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Leaching behaviors of impurities in metallurgical-grade silicon with hafnium addition

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Abstract

Hf was employed as an impurity getter to enhance the removal of impurities from metallurgical-grade Si (MG-Si) via the solidification of Si or a Si-33wt% Al solvent. The leaching behaviors of the impurities (B, Fe, Al, Ca, P, Zr, Ti, V, Mn, Hf, and Ni) within MG-Si, in the presence of 5wt% Hf, were investigated using various leaching approaches. Compared with aqua regia and HF, HCl+HF was determined to be the optimal lixiviant for the elimination of impurities from Hf-containing MG-Si. The use of a combination of HCl+HF and aqua regia reduced the quantity of impurities from 6126 ppmw to 94 ppmw. Eh-pH diagrams were calculated to discuss the leaching of HfSi_2 in aqua regia and HF solutions. The presence of Hf in the MG-Si enhanced the removal of impurities, especially P, which cannot be efficiently removed via solidification refining and hydrometallurgical treatments. Hf-containing Si-Al solvent refining is considered the most efficient approach for the elimination of impurities (except Al). The removal fractions of B and P were 94.2% and 86.2%, respectively, achieved via the solidification of the Si-33wt% Al solvent. Moreover, 99.94% and 99.9996% of the Hf, used as an impurity getter, could be eliminated through the solidification of the Si and Si-33wt% Al solvent, respectively, decreasing from 50,000 ppmw, to 28 ppmw and 0.2 ppmw, respectively.

Keywords: silicon purification; Eh-pH diagrams; hafnium; alloy refining; hydrometallurgy.

1. Introduction

Solar energy is an important renewable and green energy. Solar energy can be converted into electrical energy using solar cells, which is known as photovoltaic conversion. Si is the most common material used for the production of solar cells. However, trace amounts of impurities in Si can significantly reduce the photovoltaic conversion efficiency and render the solar cell inefficient. Therefore, the purity of Si used for photovoltaic applications must be increased to 99.9999% (solar-grade silicon or SoG-Si).

The most common approach used for the production of SoG-Si involves the purification of metallurgical-grade Si ((MG-Si), purity typically below 99.5%). A modified Siemens process can be used to upgrade MG-Si to SoG-Si; however, this process is still expensive and causes environmental problems because it consumes large quantities of energy and involves complex chemical processes. Moreover, owing to their low cost, metallurgical treatments could potentially be used for the production of SoG-Si via the upgrade of MG-Si. Many approaches have been developed to improve such metallurgical treatments, to offer environmentally friendly processes and low energy consumption.

Recently, the addition of one or more additives to MG-Si, known as alloy refining, has become a research focus. This technique uses simple equipment that is easily operated, and offers low energy consumption, low refining costs, and generates no waste slag. Alloy refining can be classified into three different approaches. One approach involves the addition of large amounts of one or more additives to form a solvent. As the liquidus temperature of the solvent is normally much lower than the melting point of Si, MG-Si can be purified at low temperature, reducing energy consumption. This approach is known as solvent refining. Examples of such solvent systems include Si-Al (Yoshikawa et al., 2005a; Gu et al., 2011; Ban et al., 2015; Li et

al., 2014a; Zou et al., 2015), Si-Cu (Mitrašinović et al., 2009; Huang et al., 2016), Si-Sn (Ma et al., 2014; Ma et al., 2012), Si-Fe (Esfahani et al., 2011; Khajavi et al., 2015), Si-Ga (Li et al., 2017), Si-Na (Morito et al., 2012; Morito et al., 2013), Si-Al-Zn (Li et al., 2014b), and Si-Al-Sn (Li et al., 2014c), as well as their combinations (Hu et al., 2013). The second approach involves the addition of small amounts of additives, which have strong affinity for certain impurities, to Si. For example, owing to their strong affinity, Ca was added to Si to enhance the removal of P (Johnston et al., 2013; Shimpo et al., 2004; Lai et al., 2015), and Ti was employed as a B getter, however, this technique was considered inefficient with regard to the removal of B (Johnston et al., 2013). In our previous study, we attempted to enhance the removal of impurities from MG-Si using Zr as an impurity getter (Lei et al., 2017). The third method involves a combination of the above two approaches; it uses solvent refining to purify MG-Si at low temperature and, simultaneously, small amounts of one or more additive are added to enhance the removal of impurities. Small amounts of Ti were employed to enhance the removal of B using a Si-Al solvent (Yoshikawa et al., 2005b). During our previous studies (Lei et al., 2016a; Lei et al., 2016b; Lei et al., 2016c; Lei et al., 2016d), we attempted to add small amounts of transition metals to a Si-Al solvent to enhance the removal of B from B-doped Si. Ca was employed to enhance the removal of impurities using a Sn-Si solvent (Hu et al., 2013).

Hf can be employed as an impurity getter because its segregation coefficient is extremely low (4.9×10^{-6} at the melting point of Si) (Lei et al., 2016c). This indicates that the added Hf can be eliminated along with other impurities, and will not contaminate the Si. Moreover, Hf has an extremely strong affinity for B according to the Gibbs energy for the formation of its boride. B is a well-known impurity that, owing to its high segregation coefficient (0.8 at the melting point of Si, 1687 K) (He et al., 2012) and low vapor pressure (lower than that of Si) (Safarian et al.,

2012), is difficult to remove from Si. According to the results of our previous study, small amounts of Hf (<6500 ppmw) (**Lei et al., 2016c**) could enhance the removal of B from B-doped Si, with a Si-Al solvent. However, if B can be eliminated efficiently via the direct addition of Hf to MG-Si (without the addition of large amounts of Al to form a Si-Al solvent), the Si purification process could become more efficient and economical. Furthermore, different lixivants must exhibit varying leaching behaviors with regard to the various impurities in Hf-containing Si, especially Hf-containing impurities; however, this has not been reported yet. In addition, Hf may have varying levels of affinity for the impurities in MG-Si, indicating that the addition of Hf may result in varying levels of efficiency with regard to the elimination of the various impurities in MG-Si; however, there have been no studies performed on this issue yet. In this study, using various lixivants, the leaching behaviors of the impurities within Hf-containing MG-Si will be evaluated to identify the most efficient lixiviant. Subsequently, the leaching behaviors of the impurities (B, Fe, Al, Ca, P, Zr, Ti, V, Mn, Hf, and Ni) in MG-Si with/without Hf will be compared. Finally, the extraction of impurities from MG-Si, with/without a Si-Al solvent, using Hf as an impurity getter, will also be discussed for comparison purposes.

