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Thermal conductivity of solidified industrial copper matte and fayalite slag

David Sibarani[1], Joseph Hamuyuni[2*], Matti Luomala[2], Mari Lindgren[2], Ari Jokilaakso[1]

[1]Aalto University School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, FI-02150 Espoo, Finland

[2]Outotec (Finland) Oy, Research Center, Kuparitie 10, PO Box 69, FI-28101 Pori, Finland.

Abstract

The thermal conductivity of various copper matte and fayalite slag was measured using laser flash analysis, a non-steady state measurement method. Industrial matte and slag samples were taken in such a way that their composition represented typical process conditions. Thermal conductivities for solid copper matte (average 64 % Cu) were found to be from 1.2 W m^{-1} K^{-1} at 300 °C to 2.1 W m^{-1} K^{-1} at 900 °C. Because arsenic is one of the most important impurities in copper matte, its effect on thermal conductivity was investigated with As-doped matte samples up to 0.59 % As. The results showed substantially lower thermal conductivity, between 0.5 and 1.3 W m^{-1} K^{-1} at 300 to 900 °C with low As matte, behavior that is analogous to that of a semiconductor. The data obtained showed that the thermal conductivity of copper matte increased linearly with temperature, but the gradient was small. The thermal conductivity of slags was found to be between 1.6 and 1.9 W m^{-1} K^{-1}, values that are consistent with earlier studies.

Key words: *copper matte, slag, conductivity measurement, diffusivity, laser flash analysis,*

Introduction

Copper flash smelting is a method used to process sulfidic copper raw materials (typically concentrates with 20-30 % Cu) into a molten copper-rich matte and, in a few cases, blister copper. At the same time, an impurity-rich and separable slag of molten oxides is generated. When smelting to matte, the copper content of matte (known as matte grade) optimally varies from 55 to 68 %. The smelting temperature is high, i.e., 1250 - 1300 °C, thus requiring a good cooling system for the furnace. Although current systems developed for the flash furnace can

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[*] Corresponding author: joseph.hamuyuni@outotec.com

already provide efficient cooling, the future of digitalization requires more process data such as thermal conductivity [1].

In particular, thermal conductivity data for matte and slag can provide more information about real time furnace temperature [1]. If these data are applied, it could result in prolonged refractory lining, increased production time, and improved safety of the working environment.

As a result of the increased throughput and capacity of flash smelting furnaces, the thermal load on their refractory linings has increased and new cooling systems have been designed for further protection. The enhanced cooling will create a freeze lining on the refractory or cooling plate surface. This freeze lining is a layer of solidified slag whose thickness is based on the thermal balance between the melt and the cooling water flowing in the water channels of the cooling element through the furnace structure. The thermal conductivity and specific heat of the solid slag or matte layers on the furnace walls are critical material properties in the thermal design of the furnace wall and cooling system, as well as the digital expert systems. The convective heat transfer coefficient from the melt to the wall is a function of the material properties of the molten phase and, therefore, the thermal conductivity of the slag and matte would be needed.

Currently, thermal conductivity data for copper smelting matte and slag are not readily available. The scarcity of data is partly caused by a lack of suitable equipment and other temperature-linked constraints of handling slag and matte in conditions comparable to industrial operations. Thermal conductivity data for some minerals and pure sulfides can be found in the literature, although they are insufficient to be used to represent actual matte and slag compositions [2]. However, for silicate slag, if the sample is rapidly cooled from high to room temperature, the crystalline structure can be preserved making low temperature measurements more reliable.

One of the most practical methods in acquiring thermal conductivity data is the laser flash method. The laser flash method, or simply laser flash analysis (LFA), is a transient indirect method of determining thermal conductivity using the thermal diffusivity of the materials. It was already in use in 1961 when Parker et al. [3] combined diffusivity and specific heat capacity to calculate thermal conductivity. By 2001[4], a single unit capable of measuring both diffusivity and heat capacity and combining them into thermal conductivity was already available. LFA has numerous advantages including the use of only small samples, its non-destructive nature, and the speed at which measurements can be taken [5]. Additionally, using this method, measurements can be made in a narrow temperature range, a feature that is useful in understanding the structural phenomena of materials at elevated temperatures. The method is also cheaper because it uses fewer components than other techniques, without compromising the quality of results. Recently, LFA has successfully been used to acquire thermal conductivities of titanium [6] and synthetic iron-free [7] slags.

