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Hydrogen Formation during Wet Grinding of Alumina and Silicon Carbide

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Alumina and silicon carbide powders were ground in water, butanol, benzene and hexane using planetary ball mill, and the gas phase inside the mill pot was analyzed by a gas chromatograph. The effect of liquid media on the grindability varied with the kind of feed powders, and the main product in the gas phase was hydrogen. The amount of it was in the order of benzene =< butanol < hexane for alumina and no gas product was detected for water. However, that for silicon carbide was considerable in water and in butanol, and was very small in benzene and in hexane. The mechanism of these mechanochemical reactions was discussed.

When mechanical actions such as grinding, friction and cutting are carried out on solids, the surface and bulk phase are activated and various chemical and physicochemical phenomena are observed. These phenomena are called mechanochemical and/or tribochemical effects. There are so many reports1) on mechanochemistry or tribochemistry, such as mechanochemically initiated polymerization, exoelectron emission, tribopolymerization, mechanoradical formation, etc.

It has been well known that the hydrogen is formed during wet grinding of inorganic powders with steel balls in water.2) Recently,Yokoyama et al.3) have investigated extensively the rate of hydrogen generation during wet grinding in water or alcohols using vibration and Planetary mills. However, it has been considered that the hydrogen formation is only due to the reactions between liquid media and steel balls, viz., iron. Mori and co-workers have investigated the specific adsorption and the reaction of organic compounds on the fresh surface of metals and ceramics. In cutting processes of metals, various organic molecules adsorbed on the fresh and active surfaces,4) and the hydrogen evolution was observed during the processes.5) While, on the fractured surface of ceramics,6) there has been no evidence for the hydrogen formation on the surface through the reaction with organic compounds and water. Authors also reported the in situ surface modification7) during grinding of alumina, silica and silicon carbide in solutions of alcohols, organosilanes and organotitanate in hexane.

Although the mechanisms of those mechanochemical phenomena were presumed and presented in many papers, particular ones of the reactions have not been well-defined. In this paper, to make clear the mechanochemical effects and reactions in wet grinding, the gas phase inside a ball mill pot after grinding was analyzed and the mechanisms of the reactions were discussed together with the effects of the liquid media on the performance of grinding.

Feed materials were alumina(WA#120) and silicon carbide(GC#120) supplied by Showa Denko Co. Ltd. of the similar particle size of about 100 μm, and were dried at 130 °C for more than 2 h before grinding. Wet grinding was conducted using a planetary ball mill(Fritsch P-7) with a rotating rate of 500r.p.m. for the duration of 20, 40 and 60 min. Inner volume of mill pot made of zirconia was 45 cm^3, and the grinding medium was zirconia balls(5 ϕ) with a fractional filling of 0.3. Feed volumes of water, butanol, benzene and hexane as liquid media were 15ml, and the powder sample used was 5 g. Distilled water was once boiled to purge dissolved oxygen, and organic substances were dried using molecular sieve. The gas phase was replaced by nitrogen using a globe box before grinding.

The gas inside the mill pot was sampled using a gas tight syringe through a Viton seal, and was analyzed by a gas chromatograph(Hitachi 163) with a molecular sieve 13X column. The amount of hydrogen evolved was determined using a calibration curve, and was corrected with a value of blank tests. Ground suspensions were centrifugally separated and the precipitates were washed by water, hexane, benzene or acetone. Then the collected powder was dried at 60 °C in vacuo. BET surface areas of these ground powders were determined by flow method using nitrogen.

It is well known that the grinding efficiency of wet grinding is much higher than that of dry grinding,$^{8)}$ and the effects of the liquid media on the grindability have been studied using various powders and many grinding methods. However, the effect of liquid media on the efficiency was not unambiguous yet. The specific surface areas of ground powders were plotted against the grinding time in Fig.1. Surface area of alumina powder ground in water was higher than those ground in butanol, benzene and hexane. Further, the surface area did not increase with the grinding time in latter cases(Fig.1). These results were attributed to the difference in the dispersibility of powders. Agglomeration of powders on the mill pot wall and on the mill balls was observed after grinding 40 and 60 min in organic media, but the phenomena were not observed for water. These results are in good agreement with those of Yokoyama et al.$^{9)}$ They studied the effects of liquid media on the grindability and reported that the dielectric constants of liquid media were the important factor in wet grinding. On the other hand, all the powders of silicon carbide ground in liquid media had almost the same specific surface area(Fig.1). In this case, agglomeration was not observed. From these results, it can be accepted that grindability depends on the feed materials and the liquid media, and one must select a suitable liquid medium for each powder.

Figure 2 shows the results of hydrogen analysis of the gas phase inside the mill pot after grinding. In the case of alumina grinding, a small amount of hydrogen evolved in hexane, while very small amount of hydrogen was detected for butanol and benzene. However hydrogen was not detected for water. Figure 3 indicates the relationship between the amount of hydrogen evolved and the specific surface area of ground powder. Since the amount of hydrogen evolved in hexane is not linear to the specific surface area of alumina, it can be considered that the hydrogen formation occurs not only on the fresh surface. This can be explained by the catalytic reaction on the alumina surface.