2. Experimental

2.1 Hf as an impurity getter in MG-Si

MG-Si (purity of 99.387%, calculated using the total concentration of B, Fe, Al, Ca, P, Zr, Ti, V, Mn, Hf, and Ni) was employed as the raw material for purification; the concentrations of the impurities are shown in **Table 1**. Prior to the experiments, the MG-Si was ground into powder (<186 μm) using an agate mortar to homogenize its composition. A Si-Mo electric resistance furnace was employed to perform the Si solidification refining, as shown in **Fig. 1**. Subsequently, 20 g of the pulverized MG-Si and shots of Hf (purity 99.5%) were charged into a graphite

crucible (outer diameter: 35 mm, inner diameter: 25 mm, length: 100 mm) of high purity and density. The composition of the mixture was set to Si-5wt% Hf, which was confirmed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) following melting and solidification. To achieve homogenization, the mixture was held at 1773 K for 2 h under an Ar gas (purity 99.99 %) atmosphere, and then cooled to 773 K at 1.5 K/min to perform solidification refining.

During solidification refining, owing to their different segregation coefficients, the impurities of the MG-Si will precipitate along the Si grain boundaries. Therefore, the solidified samples were cut in half along their cross section for chemical and morphological analyses, respectively.

For chemical analysis, one half of the sample was ground into powder ($<75\ \mu\text{m}$) using an agate mortar, and leached using aqua regia (guaranteed reagent HCl: content 36–38%; guaranteed reagent HNO_3 : content 65–68%; HCl: HNO_3 =3:1 volume ratio), HF (guaranteed reagent, content 40%), or HCl+HF (1:1 volume ratio) at $348\pm 1\ \text{K}$ for 3 h, respectively. For each leaching process, the liquid–solid weight ratio was 8:1.

Based on the leaching results of our previous study, to achieve improved leaching results, the pulverized Si was also successively leached using HCl+HF and aqua regia at $348\pm 1\ \text{K}$ for 3 h, respectively (two steps, 6 h in total). The liquid–solid weight ratios were 8:1 and 6:1, respectively. After each leaching process, the purified, pulverized Si was cleaned using deionized water several times and dried at $353\pm 1\ \text{K}$. Subsequently, the pulverized Si was dissolved in a mixture of HF and HNO_3 (HF was added dropwise into HNO_3) for subsequent chemical analysis using ICP-OES.

For morphological analysis, the other half of the sample was cut into two pieces and each piece was leached using either aqua regia or HF, respectively, at $348\pm 1\ \text{K}$ for 3 h. The

morphologies of the samples and the compositions of the precipitates, before and after acid leaching, were investigated using a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS).

2.2 Purification of MG-Si without Hf addition

For comparison purposes, the purification of MG-Si, without an addition of Hf, was investigated. The solidification refining process was identical to that used for the purification of MG-Si with an addition of Hf (as described in section 2.1). The pulverized Si was leached using HCl+HF and aqua regia, in succession, at 348 ± 1 K for 3 h (two steps, 6 h in total). The liquid–solid weight ratios used for this leaching process were 8:1 and 6:1, respectively. Subsequently, for ICP-OES analysis, the pulverized Si was dissolved using the process described in section 2.1.

2.3 Hf as an impurity getter in a Si-Al solvent

The segregation coefficients of the impurities will decrease at lower temperatures; therefore, to purify the Si at low temperature, Al was added to the Si to form a Si-Al solvent. The purification of MG-Si with a Si-33wt% Al solvent, using 5wt% Hf an impurity getter, was also investigated for comparison purposes. The solidification refining process used was identical to that described in section 2.1. The method of leaching and the technique used to dissolve the pulverized Si for ICP-OES analysis were identical to those described in section 2.2.

2.4 Eh-pH diagrams

HSC Chemistry 6.0 was employed to calculate the Eh-pH diagrams for Hf-Si-N-Cl-H₂O and Hf-Si-F-H₂O systems in order to discuss leaching of Hf-containing Si by aqua regia and HF, respectively. The value, which is unavailable in HSC Chemistry 6.0, was adopted from other source.

3. Results and discussion

3.1 Morphologies of MG-Si with 5wt% Hf

Figure 2 shows a typical precipitate located on the Si grain boundary, following the addition of 5wt% Hf. The added Hf could be expelled from the solid Si because of its low segregation coefficient (4.9×10^{-6} at the melting point of Si, 1687 K) (**Lei et al., 2016c**). Metal impurities, such as Hf, Fe, Al, Ti, Ca, and V, could be detected using EDS mapping analysis. Hf, Fe, and Al were determined to be the main precipitated impurities because of their dominant concentrations compared with those of other impurities (as shown in **Table 1**). P, a non-metallic impurity that cannot be easily removed because of its high segregation coefficient (0.35 at melting point of Si) (**He et al., 2012**), could be faintly detected in the Hf-containing phases. Owing to their strong affinity, P also coexists with Ca, as shown by the EDS mapping analysis of Ca and P in **Fig. 2**. Several researchers have performed studies on the enhancement of the removal of P from MG-Si via the addition of Ca (**Shimpo et al., 2004; Lai et al., 2015**), and reported the presence of the Ca-P phase.

The main precipitated phases are Si-Hf-Fe, Si-Hf-Fe-Al, and Si-Fe-Al, as shown in **Fig. 2**. The Si-Fe-Al phase was observed in the vicinities of the Si-Hf-Fe and Si-Hf-Fe-Al phases, owing to their various liquidus temperatures. Hf-containing phases are considered to possess higher liquidus temperatures, because the melting point of Hf (2500 K) is much higher than that of other elements. Most impurities stabilize in the Hf-containing phases (as shown in **Fig. 2**); therefore, Hf can act as an impurity getter. This suggests that impurities can be eliminated if these Hf-containing phases are soluble within a lixiviant. Therefore, the leaching behaviors of Hf-containing phases in various lixiviants are extremely important with regard to the elimination of impurities in MG-Si.

3.2 Leaching behaviors of MG-Si with 5wt% Hf

The leaching results, obtained with the use of aqua regia, HCl+HF, and HF as lixivants, are listed in **Table 1** (columns I, II, and III, respectively). The added Hf can be eliminated by both HCl+HF and HF, while only a small quantity is soluble in aqua regia. As most impurities coexist with the Hf-containing phase, a lixiviant that can eliminate Hf would be efficient with regard to the elimination of impurities. Therefore, HCl+HF and HF are efficient with regard to the removal of impurities. The total concentration of impurities (B, Fe, Al, Ca, P, Zr, Ti, V, Mn, Hf, and Ni) can be reduced from 6126 ppmw, to 231 ppmw and 353 ppmw via HCl+HF and HF leaching, respectively. Other HF-containing lixivants are also reported to be efficient to eliminate impurities in MG-Si (**Dietl, 1983; Sun et al., 2013; Kim et al., 2015; Lai et al., 2016**). Compared with HF, HCl+HF is slightly more efficient with regard to the elimination of impurities because it can eliminate Hf more efficiently. This is because the presence of HCl in HF can increase Hf dissolution rate (**James et al., 1963**) and lixivants with high HF concentrations may form insoluble fluorides (**Dietl et al., 1983**). Therefore, HCl+HF is considered the optimal lixiviant with regard to the extraction of impurities from MG-Si in the presence of Hf. The most efficient lixivants, in order of efficiency, are HCl+HF > HF > aqua regia.