Copper matte primarily contains copper and iron sulfide but can also have a lot of impurities such as arsenic, lead, bismuth, antimony, tellurium, and precious metals. There are no data in the literature that provide thermal conductivity for such compositions at smelting temperature (approx. 1250-1300 °C). However, the thermophysical property data of sulfide components of matte which are analogous, such as specific heat capacity [8,9], can be found in the literature. According to research by Nishioka [8], specific heat capacity has a close direct relationship with thermal conductivity. The heat capacity of Cu_2S at 107-677 °C ranges from 0.7 to 0.5 J g^{-1} K^{-1}[8,9]. This minor change indicates that temperature has a small influence on the heat capacity of Cu_2S (and potentially on the thermal conductivity). Duan et al. [10] have shown that changes in temperature have a significant effect on lattice structures but not necessarily on conductivity. In a narrow temperature range, thermal conductivity data for Cu_2S [11-15] and FeS_2 [16] are available in the literature. In all sources, copper and iron sulfides are classified as semiconductors (*p*-type) with thermal conductivity values between 1.2 and 1.3 $Wm^{-1}K^{-1}$. Uhlig et al. [16] have shown that doping improves thermal conductivity by modifying conductivity behavior from *p*-type to *n*-type. In their study, FeS_2 was doped with cobalt, resulting in an increase in thermal conductivity to 2.1 $Wm^{-1}K^{-1}$.

Generally, thermal conductivity studies on silicate-based, cooled (solidified) slags have shown that the crystallinity and porosity of the sample (pure solid substances) are the main factors that affect thermal conductivity [17]. Very crystalline phases tend to have higher thermal conductivities than non-crystalline ones. Pores, microcracks, and other forms of flaws reduce thermal conductivities. The thermal conductivity of molten silicate-based slag is mainly influenced by the degree of polymerization. This is because the 4-oxygen tetrahedron formed with a Si atom is covalently bonded to form a network of bonds in a melt. Thus, due to the heat transfer dependence on phonon vibration, thermal conductivity will be influenced by the number of covalent bonds (together with ionic). The thermal conductivity of fayalite slag at liquidus temperature increases with the SiO_2 content of the slag [18,19].

The main goal of this research was to investigate and measure the thermal conductivity of solid copper matte and fayalite slags between 300 and 900 °C, and that of liquid fayalite slag from 300 to 1200 °C. The motivation for this kind of research stems from the more sophisticated modeling and design tools that can simulate freeze lining formation when the thermal conductivity and specific heat capacity of matte and slag are known. LFA was used to acquire the thermal conductivities of industrial copper matte and slag.

Method

Materials

Matte and slag samples were obtained from a flash smelter. They were selected in such a way that they were representative of typical operating conditions, including temperature, matte grade etc. Sampling was done at the tap hole and at a temperature of approximately 1200 °C. A "spoon" was used to tap a sample of a few hundreds of grams from which the experimental samples were taken. The chemical analysis of matte and slag samples are shown in Table I. Three copper matte samples were in the as-taken condition, whereas two matte samples were doped with arsenic, one of the main impurities in copper smelting, to investigate its effect on thermal conductivity. For arsenic doping, two matte samples were melted in an alumina crucible up to 1200 °C in an induction furnace with a continuous flow of argon gas, and a predetermined amount of arsenic in the form of As_2O_3 was added to the melt. The melt was mixed thoroughly and held for enough time to allow mixing before rapid cooling in air. Three samples of copper matte can be distinguished by their copper content, which was measured at 62.5 wt.%, 66.0 wt.%, and 71.6 wt.% for M1, M2, and M3, respectively. Three slag samples were differentiated by their iron to silica ratio, an important parameter in determining the smelting operating conditions. Typically, the Fe to SiO_2 ratio in copper smelting operations can range between 0.7 and 2.1, depending on the process and raw materials used. Finally, two As-doped copper matte samples contained different arsenic concentrations (by percentage), 0.26 wt.% and 0.59 wt.%, but a similar copper concentration, 64-65 wt.%. The chemical analyses presented in Table I were obtained using ICP-OES (inductively coupled plasma, optical emission spectroscopy). The proportion of magnetite was determined using Satmagan equipment. The sulfur content was determined using an ELTRA 2000 analyzer (Eltra GMBH, Haan, Germany).

