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# HIGH-TEMPERATURE TRANSFORMATION OF ASBESTOS TAILINGS BY CARBOTHERMAL REDUCTION

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**Abstract**—The production and industrial use of asbestos cement and other asbestos-containing materials have been restricted in most countries because of the potential detrimental effects on human health and the environment. Chrysotile is the most common form of asbestos and investigations into how to recycle this serpentine phyllosilicate mineral have attracted extensive attention. Chrysotile asbestos tailings can be transformed thermally, at high temperature, by *in situ* carbothermal reduction (CR). The CR method aims to maximize use of the chrysotile available and uses high temperatures and carbon to change the mineral form and structure of the chrysotile asbestos tailings. When chrysotile asbestos is employed as the raw material and coke (carbon) powder is used as the reducing agent for CR transformation, stable, high-temperature composites consisting of forsterite, stishovite, and silicon carbide are formed. Forsterite ($Mg_2SiO_4$) was the most abundant crystalline phase formed in samples heat treated below 1500ºC. At 1600ºC, forsterite was exhausted through decomposition and β-SiC formed by reduction of stishovite. A larger proportion of β-SiC was generated as the carbon content was increased. This research revealed that both temperature and carbon addition play key roles in the transformation of chrysotile asbestos tailings.

**Key Words**—Asbestos Tailings, Carbothermal Reduction, Chrysotile, Forsterite, Thermal Transformation, Silicon Carbide.

## INTRODUCTION

Chrysotile, $Mg_3[Si_2O_5](OH)_4$, is considered to be a serpentine (curly) form of asbestos and is classified in the kaolin/serpentine clay mineral group with a 1:1 layer structure. The theoretical composition of chrysotile is MgO 43.0 wt.%, $SiO_2$ 44.1 wt.%, and $H_2O$ 12.9 wt.%. Chrysotile asbestos is a monoclinic serpentine-group mineral with a fibrous layer structure. It is a hydrated magnesium silicate consisting of sheets of silica tetrahedra linked to trioctahedral sheets of magnesia. Furthermore, trioctahedral-site occupancy causes the bilayers to curl into cylindrical rolls (Brindley and Brown, 1984; Auzende *et al.*, 2004).

Chrysotile has been used widely in industry in the production of asbestos cement and other asbestos-containing materials (*e.g.* insulation, fire-retardants, floor tiles, and roofing products) (Porcu *et al.*, 2005; Colangelo *et al.*, 2011). In light of the potential detrimental effects on human health caused by chrysotile asbestos, the World Health Organization (WHO) has classified all types of asbestos as carcinogenic to humans and restricts use of asbestos in structural materials (Nishikawa *et al.*, 2008). In addition, chrysotile asbestos tailings are also considered to be an environmentally destructive mineral waste. Because chrysotile is associated with coexisting gangue minerals and impurities, much of the available chrysotile material has a variable mineral composition which limits potential uses (Li *et al.*, 2012). A large amount of discarded chrysotile asbestos tailings exists, therefore, and has caused considerable environmental problems and may also have jeopardized human health. Appropriate chrysotile treatment prior to disposal in landfill sites is clearly of great importance (Gidarakos *et al.*, 2008).

Research concerning the modification (Papirer *et al.*, 1976; Valentine *et al.*, 1983; Mendelovici *et al.*, 2001; Zaremba and Peszko, 2008) and reutilization (Porcu *et al.*, 2005; Colangelo *et al.*, 2011) of asbestos has attracted a great deal of attention over the last few decades. The mineralogical and morphological transformation of chrysotile asbestos (Murphy and Rose, 1977; Gualtieri *et al.*, 2008a, 2008b, 2012; Zaremba *et al.*, 2010) is a promising and widely developed research solution for the 'asbestos problem'. Investigation of the recycling of chrysotile asbestos in various fields has made it a very important topic of research. For instance, studies have shown that high-grade chrysotile asbestos can be used to produce pure magnesium compounds or hydrated silica (Kim and Chung, 2003; Wypych *et al.*, 2005; Cheng and Hsu, 2006; Wang *et al.*, 2006). Other researchers have tried to use asbestos as a fused magnesium phosphate (fertilizer) additive (Huang, 1953), for stearic acid adsorption (Berkheiser, 1982), for carbon dioxide sequestration (Schulze *et al.*, 2004; Lin *et al.*, 2008; Pronost *et al.*, 2012), and even as a lubrication additive (Foresti *et al.*, 2003; Lyubimov *et al.*, 2011; Qi *et al.*, 2012).

