Research on the Influence of Calcination Temperature on the Content of Free Silicon Dioxide in Dust

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Abstract. In order to verify the oxidation of silicon to silicon dioxide during the calcination process of silica containing dust, silicon powder and monocrystalline silicon were calcined at different temperatures. The sample was analyzed using Fourier transform infrared spectroscopy (FTIR) and compared with the FTIR spectrum of the silica standard. The results show that the antisymmetrical stretching vibration, symmetrical stretching vibration and bending vibration absorption peak of Si-O-Si were obviously in the FTIR spectra of silicon powder and monocrystalline silicon calcined at 750°C. The positions of those absorption peaks correlate broadly with the absorption peaks of standard silica. It is concluded that when the calcination temperature was above 750°C, elemental silicon would be oxidized to silica at different levels, which would cause a higher silica content detected in dust.

Key words: Influence; Calcination temperature; FTIR spectra; Silica, Silicon.

1. Introduction

In silicon industry, it is necessary for occupational health monitoring to detect the free silica content of the dust in the workplace, as the free silica content is an important indicator to determine if the dust contains silica. The silica dust containing silicon will, in most cases, be collected during sample collection. The silicon can react with oxygen to generate silica because of its active chemical properties. According to national standard (GBZ/T192.4-2007)[1], free silica was detected by a pyrophosphoric acid method. The sample must be calcined at a high temperature by this detection method, if the dust contains silicon, the free silica content detected will become higher because that the silicon in dust will react with oxygen to generate silica at a high temperature during the detection process, which will affect the evaluation of occupational disease hazardous factors. According to the literature[2], the possibility that silicon oxidized to silica at a high temperature can be deduced by a gravimetric method, but the composition of products calcined at high temperatures were not detected.

Fourier transform infrared spectrometer is one of the most powerful tools to study molecular structure and analyze chemical composition with, many advantages including accurate detection, high measurement speed and low noise, etc. Because every material has its specific composition and structure, possess a unique infrared absorption spectrum. According to these characters, the substance can be accurately detected. The infrared absorption spectrum characteristics of silicon powder and monocrystalline silicon powder calcined at different temperatures were studied by the KBr disc technique in this paper.

Yu G et al.[3] reported that the infrared absorption spectrums of silica formed at different temperatures are not identical. Chen H et al.[4] found that the silica from eight different sources with different formation mechanisms or synthetic methods have their own characteristic spectrum. By comparison, three kinds of absorption peaks are found: the antisymmetrical stretching vibration absorption peak of Si-O-Si in 1300~1000cm−1, the symmetrical stretching vibration absorption peak of Si-O-Si at around 800cm-1 and the bending vibration absorption peak of Si-O-Si at around 500cm-1. Moreover, the antisymmetrical stretching vibration absorption peak as the characteristic peak of silica is sharp, and its intensity is larger, the symmetrical stretching vibration absorption peak and bending vibration absorption peak as the correlation peaks of silica are weak, and their intensity is smaller. The characteristic peak and the correlation peaks are related to each other. In this study, the calcination experiments of silicon powder and monocrystalline silicon at different temperatures were carried out. The samples were analyzed by Fourier transform infrared spectroscopy (FTIR) and compared with the FTIR spectra of silica standard.

2. Experiments

Base on the national standard (GBZ/T192.4-2007), the heat treatment temperature for detecting free silica is 550oC by the infrared spectrophotometry method and 800~900oC by the pyrophosphoric acid method, respectively. Therefore, the heat treatment temperatures were selected at 550oC, 650oC, 750oC, 850oC and 950oC, respectively in this study. The heat treatment time is 1h. Compared with the infrared absorption spectrums of samples calcined at different temperatures, uncalcined samples and silica standard, it can be verified whether silicon is oxidized to silica.

Infrared absorption spectra were characterized by the KBr (SP, Tianjin Ruian Technology Co., Ltd) disc technique using the Fourier Transform Infrared Spectrometer (IR-960, Tianjin Ruian Technology Co., Ltd). The resolution of the instrument is 4cm-1, the counts of scanning is 32 times. The silicon powder (99.99%, Shandong Xiya Chemical Industry Co., Ltd) or monocrystalline silicon (Hebei Ningjin Songgong Electronic Material Co., Ltd) or silica (Standard, Tianjin Ruian Technology Co., Ltd) must be mixed with KBr to form a disc with the diameter of 13mm and the thickness of 0.5mm.