Table I. Composition of slag and matte samples used in the experimental work

Element (ICP)	**Unit**	**Slag**			**Matte**				
		S1	S2	S3	M1	M2	M3	DM1	DM2
Al	wt.%	4.40	3.01	3.06	<0.01	<0.01	<0.01	0.02	0.01
Fe	wt.%	33.80	36.30	38.30	11.9	9.19	5.99	9.13	10.60
Ni	wt.%	0.08	0.09	0.08	0.76	0.79	0.69	0.80	0.72
Cu	wt.%	1.09	1.34	1.08	62.50	66.00	71.60	65.20	64.00
Zn	wt.%	3.11	3.57	3.48	1.05	0.87	0.82	0.82	0.84
As	wt.%	0.15	0.23	0.20	0.16	0.17	0.25	0.59	0.26
Pb	wt.%	0.39	0.55	0.38	0.91	0.83	0.79	0.75	0.75
SiO_2	wt.%	35.60	32.00	30.80					
Magnetite (Satmagan)	wt.%	9.40	12.90	12.60					
S(ELTRA)	wt.%				21.2	20.7	20.3	21.10	20.00
Fe/SiO_2	-	0.95	1.13	1.24					

Microstructure and phase analysis

Before the thermal conductivity measurements, the microstructures of the samples were analyzed using scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). The samples were subjected to normal metallographic methods of preparation by grinding and polishing and the polished sections were carbon coated to enhance imaging by inhibiting charging whilst improving the secondary electron signal. Carbon coating was done using a Leica EM SCD05 (Vienna) sputtering device. A LEO 1450 with Oxford X-Max EDS equipment was used for SEM-EDS. During the measurements, an acceleration voltage of 15 kV, beam emission current of 135 μA, and spot size of 90 nm were maintained.

Determination of thermal conductivities

Thermal conductivities were determined using the diffusivity and specific heat capacity of the samples. Diffusivity was measured with an LFA 457 Microflash from Netsch Gerätebau GmbH, Germany. The samples were coated with graphite and tested from room temperature to 900 °C under an inert atmosphere. The specific heat capacity, *Cp*, was obtained using the laser flash method by matching with a standard (reference) material of known *Cp*. Then the thermal conductivity at a specific temperature, *T,* was calculated using equation (1):

$\lambda(T) = \alpha(T) \cdot \rho(T) \cdot C_p(T)$,

where λ is the thermal conductivity [W/(m·K)], α is the thermal diffusivity [mm^2s^{-1}], *Cp* is the specific heat capacity [J/(g·K)], ρ is the density [g/cm^3], and *T* is the temperature [°C].

Thermal conductivity measurements on both solid and liquid slags are known to contain contributions from radiation and convection. In Netzsch LFA 427 and 457 laser flash analyzers, radiative and convective heat loss corrections are integrated in the data analysis software [20]. The standard deviation (Std. Dev/(mm^2/s)) for undoped matte was found to be between 0.001 – 0.015; for doped matte from 0.006-0.021; and for slag 0.001- 00.005.

Results and discussion

Characterization of matte and slag samples

Figs. 1-3 present back-scatter electron micrographs of the matte and slag samples showing the main phases. EDS confirmed that the compositions of the phases were within the range of typical industrial mattes and slags for fayalite slag-based copper smelting. Fig. 1 A-C are as-taken copper matte samples. The main phase was Cu_2S-FeS, which is the typical copper matte phase. Traces of Fe_2O_3 were distributed evenly in the matte phase. The presence of Fe_2O_3 can be attributed to phase formed at high temperature due to oxidation of the iron sulfide. Although the figure only shows Fe_2O_3, traces of FeO were also detected using EDS. Lead was detected in two forms, as Pb-Ni-Sn and Pb-Ni-Cu phases. It should be noted that samples are not completely homogeneous due to slow cooling in air.