In the present study, research was undertaken to better understand the mineralogical transformation of chrysotile asbestos tailings at high temperature. The

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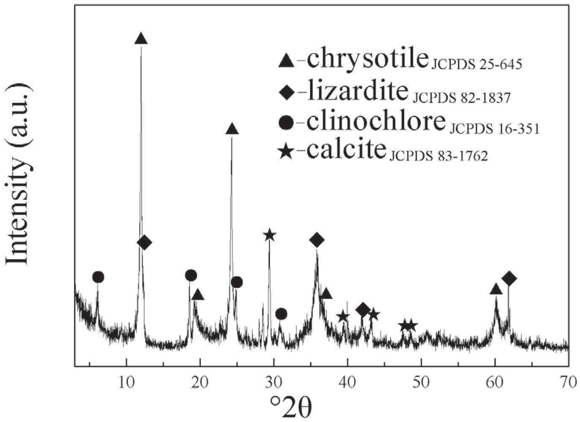


Figure 1. XRD pattern of untreated chrysotile asbestos tailings showing mineral phases.

effects of both temperature and the addition of a reductant on the mineral phases in chrysotile asbestos tailings were examined using the *in situ* CR method. By CR, the mineralogy and morphology of natural asbestos were changed to a high-temperature, stable, and harmless silicon carbide (β-SiC). The simple CR method used here may also produce forsterite/SiC/$SiO_2$ raw powders for use in refractories. The present study provides a theoretical basis for production of a forsterite/SiC-based refractory, and also provides a new perspective on high-efficiency chrysotile tailings use in the high-temperature industry.

## MATERIALS AND METHODS

Chrysotile asbestos tailings were collected from an open-pit serpentine mine in Jiangsu Province, China. The chemical composition measured was: 45.79% $SiO_2$, 39.08% MgO, 7.42% $Fe_2O_3$, 5.74% CaO, 1.02% $Al_2O_3$, 0.36% $Cr_2O_3$. X-ray powder diffraction (XRD) (Figure 1) indicated that chrysotile, lizardite, some clinochlore, and minor calcite were the mineral phases present.

The starting powder was passed through a sieve (mesh number 180) for the <0.088 mm chrysotile and through another sieve (mesh number 200) for the <0.074 mm carbon powder. The powders were mixed in a planetary ball mill (QM-WX4, NanDa Instrument Plant, Nanjing, China) for 2 h at a rotation speed of 200 rpm/min in order to achieve an homogenous mixture of the powders. The quantities used were dictated by the theoretical stoichiometry and other experiments were performed using 10, 50, and 100 wt.% excess of the theoretically established amount of coke required. Theoretical stoichiometry is defined by the proportions of chrysotile and carbon coke, with the $SiO_2$ component taken into consideration in the calculation (equation 1). The theoretical carbon value refers to the carbon content required by assuming that the $SiO_2$ component is completely reduced to silicon carbide based on the reaction

$$SiO_2 + 3C = SiC + 2CO \quad (1)$$

Based on these parameters, the proportions of chrysotile and carbon coke used in the experiments were calculated according to the theoretical stoichiometry of $SiO_2$:C = 1:3 (molar) as in Table 1. For excess carbon conditions, 10−100% more carbon than that required by the theoretical stoichiometry was added. The mixed powders were dried and pressed uniaxially into cylindrical pellets of Φ20 mm × 10 mm under a pressure of 30 MPa. The samples were then buried in carbon coke particles (0.1−1 mm) to provide a reducing atmosphere in a multi-function furnace for 4 h at a temperature range of 1300−1600ºC.

The mineral phases in synthesized samples were characterized by XRD (XD-3, CuK$\alpha_1$ radiation, $\lambda$ = 0.15406 nm, Purkinje General Instrument Co., Ltd., Beijing, China). The microstructure of the samples synthesized was examined by means of scanning electron microscopy (SEM, JEM-6460LV, Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan). The SEM instrument was equipped with an energy dispersive spectroscopy detector (EDS, OXFORD INCA X-sight, UK).

