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First-principle analysis of chemical reactions between metal oxide fine powders and Si(100) surface in EEM (Elastic Emission Machining)

K. Yamauchi[a], K. Hirose[a], H. Goto[b], M. Sakamoto[a], K. Yamamura[a], Y. Sano[a], and Y. Mori[a]

[a]Department of Precision Science and Technology, Osaka University
2-1 Yamada-oka Suita Osaka, Japan

[b]Department of Mechanical and System Engineering, Kyoto Institute of Technology
Matsugasaki, Sakyo-ku, Kyoto, Japan

Interactions between ultra-fine powder [SiO_2] and work [Si(100) surface] in EEM (Elastic Emission Machining) has been investigated by employing first principle calculations. Calculated results show the possibilities of the atomic removal from the work surface in EEM through the solid phase chemical interaction between surfaces of ultra-fine powders and works.

1. INTRODUCTION

EEM (Elastic Emission Machining)[1)~6)] which has been developed by authors is thought to be an ultra-precision machining process employing surface chemical activities of ultra-fine powders. Metal oxide powders such as SiO_2 or ZrO_2 is usually employed. When they contact to the work surface, chemical reaction between the surfaces of powder and work is induced with some probability. And when they are separated by some means, atomic removal from the work surface occurs also with some probability. Machining processes using such kinds of phenomena are called EEM[3)~6)].

EEM has been said to be best technique to make surfaces with atomic order smoothness. This technique has been successfully applied to polish the mirrors of laser jailoscope which is employed as an orbit controller of Japanese H-2 rocket. In other region, EEM technique is also successfully applied to fabricate X-ray mirrors for focusing synchrotron radiation.

To understand the mechanism of EEM process, first-principle simulation is becoming an indispensable technique. In other words, we can't perfectly understand and optimize the process only with experimental ways, because of too many process parameters.

2. EEM TECHNIQUE

As shown in this Fig. 1, EEM process is carried out in the fluid which is the mixture of water and ultra-fine powders[1)2)]. And rotating sphere made of polyurethane having low elasticity is employed to make water flow. At the region between rotating sphere and work surface, elasto-hydoro-dynamic lubricational state is induced and fluid film thickness of more than 1 μm is kept. Powders dispersed in water have diameters of smaller than 0.1 μm. So employed powders are softly transported to the work surface without contacting rotating sphere and chemically interact with work

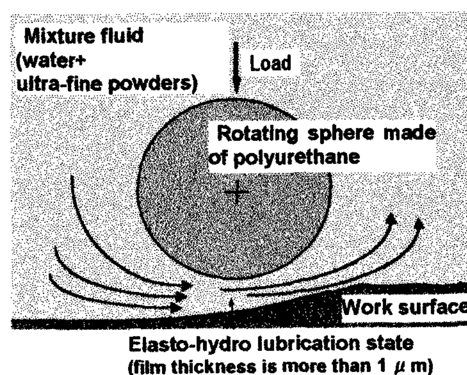
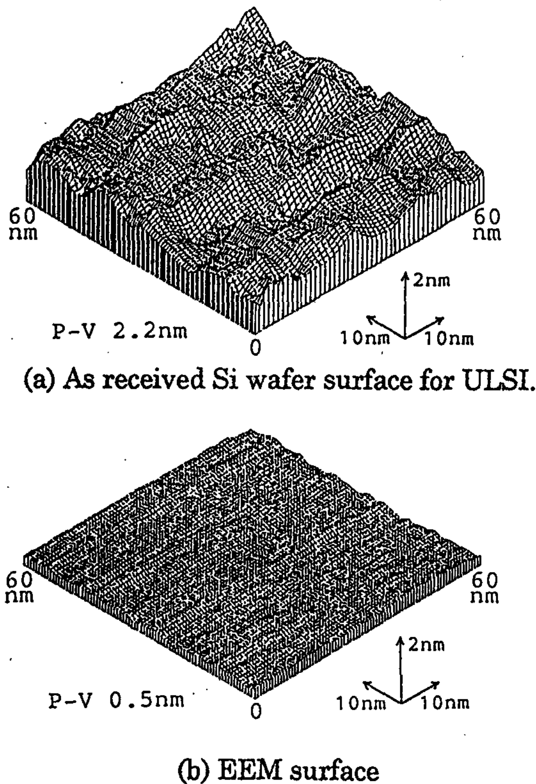


Figure 1. A method to supply ultra-fine powders to the work surface.

surface atoms. Then they are separated by the viscous drag from the water flow, atomic removal from the work surface is thought to occur.