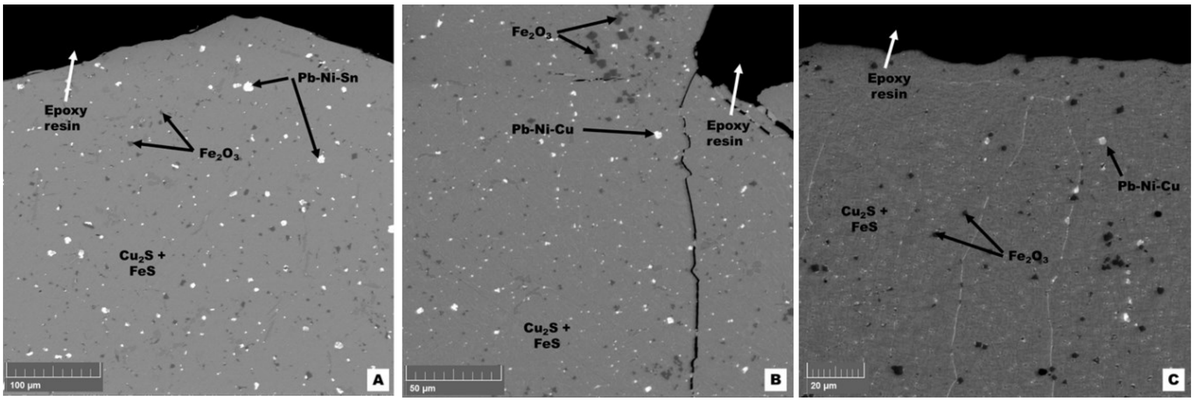


Figure 1. Backscatter scanning electron micrographs of matte-M1 (A), M2(B), and M3 (C)

Fig. 2 shows micrographs of arsenic-doped matte. The arsenic was bound to nickel in the matte phase as Ni-As (1:1 ratio) and was distributed in the form of spherical droplets, possibly a speiss phase. It can also be observed that the Pb was bound closely around the Ni-As droplets.

The association of metals Pb and Ni has been reported in earlier studies [21]. The microstructure of DM1 and DM2 looked different from that of M1-M3, as the former did not seem to contain Fe_2O_3 droplets. This can be attributed to the much faster cooling after re-melting during arsenic doping. The SEM investigation also confirmed that there were no cracks that would affect the thermal conductivity of the samples.

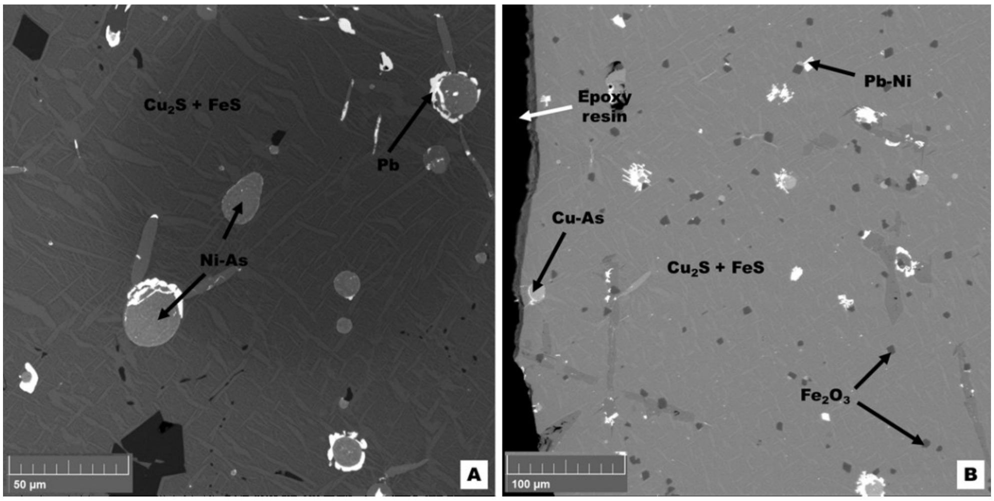


Figure 2. Backscatter scanning electron micrographs of arsenic doped matte samples-DM1(A) and DM2 (B)

SEM images of slag samples S1, S2, and S3 are shown in Fig. 3. The slag consisted of Fe_2SiO_4, Fe_2O_3, Al_2O_3-rich Fe_2SiO_4, and entrained matte droplets (Cu_2S and FeS). The Fe_2SiO_4 formed the elongated dendritic-like structures typical of cooled slags. The Cu_2S droplets were rich in arsenic (3B and 3C), which were found to be bound to the copper (or Cu-As). Furthermore, the slag did not show any cracks as observed in the matte (M1-M3). This can be attributed to the better quenching properties of slags due to the presence of SiO_2 and Al_2O_3 where phase changes are sluggish. For this reason, slags especially rich in SiO_2 tend to retain their high temperature microstructure when cooled. S1 in Fig. 3A had more elongated structures, which may be attributed to the high silica content, as shown in Table I.