## RESULTS

### *Synthesis-temperature effects on CR-product mineralogical transformations*

In order to investigate temperature effects on the mineralogical transformations in the final products, samples with 50 wt.% excess carbon were prepared *via* the CR method by heating at 1300, 1400, 1500, 1550, and 1600ºC for 4 h (see Figure 2). The main crystalline phase in the processed samples was forsterite ($Mg_2SiO_4$) at temperatures below 1500ºC. At 1550ºC, the diffraction intensity of stishovite was enhanced, while that of

Table 1. Starting compositions of samples with different carbon contents.

| Samples | Theoretical addition | Excess carbon (10%) | Excess carbon (50%) | Excess carbon (100%) |
|---|---|---|---|---|
| Asbestos tailings (wt.%) | 78.45 | 76.79 | 70.82 | 65.54 |
| Carbon coke (wt.%) | 21.55 | 23.21 | 29.18 | 35.46 |

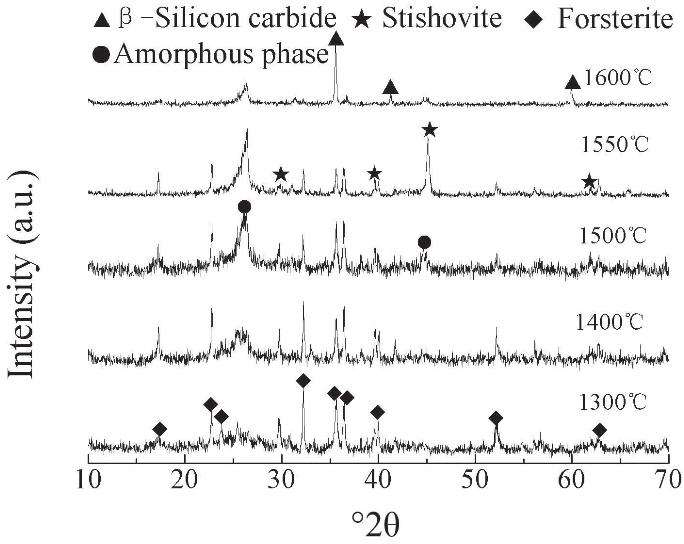


Figure 2. XRD patterns of chrysotile asbestos tailings samples mixed with 50% excess carbon and heated from 1300 to 1600ºC.

forsterite diminished. At the higher temperature of 1600ºC, stishovite and β-SiC phases both coexisted, whereas the diffraction intensity of forsterite could hardly be discerned. Remarkably, no MgO or Mg was detected in the samples.

*Effects of adding carbon coke on CR-product mineralogical transformations*

The XRD patterns (Figure 3) of samples produced after 4 h at 1600ºC in CR reactions using different amounts of carbon revealed that both $Mg_2SiO_4$ and β-SiC were formed. With increased carbon content, the β-SiC diffraction peaks became stronger while the intensity of the $Mg_2SiO_4$ peaks decreased significantly. The results suggested that $Mg_2SiO_4$ decomposes into $SiO_2$ to a greater extent and more $SiO_2$ is subsequently reduced to β-SiC. According to the XRD pattern (Figure 3) of a sample that was heated to 1600ºC with a 100% excess (*i.e.* twice the stoichimetric quantity) of carbon, the major mineral phase was β-SiC, even though a small amount of stishovite could still be detected as a remaining phase.

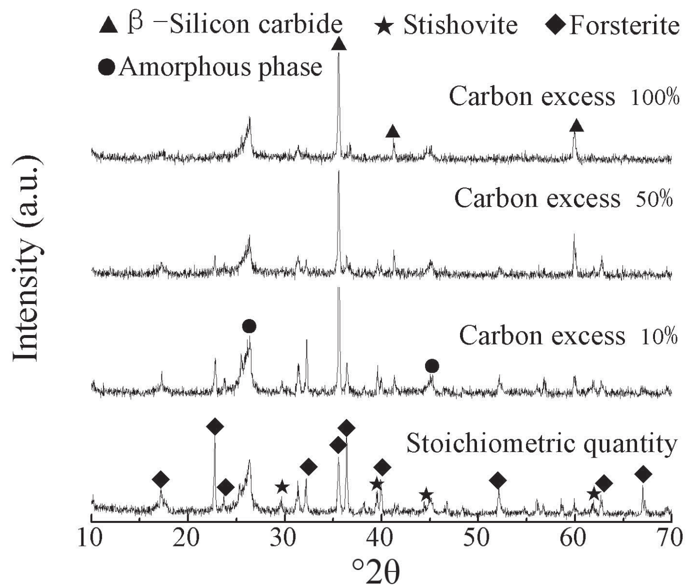


Figure 3. XRD patterns of chysotile asbestos tailings samples mixed with 0 to 100% excess carbon and heated to 1600ºC.