SEM was employed to visually observe the leaching behaviors. **Figure 3** shows SEM images of the Hf-containing phases before and after both aqua regia and HF leaching, respectively. Hf-containing phases are partially soluble in aqua regia, and following aqua regia leaching, most of them are retained in Si as Si-Hf, Si-Hf-Fe-Al, and Si-Hf-Fe phases, as shown in **Figs. 3 (a) and (b)**. This suggests that Hf, Fe, and Al were not eliminated efficiently after aqua regia leaching, as shown in column I of **Table 1**. However, Hf-containing phases are soluble in HF, and only a trace amount of Si-Hf was retained in the Si, possibly because of the insufficient leaching period. This suggests that Hf-containing phases can be efficiently eliminated using

HCl+HF or HF leaching, although the concentrations of residual Hf are still 115 ppmw and 245 ppmw, respectively (as shown in columns II and III of **Table 1**), i.e., 99.77% and 99.51% of the Hf was eliminated via HCl+HF and HF leaching, respectively.

Although aqua regia cannot efficiently eliminate impurities, it can still reduce the concentration of most impurities, as shown in column I of **Table 1**. Therefore, the pulverized sample was leached using HCl+HF and aqua regia, in succession, at 348 ± 1 K for 3 h (two steps, 6 h in total) to eliminate as many impurities as possible. The results are listed in the first column, IV, of **Table 1** (for Si-5wt% Hf). The majority of the impurities can be efficiently extracted from Si, especially Hf. The total concentration of impurities was reduced from 6126 ppmw to 94 ppmw following successive HCl+HF and aqua regia leaching. The concentration of the added Hf could be reduced from 50000 ppmw to 28 ppmw, indicating that 99.94 % of the Hf could be removed.

3.3 Eh-pH diagrams for Hf-Si-N-Cl-H₂O and Hf-Si-F-H₂O systems

The possible species in the Hf-Si-N-Cl-H₂O and Hf-Si-F-H₂O systems and their thermodynamic data are listed in **Table 2**. In this study, the leaching temperature is 348 K, the concentration of HCl and HNO₃ in aqua regia are 9 M and 3.7 M, respectively, and the concentration of HF is 23 M. The concentrations of Hf and Fe were set to 0.005 M and 0.01 M, respectively. As the Hf-Si phase was determined to be HfSi₂ by EDX analysis (Hf:Si in mole ratio is 1:2.07), other species in the Hf-Si system such as Hf₂Si, Hf₅Si₃, Hf₃Si₂, Hf₅Si₄ and HfSi are not considered. The reaction of Hf with HF (neglecting fluoride complexes) is shown in **Eq.(1)** (James et al., 1963).



The Eh-pH diagrams for the Hf-Si-N-Cl-H₂O and Hf-Si-F-H₂O systems are shown in **Fig.4(a)** and **Fig.4(b)**, respectively. The regions for Hf and Si species are represented with black and red

lines, respectively. The upper and lower dashed lines in each diagram represent O_2/H_2O and H_2O/O_2 stability boundaries, respectively. When the Hf-containing Si was leached by aqua regia, the Eh-pH diagram is shown in **Fig.4(a)**. The stable species are HfO_2 and SiO_2 from acidic to neutral pH and $SiO(OH)^{3-}$, $SiO_3(OH)^{3-}$ and $HHfO^{3-}$ in alkaline solution. $HfSi_2$ is unstable relative to oxidation to HfO_2 and SiO_2 because its Eh value is far below the water stability line, indicating that $HfSi_2$ can be easily oxidized. **Figure 4(a)** also shows that the dominant stable Hf and Si species in water is HfO_2 and SiO_2 , respectively, except in highly alkaline condition when $HHfSiO_3^-$ (pH>13.8), $SiO(OH)^{3-}$ (pH>10.7) and $SiO_3(OH)^{3-}$ (pH>11) appear. Therefore, the formation of HfO_2 and SiO_2 (as insoluble surface films) will prohibit the dissolution of $HfSi_2$ in aqua regia, which is in agreement with the low removal fraction of Hf (38.5 %, from 50000 ppmw to 30748 ppmw) in this study, as shown in **Table 1**.

When the Hf-containing Si was leached by HF solution, the Eh-pH diagram is shown in **Fig.4(b)**. Comparing **Fig.4(b)** with **Fig.4(a)**, the stable regions of HfF_4 ($0 < pH < 6.4$) and SiF_6^- ($3.1 < pH < 8$) appear, indicating that HF can remove the passivating HfO_2 and SiO_2 layers depending on the pH value. Therefore, the presence of HF can improve the leaching of $HfSi_2$, which is in agreement with the high removal fraction of Hf (99.5 %, from 50000 ppmw to 245 ppmw) in this study, as shown in **Table 1**.

The refined Si crystals may be also attacked by HF because the stable region of SiF_6^- is present in **Fig.4(b)** (between two SiO_2 stability fields). However, the dissolution of Si into HF in this study can be ignored by comparing **Fig.3 (d)** with **Fig.3(c)** (the surface of Si was still smooth after HF leaching at 384 K for 3 h).

3.4 Comparison of leaching behaviors of MG-Si with/without Hf addition

The purification of MG-Si, without Hf addition, was investigated under the same experimental conditions for comparison purposes. The results regarding the leaching of MG-Si with/without Hf addition are shown in **Table 1** (the first and second columns of IV, labeled as Si-5wt%Hf

and MG-Si, respectively). Without Hf addition, the impurities in the MG-Si could be efficiently eliminated via successive HCl+HF and aqua regia leaching. HCl + HF is considered an efficient lixiviant for the removal of impurities from MG-Si, which was reported and discussed in our previous study (Lei et al., 2017). Comparing the leaching results obtained with/without Hf addition, the extraction of impurities from MG-Si could be enhanced with an addition of Hf, especially with regard to P, as shown in **Table 1** and **Fig. 5**.

P is a typical impurity in MG-Si. The segregation coefficient of P is high (0.35 at the melting point of Si), and therefore, it is difficult to eliminate P using solidification refining and hydrometallurgical treatments. With Hf addition, the amount of P extracted from the Si increases from 25% to 59.6%, as shown in **Fig. 5**. With Hf addition, the removal of P from the Si is enhanced, because P is weakly detected in coexistence with Hf-containing phases, as shown in **Fig. 2**. Therefore, the efficient removal of the Hf-containing phases can also simultaneously eliminate P.