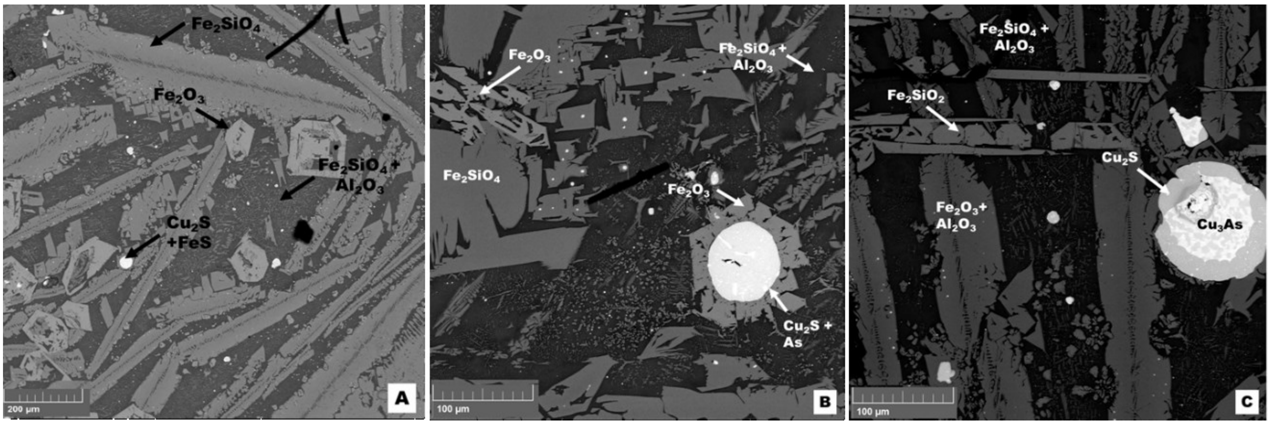
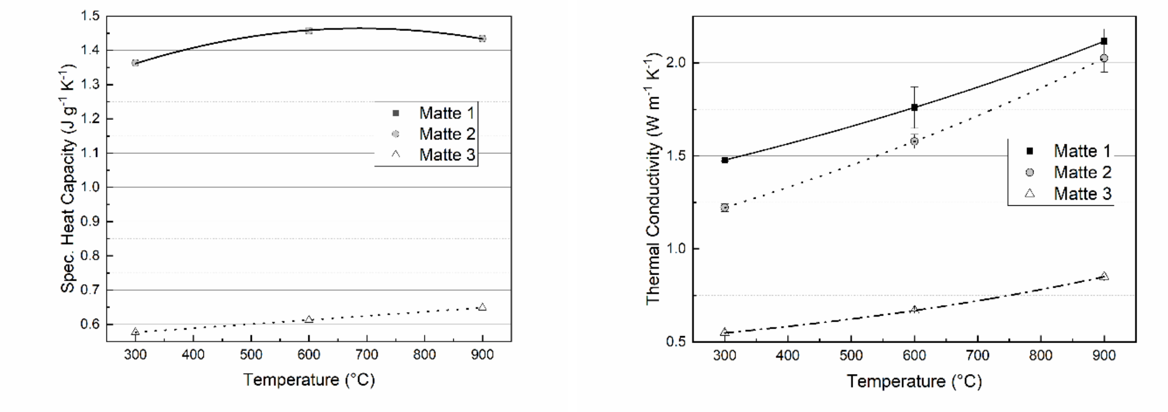


Figure 3. Backscatter scanning electron micrographs of slag samples-S1 (A), S2(B), and S3 (C)

Effect of matte grade and arsenic on thermal conductivity

Fig. 4 (A) and (B) show measured specific heat capacities and calculated thermal conductivities for the as-taken copper matte samples with varying copper grades. The thermal conductivity of M1 and M2 was between 1.2 and 2.1 W m^{-1} K^{-1} (Fig. 4(B)) in the studied temperature range of 300-900°C. On the other hand, M3 has a lower thermal conductivity than M1 and M2, which was found to be between 0.5 and 0.9 W m^{-1} K^{-1}. Observing the relation between thermal conductivity and temperature, the experimental data between M2 and M3 follow the thermal conductivity behavior of pure copper sulfide in two aspects [9]. First, M2 (Cu=66%) has a higher thermal conductivity than M3 (Cu=71%). This exceptionally low thermal conductivity is associated with the crystal structure, specifically the liquid-like copper sub-lattice that emerges on heating, and which leads to a softening of phonon modes, typical of copper-rich tetrahedrites. Copper sulfide has the lowest thermal conductivity of the sulfides, e.g., bornite and pyrite [22]. Second, there is a rise in thermal conductivity from 300 °C to 900 °C, which eliminates the possibility of copper matte being a conductor, or rather indicates that industrial copper matte is either a semiconductor or a non-conductor.

