

A SIMULATION OF REMOVAL PROCESS IN EEM(ELASTIC EMISSION MACHINING) BY AB INITIO MOLECULAR ORBITAL METHOD

R.HOSOI, K.HIROSE, K.YAMAUCHI, K.SUGIYAMA,
K.INAGAKI, K.YAMAMOTO, and Y.MORI

Department of Precision Science and Technology, Osaka University, 2-1 Yamada-oka, Suita, Osaka, Japan
FAX: 81-06-6879-7274, e-mail: ryu@pm.prec.eng.osaka-u.ac.jp

Reaction processes between the surfaces of ultrafine powders[SiO₂, ZrO₂] and work[Si(111)] in EEM(Elastic Emission Machining) has been investigated by employing ab initio molecular orbital method. Calculated results show the chemical reaction between the surfaces of Si(111) and ZrO₂ powder is more easily induced than that between the surfaces of Si(111) and SiO₂ powder. This result consists with the experimental fact that the removal rate in EEM indicated by ZrO₂ powder is faster than that by SiO₂ powder.

Key words: EEM, ab initio, molecular orbital method, metal oxide, silicon

1. INTRODUCTION

EEM(Elastic Emission Machining) is one of the ultraprecision machining process that can make extremely flat surfaces without crystallographic damages. In EEM process, ultrafine powders of metal oxide (SiO₂ or ZrO₂ etc.) dispersed in water are employed as reactive species against to the work surface and they are transported to the work surface by the flow of the water. When they contact to the work surface, chemical reactions between the surfaces of the powders and the work is induced with some probability. And when they are separated by the drag force from the water, atomic removal from the work surface occurs. Those are thought principal mechanisms of EEM process.

The purposes of this study are to analyze the reaction processes between the surfaces of ultrafine powders and work, and to predict machining properties such as removal rate by employing ab initio molecular orbital method. In this theoretical analysis, the cluster models of SiH₃-OH [as Si(111) surface], Si(OH)₄ [SiO₂ ultrafine powder] and Zr(OH)₄·2H₂O [ZrO₂ ultrafine powder] were used. Calculated results show the chemical reaction between the surfaces of Si(111) and ZrO₂ powder is induced more easily than that between the surfaces of Si(111) and SiO₂ powder. It can be thought that the stronger chemical reactivity, the faster removal rate of EEM. This result corresponds to the experimental fact of removal rate in EEM.

2. EEM TECHNIQUE

As shown in Fig.1, EEM process is carried out in the fluid which is the mixture of water and ultrafine powders¹⁾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-hydro-dynamic lubricational state is induced and fluid film thickness of more than 1μm is kept. Powders dispersed in water have diameters of smaller than 0.1μm. So employed powders are softly transported to the work surface without contacting rotating sphere and chemically interact with work

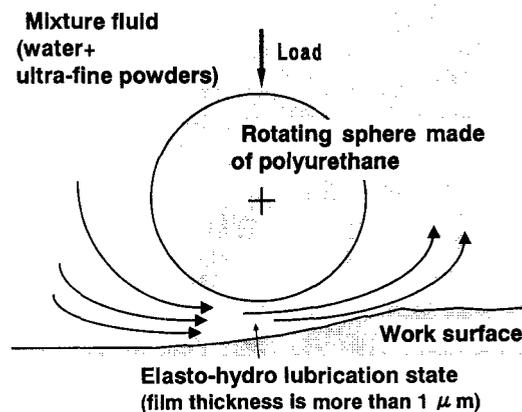


Fig.1 A method to supply ultrafine powders to the work surface in EEM.

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 obtained⁵⁾.

Secondly, finished surfaces have no crystallographic damage. EEM surface has almost same surface state density as the chemically etched surface with HF and HNO₃ system. And surface state density of EEM surface is smallest.

Third feature is the most important to understand removal mechanism in EEM. Removal rates strongly depend on combinations between materials of powders and works³⁾⁴⁾. Fig.2(a) shows the wide variations of removal rates by ZrO₂ powder with differences of work materials. Also Fig.2(b) shows the wide variations of removal rates for Si(100) with differences of employed powder materials. No such variation appears in conventional mechanical polishing methods.

