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Effect of Particle Size on Infrared Spectra of Inorganic Powders*1,*2

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In our studies of the analysis of the inclusions in iron and steel by infrared absorption spectroscopy,[1-7] it was found that the effect of the particle size of inorganic powders is remarkable in its quantitative measurement. The effect is, of course, also connected with the physical properties of iron and steel as well as with the quantitative investigation of these substances. One effect of the particle size in the infrared spectra of inorganic powders had already been studied by the Liege investigators,[8-10] who proposed a theoretical formula. At that time, it was, however, difficult to separate inorganic powders into different particle sizes according to the order of micron. Lejeune and co-worker[8] identified each particle size of powders by means of a microscope. Since then, the problem on the particle size has not been discussed, because no

*1 Infrared Absorption Spectra and its Application to the Studies on Iron and Steel. Part VII. Part VI of this series: Ō. Kammori, K. Sato and F. Kurosawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **72**, 1258 (1969).

*2 Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

1) Ō. Kammori, N. Yamaguchi and K. Sato, *Bunseki Kagaku (Japan Analyst)*, **16**, 1050 (1967).

2) K. Sato, F. Kurosawa, N. Yamaguchi and Ō. Kammori, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 208 (1968).

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4) Ō. Kammori, I. Taguchi and K. Sato, *J. Japan Inst. Metals*, **32**, 634 (1968).

5) Ō. Kammori, N. Yamaguchi, K. Sato and F. Kurosawa, *ibid.*, **32**, 779 (1968).

6) Ō. Kammori, K. Sato and F. Kurosawa, *Bunseki Kagaku (Japan Analyst)*, **17**, 1270 (1968).

7) Ō. Kammori, K. Sato and F. Kurosawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **72**, 1258 (1969).

8) R. Lejeune and G. Duyckaerts, *Spectrochim. Acta*, **6**, 194, (1954).

9) G. Duyckaerts, *ibid.*, **7**, 25 (1955).

10) Mille. J. Bonhomme, *ibid.*, **7**, 32 (1955).

technique for separating powders has been developed.

A new method of separating particles with ultrasonic waves was recently developed in our laboratory,[11] and it was applied to the study of the effect of the particle size on the infrared spectra of inorganic powders. The present paper will describe the variation in the absorption bands in the infrared spectra of several inorganic powders separated by means of the new screening method mentioned above.

Experimental

Materials. Three inorganic powders, α-SiO_2, $CaCO_3$, and α,β-Si_3N_4, were used as samples, since they have more absorption bands than the other metal oxides, carbides, nitrides and sulfides reported on in our previous papers.[1,6)]

Separation of Powders with Particles of Different Sizes. The three inorganic powders were separated into each particle size according to the order of micron by means of a new apparatus with ultrasonic waves developed in our laboratory.[11] The outline of the technique is as follows. The inorganic powders used are uniformly suspended in methanol with ultrasonic waves and are then filtered with metal sieves. In this experiment, the powdered samples were separated into four particle sizes by using sieves of 2, 10, and 20 μ. A micrograph of the 5 μ sieve is shown in Photo. 1.

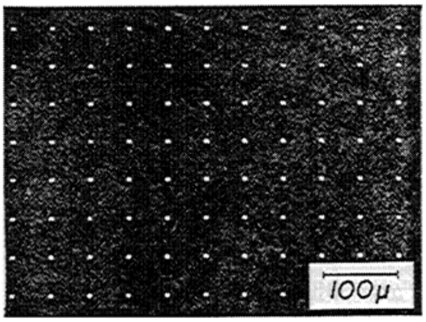

Photo. 1. An exampe of 5 μ sieve used in this experiment.