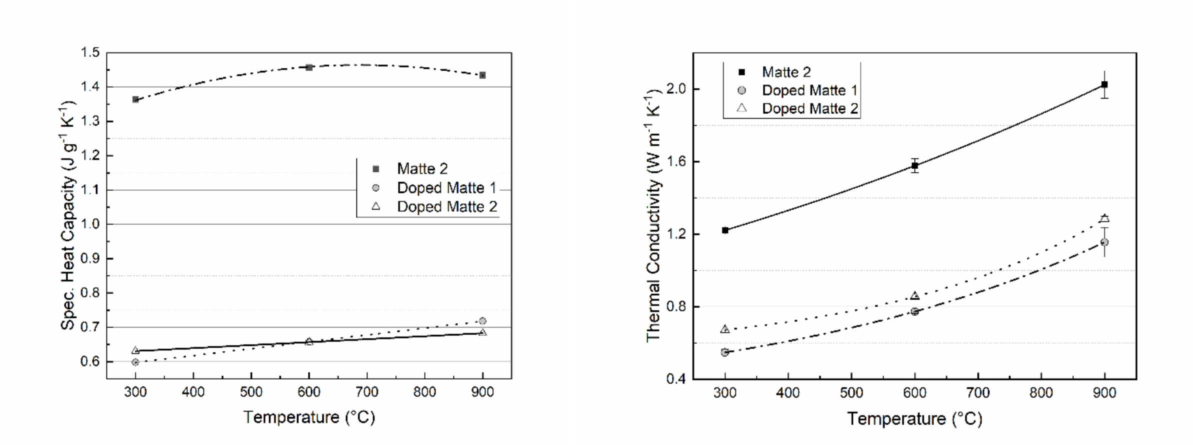


(A) (B)

Figure 4. Measured specific heat capacity (B) and thermal conductivity (B) of copper matte. Note in (A) that M1 and M2 have identical specific heat capacities.

Sample M3, on the other hand, has a much lower specific heat capacity than M1 and M2, between 0.5 and 0.7 J g^{-1} K^{-1} (Fig. 4 (A)). The only significant difference in chemical composition between them is the slightly high arsenic amounts in M3. Arsenic may have lowered the thermal conductivity of M3 to be less than M1 and M2.

Two matte samples (DM1 and DM2), of a similar copper grade to sample M2 (64.00 and 65.20 wt.% Cu), were doped with arsenic so that the resultant arsenic in the matte was 0.59 and 0.26 wt.%, respectively. After doping, SEM-EDS analysis of the samples showed that there were only minor changes to the main phases both in size and shape despite the different cooling conditions. Their thermal conductivities, however, ranged between 0.5 and 1.3 W m^{-1} K^{-1} (Fig. 5B), which is close to that for sample M3 rather than that for M2, suggesting a link between arsenic concentration and the changes in thermal conductivity.