3. Results and discussions

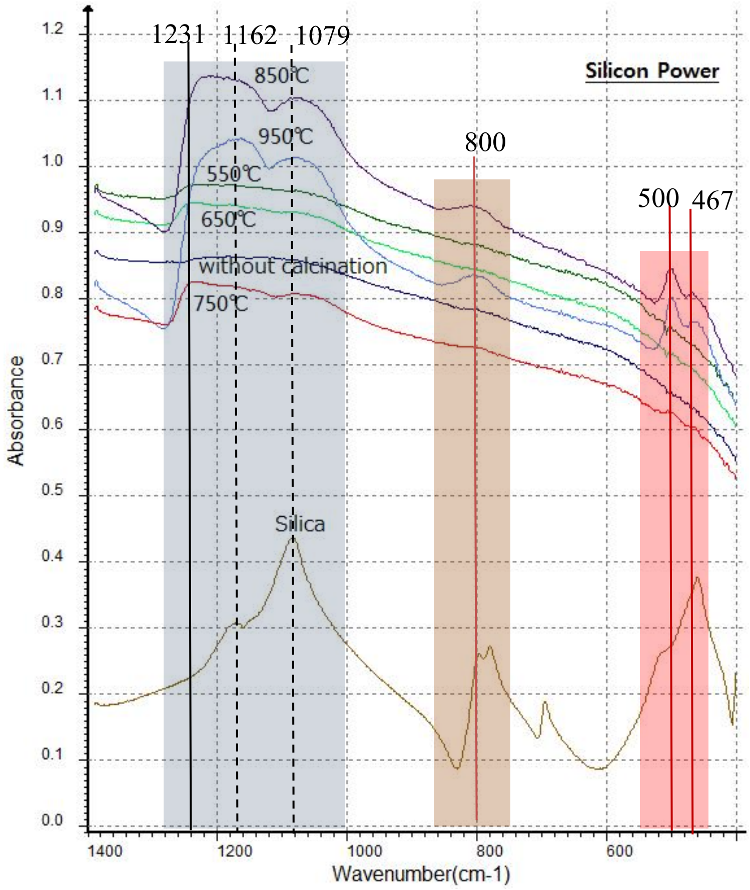

Fig.1 FTIR spectra of silica powder calcined at different temperatures

From Fig.1, it can be seen that three vibration absorption peaks of silicon powder at three absorption regions had obvious changes with the increasing heat treatment temperature.

The antisymmetrical stretching vibration absorption peak of Si-O-Si rises with the increasing calcination temperature in 1300~1000cm-1. When silicon powder was calcined at 550oC, 650oC and 750oC, a broad and weak antisymmetrical stretching vibration absorption peak of Si-O-Si occurs at 1231cm-1, when the calcination temperature reaches to 850oC, the absorption peak is split into two peaks and the peaks had shifted, and then the left peak shifts to 1210cm-1. The temperature continues to rise to 950oC, the left peak shifts to 1162cm-1, and the two peaks are consistent with the antisymmetrical stretching vibration absorption peaks of Si-O-Si in the FTIR spectra of silica standard.

Compared with uncalcined silicon power, the symmetrical stretching vibration absorption peak of silicon power calcined at 750oC appears at 800cm-1. When the calcination temperature reaches to 850oC, and the absorption peak becomes broad and weak. Similarly, the symmetrical stretching vibration absorption peak of Si-O-Si in the FTIR spectra of silica standard also occurs at 800cm-1.

The change of the bending vibration absorption peak of Si-O-Si at 500cm-1 with the increasing calcination temperature is consistent with that of the symmetrical stretching vibration absorption peak of Si-O-Si at 800cm-1. When the calcination temperature is 750oC, there is less obvious absorption peak near 500cm-1. When the calcination temperature reaches to 850oC, two very sharp absorption peaks appear at 500cm-1 and 467cm-1, which are consistent with the bending vibration absorption peaks of Si-O-Si in the FTIR spectra of silica standard, though the shape of peaks are different, and the peak in the FTIR spectra of silica standard at 500cm-1 is a shoulder peak.

Compared with the FTIR spectra of silica standard, all of three types of vibration absorption peaks began to appear and is becoming more apparent over 750oC, and the absorption peaks are consistent with those of silica standard, it can show that silicon powder turned into silica.