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

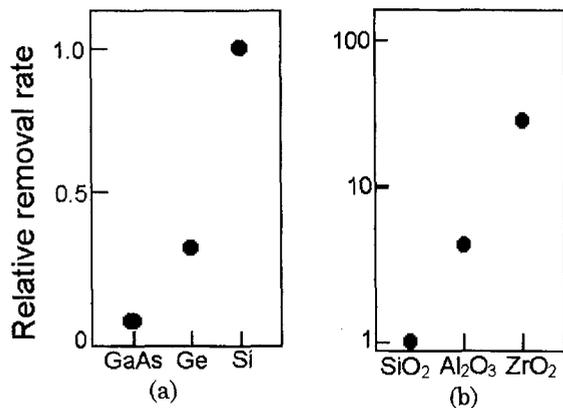


Fig.2 Relationship between removal rates and combinations of work and powder materials.; (a) Variations of removal rate with difference of work material. Powder employed in this figure is ZrO₂; (b) Variations of removal rate with difference of powder material. Work materials employed in this figure is Si(100).

4. REMOVAL MECHANISM IN EEM

The proposed atomic removal mechanism in EEM is shown in Fig.3.

In the water, the surface of ultrafine powder is terminated by hydro-oxide species. Also it is known that exchanges from surface hydrogen termination to hydro-oxide species occur during Si etching in ultra-pure water. These are shown in Fig.3(a). Then, ultrafine powders are carried by water flow induced by the rotating sphere. When they contact to the work surface,

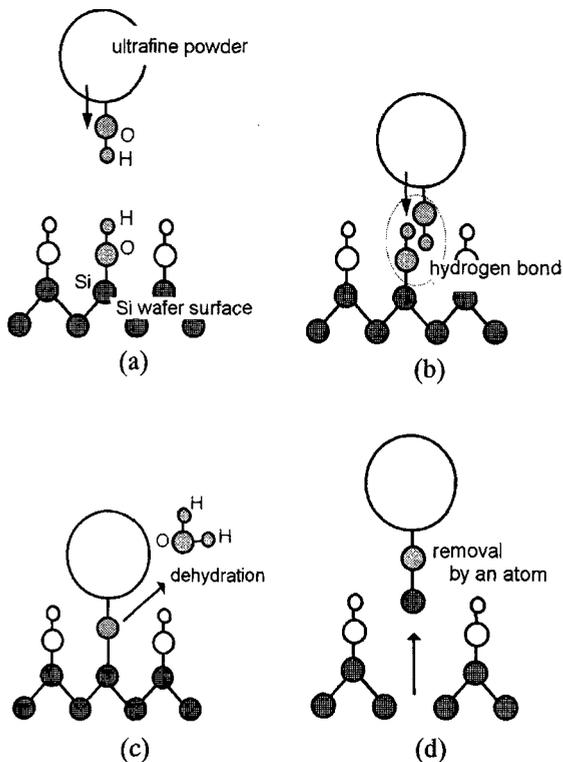


Fig.3 An atomic removal mechanism in EEM; (a) surface structures before interaction; (b) hydrogen bonding between two surfaces; (c) chemical reaction via oxygen; (d) removal process with atomic unit

with some possibility, the hydro-oxide species on the surfaces of ultrafine powder and work make hydrogen bond each other as shown in Fig.3(b). Next, dehydration occurs on this site also with some possibility. As a result of this, the interface between the surface of ultrafine powder and that of work is formed as shown in Fig.3(c). This interface structure is made of oxygen atoms being placed between two metal ions, one is a part of powder, the other is a part of work surface. This kind of atomic configuration is same as usual metal oxides such as SiZrO₄. Concerning 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. However near the interface, valence electron distribution is distorted. Especially in the configuration as shown in Fig.3(c), interfacial atom is oxygen atom having high electro-negativity so that valence electrons at the region between work atoms on surface layer and second layer are captured by interfacial oxygen atom. Consequently, binding force between the atoms on first layer and second layer is weakened. When ultrafine powder leaves by water flow, an atom on first layer is removed together as shown in Fig.3(d).

It can be thought that removal rate of EEM depends on the reactivity between hydro-oxide species on the surface of ultrafine powder and that of work. The purpose in this report is to study the relationship between the experimental removal rate in EEM and the theoretically analyzed reactivity between the powder surface and the work surface.

