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Thermodynamic evaluation of Sr-containing Si metals and silicate melts for Si-Sr alloy production

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Synopsis

Reliable thermodynamic descriptions of the Si-based Sr-Al-Ca-Fe-Mg metal system and SiO_2-SrO-CaO-MgO-Al_2O_3 oxide system are essential for the understanding and optimizing the production of Si-Sr alloys. Phase relations of all SrO containing binary and ternary subsystems were evaluated and thermodynamically modelled based on the existing literature data. Phase equilibria in the SiO_2-SrO-CaO-MgO-Al_2O_3 higher-order oxide system were thus possible to calculate by the CALPHAD method. A thermodynamic description of the Si-Sr-Al-Ca-Fe-Mg metal system was developed based on assessment of all binary systems as well as all Si containing ternary subsystems. The newly developed thermochemical databases can be used to calculate the equilibrium distribution of Sr between metal and slag. The theoretical Sr distribution maps for both pure Si and 75FeSi alloys in different SrO-containing slags are reported.

Keywords

thermodynamic evaluation, Si-Sr-Al-Ca-Fe-Mg metal, SiO_2-SrO-CaO-MgO-Al_2O_3 oxide, Sr equilibrium distribution.

Introduction

Strontium distribution equilibria between the Si-based metals and SrO-containing silicate melts are of great importance for the development of new ferrosilicon products. To describe the complex phase equilibria between the Sr-containing Si metals and silicate slags, thermodynamic descriptions of the Sr-containing metal and oxide phases are essential. This paper summarizes our recent work on thermodynamic modelling of the Si-rich Si-Sr-Al-Ca-Fe-Mg metal and SiO_2-SrO-CaO-MgO-Al_2O_3 oxide systems.

Thermochemical descriptions of the above metal and oxide phases were input into databases for the FactSage™ software package. The model calculations for the phase equilibrium relations in the SiO_2-SrO-Al_2O_3 ternary oxide system were verified by laboratory experiments. The metal/slag strontium distribution equilibria at elevated temperatures were then evaluated thermodynamically. The present equilibrium simulations can serve as a 'map' for the metallurgist to design and optimize Si-Sr ferroalloy production.

Thermodynamic assessments

The metal system

Thermodynamic descriptions of the liquid and solid Si-based Si-Al-Ca-Sr-Fe-Mg alloy phases have been set up based mainly on the experimental data available in the literature. The compound energy formalism is applied to liquid and all the mixture phases as well as stoichiometric compounds.

The six-element metal system contains 15 binary, 20 ternary, 15 quaternary, and 6 quinary subsystems. Since the metal system is in the Si-rich domain, the Si-free ternary and higher-order subsystems are not considered in the present study. To ensure the reliability of the model calculation, all 15 binary subsystems were modelled to cover the whole composition range, and temperatures from the liquid phase to the sub-liquidus solid phases.

The calculated Sr-Si binary phase diagram, based on the assessment of Li *et al.* (2011), is shown in Figure 1. Experimental phase equilibrium data reported by Palenzona and Pani (2004) and Rygalin *et al.* (2010) is also shown in the diagram. The assessment emphasized the eutectic and peritectic reaction temperatures and compositions.

The experimental Sr-Al phase equilibria reported by Closset and Gruzleski (1982), Vakhobov, Eshonov, and Dzhurayev (1979), and Bruzzone and Merlo (1975) can be reproduced using the model parameters assessed by Zhong *et al.* (2004). The calculated phase diagram is shown in Figure 2.

