Equilibrium Phase Relations of a SiO$_2$–Al$_2$O$_3$–FeO$_x$ System with 10 wt % CaO Addition for the Production of Continuous Basalt Fibers

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ABSTRACT: The continuous basalt fibers have been regarded as one of the most promising green materials in modern society; however, key thermodynamic equilibrium data are insufficient for a better understanding of the crystallization mechanism during the fiber forming process. In the present study, the equilibrium phase relations of the core SiO$_2$–Al$_2$O$_3$–FeO$_x$ subsystem with fixed 10 wt % CaO were experimentally determined using the classic equilibrium-quenching technique with the scanning electron microscopy–energy-dispersive X-ray spectroscopy analysis. All samples were presented as liquid-silica coexisting within the basalt composition range. The 1300 and 1400 °C isotherms were constructed based on the experimental results. However, significant discrepancies were confirmed with further comparison of the experimental results with FactSage predictions, indicating that more efforts are needed for the optimization of the basalt oxide-related thermodynamic databases.

1. INTRODUCTION

With the promotion of carbon neutral policies,1,2 stricter regulations have been issued regarding environmental protection during the production of different kinds of materials.3–5 The continuous basalt fibers (CBFs),6,16 produced by the natural basalt rock,7 have been regarded as “The 21st-century non-pollution green materials”6 because no chemical additives, solvents, and any other hazardous materials are added or generated during their production. CBFs and their composites are therefore widely used in many fields6,8–11 such as highway, aerospace power engineering, civil and industrial construction, and firefighting due to the superior performance,12–13 that is, high thermal conductivity, high electrical resistivity, and unique resistance to high temperatures (up to 700 °C). CBFs were first successfully developed by the former Soviet Union around 1953,14 while the core advanced technology is held in a few countries, that is, Ukraine, Russia, USA, Canada, and Belgium. During the production of CBFs,6 the crushed and washed basalt rock is premelted at above 1450 °C; afterward, the molten rock is homogenized in a secondary controlled heat zone, and then the filaments are formed by passing through small nozzles in a platinum–rhodium alloy at around 1350 °C. The CBFs are finally wounded with an automatic speed control to make the filaments down to their precise diameter.

The crystallization of the molten basalt rock during the fiber forming process must be carefully controlled to ensure continuity for the production of CBFs;15 however, the filament forming process is sensitive to the fluctuations of compositions of the basalt rock mined from different ore deposits.16 It is therefore essential to have a comprehensive understanding of the thermodynamic/kinetic properties, that is, melting temperature,17 equilibrium phase relation,18 viscosity,19 surface tension,20 etc. with varying compositions. The phase diagrams for basalt oxide systems, visually presenting the melting behavior and crystallization process, are preferentially needed for adjusting the industrial parameters to adapt to the fluctuation of the compositions caused by the different sources of the basalt ore.

The basalt oxide system can be basically described as a SiO$_2$–Al$_2$O$_3$–FeO$_x$–MeO$_y$ (Me = Ca, Ti, Na, K, etc.) system with reference to the main compositions in the basalt rock.16 The primary crystal phase during the fiber forming process was considered as silica due to the high concentration of SiO$_2$ (>42 wt %),5,16 however, the precipitation phase was easily transformed to mullite or spinel when the composition fluctuations occurred in Al$_2$O$_3$ or FeO$_x$.21 The optimized industrial parameters corresponding to the varying oxide...
compositions could be dynamically adjusted if a comprehensive thermodynamic basalt oxide database has been established. However, most of the thermodynamic studies regarding the phase diagrams were focused on sub-binary and subternary systems, that is, SiO$_2$−Al$_2$O$_3$ [22] SiO$_2$−CaO−Fe$_2$O$_3$ [23] SiO$_2$−CaO−TiO$_2$ [24] SiO$_2$−Al$_2$O$_3$−MgO−CaO [25] SiO$_2$−CaO−Al$_2$O$_3$−TiO$_2$ [26,27] etc. The high-order basalt oxide systems were insufficiently investigated due to the complex phase relations and experimental difficulties. Nowadays, the rapid development of the CALculation PHase Diagram (CALPHAD) technique [28] resulted in the establishment of different kinds of thermodynamic databases including FactSage [29] MTDATA [30], HSC [31], and Thermo-Calc [32] among which FactSage is famous for its wide application in the ferrous metallurgy industry. However, the predicted thermodynamic properties are mainly reliable for lower binary and ternary systems, such as CaO−SiO$_2$ [33] CaO−SiO$_2$−Al$_2$O$_3$ [34] CaO−SiO$_2$−ZrO$_2$ [35] and SiO$_2$−Al$_2$O$_3$−TiO$_2$ [36] while the calculated thermodynamic information for high-order systems is still far from sufficient due to the lack of accurate experimental data. [37,38] It is then necessary to conduct basic thermodynamic studies to lay the foundation for further comprehensive construction of the basalt oxide thermodynamic databases.