Measurement. The spectra were obtained using a Perkin Elmer model 521 grating spectrometer with the KBr disk technique over the 400—1400 cm^{-1} region. The KBr powders were prepared by pulverizing single crystals into particle sizes smaller than 300 mesh, and the amount of KBr in the disk for one sample (about 0.5 mg) was unified to 300 mg in a disk preparation. The disk prepared was about 1 mm thick and 13 mm in diameter.The thickness of the disk was not measured exactly in this experiment. We spent 15—20 min mixing inorganic powder with KBr powder in an agate mortar, according to the method described in our previous papers.[5,7]

Results and Discussion

The micrograph of $CaCO_3$ separated into four ranges of particle sizes by the screening method with ultrasonic waves is shown in Photo. 2 as an example. It seems to be nicely separated by particle size. The infrared spectra of $CaCO_3$ for each particle size are shown in Fig. 1, which shows that each absorption band becomes sharper and its spectral intensity stronger as the particle size becomes smaller. Figure 2 shows the variation in the infrared spectrum for each particle size of α-SiO_2. The absorption band at about 800 cm^{-1} hardly splits at all in the larger particle size, while it separates remarkably into two bands in the sizes smaller than 2 μ. For the 460 cm^{-1} band with a shoulder at 512 cm^{-1} in the sample of a particle size larger than 2 μ, the 512 cm^{-1} band is separated remarkably

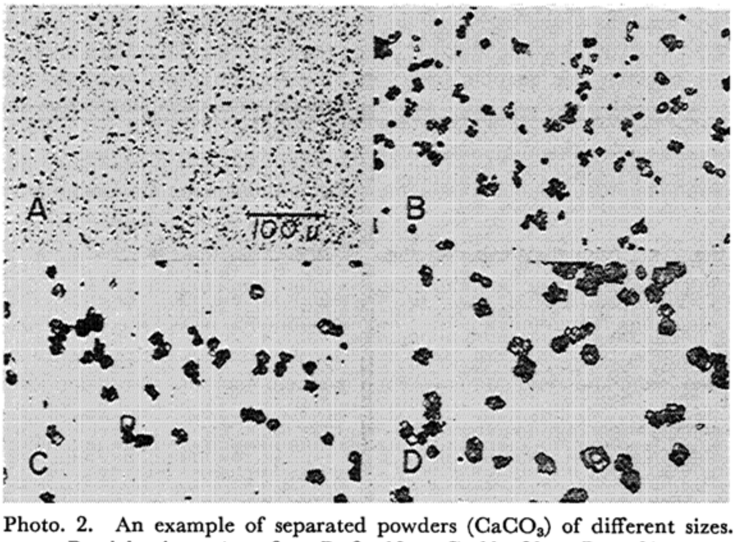

Photo. 2. An example of separated powders ($CaCO_3$) of different sizes.
Particle sizes: A, $<2\,\mu$ B, 2—10 μ C, 10—20 μ D, $>20\,\mu$

11) Ō. Kammori, I. Taguchi and K. Takimoto, *J. Japan Inst. Metals*, **33**, 669 (1969).

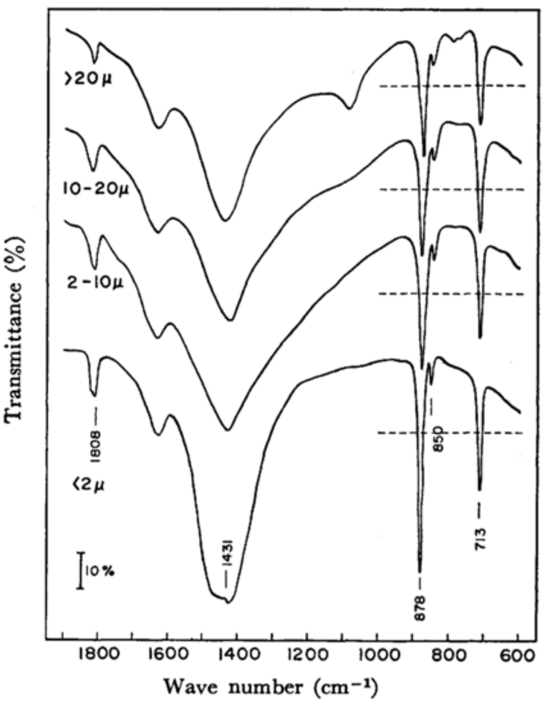

Fig. 1. Infrared spectrum of $CaCO_3$ with particles of different size.
---- : 50% transmittance line