The Ca-Sr phase diagram, assessed by the present authors based on the experimental liquidus and solidus data by Schottmiller,

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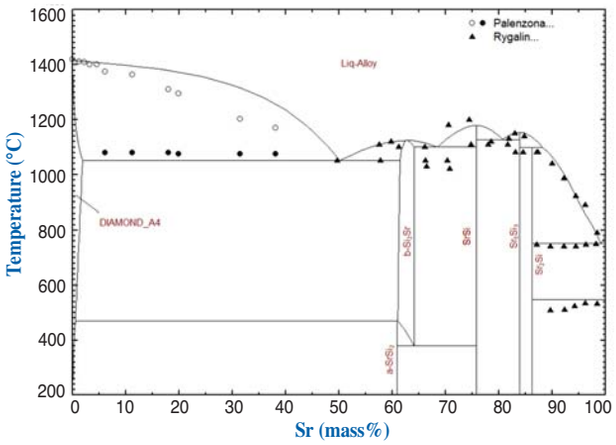

Figure 1—Calculated Si-Sr binary phase diagram (after Li *et al.*, 2011)

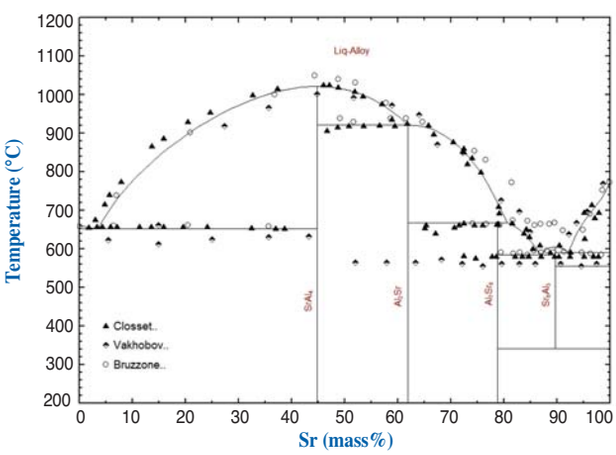

Figure 2—Calculated Sr-Al binary phase diagram (after Zhong *et al.*, 2004)

King, and Kanda (1958) is shown in Figure 3. These three binary subsystems, together with the Sr-Fe binary, are of great importance for the phase equilibria and elemental distributions of Sr-containing alloys.

There exist 10 Si-containing ternary subsystems which are also very important for the present thermodynamic descriptions, as shown in Table I. Only a few ternary systems have been thermodynamically assessed in the literature. Since the Sr concentrations in pure Si and FeSi alloys are in the range of dilute solution, *i.e.* < 5 wt%, ternary and higher-order contributions to the melts will not be significant. This means that the present database can represent thermochemical properties of the Si-based Sr-Al-Ca-Fe-Mg alloys at elevated temperatures.

The calculated Al-Al_2Si_2Sr pseudo-binary phase diagram is shown in Figure 4. In this ternary alloy system, the model calculation can reproduce the experimental phase boundaries (Sato *et al.*, 1985) quite well. The agreement between the calculated and measured phase equilibria by Vakhobov, Eshonov, and Dzhurayev (1979) is also satisfactory in the low-Sr composition domain.

Thermodynamic model calculations for the phase equilibria in the Si-Mg-Sr ternary as well as in the Si-Al-Ca-