Al is another typical impurity in MG-Si. It is highly soluble in solid Si (as much as 340 ppmw) (Murray and McAlister, 1984) and is therefore difficult to remove using solidification refining and hydrometallurgical treatments. With Hf addition, the removal of Al is slightly enhanced, as shown in **Table 1** and **Fig. 5**. A typical precipitate within MG-Si (without Hf addition) is shown in **Fig. 6**. According to its EDS mapping analysis, Al is primarily stabilized in Si-Fe-Al-based phases, indicating that Fe can act as an Al getter. However, when the MG-Si is alloyed with 5wt% Hf, Al is not only stabilized in the Si-Fe-Al-based phases but also in the Si-Hf-Fe-Al phases (as shown in **Fig. 2**), indicating that both Hf and Fe can act as Al getters. This suggests that the removal of Al could be slightly enhanced with Hf addition.

In this study, 98.6% of Al (from 1608 ppmw to 22 ppmw) could be eliminated from the MG-Si. However, this value was determined to be only 85% (from 1243 ppmw to 186 ppmw after HCl+HF leaching) in our previous study (Lei et al., 2017). This indicates that the leaching

approach was improved in this study. In the previous study (Lei et al., 2017), the size of the pulverized Si was lower than 186 μm . However, it is lower than 75 μm in this study. The lixiviant employed in the previous study (Lei et al., 2017) was HCl+HF, while HCl+HF and aqua regia are both used in this study. In addition, the leaching time used in this study (3 h) is longer than that used in the previous study (2.5 h) (Lei et al., 2017).

3.5 Comparison of the leaching behaviors of MG-Si with/without Si-Al solvent, using Hf as an impurity getter

B was expected to be eliminated efficiently with Hf addition. This is because Hf has the strongest affinity for B (to our knowledge) according to the Gibbs energy of formation of HfB_2 , as shown in Eqs. (2) and (3).



$$\Delta G_1^{\circ f} = -459000 + 64.4T \text{ J/mol (Turkdogan, 1980)} \quad (3)$$

However, with an addition of 5wt% Hf to the MG-Si, the highest removal fraction of B is only 56.7% (from 12 ppmw to 5.2 ppmw) (Table 1). According to the results of our previous study (Lei et al., 2016a), 97% of B (from 60 ppmw to 1.8 ppmw) could be extracted from Si following the addition of 0.65wt% Hf to the Si-54wt% Al solvent (liquidus temperature of 1273 K). In the two studies, the different extraction behaviors of the B can be attributed to the different liquidus temperatures. It is well known that compared with a high refining temperature, a lower refining temperature is more favorable for the extraction of impurities from Si. This is because the segregation coefficient of most impurities will decrease as the temperature decreases (Morita and Yoshikawa, 2011). In addition, HfB_2 is also more stable at lower temperature, as shown by Eq. (3). Therefore, Si-Al solvent refining was also performed in this study for comparison purposes.

The leaching results regarding the Si-33wt% Al solvent, with the presence of 5wt%Hf,

following solidification refining, are listed in **Table 1** (the third column of IV, labeled as Si-Al-5wt%Hf). Most impurities can be further eliminated with Si-33wt% Al solvent refining, especially B, P, and Hf. The removal fractions of B, P, and Hf were enhanced to 94.2%, 86.2%, and 99.9996%, respectively. Although residual Al was found in the refined Si, owing to the high solubility of Al in solid Si (as much as 340 ppmw) (**Murray and McAlister, 1984**), the residual Al in solid Si can be removed using vacuum melting owing to the significant difference between the vapor pressures of Al and Si (**Safarian et al., 2012**).

4. Conclusions

The use of solidification refining technology for the purification of MG-Si, with Hf addition, was investigated in this study. Using aqua regia, HCl+HF, and HF as lixivants, the leaching behaviors of MG-Si, with 5wt% Hf, were investigated. HCl+HF was determined to be the optimal lixiviant with regard to the elimination of impurities within the Hf-containing MG-Si. Using a combination of HCl+HF and aqua regia, the removal of impurities was determined to be more efficient (from 6126 ppmw to 94 ppmw). Eh-pH diagrams for Hf-Si-N-Cl-H₂O and Hf-Si-F-H₂O systems were calculated to discuss the leaching of HfSi₂ in aqua regia and HF solutions, respectively. The addition of Hf to MG-Si was determined to enhance the removal of impurities, especially P, compared with that without the addition of Hf. Hf-containing Si-Al solvent refining is considered the most efficient approach for the elimination of impurities (except Al). Most impurities can be further eliminated with the use of Si-33wt% Al solvent refining using Hf as an impurity getter, especially with regard to B, P, and Hf. The removal fractions of B, P, and Hf were determined to be as high as 94.2%, 86.2%, and 99.9996%, respectively.

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References

- T. Yoshikawa, K. Morita, 2005a, Refining of Si by the solidification of Si-Al melt with electromagnetic force, *ISIJ Int.* 45, 967–971.
- X. Gu, X. Yu, D. Yang, 2011, Low-cost solar grade silicon purification process with Al-Si system using a powder metallurgy technique, *Sep. Purif. Technol.* 77, 33–39.
- B. Y. Ban, Y. L. Li, Q. X. Zou, T. T. Zhang, J. Chen, S. Y. Dai, 2015, Refining of metallurgical grade Si by solidification of Al-Si melt under electromagnetic stirring, *J. Mater. Process. Technol.* 222, 142–147.
- J. Li, Z. Guo, 2014a, Thermodynamic evaluation of segregation behaviors of metallic impurities in metallurgical grade silicon during Al-Si solvent refining process, *J. Cryst. Growth* 394, 18–23.
- Q. C. Zou, J. C. Jie, J. L. Sun, T. M. Wang, Z. Q. Cao, T. J. Li, 2015, Effect of Si content on separation and purification of the primary Si phase from hypereutectic Al-Si alloy using rotating magnetic field, *Sep. Purif. Technol.* 142, 101–107.
- A. M. Mitrašinović, T. A. Utigard, 2009, Refining silicon for solar cell application by copper alloying, *Silicon* 1, 239–248.
- L. Huang, H. Lai, C. Lu, M. Fang, W. Ma, P. Xing, J. Li, X. Luo, 2016, Enhancement in extraction of boron and phosphorus from metallurgical grade silicon by copper alloying and aqua regia leaching, *Hydrometall.* 161, 14–21.
- X. Ma, T. Yoshikawa, K. Morita, 2014, Purification of metallurgical grade Si combining Si-Sn solvent refining with slag treatment, *Sep. Purif. Technol.* 125, 264–268.
- X. Ma, T. Yoshikawa, K. Morita, 2012, Phase relations and thermodynamic property of boron in the silicon-tin melt at 1673 K, *J. Alloy Compd.* 529, 12–16.
- S. Esfahani, M. Barati, 2011, Purification of metallurgical silicon using iron as impurity getter,

part II: extent of silicon purification, *Mel. Mater. Int.* 17, 1009–1015.