## DISCUSSION

### *Thermodynamic analysis of the CR process*

*Idealized thermodynamic analysis in the MgO–SiO$_2$ system.* Thermodynamic analysis was also undertaken to further verify the results above. According to the redrawn binary MgO–SiO$_2$ stability phase diagram (Figure 4) of Bowen and Anderson (1914), forsterite (2MgO.SiO$_2$) and periclase (MgO) are formed at temperatures of <1850ºC with <42% SiO$_2$. For SiO$_2$ contents of 42–59%, forsterite and clinoenstatite (MgO·SiO$_2$) form at 1500ºC and clinoenstatite melts at ~1557ºC. At temperatures <1543ºC with >59% SiO$_2$, cristobalite (SiO$_2$) and clinoenstatite coexist, but at >1543ºC clinoenstatite melts. The chrysotile asbestos tailings used in the experiment contained a greater amount of SiO$_2$, which accounted for 54% of the total magnesia and silica, calculated according to the chemical composition of the chrysotile asbestos. Based on the analyses above, forsterite and clinoenstatite will initially be expected as the main phases using the CR route. In the experiment, no sign of clinoenstatite was observed in the XRD patterns. The major mineral phases in samples heated at 1300–1550ºC were forsterite, stishovite, and an amorphous phase (Figure 2). One could assume that clinoenstatite would be unstable and formation would be limited in a complex reducing environment.

The standard Gibbs free energy of formation, $\Delta G_f^0$, at 25ºC, and the corresponding values at 1300 and 1600ºC, are given in Table 2. At temperatures between 1300 and 1600ºC, the standard Gibbs free energies of the solid and liquid states of 2MgO·SiO$_2$ and MgO·SiO$_2$ were calculated. As can be seen from the data (Table 2), (forsterite) 2MgO·SiO$_2$ (s) formation was more likely than (clinoenstatite) MgO·SiO$_2$ (s) formation under the same conditions. The following reaction for the thermal transformation of serpentine minerals to forsterite was suggested by Brindley and Zussman (1957):

$$2Mg_3Si_2O_5(OH)_4 = 3Mg_2SiO_4 + SiO_2 + 4H_2O \quad (2)$$

From the discussion above, the CR of asbestos tailings passes through two decomposition reactions in the first stage at temperatures below 1550ºC. Over the temperature range from 1300 to 1550ºC, the reaction process in the system was controlled by the decomposition of chrysotile. The decomposed products under a reducing atmosphere were mainly forsterite, an amorphous phase, and a small amount of stishovite (SiO$_2$). As temperature was increased, the forsterite generated began to decompose to stishovite and MgO. Forsterite decomposition was greatest at 1550ºC, which explained the dramatically strengthened diffraction intensity of stishovite at 1550ºC. At 1600ºC, with forsterite decomposition almost complete, the CR of SiO$_2$ took control of the second stage of the reaction, and more stishovite was reduced to SiC. At the same time, no Mg phases were detected in the XRD patterns, indicating that increased foresterite decomposition was accompanied by the loss