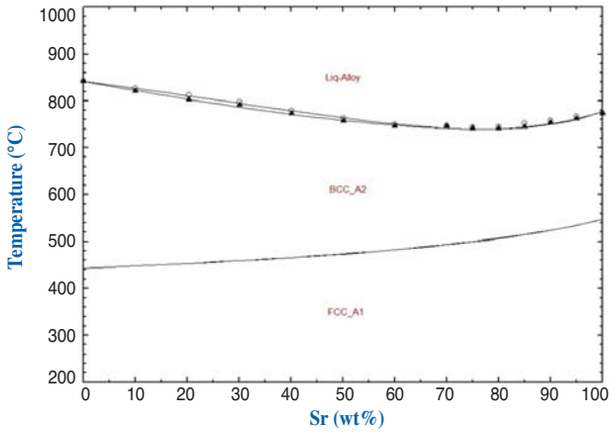

Figure 3—Calculated Ca-Sr binary phase diagram

Table I

Ternary subsystems used in the present database

No.	System			References
1	Si	Al	Sr	Sato *et al.* (1985), Vakhobov, Ganiev, and Djuraev (1975), Janz and Schmid-Fetzer (2009)
2	Si	Ca	Sr	No ref.
3	Si	Fe	Sr	No ref.
4	Si	Mg	Sr	Rokhlin and Dobatkina (2001), Gil-Santos *et al.* (2016)
5	Si	Al	Ca	Effenberg and Ilyenko (2004), Anglezio, Servant, and Ansara (1994a, 1994,)
6	Si	Al	Fe	Anglezio, Servant, and Ansara (1994a, 1994b)
7	Si	Ca	Fe	Anglezio, Servant, and Ansara (1994a, 1994b)
8	Si	Mg	Fe	Duo *et al.* (2007)
9	Si	Ca	Mg	Gröbner, Chumak, and Schmid-Fetzer (2003), Rokhlin, Evgeniya Lysova, and Materials Science International Team (2000)
10	Si	Al	Mg	Tang *et al.* (2012, Feufel *et al.* (1997)

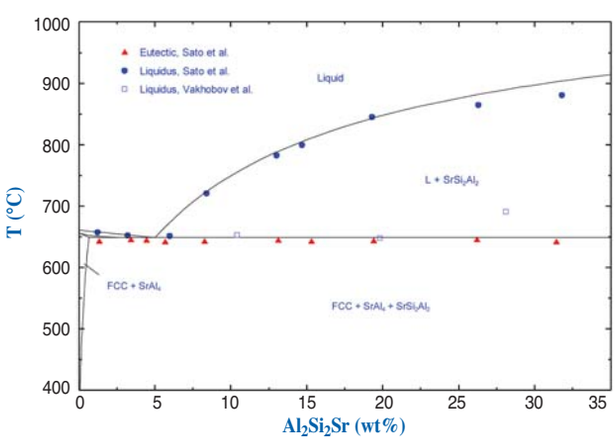

Figure 4—Calculated Al- Al_2Si_2Sr pseudo-binary phase diagram

Fe quaternary system were also examined with the experimental data in the literature. For the sake of simplicity, they are not presented here.

Thermodynamic properties of the Si-Sr-Al-Ca-Fe-Mg system are all extrapolated from the above assessed binaries and some ternaries, as well as Si-Al-Ca-Fe quaternary subsystems.

Oxide systems

The SiO_2-CaO-Al_2O_3-SrO-MgO oxide system consists of 10 binaries and 10 ternaries. Unlike the Si-rich metals, the slags vary over a large composition range. It is thus necessary to evaluate whole binary and ternary oxide subsystems in their entirety. To define the oxide equilibrium contents, both the liquid slag and solid oxide phases need to be correctly modelled. In the present work, the molten slag phase was modelled using the modified quasichemical solution model (Pelton and Blander, 1986). Solid non-stochiometric phases, for instance the monoxide phases, were modelled using the compound energy formalism.

Thermodynamic models of the SrO-free SiO_2-CaO-Al_2O_3-MgO oxide system can be found in the literature. Four SrO-containing binary and three SrO-containing ternary subsystems were modelled in the present work. Table II lists the binary oxide subsystems used.

The liquid SiO_2-SrO phase was assessed based on the phase equilibrium data available in the literature (Fields, Dear, and Brown, 1972; Hageman and Oonk, 1986; Huntelaar, Cordfunke, and Ouweltjes, 1992; Ghanbari-Ahari and Brett, 1988). All solid mixture phases in the present work are treated as stoichiometric compounds.

The experimental phase equilibria data related to liquid SrO-Al_2O_3 slag were mainly based on the experimental results of Hanic, Chemekova, and Udalov (1979) and Starczewski (1964). The present assessment was based on the experimental data of Starczewski (1964). The calculated SrO-Al_2O_3 phase diagram is shown in Figure 6. The model calculations fit the experimental equilibrium data by Starczewski (1964), since his data fits well to the SrO-SiO_2-Al_2O_3 ternary phase equilibria.