3. DISTINCTIVE FEATURES OF EEM

Distinctive features of EEM process are as follows. Firstly, in EEM, extremely smooth surfaces (atomically flat surfaces) can be obtained[5]. Figure 2(a) shows the micro roughness of as received Si(100) wafer surface. And Fig. 2(b) shows EEM machined surface finished to have smoothness of the atomic order. Secondly, Finished surfaces have no crystallographic damage. Figure 3 shows the surface state densities of finely-prepared Si(100) surfaces which are observed by surface photo-voltage spectroscopy. EEM surface has almost same surface state density as the chemically etched surface with HF and HNO_3



(a) As received Si wafer surface for ULSI.

(b) EEM surface

Figure 2. STM (Scanning tunneling microscopy) observations.

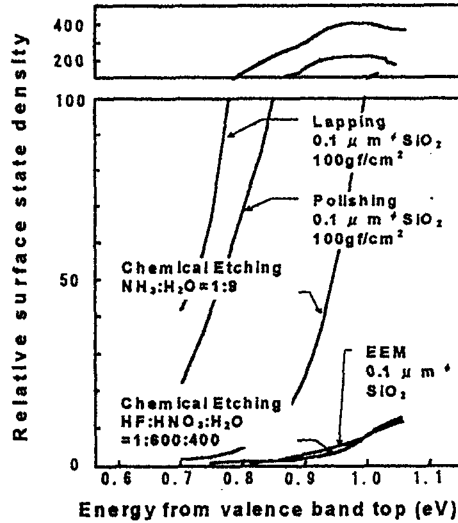


Figure 3. Surfaces state densities of finely prepared Si surfaces obtained by surface photo-voltage spectroscopy.

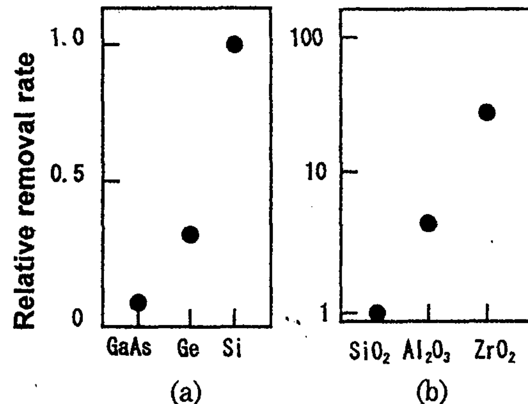


Figure 4. Relationship between removal rates and combinations of work and powder materials. (a) Wide variations of removal rate with difference of work material. Powders employed in this figure is ZrO_2. (b) Wide variations of removal rate with difference of powder material. Work materials employed in this figure is Si.

system. And surface state density of EEM surface is smallest.

Third feature is most important to understand removal mechanism in EEM. Removal rates strongly depend on combinations between materials of powders and works[3][4]. Figure 4(a) shows the wide variations of remo-

val rates with differences of work materials. Also Fig. 4(b) shows the wide variations of removal rates with differences of employed powder materials. Such wide variations don't appear in conventional mechanical polishing methods.

These three features of EEM strongly show that the atomic removal mechanism in EEM is chemical.

4. REMOVAL MECHANISM IN EEM

An atomic removal mechanism in EEM has been already proposed as shown in Fig. 5. In the water, both surfaces of ultra-fine powder and work are said to be terminated by hydroxide species as shown in Fig. 5(a). And ultra-fine powders are carried by water flow which is induced by the rotating sphere. And when they contact to the work surface, interface

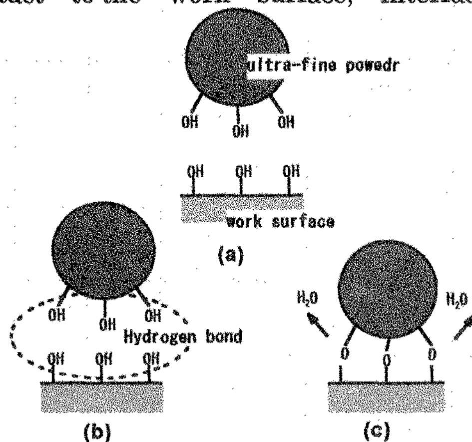


Figure 5. Interactions between surfaces of ultra-fine powders and works.
(a)Surface structures before interaction.
(b)Hydrogen bonding between two surfaces.
(c)Final interface structure.

structures as shown in Fig. 5(c) might be constructed through hydrogen bonding state as shown in Fig. 5(b). This interface structure is constructed by oxygen atoms being placed between two metal ions belonging both to powder and to work. This kind of atomic configuration is same as usual metal oxides such as $SiZrO_4$. Concerning to the back-bond strength to be broken during atomic removal, following idea has been also proposed. In the crystal, ideal binding force between atoms appears. But near the interface, valence electron distribution is distorted. Especially in the configuration as shown in Fig. 5(c), interface atoms are oxygen atoms having high electronegativity so that valence electrons at the region between work atoms on surface layer and second layer is captured by interface oxygen atoms. Consequently, binding forces between the atoms on first layer and second layer are weakened. These kinds of ideas have been proposed to explain the machining properties, as the stronger this kind of distortion, the higher the machining rate is. Employing these kinds of phenomena, influences of the variations of combinations between materials of ultra-fine powders and works could be explained.