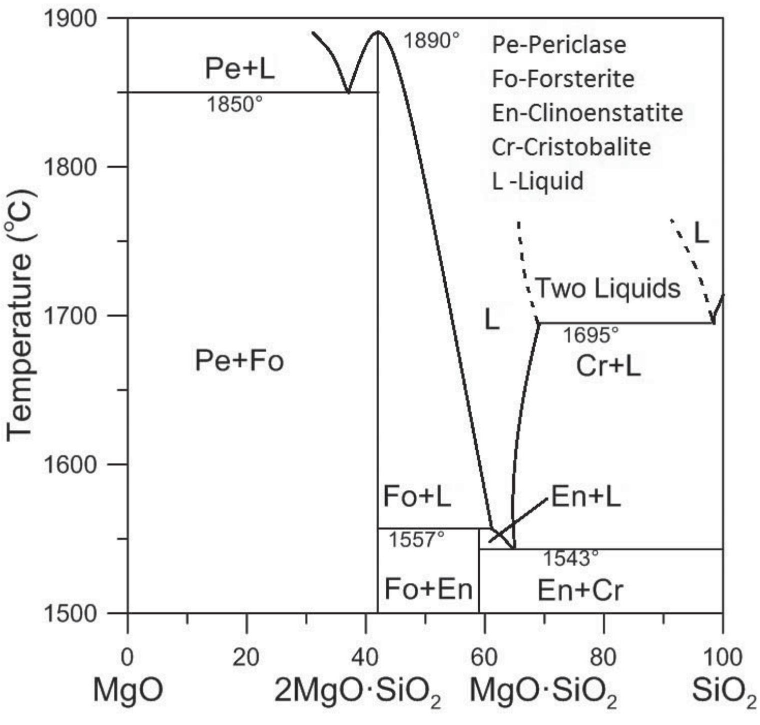


Figure 4. Stability phase diagram of the MgO–SiO$_2$ system.

Table 2. Standard Gibbs free energy ($\Delta G_f^0$) of formations at 25ºC, as well as the corresponding values at 1300 and 1600ºC.

| Chemical reactions | $\Delta G_f^0$ (J/mol) | $\Delta G_f^0$/1300ºC (J/mol) | $\Delta G_f^0$/1600ºC (J/mol) |
|---|---|---|---|
| $2MgO(s) + SiO_2(s) = 2MgO{\cdot}SiO_2(s)$ | $-67200 + 4.31T$ | −60420.4 | −59127.4 |
| $2MgO{\cdot}SiO_2(s) = 2MgO{\cdot}SiO_2(l)$ | $71100 - 32.60T$ | 19820.2 | 10040.2 |
| $MgO(s) + SiO_2(s) = MgO{\cdot}SiO_2(s)$ | $-41100 + 6.10T$ | −31504.7 | −29674.7 |
| $MgO{\cdot}SiO_2(s) = MgO{\cdot}SiO_2(l)$ | $75300 - 40.60T$ | 11436.2 | −743.8 |

of magnesium as a vapor phase. If carbon was used as a reductant under vacuum conditions, a temperature >1352ºC was required to reduce and transform pure MgO into Mg vapor (Li *et al.*, 2005). Similar results were found in other studies. For example, nitridation on SiC and talc (37% MgO) was performed by Mazzoni and Aglietti (1998) and Mg volatilization occurred at high temperatures. Furthermore, vaporization was enhanced in a reducing atmosphere with high $N_2$ flow rates. Similarly, in the research of Lou *et al.* (1985), gaseous Mg loss at high temperatures (1630ºC) was also enhanced quantitatively by MgO volatilization with the reducing gases.

*Idealized thermodynamic analysis of chemical reactions in a Si–C–O complex system.* At 1600ºC, a Si–C–O system was involved in the second stage of the CR process. In a closed system with sufficient carbon, gas-phase CO accounted for almost 100% of the gas composition. The potential phases involved in the Si–C–O system are SiO, CO, Si, $SiO_2$, and SiC.

Based on the standard Gibbs free energies of formation of the main system components (Table 3), the possible reactions, the reaction standard Gibbs free energies, and the logarithms of the SiO partial pressures (for $p_{CO} = p^0 = 1.0 \times 10^5$Pa) are as follows:

$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)$ (3)
$\Delta G_3^0 = 603150 - 331.98T$, $T \equiv = 1817$(K)

$SiO_2(s) + C(s) = SiO(s) + CO(g)$ (4)
$\Delta G_4^0 = 676720 - 330.69T$, $\ln(p_{SiO_2}/p^0) = -35349/T$ (K) + 17.274

$SiO(g) + 2C(s) = SiC(s) + CO(g)$ (5)
$\Delta G_5^0 = -73570 - 1.29T$, $\ln(p_{SiO}/p^0) = -3843/T$ (K) $-0.067$

$SiO(g) + SiC(s) = Si(l) + CO(g)$ (6)
$\Delta G_6^0 = 155239 - 75.69T$, $\ln(p_{SiO}/p^0) = 8109/T$ (K) $- 3.954$

