

Communications

Density and Interfacial Tension of Liquid Fe-Si Alloys

C. DUMAY and A.W. CRAMB

Numerous metallurgical processes such as the production and refining of iron-silicon alloys involve slag/metal reactions. The control of these processes requires a fundamental understanding of emulsification and entrainment phenomena; therefore, slag and metal densities, as well as metal/slag interfacial tension, have to be accurately determined. This work documents liquid Fe-Si alloy density measurements and Fe-Si/slag ($\text{Al}_2\text{O}_3/\text{CaO}/\text{SiO}_2$) interfacial tension measurements. The experiments were performed using the X-ray sessile drop technique at 1450 °C, which enabled the measurement of both parameters simultaneously.

The metal and slag systems were contained in high-purity alumina crucibles resting in a SiC resistance furnace. An X-ray unit was employed to determine the shape of sessile metal drops. Densities and interfacial tensions were obtained, from the contour of the droplets on the X-ray pictures, by numerically solving the Young-Laplace equation. The experimental setup, image processing, and numerical resolution are detailed in References 1 through 5.

The Fe-Si alloys were prepared by melting solid pieces of the two pure components in a resistance furnace equipped with a horizontal alumina tube sealed at both ends with two gas tight water-cooled aluminum jackets. The solid iron and silicon pieces contained in high-purity alumina crucibles were pushed through this tube under an argon/hydrogen atmosphere and left for about 1 hour in the hot (middle) zone for melting and homogenization. The solidification of the samples was then obtained by pushing the crucible toward the cold end of the furnace tube. The metallic purity of iron (from Noah Technology, San Antonio, TX) was 99.5 pct and that of silicon (Johnson-Mathey, Ward Hill, MA) was 99.9995 pct with about 2000 ppm of antimony.

The alloy pieces used for the sessile drop experiments were roughly conical in order to avoid drop pinning on the bottom of the crucibles during the experiments: advancing metal drops were produced while the metal/slag system was melting. The alloy samples were sandblasted in order to remove the oxide crust that could be seen at the surface. The pieces were then washed with ethanol, carefully weighted, placed in the alumina crucible, and covered with slag particles. The composition of each metal drop was determined after experiment by wet chemical analysis.

The measurements reported here were, unless noted, all performed with an identical slag chemistry (12 wt pct Al_2O_3 , 29 wt pct CaO, and 59 wt pct SiO_2). This slag

was prepared with high-purity oxide powders (Al_2O_3 99.5 pct, Fisher Scientific, Pittsburgh, PA, CaO 99.3 pct Baker Analyzed Reagent, 99.5 pct, SiO_2 , Johnson-Mathey) in a resistance furnace with an air atmosphere.

The slag cover reduces the overall contrast of the X-ray pictures, especially in the case of silicon-rich alloys. The accuracy of the drop profile determination is then lower than that of surface tension experiments. Small gas bubbles were often found trapped at the metal/slag interface. These bubbles were formed during the melting of the metal/slag system and occasionally lead to small perturbations of the drop shape. The slag protected the metal drop from oxidation during the experiments that were carried in an argon/carbon monoxide atmosphere. In presence of slag, the Fe-Si alloys are very nonwetting (contact angles >160 deg) with respect to the substrate (alumina), and this helps in the formation of symmetrical drops. Since the interfacial tension measurement consists in a comparison of gravity and interfacial effects, the slag cover enables the use of larger metal drops, and this balances the loss of accuracy resulting from the reduction in contrast described earlier.