L. T. Khajavi, K. Morita, T. Yoshikawa, M. Barati, 2015, Thermodynamics of boron distribution in solvent refining of silicon using ferrosilicon alloys, *J. Alloy Compd.* 619, 634–638.

J. Li, B. Ban, Y. Li, X. Bai, T. Zhang, J. Chen, 2017, Removal of impurities from metallurgical grade silicon during Ga-Si solvent refining, *Silicon* 9, 77–83.

H. Morito, T. Karahashi, M. Uchikoshi, M. Isshiki, H. Yamane, 2012, Low-temperature purification of silicon by dissolution and solution growth in sodium solvent, *Silicon* 4, 121–125.

H. Morito, M. Uchikoshi, H. Yamane, 2013, Boron removal by dissolution and recrystallization of silicon in a sodium-silicon solution, *Sep. Purif. Technol.* 118, 723–726.

Y. Q. Li, Y. Tan, J. Y. Li, K. Morita, 2014b, Si purity control and separation from Si-Al alloy melt with Zn addition, *J. Alloy Compd.* 611, 267–272.

Y. Q. Li, Y. Tan, J. Y. Li, Q. Liu, Y. Liu, 2014c, Effect of Sn content on microstructure and boron distribution in Si-Al alloy, *J. Alloy Compd.* 583, 85–90.

L. Hu, Z. Wang, X. Gong, Z. Guo, H. Zhang, 2013, Impurities removal from metallurgical-grade silicon by combined Sn-Si and Al-Si refining processes, *Metall. and Mater. Trans. B* 44B, 828–836.

M. D. Johnston, M. Barati, 2013, Calcium and titanium as impurity getter metals in purification of silicon, *Sep. Purif. Technol.* 107, 129–134.

T. Shimpo, T. Yoshikawa, K. Morita, 2004, Thermodynamic study of the effect of calcium on removal of phosphorus from silicon by acid leaching treatment, *Metall. and Mater. Trans. B* 35B, 277–284.

H. Lai, L. Huang, C. Lu, M. Fang, W. Ma, P. Xing, J. Li, X. Luo, 2015, Leaching behavior of impurities in Ca-alloyed metallurgical grade silicon, *Hydrometall.* 156, 173–181.

Y. V. Meteleva-Fischer, Y. Yang, R. Room, B. Kraaijveld, H. Kuntzel, 2012, Microstructure of metallurgical grade silicon during alloying refining with calcium, *Intermetal.* 25, 9–17.

- Y. Lei, W. Ma, G. Lv, K. Wei, S. Li, K. Morita, 2017, Purification of metallurgical-grade silicon using zirconium as an impurity getter, *Sep. Purif. Technol.* 173, 364–371.
- T. Yoshikawa, K. Arimura, K. Morita, 2005b, Boron removal by titanium addition in solidification refining of silicon with Si-Al melt, *Metall. and Mater. Trans. B* 36B, 837–842.
- Y. Lei, W. Ma, L. Sun, J. Wu, K. Morita, 2016 a, Effects of small amounts of transition metals on boron removal during electromagnetic solidification purification of silicon with Al-Si solvent, *Sep. Purif. Technol.* 162, 20–23.
- Y. Lei, L. Sun, W. Ma, K. Wei, K. Morita, 2016b, Enhancing B removal from Si with small amounts of Ti in electromagnetic solidification refining with Al-Si alloy, *J. Alloy Compd.* 666, 406–411.
- Y. Lei, W. Ma, L. Sun, J. Wu, Y. Dai, K. Morita, 2016c, Removal of B from Si by Hf addition during Al-Si solvent refining process, *Sci. Technol. Adv. Mat.* 17, 12–19.
- Y. Lei, W. Ma, L. Sun, Y. Dai, K. Morita, 2016d, B removal by Zr addition in electromagnetic solidification refinement of Si with Si-Al melt, *Metall. and Mater. Trans. B* 47B, 27–31.
- L. Hu, Z. Wang, X. Gong, Z. Guo, H. Zhang, 2013, Purification of metallurgical-grade silicon by Sn-Si refining system with calcium addition, *Sep. Purif. Technol.* 118, 699–703.
- F. L. He, S. Zheng, C. Chen, 2012, The effect of calcium oxide addition on the removal of metal impurities from metallurgical-grade silicon by acid leaching, *Metall. and Mater. Trans. B* 43B, 1011–1018.
- J. Safarian, G. Tranell, M. Tangstad, 2012, Processes for upgrading metallurgical grade silicon to solar grade silicon, *Energy Procedia* 20, 88–97.
- J. Dietl, 1983, Hydrometallurgical purification of metallurgical-grade silicon, *Sol. Cells* 10, 145–154.
- Y. H. Sun, Q. H. Ye, C. J. Guo, H. Y. Chen, X. Lang, F. David, Q. W. Luo, C. M. Yang, 2013, Purification of metallurgical-grade silicon via acid leaching, calcination and quenching before

boron complexation, *Hydrometall.* 139, 64–72.

J. Kim, J. No, S. Choi, J. Lee, B. Jang, 2015, Effects of a new acid mixture on extraction of the main impurities from metallurgical grade silicon, *Hydrometall.* 157, 234–238.

H. Lai, L. Huang, C. Gan, P. Xing, J. Li, X. Luo, 2016, Enhanced acid leaching of metallurgical grade silicon in hydrofluoric acid containing hydrogen peroxide as oxidizing agent, *Hydrometall.* 164, 103-110.

J. C. Zhao, B. P. Bewlay, M. R. Jackson, Q. Chen, 2000, Hf-Si binary phase diagram determination and thermodynamic modeling, *J. phase equilib.* 21, 40-45.

W. J. James, J. W. Johnson and M. E. Straumanis, 1963, The difference effect and anodic behavior of hafnium dissolving in hydrofluoric acid, *Corros. Sci.* 3, 273-279.

J. L. Murray, A. J. McAlister, 1984, The Al-Si (Aluminum-Silicon) system, *Bull. Alloy Ph. Diagr.* 5, 74–84.

E. T. Turkdogan, 1980, *Physical Chemistry of High Temperature Technology*, Academic Press, New York.

K. Morita, T. Yoshikawa, 2011, Thermodynamic evaluation of new metallurgical refining processes for SOG-silicon production, *Trans. Nonferrous Met. Soc. China* 21, 685–690.