$SiO_2(s) + SiO(g) + 3C(s) = 2Si(l) + 3CO(g)$ (7)
$\Delta G_7^0 = 758380 - 407.67T$, $\ln(p_{SiO}/p^0) = 39615/T$ (K) $- 21.295$

and

$SiO_2(s) + Si(l) = 2SiO(g)$ (8)
$\Delta G_8^0 = 635890 - 292.2T$, $\ln(p_{SiO}/p^0) = -16605/T$ (K) + 7.63

Using the thermodynamic data above, first let $\Delta G_3^0 = 0$, so that the starting reaction temperature from equation 3 can be obtained in the standard state: $T = 603150/331.98 = 1817$ K (1544ºC) (when $T \geqslant 1817$ K, with $p_{CO} = p^0 = 1.0 \times 10^5$ Pa), $SiO_2$(s) reacts with C(s) to generate SiC(s). In fact, the CR process involves a series of step-by-step reactions [equations 4 and 5], and is promoted by the reactive vapor intermediates, CO and SiO. Thus, the equilibrium partial pressure of SiO cannot be ignored. The values of $\ln(p_{SiO}/p^0)$ at different temperatures were obtained using the formula $\Delta G_f^0 = -RT\ln K^0$. According to the equilibrium relationships obtained by plotting $\ln(p_{SiO}/p^0)$ *vs.* $1/T$ (Figure 5), SiC can be synthesized at any particular temperature when CO and SiO partial pressures are sufficient. This result is in agreement with the above phase equilibrium analysis, whereupon SiC could be formed at at least 1817 K (1544ºC) under standard pressure.

Thus, in the second stage of CR at the higher temperature range (1550−1600ºC), the reduction of $SiO_2$ to β-SiC would be the dominant factor that affects the mineralogical transformation of asbestos tailings. With increased carbon contents, more of the $Mg_2SiO_4$ that is formed decomposes into $SiO_2$ and is subsequently reduced to β-SiC. Greater amounts of β-SiC can be produced by heating samples at 1600ºC for 4 h using a

Table 3. Gibbs free energies of the main components in the Si–C–O system.

| Chemical reactions | $\Delta G_f^0$ (J/mol) |
|---|---|
| C (s) + $1/2O_2$ (g) = CO (g) | $\Delta fG^0_{CO} = -114400 - 85.77T$ |
| Si (l) + $1/2O_2$ (g) = SiO (g) | $\Delta fG^0_{SiO} = -155230 - 47.28T$ |
| Si (l) + $O_2$ (g) = $SiO_2$ (s) | $\Delta fG^0_{SiO_2} = -946350 + 197.64T$ |
| Si (l) + C (s) = SiC (s) | $\Delta fG^0_{SiC} = -114400 + 37.20T$ |
| Si (l) + $O_2$ (g) = $SiO_2$ (l) | $\Delta fG^0_{SiO_2} = -921740 + 185.91T$ |

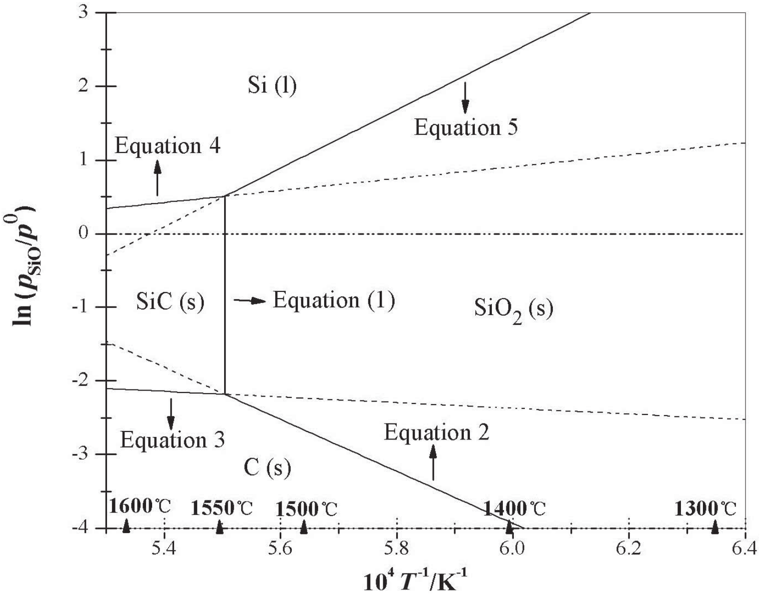


Figure 5. Stable regions of the condensed phases in Si–C–O system assuming that $p_{CO} = p^0 = 1.0 \times 10^5$ Pa.