In the present work, density measurements have been performed at 1450 °C for Fe-Si alloys with a silicon content ranging from 15 to 80 wt pct. The results are reported in Table I and plotted in Figure 1 along with previous data from Dzhemilev *et al.*^[6] at 1550 °C, Kawai *et al.*^[7] at 1550 °C, and Gertman *et al.*^[8] at 1500 °C. Considering the order of magnitude of typical thermal expansion coefficients for liquid metals, as well as the values measured by Kawai *et al.*,^[7] there is an excellent agreement between this study and the previous investigations by Dzhemilev *et al.* and Kawai *et al.*

Expressed in terms of molar volumes (Table I), the results could be interpreted by two apparent linear regions corresponding to conditions where the change in the partial molar volumes of iron and silicon are a very weak function of composition. The molar volumes are plotted in Figure 2 where the data point shown for pure metastable liquid iron at 1450 °C was calculated from Reference 9, and the data point added for pure liquid silicon was obtained from the same reference.

By definition,

$$V_m = X_{\text{Fe}} \bar{V}_{\text{Fe}} + X_{\text{Si}} \bar{V}_{\text{Si}} \quad [1]$$

where V_m is the molar volume of the Fe-Si solution, \bar{V}_{Fe} and \bar{V}_{Si} are the partial molar volumes of the pure components, and X_{Fe} and X_{Si} are the mole fractions.

From the experimental data shown in Figure 2, for X_{Si} lower than 0.6, the partial molar volume of iron in solution is approximately 7.8 cm³/mol with that of silicon being approximately 9.1 cm³/mol. For X_{Si} greater than 0.6, the partial molar volumes for iron and silicon are approximately 4.3 and 11.1 cm³/mol, respectively.

For an ideal liquid solution, the partial molar volumes of iron and silicon would be constant over the entire range of composition. The molar volume of Fe-Si alloys exhibits a very strong negative deviation from ideality in accordance with the behavior of the activities and the heat of mixing in this system.

The interfacial tensions of Fe-Si alloys in contact with a CaO-SiO₂-Al₂O₃ covering slag are presented in

C. DUMAY is with Pechiney Electrometallurgie, France. A.W. CRAMB is with the Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213.

Manuscript submitted August 3, 1994.

Table I. Density and Molar Volume of Fe-Si Alloys at 1450 °C

Number of Measurements	Silicon Content of the Alloy (Wt Pct)	Density (g/cm ³)	Molar volume (cm ³ /mol)
3	16.3	6.039	7.96
1	18.1	5.784	8.20
2	24.4	5.472	8.23
1	30.3	5.226	8.22
2	35.6	4.828	8.55
1	41.2	4.715	8.41
2	46.2	4.342	8.83
4	56.0	3.861	9.27
3	61.8	3.631	9.55
3	64.1	3.570	9.58
6	65.93	3.478	9.76
7	67.03	3.395	9.92
3	77.97	3.069	10.27

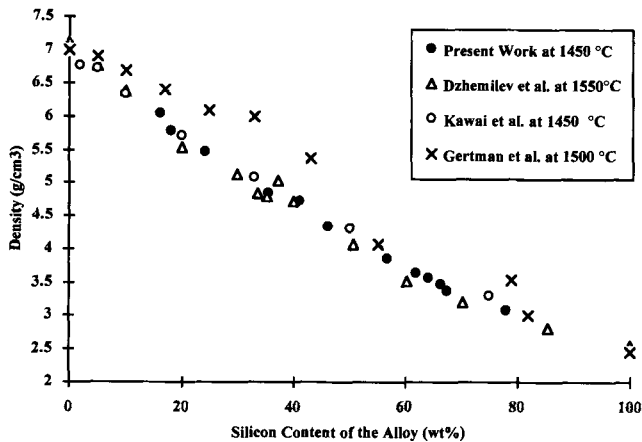


Fig. 1—Density measurements of Fe-Si alloys at 1450 °C.

Table II and are average values taken over the various experiments performed with identical or very close alloy compositions. The scatter observed for the calculated values was high (up to ± 15 pct for high silicon contents in the metal) since the calculated value for the interfacial tensions is extremely sensitive to small changes in the drop profile. The calculation of interfacial tension requires an accurate value for the density of the slag since the metal/slag density difference becomes quite low when high silicon contents in the metal are considered. A value of 2.6 g/cm³ for the slag (12 wt pct Al₂O₃, 29 wt pct CaO, and 59 wt pct SiO₂) at 1450 °C was determined from sessile drop measurements performed on slag drops contained in graphite crucibles.