5. ANALYSIS OF REACTION OF EEM

Atomic removal processes in EEM as shown in Fig.3(d) has already investigated. In this study, we calculate the dehydrating reaction process between the surfaces of ultrafine powder and that of work as shown in Fig.3(b)-(c). Employed cluster models for the Si surface, the SiO₂ ultrafine powder surface and the ZrO₂ ultrafine powder surface are SiH₃-OH, Si(OH)₄ and Zr(OH)₄·2H₂O⁷ respectively. Fig.4(a) and (b) show the reacting configurations between the SiO₂ ultrafine powder surface and the Si work surface, and between the ZrO₂ ultrafine powder surface and the Si work surface respectively. These configurations of the

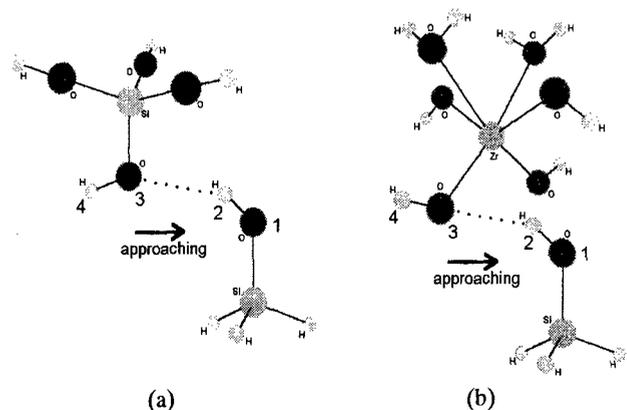


Fig.4 (a) Cluster model for Si surface is SiH₃-OH and model for SiO₂ powder is Si(OH)₄; (b) Cluster model for Si surface is SiH₃-OH and model for ZrO₂ powder is Zr(OH)₄·2H₂O

reaction models are decided so that electron transfer from HOMO(Highest Occupied Molecular Orbital) to LUMO(Lowest Unoccupied Molecular Orbital) occurs. Only the positions of the atoms with numbers in this figure are structurally optimized. This simulation has been carried out by LCAO method based on Hartree-Fock approximation. Electrons considered here are $((3s)^2(3p)^2)$ for Si, $((2s)^2(2p)^4)$ for O and $((1s)^1)$ for H respectively. Potentials from nuclei and contributions from inner electrons are considered by ECP (Effective Core Potential) method.

Fig. 5 shows the valence electron charge density distribution with two clusters approaching each other. It is shown by wire-frame in Fig.5(a-1) and Fig.5(b-1), and it is shown by clouds in the others. In the model (b), the bond between H(in the Si surface model) and O(in the ZrO_2 model) is formed, but no reaction occurs in the model (a).

These results are clearly shown by bond order analysis. Fig.6 shows bond order between both atoms in the Si surface model and in powders surface in the cases of before and after approaching. (a) is the case of the