100% excess of carbon powder (*i.e.* twice the stoichiometric quantity) as the reducing agent.

*Morphology of CR-product mineralogy by SEM*

Scanning electron microscopy (SEM) of the samples (Figure 6) revealed asbestos-like structures in a natural chrysotile (Figure 6a) that are destroyed completely (Figure 6b) after a 4 h CR treatment at 1600ºC with twice the stoichiometric quantity of carbon added to the raw samples. This may have been a consequence of both chemical and melting transformations (Porcu *et al.*, 2005), which completely altered the natural chrysotile structure. The SEM observations were consistent with the XRD patterns (Figure 3) and confirmed that the initial mixture was completely converted to β-SiC, forsterite, and stishovite. The final products had morphologies that (Figure 6b) were consistent with well formed β-SiC and an undefined form of unreacted forsterite.

## CONCLUSIONS

When chrysotile asbestos tailings were used as a raw material mixed with carbon coke powder as a reducing agent, both the temperature and the addition of carbon affected significantly the mineralogical transformation of chrysotile by CR. The CR process occurred in two stages. In the first, <1550ºC decomposition stage, natural chrysotile asbestos decomposed and generated forsterite as the major mineral phase at 1500ºC or below, while at

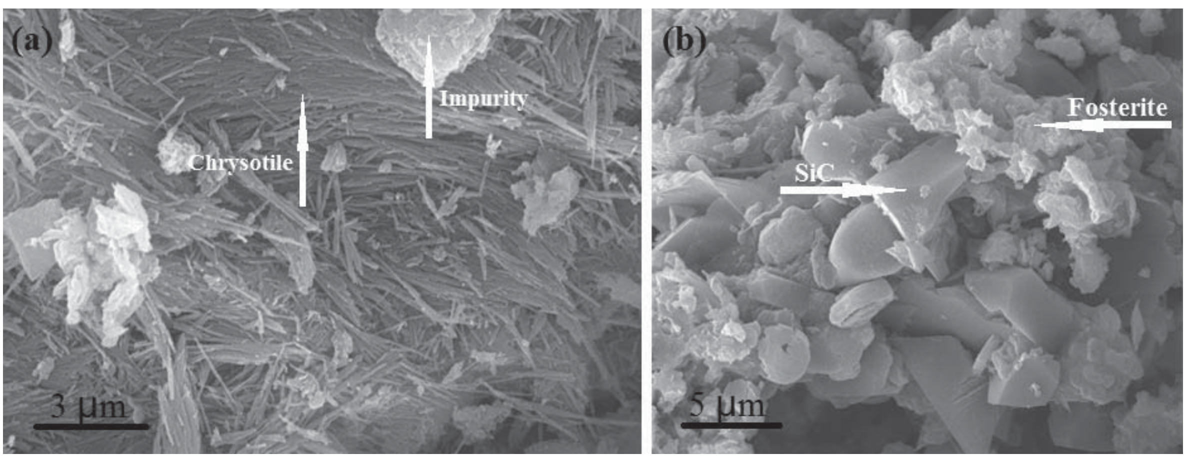


Figure 6. SEM images of (a) natural chrysotile asbestos tailings and (b) final products after heat treatment at 1600ºC for 4 h.

the higher temperature (1550ºC) the system reaction was controlled by decomposition of forsterite to stishovite with Mg lost as a vapor phase. In the higher temperature (1600ºC) reduction stage, thermal reduction of stishovite to β-SiC was the dominant process and a greater proportion of stishovite was reduced to β-SiC as the carbon content was increased. After a high-temperature CR treatment, natural chrysotile structures were replaced by more stable β-SiC and forsterite. The optimal parameters for obtaining greater amounts of β-SiC were: (1) twice the theoretically required amount of carbon powder as a reducing agent, and (2) CR heat treatment at 1600ºC for 4 h.

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