Monitoring Chemical Reactions in the Solid State by EXAFS Spectroscopy: Study of the Fe–Si Binary System

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Chemical reactions of the transition metal–silicon systems are of great interest because of their applicatons in electronic devices and composite materials.[1-3] They also represent a typical reaction process in the solid state,[4] which in general is not fully understood.[5] The Fe–Si reaction couple is one of the systems that have been studied extensively.[6-19] Nevertheless, many kinetic properties and microscopic details of the reaction are unknown. Synchrotron radiation is a powerful tool for investigating bonding and atomic arrangement of crystalline and amorphous solid state materials.[20] In this contribution we report a study of the solid state reaction of the Fe–Si binary system using synchrotron radiation. We monitored the charge transfer and making and breaking of bonds in the Fe–Si binary reaction system by measuring the change of the X-ray absorption fine structure (EXAFS) of the Si K-edge.

Fe and Si powders (>99.9%, Strem) were mixed in 1:1 molar ratio (total weight, 1.803 g) and placed in a quartz ampule. The ampule was sealed under a vacuum of 10^{-4} Torr. A computer-controlled furnace was used to heat the ampule to a final temperature T_f in 1 h. The ampule was then quickly removed from the furnace and quenched to room temperature in air. The ampule was opened, and the power sample was ground again and mounted on a sample holder immediately prior to the Si K-edge absorption measurement. The Si K-edge absorption spectra were recorded at the Canadian Synchrotron Facility at the Synchrotron Radiation Center of the University of Wiscon-

Figure 1. Absorption edge of the Si K-shell in the binary Fe–Si reaction system at various final reaction temperatures.

sin. A double crystal monochromator was employed. The peak positions were accurate within 0.1 eV.

Figure 1 is the Si 1s electron absorption edge (K-edge) of the binary reaction system heated to various final temperatures. It shows that the absorption edge shifts to a higher energy value as the final temperature of the chemical reaction increases. At room temperature (25 °C), there is obviously no reaction; the absorption edge (~1840 eV) is simply that of pure, elemental Si. At higher temperatures, the chemical reaction proceeds at a faster rate, and a larger amount of the reactants becomes metal silicide. The shift of the absorption edge can be caused by either a charge transfer from Si to Fe or a move of empty p states to higher energy. In the case of a charge transfer, the excitation of a K-shell electron requires higher energy, thus the absorption edge moves to a higher energy value. Our extended Hückel calculation supports the charge transfer mechanism.[21]

Because the intensity is measured as the total electron yield, the choice of zero and scale is arbitrary. Therefore, we can normalize the intensity of peak B such that it is 0 at 25 °C and 1 at 1250 °C. The intensity should then relate to the molar fraction of the product (metal silicides), x, assuming $x = 0$ at 25 °C and $x = 1$ at 1250 °C. Similarly, we can correlate the normalized intensity of peak A to $1 - x$, i.e., the amount of the reactant (Si). Figure 2 shows the change of x calculated from the intensities of peaks A and B, as a function of the final reaction temperature. In this figure, the most dramatic change occurs between 800 °C and 900 °C. This is an indication of a phase transition in this temperature range. This temperature range is the region in which FeSi and Fe_5Si_3 are stable in the equilibrium bulk phase diagram.[22,23] The discrepancy between peak A and peak B is likely due to the background noise in peak A region when the intensity of this peak reduces to zero at high temperatures.

We can also try to fit the data into a kinetic model A → B, where A is the reactant (elemental Si) and B is the product (metal sicilides). A first-order reaction, for example, will be described by the equation $dx/dt = k(T)(1 - x)$. $k(T)$ is the rate constant and is related to the activation energy through the equation $k = C \exp(-E/RT)$ in the transition state theory, where

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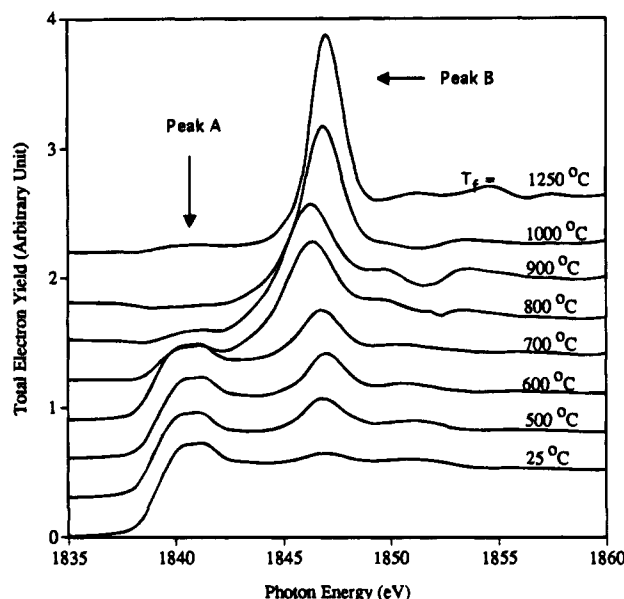(20) Teo, B. K.; Joy, D. C. *EXAFS Spectroscopy Techniques and Applications*; Plenum: New York, 1979.