Therefore, a long-term project for the fundamental thermodynamic investigation of the equilibrium phase relations has been proposed for the efficient production of CBFs. In the former studies of the phase relations of the SiO$_2$−Al$_2$O$_3$−Fe$_2$O$_3$ system, [39] the FeO fluctuation has been discussed based on the experimental results in air. In the present work, the equilibrium phase relations with the addition of 10 wt % CaO to the SiO$_2$−Al$_2$O$_3$−Fe$_2$O$_3$ system will be further explored to clarify the influence of the varying CaO concentration. The experimentally determined equilibrium results at 1300 and 1400 °C will be thoroughly compared with the predictions by FactSage to estimate the requirements for the update of the current basalt oxide-related thermodynamic databases.

### 2. EXPERIMENTAL SECTION

#### 2.1. Raw Materials and Compositions

Reagent oxides of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, and CaO with purity higher than 99.9 wt % from Sinopharm Chemical Reagent Co., Ltd., China were used as the raw materials. The initial compositions of the samples were designed within the basalt rock composition range [39] as shown in Table 1, while the concentration of CaO was fixed at 10 wt % to reflect the addition of CaO on the equilibrium phase relationships. Each reagent powder was weighted to an accuracy of 0.1 mg, then thoroughly mixed and pressed into a cylinder (with diameter 4 mm), and stored in a desiccator for further experiments.

#### 2.2. Determination of the Equilibrium Phase Relations

The methods for experimental determination of the phase diagram have been divided into two kinds, [40] that is, the dynamic and static techniques. The static method of the equilibrium-quenching technique is perfectly suitable for the basalt oxide system due to its high viscosity and sluggishness of crystallization caused by its high SiO$_2$ concentration. [41] In the present work, the heating program shown in Figure 1 was applied to the equilibrium-quenching process. The pressed cylinder sample was placed inside a platinum foil, which was then suspended within an even temperature area in a vertical tube furnace (Shanghai Yetuo Technology Co., Ltd., MFLGL306-18). The furnace was heated using MoSi$_2$ heating elements, and the temperature adjacent to the sample was monitored using a regular calibrated B-type thermocouple with an accuracy of ±3 °C. Before the temperature was adjusted to the equilibrium temperature, the sample was first heated to 1500 °C for 60 min to accelerate the homogenization process. The sample was then kept at 1300 and 1400 °C for at least 1440 min for reaching the equilibrium state. Preliminary experiments and literature studies proved that 1440 min was sufficient to achieve equilibrium from the results using systems of CaO−SiO$_2$−TiO$_2$ [24] CaO−SiO$_2$−MgO−Al$_2$O$_3$−TiO$_2$ [41–43] etc. After the equilibrium state was reached, the platinum foil containing the sample was rapidly dropped into ice water placed below the tube furnace. The phase assemblies and compositions were therefore retained at room temperature due to the high viscosity of the molten basalt. [44] The quenched sample was then dried and stored in a desiccator for further analysis.