The surface activity of antimony and sulfur was also checked since these two impurities are known to significantly reduce the surface tension of liquid iron. Several experiments were carried with samples made out of silicon containing less than 50 ppm of antimony, and the values obtained for the interfacial tension were not significantly different from those obtained with regular alloy samples (prepared with Si containing about 2000 ppm of antimony). These results are shown in Table III. Sulfur, very surface active in liquid iron, was

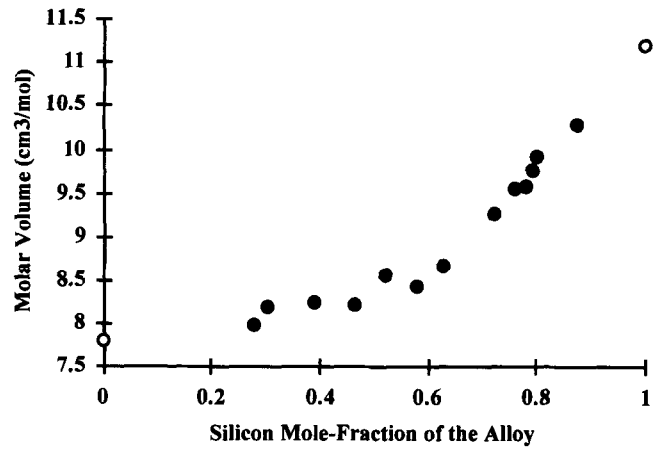


Fig. 2—Molar volumes of Fe-Si alloys at 1450 °C.

Table II. Interfacial Tension of Fe-Si Alloys in Contact with a Lime-Alumina-Silica Slag at 1450 °C

Silicon Content of the Alloy (Wt Pct)	Interfacial Tension (mN/m)
16.3	1395
18.1	1404
24.4	1281
30.3	1062
35.6	975
41.2	896
46.2	1004
56.8	772
66.2	778
78	784

Table III. Effect of Alloy Antimony on Interfacial Tension

Silicon Content of the Alloy (Wt Pct)	Estimated Antimony Content of the Alloy (ppm)	Interfacial Tension (mN/m)
16.3	300	1395
18.1	<50	1404
24.4	500	1281
30.3	<50	1062
35.6	700	975
41.2	<50	896

not found to be as significantly surface active in the silicon-rich alloys covered with a slag (Table IV) where an increase in metal sulfur content of 180 ppm caused only a 46-mN/m decrease in interfacial tension.

Aluminum and calcium levels set by the metal/slag equilibrium are below 500 ppm. This should not change noticeably the interfacial tension since metals are generally not very surface active in liquid iron or liquid silicon.^[10,11] Other impurity levels (metals and rare earths) are below 10 ppm in the alloy, and their effect on the interfacial tension is thus believed to be negligible.

For the present work, the oxygen potential in the

Table IV. Effect of Alloy Sulfur Content on Interfacial Tension

Wt Pct Al ₂ O ₃	Wt Pct CaO	Wt Pct SiO ₂	Sulfur Content	Estimated Slag Density (gm/cm ³)	Interfacial Tension (mN/m)
12	29	59	<20 ppm	2.6	778
11.7	29.6	58.5	200 ppm	2.6	732
12.1	29.3	59.0	6,000	2.6	637
11.7	29.4	57.7	15,000	2.6 (2.7)	780 (689)

system was set by the silicon/silica equilibrium and was very low ($P_{O_2} < 10^{-18}$ atm for wt pct Si > 40; $P_{O_2} < 10^{-16}$ atm for wt pct Si > 15). Consequently, the authors believe that the studied systems did not contain any significant concentration of surface-active impurities.

