 0 $\bar{1}$ 0)
Vickers hardness† (kg mm^{-2})	1900	3000–4000
Ratio of time required to have given wear volume	1	2–4
Thickness of strengthened surface (μm)	–	1–3

*Sapphire crystal.
†Measured at 25 g.

Acknowledgement

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