#### 2.3. Analysis

In order to determine the equilibrium phase assemblies and compositions, the particle sample (about 1−2 mm diameter) was mounted in epoxy resin, polished, and carbon-coated for better electrical conductivity. A scanning electron microscope (SEM, Ultra Plus, Zeiss) equipped with an energy-dispersive X-ray spectrometer (EDS, Thermo Fisher Scientific, Waltham, MA, USA) was selected for the detection. An accelerating voltage of 15 kV and a beam current of 10 nA on the sample surface were used for the detection. The Proza (Phi-Rho-Z) matrix correction procedure was used for processing the raw data. The external standards utilized in the EDS analyses were anhydride (for Ca, Kz), quartz (for O, Kz and Si, Kα), Al metal (for Al, Kα), and Fe metal (for Fe, Kα). At least six analysis points were randomly selected from each phase for statistical reliability.

#### 2.4. Thermodynamic Calculation

The experimental results from the present work were further compared with the predictions by FactSage thermodynamic software. The solution phases in FactSage were described by the quasi-chemical model, [45] and the “FactPS” and “FToxid” databases in the “Phase Diagram” module were used for the calculation, while the oxygen partial pressure was set as 0.21 atm.

### Table 1. Composition Characteristics of the Basalt Rock

| chemical | SiO$_2$ | Al$_2$O$_3$ | Na$_2$O | K$_2$O | CaO | MgO | FeO | Fe$_2$O$_3$ | TiO$_2$ | MnO |
|----------|---------|-------------|---------|--------|-----|-----|-----|-----------|--------|-----|
| content, wt % | 45−52 | 12−16 | 1.5−3.0 | 0.9−2.9 | 7.1−10.3 | 4.1−7.2 | 2.7−9.5 | 5.7−9.6 | 2.2−4.1 | 0.1−0.3 |

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Figure 1. Experimental process for the equilibrium-quenching technique.
3. RESULTS AND DISCUSSION

3.1. Valence State of Fe. Both FeO and Fe$_2$O$_3$ are present in the natural basalt rock; during the premelting of basalt in the CBF production, the divalent ion will be oxidized to a trivalent ion. It was also reported that the $w$(FeO)/$w$(Fe$_2$O$_3$) ratio has a significant influence on the crystallization process and the corrosion of the platinum–rhodium alloy. Therefore, it is essential to determine the valence state of Fe during the equilibrium experiments at 1300 and 1400 °C in air. The Fe–O predominant phase diagram was then calculated using FactSage 7.3 with the “Phase Diagram” module and is presented in Figure 2 to reveal the influence of oxygen partial pressures and temperatures on the oxidation state of Fe. As can be seen, Fe can be stable as Fe, FeO, Fe$_3$O$_4$ (spinel), and Fe$_2$O$_3$ with the decreasing temperature and increasing oxygen partial pressure. Under the present experimental conditions in air, Fe was stable as Fe$_2$O$_3$ at 1300 °C, as shown by point M in Figure 2, while Fe$_2$O$_3$ partly transformed to Fe$_3$O$_4$ (spinel, point N shown in Figure 2) when the temperature was increased to 1400 °C.

3.2. Equilibrium Phase Relations at 1400 and 1300 °C. The micrographs and compositions for the equilibrium phases at 1400 °C for the SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$–10 wt % CaO system are presented in Figure 3 and Table 2, respectively, while the experimental results for 1300 °C are shown in Figure 4 and Table 3, correspondingly. It can be observed from Figure 3a–e and Figure 4a–e that samples FSAC-1 to FSAC-6 were all present as a liquid-silica two-phase equilibrium state at 1300 and 1400 °C in air, indicating that the designed initial compositions were all located within the primary phase field of silica. In the figures, the liquid was shown by a light gray phase, while the corresponding equilibrium silica phase was presented as a rodlike, big block or a spheroid shape.