Phase equilibria in the SrO-SiO_2-Al_2O_3 system are of crucial importance for the determination of the Sr distribution between slag and metal. There are three ternary compounds reported by Dear (1957), namely $Si_2SrAl_2O_8$, $Si_2Sr_6Al_{18}O_{37}$, and $SiSr_2Al_2O_7$. Thermodynamic properties of these compounds were also reported in the literature (Lapina, Semenov, and Khodakovskii, 1989; Massazza and Sirchia, 1959). Based on the literature data, properties of these ternary compounds were estimated.

Table II

Binary subsystems used in the present database

No.	System		Reference
1	SiO_2	SrO	This work
2	SiO_2	Al_2O_3	Eriksson and Pelton (1993)
3	SiO_2	CaO	Eriksson and Pelton (1993)
4	SiO_2	MgO	Decterov, Jung, and Pelton (2002)
5	Al_2O_3	CaO	Eriksson and Pelton (1993)
6	Al_2O_3	SrO	This work
7	Al_2O_3	MgO	Jung, Decterov, and Pelton (2004a)
8	CaO	SrO	This work
9	CaO	MgO	Wu, Eriksson, and Pelton (1993)
10	MgO	SrO	This work

The calculated liquidus projection of the SiO_2-SrO-Al_2O_3 ternary oxide system is shown in Figure 7. It is seen that this ternary system is similar to the well-known SiO_2-CaO-Al_2O_3 ternary system. Two SrO-containing compounds precipitate in the middle of the composition range, where the slags exhibit low smelting temperatures.