In the case of grinding in butanol, hydrogen was formed with the amount smaller than that in hexane as shown in Fig.2. Hydrogen does not evolve if the formation of only butoxyl and hydroxyl groups proceeds on the fresh surface through the following reaction,

$$>\mathrm{Al-O-Al}< \xrightarrow{\mathrm{C_4H_9OH}} >\mathrm{Al-O-C_4H_9} + >\mathrm{Al-O-H} \qquad (1)$$

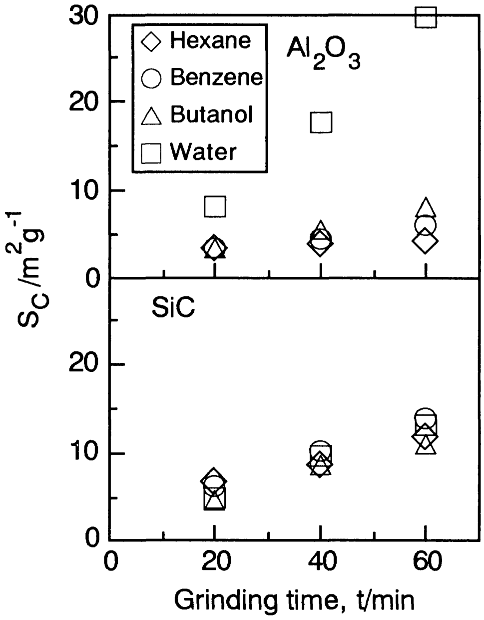

Fig.1. Increase in specific surface area, S_C, by grinding.

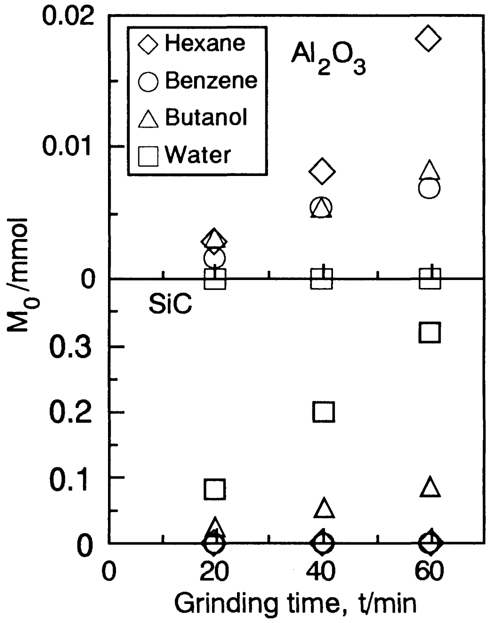

Fig.2. Amount of hydrogen evolved, M_0, against grinding time.

Then the hydrogen formation may imply progress of a complex reaction on the ground surface. As hydrogen was not detected during grinding in water, it is natural to consider that the most part of the fresh surface reacts with water as follows:

$$>Al-O-Al< \xrightarrow{H_2O} 2 >Al-O-H \qquad (2)$$

As shown in Fig.2, the hydrogen evolution is remarkable during grinding of silicon carbide in water and in butanol, while in benzene and hexane only trace amount of hydrogen was detectable. From the linearity of the amount of hydrogen to the specific surface area(Fig.3), the hydrogen formation is inferred to proceed on the fresh surface. The mechanisms in these cases will be described as follows: (1)Scission of silicon-carbon bond occurs, and simultaneously surface mechanoradicals are created, (2)Water or butanol molecules react with the surface to form mainly surface hydroxyl or butoxyl groups, (3) Hydrogen atoms formed by these reactions are recombined with each other. On the other hand, very small amount of hydrogen was detected in cases of grinding in benzene and in

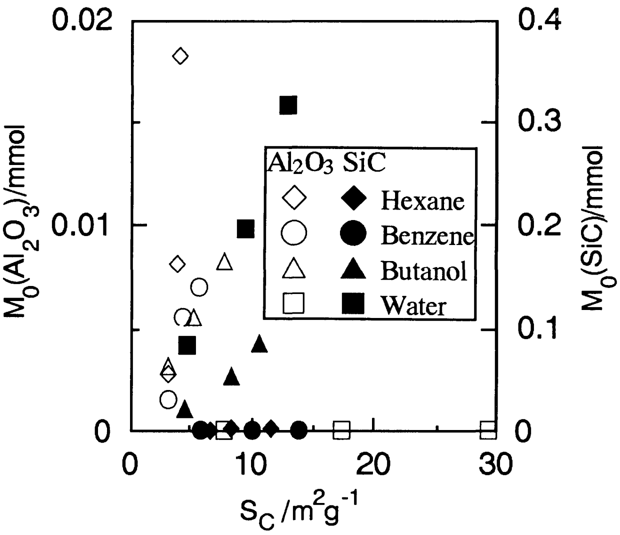

Fig.3. Relationship between M_0 and S_C.

hexane. So the thermal analysis, temperature programed desorption - mass spectrometry, of ground powders were carried out. From these measurements, hydrogen was recognized to evolve at the temperature range of 400 to 800 °C. Then it was considered that the hydrogen was adsorbed chemically on the surface or absorbed atomically in the bulk of silicon carbide powders.

Additionally, methane was detected in the systems of alumina-hexane, silicon carbide-water and silicon carbide-butanol. Heinicke et al.10) reported that methane, ethane and other hydrocarbons were generated in dry grinding of silicon carbide in the atmosphere of hydrogen. Then the methane formation in our system is considered to be caused by the similar mechanism of tribosorption of hydrogen atom.

Concludingly, in many cases hydrogen evolves during wet grinding of ceramic powders which has been considered to be stable, and one must care for the hazard of hydrogen combustion in not only metal but also ceramic grinding. Furthermore, the selection of a suitable liquid medium in wet grinding depends on the nature of chemical bond of solid such as covalency, but more elaborate experimental confirmation is needed.

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