It is worth mentioning that the sample FSAC-1 was Al$_2$O$_3$-free; therefore, the equilibrium result of sample FSAC-1 could be explained by the SiO$_2$–FeO$_x$–CaO ternary phase diagram, as shown in Figure 5. In Figure 5, the distribution of the 1400 °C isotherm was shown with reference to the locations of the primary phase fields of SiO$_2$, CaO-SiO$_2$, 3CaO·2SiO$_2$, 2CaO·SiO$_2$, and Fe$_3$O$_4$. The composition of the equilibrium liquid phase for sample FSAC-1 was then projected in Figure 5 to compare with the 1400 °C isotherm, and the comparison indicated that the present experimental result is in well agreement with the constructed SiO$_2$–FeO$_x$–CaO phase diagram from the literature.

3.3. Projection of the 1300 and 1400 °C Isotherms. Based on the experimental results discussed above, the 1300
and 1400 °C isotherms were projected on a quasi-ternary SiO$_2$−Al$_2$O$_3$−FeO$_x$ phase diagram with the CaO concentration fixed at 10 wt %, as shown in Figure 6. The magenta solid line connecting the magenta symbols was the 1400 °C isotherm, while the blue solid line passing through the blue symbols was the 1300 °C isotherm. The isotherms have similar trends with the varying compositions, and the 1400 °C isotherm moved toward higher SiO$_2$ concentrations.

Table 2. Compositions for the Equilibrium Phases in Air at 1400 °C

| no. | initial compositions, wt % | $T_r$ °C | equilibrium phases | equilibrium compositions, wt % |
|-----|-----------------------------|----------|--------------------|--------------------------------|
|     | Fe$_2$O$_3$ | SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | SiO$_2$ | Al$_2$O$_3$ | CaO |
| FSAC-1 | 9.0 | 81.0 | 0.0 | 10.0 | 1400 | liquid | 29.8 ± 0.1 | 47.2 ± 0.2 | 0.0 ± 0.0 | 23.0 ± 0.08 |
| FSAC-2 | 4.5 | 81.0 | 4.5 | 10.0 | 1400 | liquid | 18.3 ± 0.4 | 60.1 ± 0.4 | 10.1 ± 0.3 | 11.6 ± 0.4 |
| FSAC-3 | 13.5 | 72.0 | 4.5 | 10.0 | 1400 | liquid | 0.4 ± 0.2 | 99.2 ± 0.4 | 0.4 ± 0.2 | 0.0 ± 0.0(2) |
| FSAC-4 | 9.0 | 72.0 | 9.0 | 10.0 | 1400 | liquid | 24.2 ± 0.5 | 55.0 ± 0.7 | 6.7 ± 0.2 | 14.2 ± 0.3 |
| FSAC-5 | 13.5 | 72.0 | 4.5 | 10.0 | 1300 | liquid | 0.6 ± 0.2 | 99.2 ± 0.3 | 0.1 ± 0.1 | 0.0 ± 0.0 |
| FSAC-6 | 9.0 | 72.0 | 9.0 | 10.0 | 1300 | liquid | 10.6 ± 0.7 | 65.3 ± 0.6 | 12.6 ± 0.2 | 11.5 ± 0.2 |