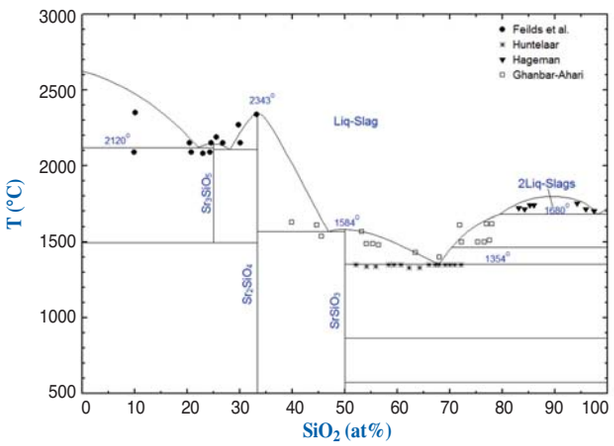

Figure 5—Calculated SiO_2-SrO phase diagram

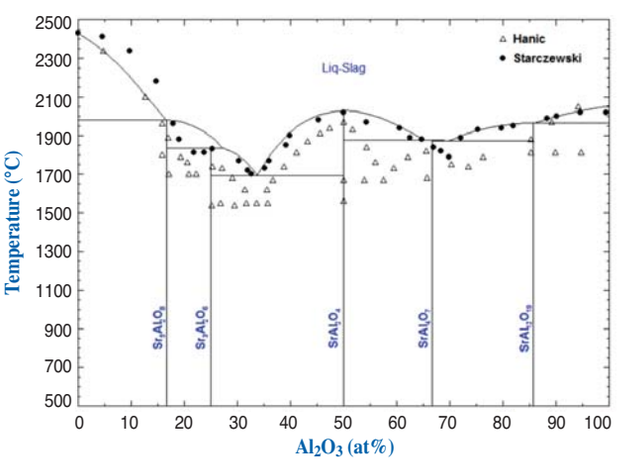

Figure 6—Calculated Al_2O_3-SrO phase diagram

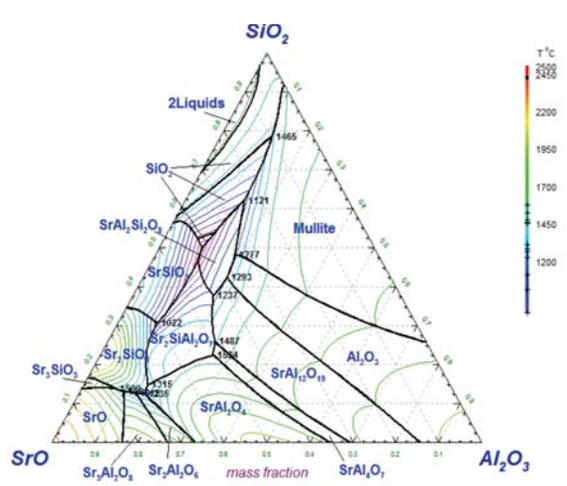

Figure 7—Calculated liquidus projection of the SiO_2-Al_2O_3-SrO system

For the sake of simplicity, detailed descriptions of the experimental data as well as model assessment will not be presented here. The information related to other ternary oxide subsystems is summarized in Table III.

Slag/metal equilibria

The slag/metal Sr partition equilibria are the most interesting aspect of the present study. The partition of Sr between Si-Sr metals and SrO-SiO_2 binary slags at different temperatures is shown in Figure 8. The Sr distribution equilibria between 75FeSi alloys and SrO-SiO_2 binary slags at 1600°C are also shown in the same diagram.

It is notable that the Sr contents in 75FeSi are about 10 times lower than those in Si metals. This is due to the strong positive interaction between Fe and Sr, which can also be observed by the immiscibility of Fe and Sr.

Figure 9 shows the iso-Sr composition contours for pure Si in equilibrium with the ternary SiO_2-SrO-Al_2O_3 slags at 1600°C. The amphoteric property of Al_2O_3 is rather obvious, *i.e.* Al_2O_3 acts as a basic oxide in the SiO_2-rich area and an acid oxide in the SrO-rich domain. Figure 10 shows the similar equilibrium iso-Sr contours for the same system at 1700°C.

By comparing Figure 10 to Figure 9, we see that temperature does not play a key role in the Sr partition equilibria in this ternary slag system. This means that the silicothermic reduction of SrO is relatively independent of temperature. However, slag composition plays a vital role in the Sr contents in Si metals, in particular for the higher SrO slags. By increasing the SrO content in the slag from 55 wt% to 60 wt%, the final equilibrium Sr content in Si will increase from around 6-7 wt% to 18-31 wt% at 1600-1700°C.

The present thermodynamic models can also be used to evaluate the solidification of Si/75FeSi alloys, smelting behaviour of SrO-containing slags, as well as materials and energy balances during metallurgical processes. This will be discussed in our next publication.

Conclusions

Thermodynamic descriptions of the Si-based Sr-Al-Ca-Fe-Mg metal and SiO_2-SrO-CaO-MgO-Al_2O_3 oxide systems have been established and implemented in the commercial software package FactSage. Thermodynamic modelling of the Si-based Si-Sr-Al-Ca-Fe-Mg metal system was developed based on assessments of all binary systems as well as the Si-Sr-Al, Si-Sr-Mg, Si-Al-Mg ternary, and Si-Al-Ca-Fe quaternary subsystems.

Table III

Ternary subsystems used in the present database

No.	System			Reference
1	SiO_2	Al_2O_3	CaO	Eriksson and Pelton (1993)
2	SiO_2	Al_2O_3	SrO	This work
3	SiO_2	Al_2O_3	MgO	Jung, Decterov, and Pelton (2004b)
4	SiO_2	CaO	SrO	This work
5	SiO_2	MgO	SrO	This work
6	Al_2O_3	CaO	SrO	This work
7	Al_2O_3	CaO	MgO	Jung, Decterov, and Pelton (2004b)
8	CaO	MgO	SrO	This work
9	Al_2O_3	MgO	SrO	This work