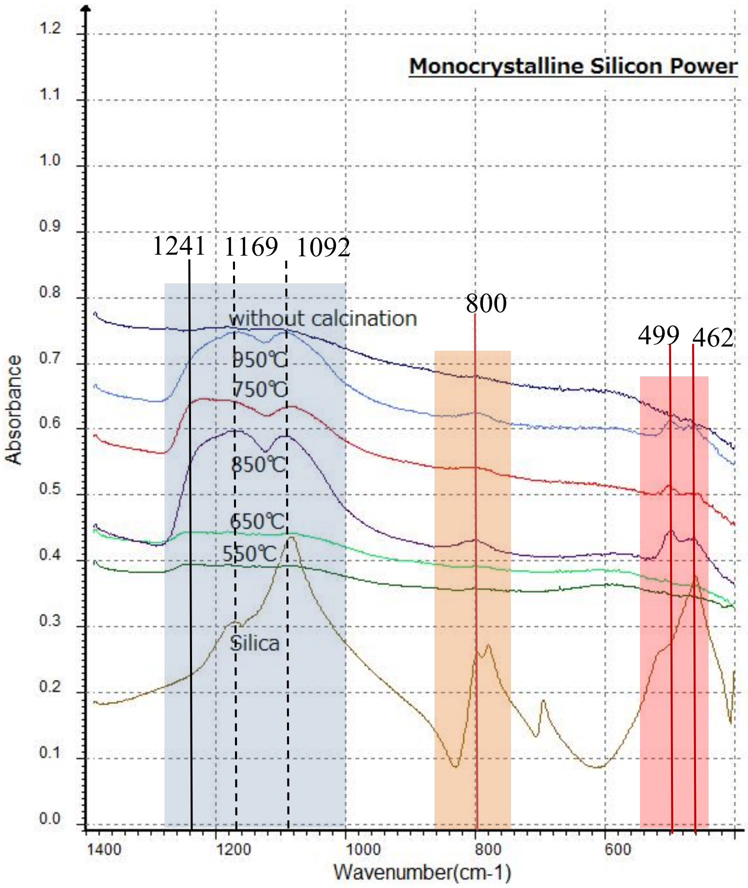

Fig. 2 FTIR spectra of monocrystalline silicon powder calcined at different temperatures

From Fig.2, it can be found that the changing trend of vibration absorption peaks with increasing calcination temperature is consistent with silicon powder.

The antisymmetrical stretching vibration absorption peaks of Si-O-Si in FTIR spectra of monocrystalline silicon power began to appear with the increasing calcination temperature in 1300~1000cm-1. Compared with silicon powder, when monocrystalline silicon power is calcined at 550oC or 650oC, a broad and weak antisymmetric stretching vibration absorption peak of Si-O-Si appears at 1241cm-1, when the calcination temperature reaches to 750oC, the absorption peak is split to two peaks. The left absorption peak shifts to low wave number region, and it is from 1241cm-1 at 550oC and 650oC to 1216cm-1 at 750oC, and then to 1169cm-1 at 850oC and 950oC. By contrast, the right absorption peak shifts gradually to high wave number, and it is from 1082cm-1 at750oC to 1092cm-1 at 850oC and 950oC. The two peaks are consistent with antisymmetric stretching vibration absorption peaks of Si-O-Si in FTIR spectra of silica standard.

The symmetrical stretching vibration absorption peak at 800cm-1 began to appear at 750oC, and form gradually two broad and weak peaks at 850oC and 950oC. Similarly, the peaks can be found at 800cm-1 in FTIR spectra of silica standard.

The bending vibration absorption peak at 499cm-1and the symmetrical stretching vibration absorption peak at 800cm-1 in FTIR spectra of monocrystalline silicon power have the same trend with the increasing calcination temperatures, respectively. The difference with FTIR spectra of slicon power is that the bending vibration absorption peak of Si-O-Si in FTIR spectra of monocrystalline silicon power can appear at lower temperature, when the calcination temperature is 750oC, the peaks are obvious, larger intensity and very sharp. Similarly, two peaks are consistent with the antisymmetrical stretching vibration absorption peak of Si-O-Si in FTIR spectra of silica standard.

Comparing above three types absorption peaks of monocrystalline silicon powder with silica standard, it can be found that when monocrystalline silicon powder was calcined at above 750oC, all absorption peaks of Si-O-Si began to appear and became obvious gradually. The peaks are consistent with the FTIR spectra of silica standard demonstrating, that monocrystalline silicon turned into silica.

It is noticed that the antisymmetric stretching vibration absorption peak of Si-O-Si in 1300~1000cm-1 is becoming more obvious with the increasing calcination temperature, and the absorption peak is split gradually from a single broad and weak absorption peak into two strong absorption peaks. It was attributed to Fermi Resonance during calcination process, when one type vibration overtone is near another type vibration base band, the vibration coupling can be generated and form strong absorption peak or spectral peak splitting, which will form two stronger absorption peaks. Additionally, the spectral bands of silicon powder did not begin to change until the calcination temperature exceeding 850oC, and the spectral bands of monocrystalline silicon power begin to change at 750oC. This is due to the spectral band shape related to crystallinity[5]. The crystallinity can change vibration frequency, and then cause a change of spectral band shape.

4. Summary

The silicon powder and monocrystalline silicon powder calcined at different temperatures were detected by Fourier transform infrared spectroscopy and compared with the silica standard.The results indicate that whether it is calcined silicon containing dust or monocrystalline silicon power, the final product will be oxidized to form silicon dioxide at high temperatures. Moreover, the extent of oxidation is more obvious at 850oC. Accordingly, the temperature design of 800~900oC is inappropriate in the standard method of the free silica content detected by the pyrophosphoric acid method. If the dust contains silicon, the free silica content detected will be higher because that silicon of dust will react with oxygen to generate silica resulting in an overestimation of the actual values. Therefore, the calcination temperature should be corrected. On the contrary, free silica content detected at 550oC by infrared spectrophotometry is more reasonable and this method can exactly detect the silica content of dust.

Acknowledgements

Doctoral Initiation Project: 19BS002; 19BS003

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