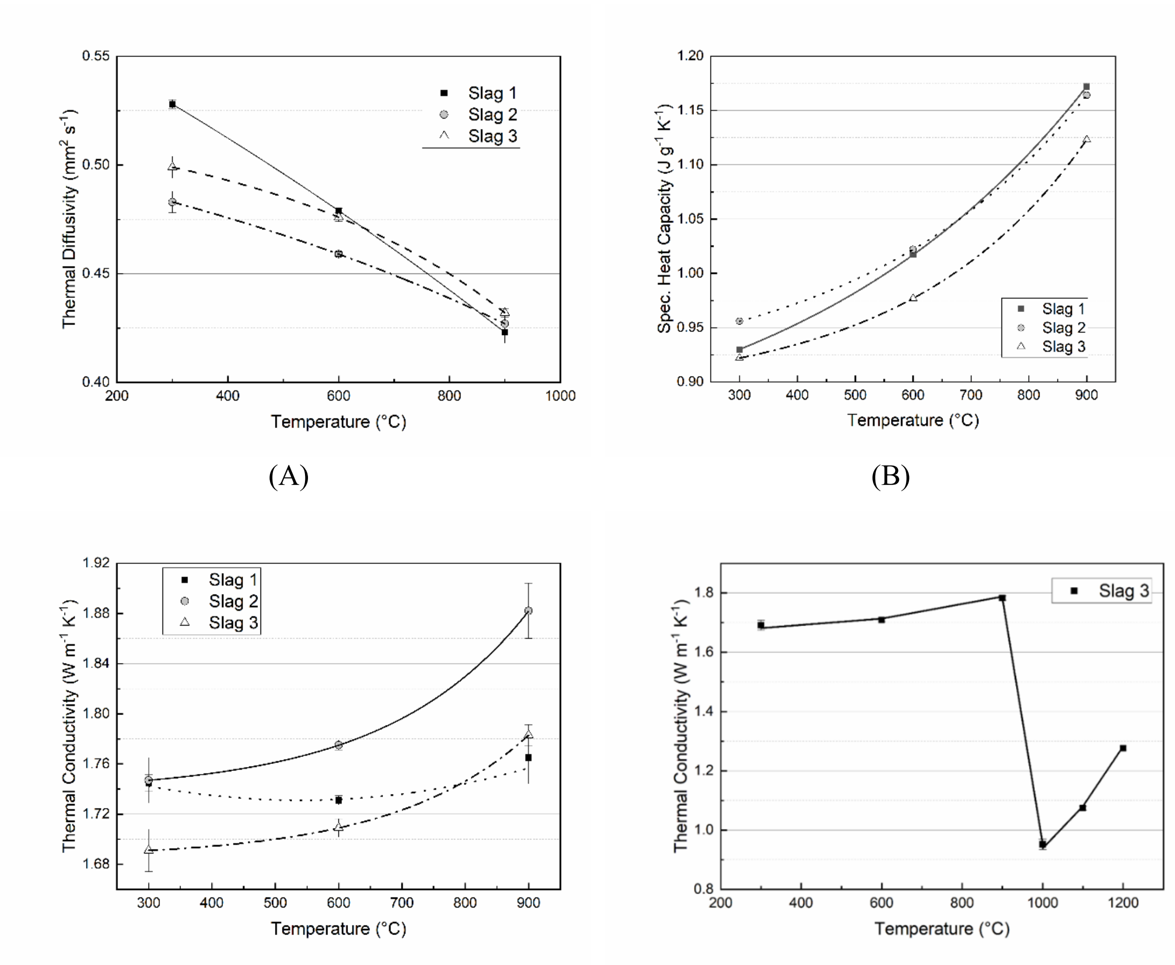
(A) (B)

Figure 5. Measured specific heat capacity (A) and thermal conductivity (B) of arsenic-doped copper matte

DM1 has a higher arsenic and copper grade than DM2, whereas M2 has only a small amount of arsenic. Comparison of DM1, DM2, and M3 shows that thermal conductivity in arsenic-doped copper matte has a negative relation with both arsenic content and copper grade. The range of thermal conductivity of the three arsenic-containing samples are 0.5 – 1.2 W m^{-1} K^{-1} (DM1), 0.7 – 1.3 W m^{-1} K^{-1} (DM2), and 0.5-0.9 W m^{-1} K^{-1} (M3). However, it should be mentioned that the relationship observed may not be exclusively due to arsenic because of the different conditions in which the samples were cooled. The authors could not find a reference in the literature regarding the effect of arsenic on the thermal conductivity of copper matte.

Influence of Fe/SiO₂ ratio on thermal conductivity of slag

The thermal conductivity and the other thermophysical properties of three slag samples (S1, S2, S3) with different Fe/SiO_2 ratios are compared to each other in Fig. 6. Conductivity of molten slag as a function of Fe/SiO_2 ratios is given in Fig. 7. Generally, thermal diffusivity decreased with increasing temperature, whereas specific heat and thermal conductivity showed the opposite behavior. The thermal conductivity values ranged from 1.7 and 1.9 W m^{-1} K^{-1} in the temperature range of 300-900°C (Fig. 6C), which is consistent with the values reported in the literature for solid fayalite slag [17].



(A) (B)

(C) (D)

Figure 6. Thermophysical properties of the slag samples: (A) thermal diffusivity, (B) specific heat, (C) thermal conductivity of the solid phase, and (D) thermal conductivity of molten slag