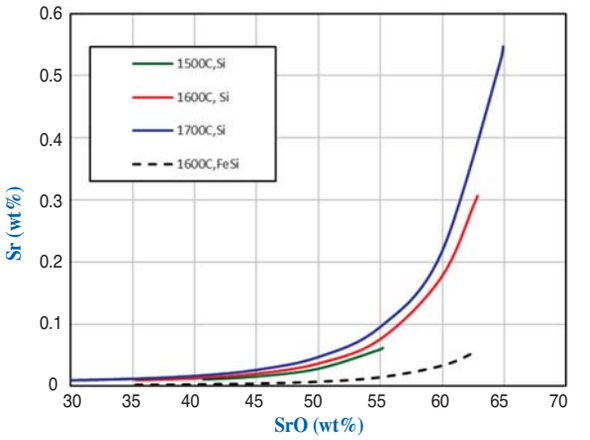

Figure 8—Calculated Sr distribution between Si75FeSi and SiO_2-SrO slag at different temperatures

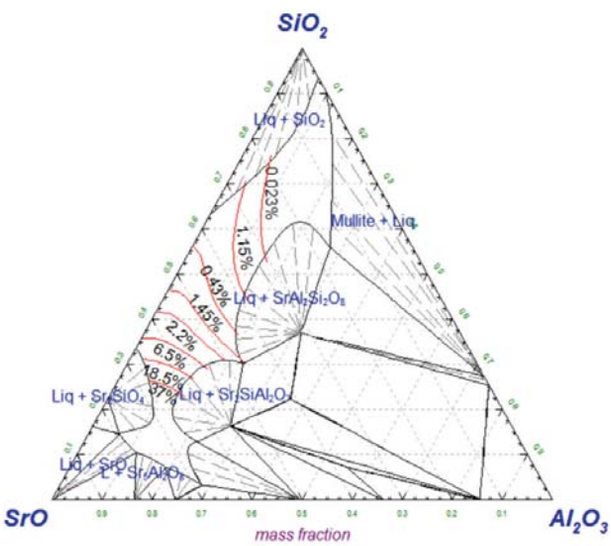

Figure 9—Calculated iso-Sr composition lines in Si metals represented in the SiO_2-SrO-Al_2O_3 ternary system at 1600°C

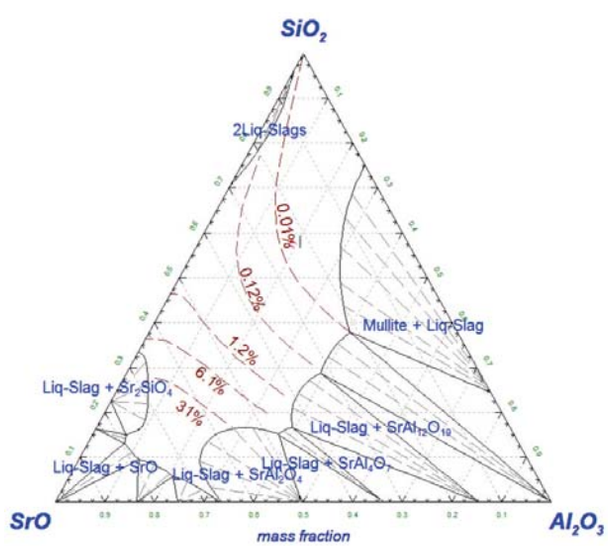

Figure 10—Calculated iso-Sr composition lines in Si metals represented in the SiO_2-SrO-Al_2O_3 ternary system at 1700°C

Phase relations in the SiO_2-SrO, SrO-Al_2O_3 binary as well as the SiO_2-SrO-Al_2O_3, SiO_2-SrO-CaO, and SiO_2-SrO-MgO ternary system were evaluated and thermodynamically modelled based on existing literature data. Phase equilibria in the SiO_2-SrO-CaO-MgO-Al_2O_3 higher-order oxide system were thus possible to calculate by the CALPHAD method.

The thermochemical databases have been applied to evaluate the Sr distribution equilibria between pure Si and SiO_2-SrO slags as well as FeSi and SiO_2-SrO slags. In addition, the equilibrium distribution of Sr between pure silicon and SiO_2-SrO-CaO-Al_2O_3 slags was calculated. It is found that the Sr contents in Si metals are much higher than those in 75FeSi alloys. The Sr contents in Si metals will depend strongly upon the slag composition, and weakly upon the temperature.

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