Some surface-tension measurements have been previously reported on Fe-Si alloys, and the reported values show a surprising similarity to the results of this study. Figure 3 presents the results of this study as well as the surface-tension values reported by Dzhemilev *et al.*,^[6] Kawai *et al.*,^[7] and Ixanov *et al.*^[12] Other studies by Popel *et al.*^[13] and Monma and Suto^[14] present results that are in good agreement with those of Dzhemilev *et al.* and Kawai *et al.* Hence, the values measured by Monma *et al.* seem slightly high in comparison to the other works.

The measured interfacial tension and surface-tension values are very close, and the shape of the curve is identical for the slag composition studied in the present work. This indicates little interaction between the slag and the metal. It is worth noting that silica was found to be surface active in alumina-lime-silica-base slags. This suggests that the surface of a silica-rich slag is close to saturation with silica.

Published data on interfacial tension measurements regarding Fe-Si alloys are very scarce, and only one study was found regarding high silicon content alloys. This work performed by Popel^[15] indicates lower interfacial tension values than the ones that were obtained in this study. The slag composition was 18 wt pct alumina, 46 wt pct lime, and 36 wt pct silica.

In the course of our study, a value of 492 mN/m was obtained for the interfacial tension between an alloy containing 65 wt pct silicon and a slag containing 16 wt pct alumina, 42 wt pct lime, and 42 wt pct silica. This result agrees quite well with the measurements reported by Popel: an increase of the ratio of the lime content over silica content of the slag lowers the interfacial tension, and this indicates an increase of the metal slag interaction. This measurement (slag 2) is reported in Figure 4 along with Popel's results and the values obtained with the slag composed of 12 wt pct alumina, 29 wt pct lime, and 59 wt pct silica (slag 1).

The densities of the Fe-Si alloys measured in this work were found to be in good agreement with the measurements by Dzhemilev *et al.*^[6] and Kawai *et al.*^[7] The molar volume curve exhibits a strong negative deviation from ideality. Interfacial tensions measured with a slag containing 12 wt pct alumina, 29 wt pct lime, and 59 wt pct silica at 1450 °C were found to be a function of silicon content of the alloy, ranging from 1.4 N/m at 20 wt pct silicon to 0.8 N/m at 80 wt pct silicon.

The authors would like to thank the members of the

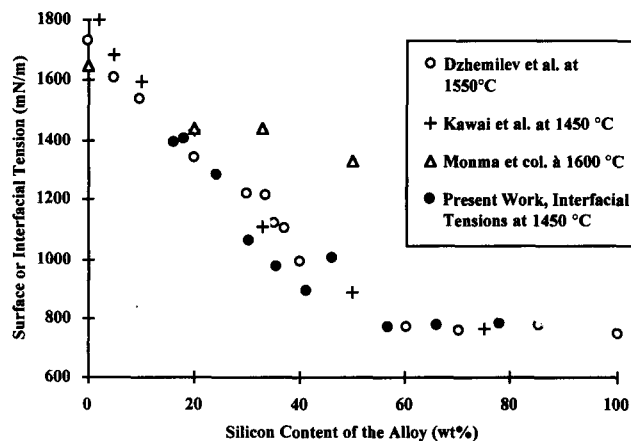


Fig. 3—Surface and interfacial tension measurements of Fe-Si alloys at 1450 °C.