Table 3. Compositions for the Equilibrium Phases in Air at 1300 °C

| no. | initial compositions, wt % | $T_r$ °C | equilibrium phases | equilibrium compositions, wt % |
|-----|-----------------------------|----------|--------------------|--------------------------------|
|     | Fe$_2$O$_3$ | SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | SiO$_2$ | Al$_2$O$_3$ | CaO |
| FSAC-2 | 4.5 | 81.0 | 4.5 | 10.0 | 1300 | liquid | 9.5 ± 0.1 | 62.2 ± 0.2 | 11.0 ± 0.0 (7) | 17.4 ± 0.1 |
| FSAC-3 | 13.5 | 72.0 | 4.5 | 10.0 | 1300 | liquid | 25.0 ± 0.9 | 52.5 ± 0.7 | 7.3 ± 0.3 | 15.2 ± 0.2 |
| FSAC-4 | 9.0 | 72.0 | 9.0 | 10.0 | 1300 | liquid | 0.5 ± 0.1 | 99.2 ± 0.1 | 0.3 ± 0.1 | 0.0 ± 0.0 |
| FSAC-5 | 4.5 | 72.0 | 13.5 | 10.0 | 1300 | liquid | 11.5 ± 0.1 | 62.5 ± 0.0 (7) | 15.6 ± 0.0 (4) | 10.3 ± 0.0 (4) |
| FSAC-6 | 9.0 | 67.5 | 13.5 | 10.0 | 1300 | liquid | 6.4 ± 0.1 | 68.3 ± 0.3 | 15.5 ± 0.1 | 9.8 ± 0.1 |

Figure 4. SEM micrographs for the equilibrium phases in air at 1300 °C (a: FSAC-2, b: FSAC-3, c: FSAC-4, d: FSAC-5, and e: FSAC-6).
calculations indicated that more experimental data are needed for verifying the accuracy of the current thermodynamic database, and more efforts are required for better optimization of the thermodynamic database regarding the complex basalt oxide systems.

4. CONCLUSIONS

In the present work, the equilibrium phase relations for the core subsystem of SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$–10 wt % CaO were experimentally determined in air. Within the composition range designed in the present work, all samples were present as a liquid-silica two-phase equilibrium state. The 1300 and 1400 °C isotherms with 10 wt % CaO addition were constructed and projected on a quasi-ternary SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$ phase diagram. However, further comparison with predictions by FactSage verified that significant discrepancies existed in the primary phase fields of silica and Fe$_2$O$_3$, indicating that more efforts are needed for a better optimization of the current basalt-related oxide thermodynamic database, and the crystallization behavior of the basalt melt during the fiber process could then be properly controlled for the basalt fiber industry.

Figure 5. Comparison of the experimental result of sample FSAC-1 at 1400 °C with the CaO–SiO$_2$–Fe$_2$O$_3$ phase diagram. Reprinted with permission from [ref 46]. Copyright [1995] [Verlag Stahleisen GmbH].

Figure 6. Comparison of the experimentally determined 1300 and 1400 °C isotherms with the predictions by FactSage.

Figure 6 shows the calculated 1300 and 1400 °C isotherms by FactSage with an Equilib module for comparison. The distribution of the primary phase fields was projected as well for a better understanding of the equilibrium phase relations. The distribution of the primary phase fields of M$_2$O$_3$ (corundum), Ca(Al,Fe)$_{12}$O$_{19}$ mullite, spinel, Fe$_2$O$_3$, and silica was clearly presented using the calculations; meanwhile, the prediction from FactSage indicated that 10 wt % CaO addition was favorable for the formation of at a SiO$_2$ content lower than ~40 wt %, which was not located within the composition range studied in the present work. Although significant discrepancies have been found from the comparisons for the composition range investigated in the present research, the most obvious difference was that the experimentally determined 1300 and 1400 °C isotherms were found to be located within the calculated primary phase field of Fe$_2$O$_3$, while the experimental results proved that it should be in equilibrium with silica. The experimentally confirmed and FactSage-predicted 1400 °C isotherms have a similar change trend with the varying compositions, while for the 1300 °C isotherm, the experimentally determined line extended to the significant higher FeO$_2$ area. The discrepancies between experiments and
ACKNOWLEDGMENTS

This study received financial support from the China Postdoctoral Science Foundation (Grant numbers 2020TQ00059 and 2020M680967), the Natural Science Foundation of Liaoning Province, the Fundamental Research Funds for the Central Universities (N2125010), open project from the Key Laboratory of Ecological Utilization of Multimetallic Mineral of Education Ministry (NEMM2018003), and the research project from the Chongqing Committee of Education (KJQN201910404 and KJZD-M201810410).

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