5. FIRST-PRINCIPLE ANALYSIS OF ATOMIC REMOVAL PROCESSES

First principle simulations are employed to analyze EEM mechanism and to aim to predict machining properties such as removal rates non-empirically. Interactions between ultra-fine powder [SiO_2] and work [Si(100) surface] has been investigated as an initial trial. Employed cluster model is shown in Fig. 6. Cluster model for Si(100) surface is $Si_{10}H_{14}$. And cluster model for SiO_2 powder is $Si_3O_{10}H_6$ having crystobalite structure. And surface atoms are terminated by hydrogen being employed as cap atoms. Simulation has been carried out by LCAO method based on Hartree Fock approximation. Electrons considered hear are $((3s)^2(3p)^2)$ for Si, $((2s)^2(2p)^4)$ for O and $((1s)^1)$ for H. Inner electrons are considered by ECP (Effective Core Potential).

Figure 7 shows valence electron density distributions on the planes including back bonds of the top Si atom of $Si_{10}H_{14}$ cluster with and without $Si_3O_{10}H_6$. Valence electrons concerning to the back-bond of the top Si atom decrease by interacting with $Si_3O_{10}H_6$ cluster.

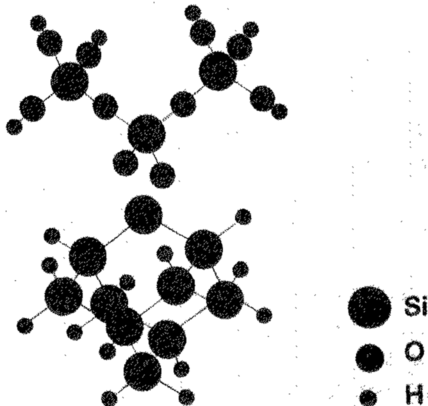


Figure 6. Employed cluster model.

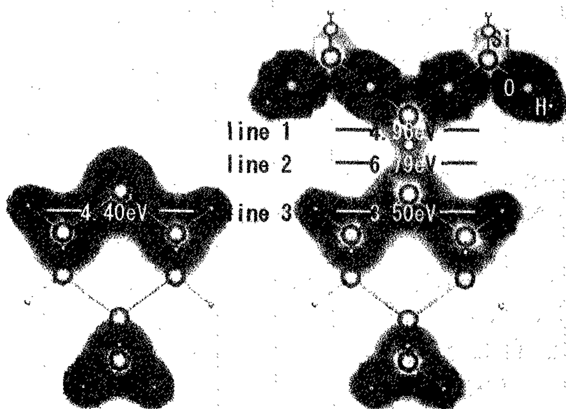


Figure 7. Calculated valence electron densities and binding energies of various boundaries.
(a) $Si_{10}H_{14}$ cluster (b)$Si_{10}H_{14}$ with $Si_3O_{10}H_6$ cluster.

Furthermore, we tried to estimate binding energies between the boundaries at the line 1, 2 and 3 as shown also in Fig. 7. Binding energy at the line 3 shows the back-bond energy. Binding energy at the line 1 shows the binding energy between the interface oxygen and Si of powder and binding energy at the line 2 shows the binding energy between the interface oxygen and surface Si. These energies should be larger than the binding energy at the line 3, for occurrences of atomic removal from the work surface. Binding energy at line 3 decreases from 4.40eV to 3.50eV as the consequence of interacting with employed cluster. And this energy is understood to be small enough for the atomic removal of the Si atom from the $Si_{10}H_{14}$ cluster by comparing to the binding energies of 4.96eV at the line 1 and 6.79eV at the line 2.

6. CONCLUSIONS

Interactions between ultra-fine powder [SiO_2] and work [Si(100)surface] has been investigated as an initial trial. Obtained conclusions are summarized as follows.
(1) From the calculations of valence electron density, back-bond strength of surface Si interacting with $Si_3O_{10}H_6$ cluster is predicted to be weakened.
(2) Back-bond energy is understood to decrease from 4.40eV to 3.50eV in consequence of interacting with the $Si_3O_{10}H_6$ cluster. And this value is smaller enough than those of other boundaries.
(3)These facts are thought to show the possibilities of atomic removal in EEM through the mechanisms, previously proposed.

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