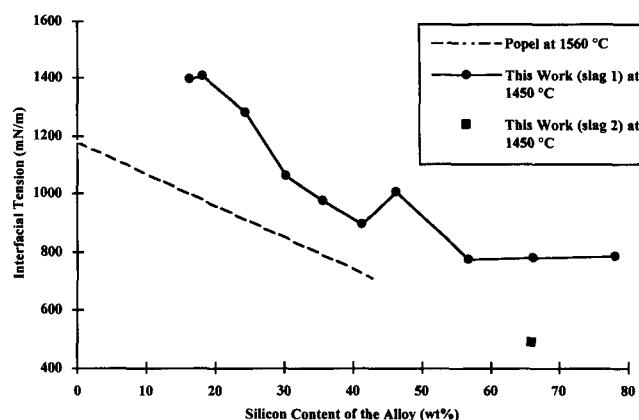


Fig. 4—Interfacial tension measurements of Fe-Si alloys at 1450 °C.

research center of Péchiney Electrometallurgie (LCR) for their technical and financial support. The work was also partially funded through the Center for Iron and Steelmaking Research at Carnegie Mellon University. The authors would also like to express special gratitude to Dr. A. Sharan for useful discussions and Dr. I. Jimbo for technique development.

REFERENCES

- I. Jimbo, A. Sharan, and A.W. Cramb: *Proc. 76th Steelmaking Conference of the Iron and Steel Society*, Dallas, TX, 1993, pp. 485-94.
- I. Jimbo and A.W. Cramb: *Metall. Trans. B*, 1993, vol. 24B, pp. 5-10.
- Y. Rotenberg, L. Boruvka, and A.W. Neumann: *J. Colloid Interface Sci.*, 1983, vol. 93 (1), pp. 169-83.

4. I. Jimbo and A.W. Cramb: *Proc. 6th Int. Iron and Steel Congress*, The Iron and Steel Institute of Japan, Nippon, 1990, pp. 499-504.
5. I. Jimbo and A.W. Cramb: *Iron Steel Inst. Jpn. Int.*, 1992, vol. 32 (1), pp. 26-35.
6. N.K. Dzhemilev, S.I. Popel, and B.V. Tsarevskii: *Phys. Met. Metallogr.*, 1964, vol. 18, pp. 77-78.
7. Y. Kawai, K. Mori, M. Kishimoto, K. Ishikura, and T. Shimada: *Tetsu-to-Hagané*, 1974, vol. 60 (1), pp. 29-31.
8. Y.M. Gertman and P.V. Gel'd: *Zh. Fiz. Khim.*, 1962, vol. 36, p. 1477.
9. L.D. Lucas and G. Urbain: *Compt. Rend.*, 1962, vol. 255, pp. 2414-16.
10. B.J. Keene: *Int. Mater. Rev.*, 1988, vol. 33 (1), pp. 1-50.
11. B.J. Keene: *Surf. Interface Anal.*, 1987, vol. 10, pp. 367-83.
12. B. Ixanov, P. Laty, J.-C. Joud, and P. Desré: *Cheml. Phys.*, 1978, vol. 75 (5), pp. 35-40.
13. S.I. Popel, L.M. Shergin, and B.V. Tsarevskii: *Russ. J. Phys. Chem.*, 1970, vol. 1 (44), p. 37.
14. K. Monma and H. Suto: *J. Jpn. Inst. Met.*, 1960, vol. 1, pp. 42-47.
15. S.I. Popel: *Sb. Nauchno. Tr. Ural'sk. Polit.*, 1963, No. 126, p. 5.

Purifying Effects and Product Microstructure in the Formation of TiC Powder by the Self-Propagating High-Temperature Synthesis

DAE KYU CHANG, CHANG WHAN WON, BYUNG SUN CHUN, and GUN CHOO SHIM

In self-propagating high-temperature synthesis (SHS), the exothermic heats of reaction usually involving solid reactants are sufficient for the process to sustain itself once the reactant mixture is ignited. Much research has been done on the application of SHS for the synthesis of many high-temperature materials.^[1,2,3] The SHS process has also been applied to the joining of ceramics to metals.^[4] Advantages of SHS include the simplicity of apparatus as well as the absence of the need for external heating other than the small amount of heat for ignition. Furthermore, due to the fact that the SHS process typically takes place above 2000 °C, many of the impurities volatilize, often yielding a product containing less impurities than in the reactant mixture. Among the numerous materials synthesized by SHS, TiC has attracted much attention because of its superior high-temperature resistance and strength, hardness, and wear resistance.