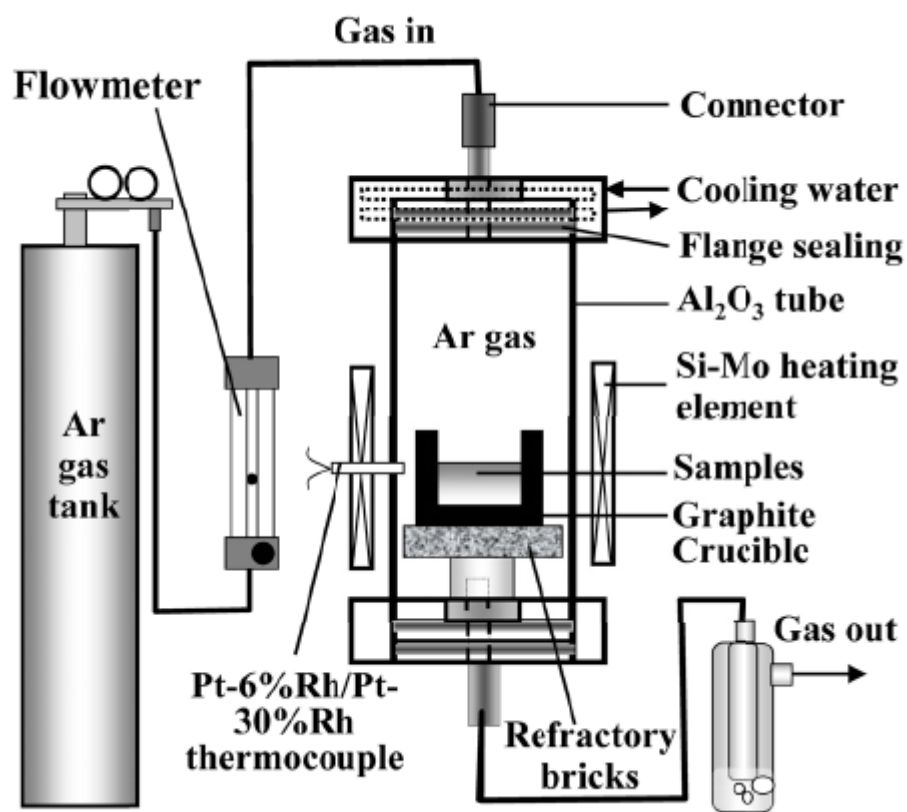


Fig. 1. Schematic of electric resistance furnace used for Si solidification refining.

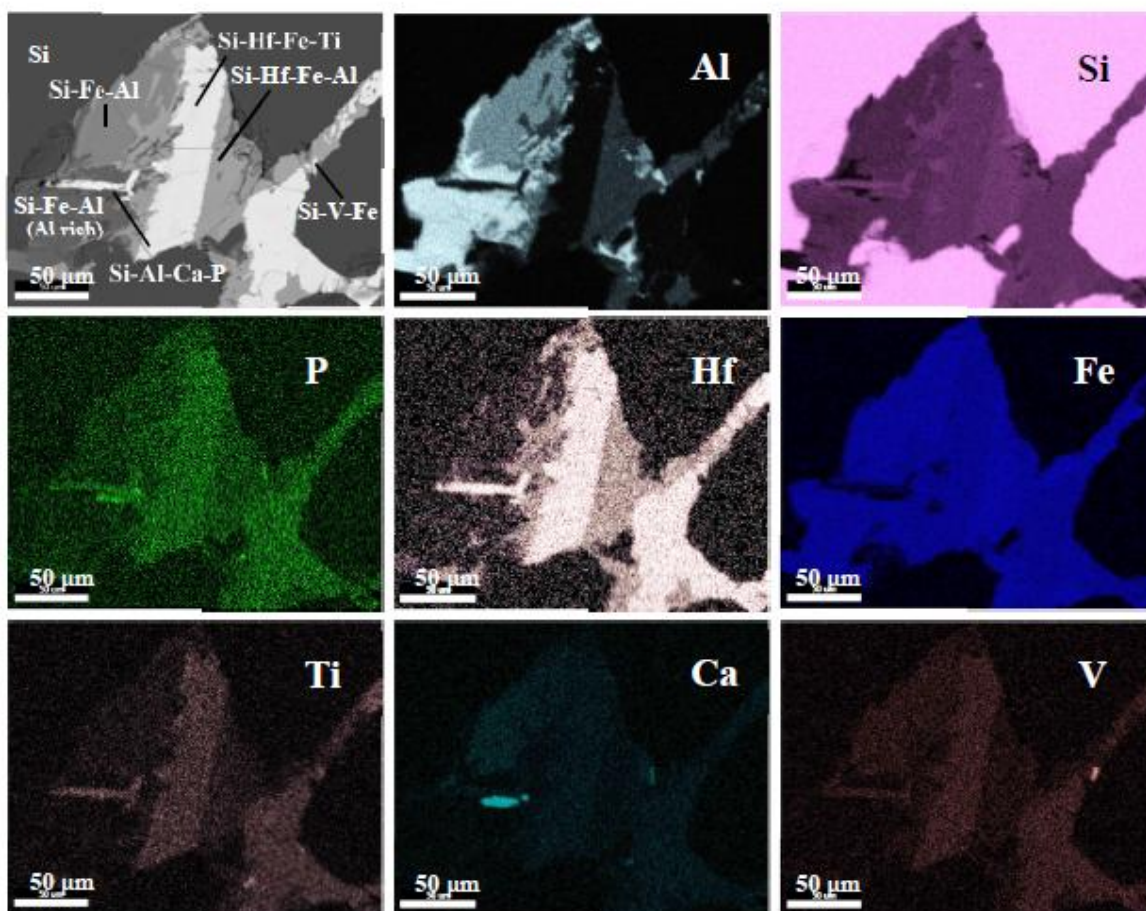


Fig. 2. A typical precipitate in Si with presence of 5 wt% Hf prior to acid leaching, as well as the results of the EDS mapping analysis