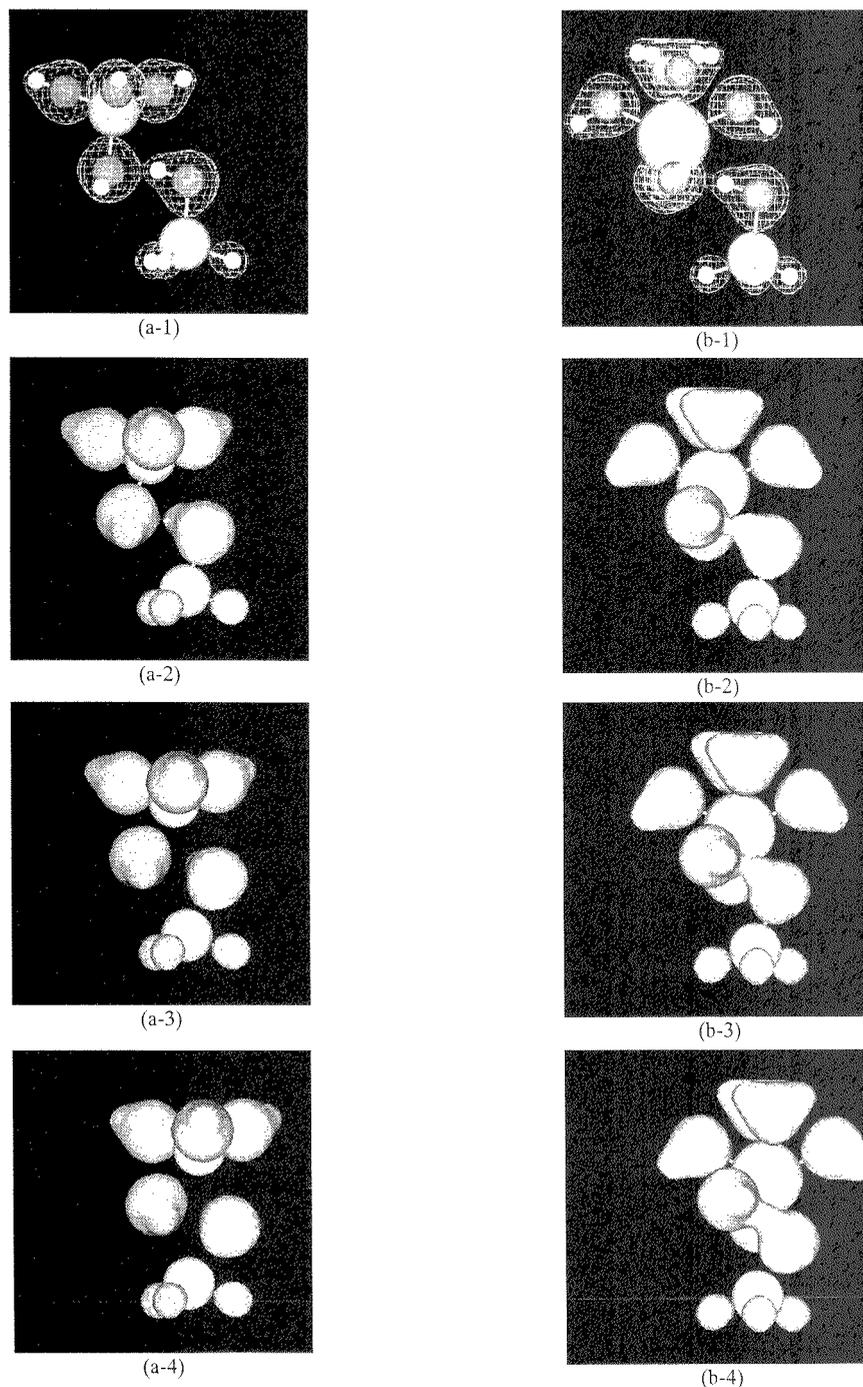


Fig.5 Equipotential surface of charge density with approaching Si surface model and powder surface models. Interfacial two OH are structurally optimized in all configurations. No binding between OH in the reaction between SiH_3-OH and $Si(OH)_4$ is observed as shown in (A-1)~(A-4), but it is observed in the reaction between SiH_3-OH and $Zr(OH)_4 \cdot 2H_2O$ as shown in (B-1)~(B-4).