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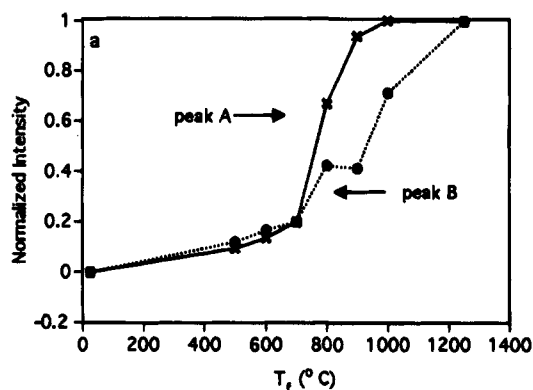(23) Hansen, M. *Constitution of Binary Alloys*; McGraw-Hill: New York, 1958.

Figure 2. Normalized peak intensity as a function of the final reaction temperature in the Fe—Si reaction system. Peak A in Figure 1 is normalized to $1 - x$ and peak B to x, with $0 \leq x \leq 1$.

C is the preexponential factor and R the gas constant. Since the reaction couple was heated from room temperature to a final temperature T_f with a given heating rate, we can integrate the rate equation over the temperature range and relate the molar fraction of the product (x) to the activation energy (E). If the activation energy E is much larger than RT, as is the case for most high-temperature solid state reactions, the rate will be dominated by the final temperature T_f. For a first-order reaction, for instance, the relationship between x and T_f is $\ln[\ln(1/1 - x)] \propto -E/RT_f$.

The data, however, do not fit into a single-step kinetic model, whether it is a zeroth-order, first-order, second-order, or diffusion-controlled ($dx/dt = k/x$), when we use the x calculated from peak A, peak B, or the average of the two peak intensities. It is likely the reaction proceeds in two or more stages with a phase transition between 800 °C and 900 °C. Under this assumption, the data can be best fitted to a first-order model.

The EXAFS region of the absorption spectra can be Fourier-transformed to yield the radial distribution of the neighboring atoms of the absorber (Si). Figure 3 shows the Fourier transform of the EXAFS of the reaction system heated to several final temperatures. At 25 °C, the peak at 2.1 Å (peak II) is the first coordination shell of Si. The Si—Si distance is 2.35 Å in crystalline Si; however, EXAFS is known to underestimate the bond distance by up to 0.5 Å when the data are not filtered. As temperature increases, a second peak (peak I) at a smaller distance emerges, which can be identify as the Fe—Si bond in FeSi, which is shorter (2.1 Å) than the Si—Si bond. FeSi is known to be the first phase formed.[24] At 1250 °C, peak II vanishes, indicating that most Si—Si bonds are broken. It is

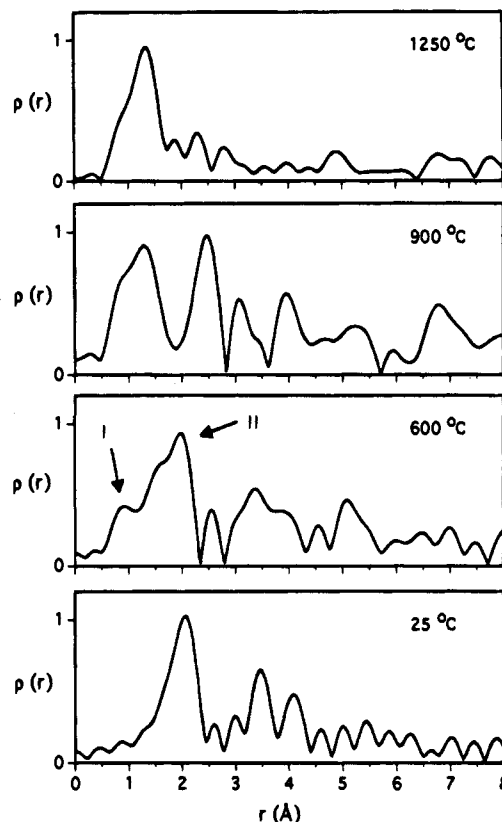(24) Walser, R. M.; Bené, R. W. *Appl. Phys. Lett.* **1976**, *28*, 624.

Figure 3. Fourier transform of the EXAFS of the Fe—Si reaction system at several final temperatures. Peaks I and II can be identified as Fe—Si and Si—Si bonds.

also interesting to note that a third peak around 2.5—3 Å appears at 600 °C and persists until after 900 °C. It may be associated with the Si—Si bond (~2.8 Å) in the second coordinate sphere of Si in FeSi and Fe_5Si_3.

Understanding thermodynamic and kinetic aspects helps chemists to design best reaction conditions (temperature, pressure, etc.) for solid state synthesis. EXAFS spectroscopy is a useful tool in this aspect, especially in the case where the reaction intermediate is amorphous. From our study, the reaction temperature for the Si—Fe system should be above 800 °C in order to achieve a faster rate.

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