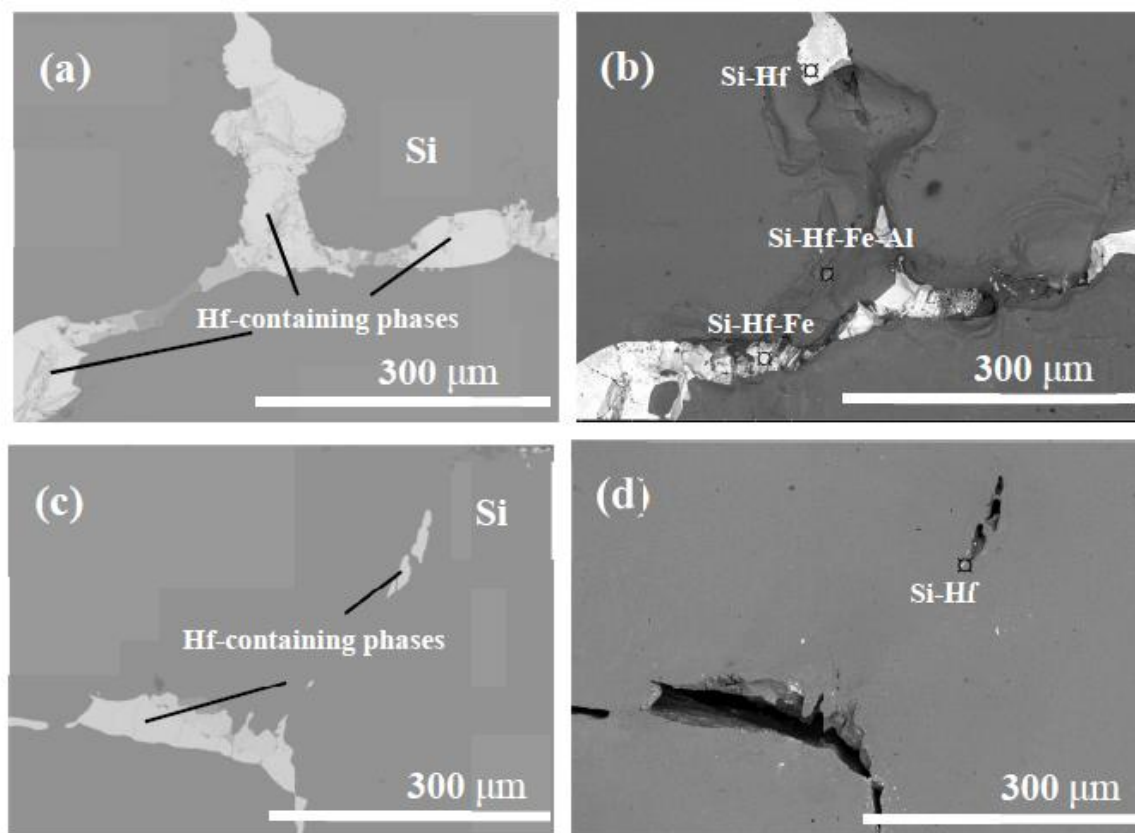


Fig. 3. SEM images of Si with 5wt% Hf (a) before leaching with aqua regia, (b) after leaching with aqua regia, (c) before leaching with HF, and (d) after leaching with HF.

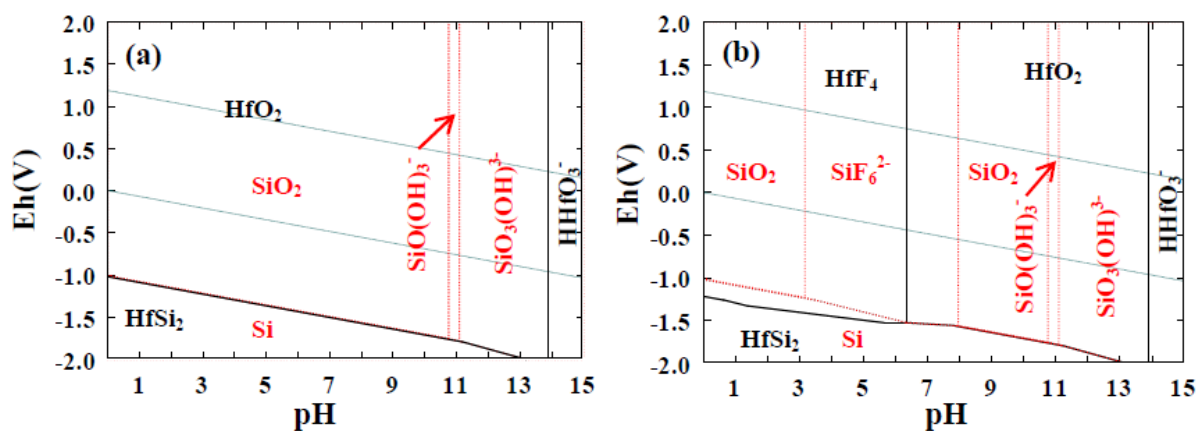


Fig. 4. Eh-pH diagrams for the systems at 348 K (a) Hf-Si-N-Cl-H₂O ($\{Hf\}=0.005$ M, $\{Si\}=0.01$ M, $\{N\}=3.7$ M, $\{Cl\}=9$ M), (b) Hf-Si-F-H₂O ($\{Hf\}=0.005$ M, $\{Si\}=0.01$ M, $\{F\}=23$ M).

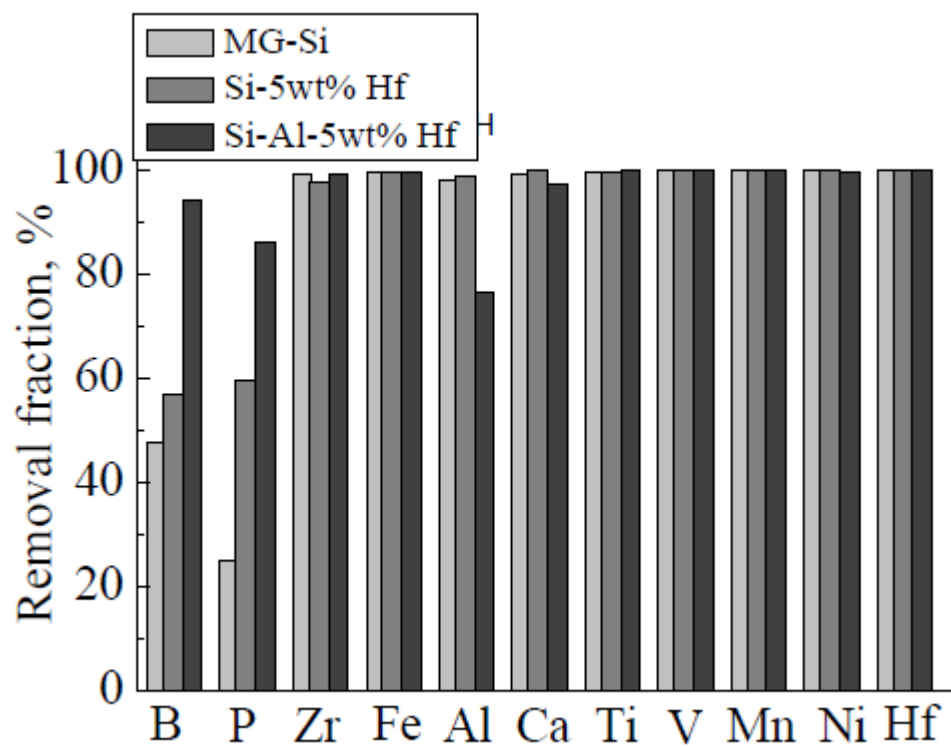


Fig. 5. Removal fractions of the impurities achieved via solidification of MG-Si, Si-5wt% Hf, and Si-Al-5wt% Hf, respectively, following successive leaching with HCl+HF and aqua regia.