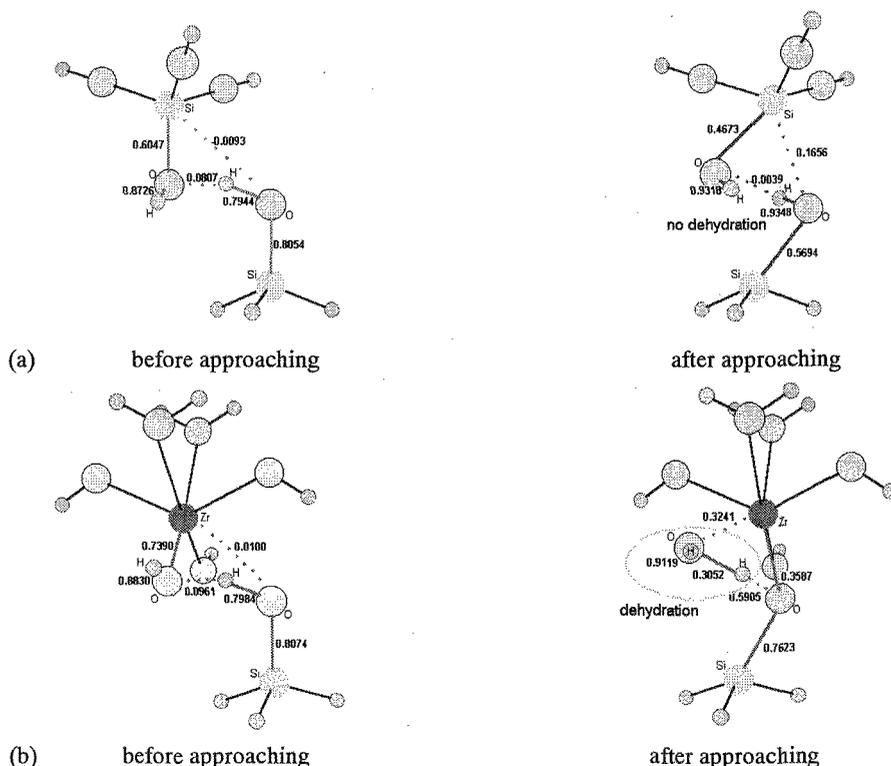


Fig. 6 Change of bond order with powder surface models and Si surface model approaching each other. Binding between Si surface atom and the atoms(Si or Zr) in powder via oxygen atom is observed in each case. However dehydration reaction is observed only in the case of ZrO_2 - Si model; (a) the reaction of SiH_3 -OH and $Si(OH)_4$; (b) the reaction of SiH_3 -OH and $Zr(OH)_4 \cdot 2H_2O$

SiO_2 ultrafine powder and the Si surface, and (b) is that of the ZrO_2 powder and the Si surface. In (a), two Si atoms begin to make bond via oxygen. However no attraction between released OH from the SiO_2 model and H from the Si surface model is observed. The increase of total energy when the SiO_2 powder model approaching the Si surface is 3.86eV. In (b), Si and Zr atoms also begin to make bond via oxygen. Moreover, H_2O is made by the reaction between released OH from the ZrO_2 model and H from the Si surface model. This phenomenon shows acid-base reaction. In this reaction, the increase of total energy is 3.19eV. It is smaller than that in the case of the SiO_2 ultrafine powder.

These results show that OH on ZrO_2 ultrafine powder more easily reacts with OH on Si than that on SiO_2 ultrafine powder. This result consists with the experimental fact that removal rate in EEM indicated by ZrO_2 powder is faster than that by SiO_2 powder.

6. CONCLUSION

Reactions between ultrafine powders [SiO_2 , ZrO_2] and work [Si surface] has been investigated as a trial of the attracting process indicated in Fig.3(b) and (c). Obtained results are summarized as follows.

- (1) OH on ZrO_2 ultrafine powder reacts with OH on Si surface with the 3.19eV rise of total energy with forming H_2O molecule.
- (2) The reaction between OH on SiO_2 ultrafine powder and OH on Si surface rises total energy by 3.86eV without forming H_2O molecule.
- (3) According to (1) and (2), ZrO_2 ultrafine powder more easily reacts with Si surface than SiO_2

ultrafine powder. This result consists with the experimental fact that removal rate in EEM indicated by the ZrO_2 powder is faster than that by the SiO_2 powder.

ACKNOWLEDGEMENT

This work was partially supported by a Grant - in - Aid for COE Research (No. 08CE2004) from the Ministry of Education, Science, Sports and Culture, and by the Japan Science and Technology Corporation. In this work, AMOSS (Ab initio Molecular Orbital System for Supercomputers; NEC) installed to computation center of Osaka University was used.

REFERENCE

1. Y. Mori, N. Ikawa, T. Okuda, K. Sugiyama, and K. Yamauchi, *Proc. Japan Soc. Prec. Eng.*, **49**(1983)1540 (in Japanese).
2. Y. Mori, T. Okuda, K. Sugiyama, and K. Yamauchi, *Proc. Japan Soc. Prec. Eng.*, **51**(1985)1033 (in Japanese).
3. Y. Mori, K. Yamauchi, and K. Endo, *Precision Engineering.*, **9**(1987)123.
4. Y. Mori, K. Yamauchi, and K. Endo, *Precision Engineering.*, **10**(1988)24.
5. Y. Mori, K. Yamauchi, K. Endo, T. Ide, H. Toyota, K. Nishizawa, and M. Hasegawa, *J. Vac. Sci. Technol.*, **A,8**(1990)621.
6. Y. Mori, K. Yamauchi, and K. Endo, *Proc. Japan Soc. Prec. Eng.*, **57**(1991)36 (in Japanese).
7. F. Babou, B. Bigot, and P. Sautet, *J. Phys. Chem.*, **97**, 11501-11509 (1993).