DAE KYU CHANG is with the Korea Institute of Energy and Resources, Daedeok Science Town, Daejeon, Korea 305-343. CHANG WHAN WON and BYUNG SUN CHUN, Professors, are with the ERC for Rapidly Solidified Advanced Materials and the Department of Metallurgical Engineering, Chungnam National University, Daejeon, Korea 305-764. GUN CHOO SHIM is with Korea Institute of Geology, Mining and Materials, Daejeon, Korea 305-350.

Manuscript submitted February 8, 1993.

Conventional TiC production methods such as the carbothermic reduction of titanium dioxide, the titanium hydride process, and chemical vapor deposition suffer from the shortcomings of high oxygen or hydrogen content and low purity, which adversely affect the mechanical properties of the product. Most published articles on SHS so far deal with mathematical modeling,^[5] materials synthesis,^[6] or materials synthesis by reactive sintering under pressure.^[7] The main objectives of this work were to study the effect of SHS on lowering the impurity content of the product and to examine the effect of the reactant mixing ratio on the product microstructure.

As shown in Figure 1, the experimental apparatus consisted of a stainless reaction chamber, a vacuum system, and a power supply for igniting the sample. Titanium and carbon powders were weighed to give C/Ti ratios of 0.5 to 0.9. These ratios fall within the TiC_x phase field of the Ti-C phase diagram.^[8] Some runs were made with C/Ti ratios up to 1.3 for comparison. The particle size and chemical composition of the titanium and carbon powders used in this experiment are shown in Table I. The powders were mixed in a polyethylene container and thoroughly mixed after adding a small amount of alcohol to facilitate mixing and pelletizing. The mixture was dried completely under vacuum at 70 °C for 24 hours and then pressed into pellets of a 25-mm diameter and 20 to 30 mm in length.

The reactor was evacuated and refilled with argon to a slightly positive pressure. The pellet was placed on a graphite plate and ignited. After the reaction, the impurity material condensed on the reactor wall was analyzed by proton-induced X-ray emission (PIXE). The product was examined by X-ray diffraction, and the impurity contents before and after the reaction were analyzed by atomic absorption spectroscopy. In addition, the morphology of the product as affected by the initial mixing ratio was evaluated with scanning electron microscopy (SEM).

After reacting the carbon and titanium powders, the X-ray diffraction pattern showed only TiC_x peaks for samples with the initial C/Ti ratios of 0.5, 0.7, 0.8, and 0.9, as shown in Figure 2. Some unreacted carbon appeared at higher C/Ti ratios.

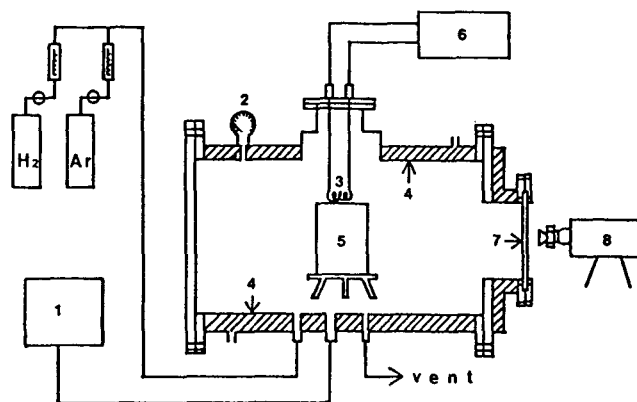


Fig. 1—Schematic diagram of experimental apparatus: (1) vacuum pump; (2) vacuum gauge; (3) tungsten filament; (4) cooling device; (5) sample; (6) power supply; (7) heat-resistant glass; and (8) optical pyrometer.