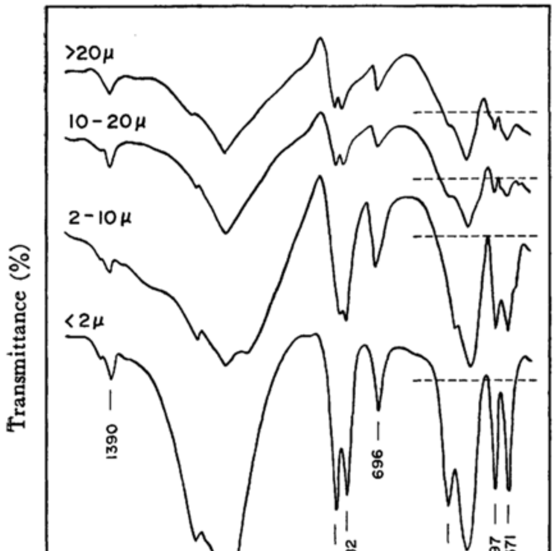

Fig. 2. Infrared spectrum of α-SiO_2 with particles of different size.
---- : 50% transmittance line

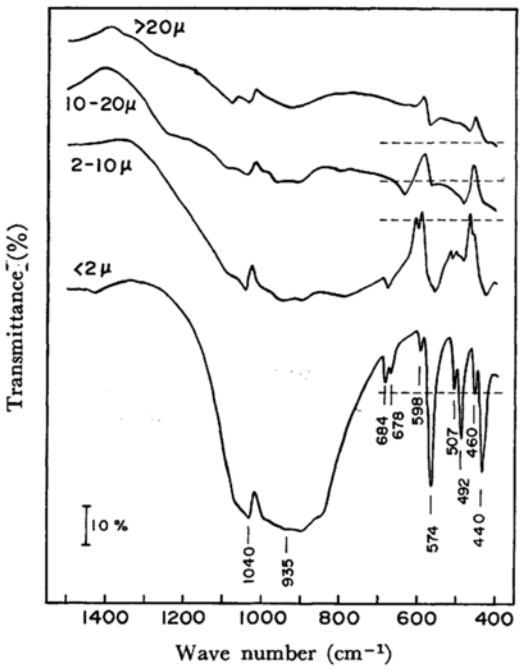

Fig. 3. Infrared spectrum of α,β-Si_3N_4 with particle of different size.
---- : 40% transmittance line

in the particles smaller than 2 μ. We observed a similar phenomenon for the 371 and 397 cm^{-1} bands. Si_3N_4 cannot be separated into α- and β-forms, so it was used as a mixture. The variation in the infrared spectra in each particle size of α,β-Si_3N_4 is shown in Fig. 3. In the case of larger particle sizes, each absorption band is hardly split at all, while the separation of each band is fine in the sizes less than 2 μ.

In the infrared spectra of inorganic powders, each absorbance at characteristic absorption bands varies according to its particle size, as has been mentioned above. In general, the smaller the particle size, the larger its absorbance. In some particles of the smaller size, it seems that the tendency of absorbance becomes definite; this finding agrees with Duyckaerts'.[9] In the separation of each particle size of a mixture, there is still a difference in the particle size of each component. Therefore, when a mixture involves substances in different particle-size meshes, the spectrum for each mesh may show something unusual. The corresponding examples are the 1090 cm^{-1} band in the spectrum of 2μ up-separated $CaCO_3$ and the 1030 cm^{-1} band in α-SiO_2 with sizes between 2 and 10μ. Accordingly, we must pay attention to the point of the spectral abnormality. At the same time, it is indispensable that a sample be very pure in a study of the variation in the infrared spectrum for inorganic powders of different particle sizes.

On the other hand, it is very useful to separate powders into each size of particle when the iron ores, the corrosion product of steel, and the non-metallic inclusion in steel are used as the samples for separation. In the present technique, only the sieves with meshes larger than 2μ can be manufacutured; it is difficult to make a mesh less than this size.

In any case the study of infrared spectra by the separation of powders into each particle size is important not only for a quantitative analysis but also for a study of the properties of an inorganic substance.

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