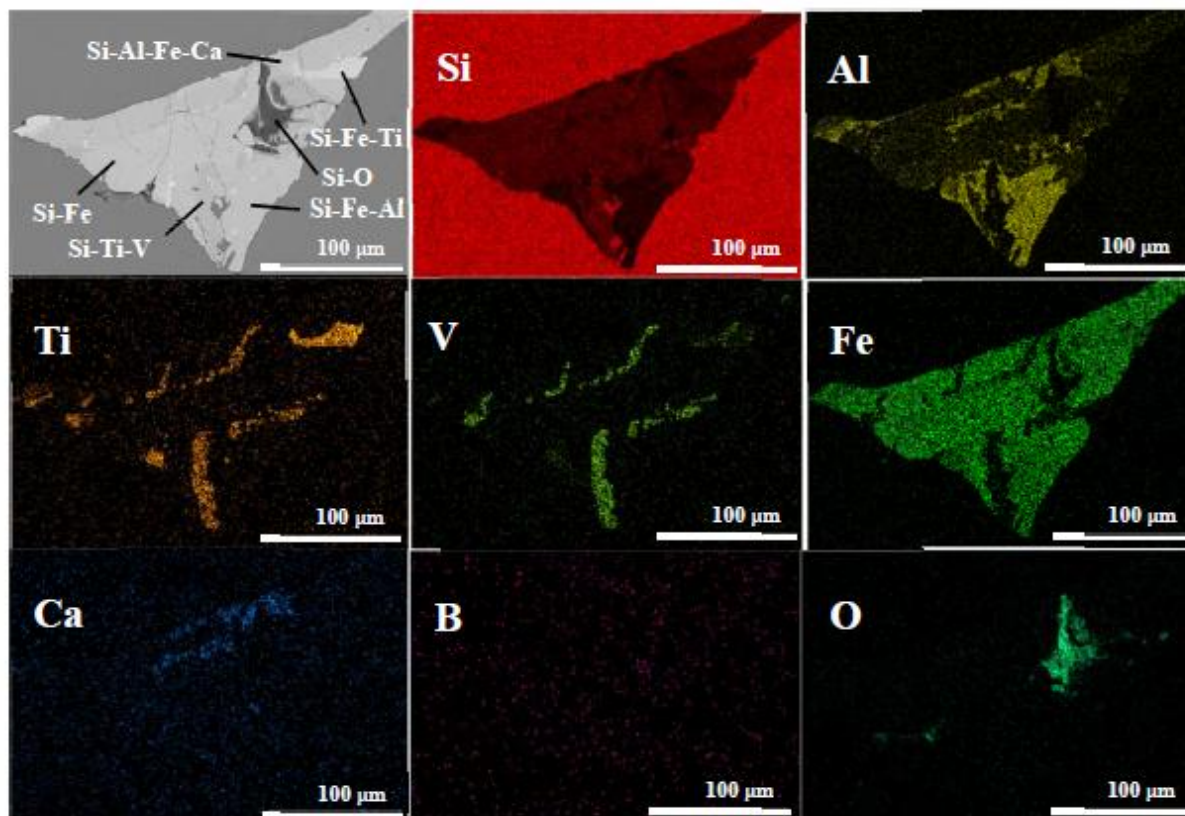


Fig. 6. A typical precipitate in MG-Si prior to acid leaching, as well as the results of the EDS mapping analysis.

Table 1. Concentrations of impurities within initial MG-Si and Si following acid leaching (I , II , and III indicate that leaching with aqua regia, HF+HCl, and HF was performed, respectively; IV indicates that leaching was performed using HF+HCl and aqua regia successively; “-” indicates the analysis limit of ICP-OES).

Impurity	Initial MG-Si	Si-5wt%Hf				MG-Si	Si-Al-5 wt%Hf
		I	II	III	IV	IV	IV
B	12	10	8	9.7	5.2	6.3	0.7
P	52	28	30	28	21	39	7.2
Zr	13	3.4	1.2	0.9	0.3	0.1	0.1
Fe	3494	2308	17	17	16	16	12
Al	1608	663	42	33	22	35	381
Ca	165	11	16	18	-	1.6	4.5
Ti	236	137	0.5	0.7	1.2	1.2	0.7
V	229	133	0.3	0.3	-	-	-
Mn	184	53	0.1	0.3	-	-	-
Ni	132	31	0.4	-	-	-	0.5
Hf	0.5	30748	115	245	28	-	0.2
Total	6126	34125	231	353	94	99	407
Purity of Si (<)	99.387	96.587	99.977	99.965	99.991	99.99	99.959

Table 2. Selected thermodynamic data at 348 K.

[1] HSC Chemistry 6.0, [2] Zhao et al.

Species	$\Delta G_{f,348\text{ K}}^{\circ}$ (kcal/mol)	Reference	Species	$\Delta G_{f,348\text{ K}}^{\circ}$ (kcal/mol)	Reference
F ⁻	-65.06	[1]	HHfO ₂ ⁺	-226.02	[1]
HF ₂ ⁻	-136.45	[1]	HHfO ₃ ⁻	-279.85	[1]
HF(aq)	-70.66	[1]	Hf ⁴⁺	-129.67	[1]
Cl ⁻	-29.80	[1]	HfO ²⁺	-183.492	[1]
HCl (aq)	-28.53	[1]	HfOH ³⁺	-185.32	[1]
NO ₃ ⁻	-22.52	[1]	Hf(OH) ₂ ²⁺	-243.64	[1]
HNO ₃ (aq)	-21.26	[1]	SiO ₂	-202.51	[1]
Si	0	[1]	SiF ₆ ²⁻	-517.80	[1]
HfSi ₂	-47.40	[2]	HSiO ₃ ⁻	-237.41	[1]
HfCl ₄	-211.84	[1]	Si(OH) ₄ (aq)	-306.45	[1]
HfF ₄	-433.43	[1]	SiO(OH) ₃ ⁻	-291.71	[1]
HfO ₂	-250.89	[1]	SiO ₂ (OH) ₂ ²⁻	-272.22	[1]
HfOCl ₂	-238.83	[1]	SiO ₃ (OH) ₂ ³⁻	-256.36	[1]

Highlights:

- Hf enhanced the removal of impurities from MG-Si, especially P.
- Eh-pH diagrams for leaching HfSi_2 were calculated.
- The highest removal fractions for B and P were 94.2% and 86.2%, respectively.
- The quantity of impurities within Si was reduced from 6126 ppmw to 94 ppmw.
- The amount of added Hf was reduced from 50,000 ppmw to 0.2 ppmw.

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