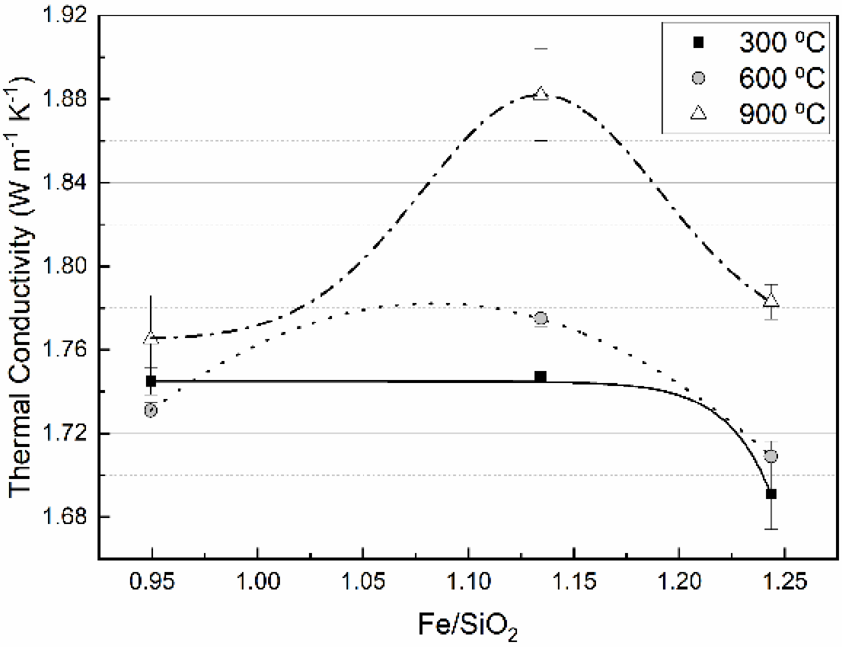


Figure 7. Thermal conductivity of molten slag as a function of Fe/SiO$_2$ ratio

Figure 6D, between 300 and 900 °C, conductivity slightly increase from 1.7 W m^{-1} K^{-1} to about 1.8 W m^{-1} K^{-1} before sharply dropping to about 0.95 W m^{-1} K^{-1}. It then starts to rise again up to nearly 1.4 at 1200 °C. Theoretically, a higher Fe/SiO$_2$ ratio leads to lower thermal conductivity because of the reduced silica content, which can negatively affect the microstructure [19]. The thermal conductivity of S2 and S3 follow this behavior at elevated temperature. However, experimental data do not show coherency with S1, which has the lowest Fe/SiO$_2$ ratio. The glass transition temperature of the samples cannot be determined unless more thermal conductivity data are collected between 700 and 900 °C.

Conclusions

The thermal conductivity of solid copper matte, solid and liquid fayalite slag, and copper has been determined using LFA apparatus on five matte samples and three slag samples. The matte and slag samples were taken from an operating Outotec flash smelter.

Based on the results of this work, the following conclusions can be drawn:

- The thermal conductivity of solid copper matte containing an average of 64% Cu was found to range from 1.2 W m^{-1} K^{-1} at 300 °C to 2.1 W m^{-1} K^{-1} at 900 °C;

- The thermal conductivity of solid fayalite slag having an average Fe/SiO_2 ratio of 0.95 was found to range from 1.7 W m^{-1} K^{-1} at 300 °C to 1.9 W m^{-1} K^{-1} at 900°C, the temperature above which the material has the characteristics of a glassy slag. Molten slag at 1200 °C having an average Fe/SiO_2 ratio of 1.24 was found to have a thermal conductivity of approx. 1.85 W m^{-1} K^{-1};
- As the matte grade was increased over the range of 62.5% Cu to 71.6% Cu, the thermal conductivity decreased due to more copper sulfide (which tends to lower the thermal conductivity) being present in the higher matte grades;
- A higher arsenic concentration in the matte was found to decrease thermal conductivity; for a copper matte averaging 64% Cu, the thermal conductivity decreased from approx. 2.1 W m^{-1} K^{-1} (low As matte – 0.16% As) to approx. 1.2 W m^{-1} K^{-1} when the matte was doped to an average level of 0.59% As;
- The effect of the Fe/SiO_2 ratio in fayalite slag on thermal conductivity was not clear cut. At 900 °C, the solid slag with a Fe/SiO_2 ratio of 1.13 had a higher thermal conductivity (1.88 W m^{-1} K^{-1}) than slags with an Fe/SiO_2 ratio of either 1.24 or 0.95 (thermal conductivity about 1.78 W m^{-1} K^{-1} and 1.75 W m^{-1} K^{-1}, respectively).

The thermal conductivity and specific heat of solid matte, and solid and liquid slag are of special interest for furnace designers and operators. It is believed that the present results will be useful in this regard.

Increasingly, secondary and scrap feed materials are handled at copper smelters, thus potentially influencing matte composition with respect to minor elements, hence it will be important to understand the impact of such feed as it affects the thermal conductivity of matte and slag.

The Metallurgy Research Group at the Aalto University School of Chemical Engineering anticipates further studies to provide a better understanding of the parameters affecting the thermal conductivity of matte and slag for a range of compositions.

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References

1. J. Jansson, L. Pesonen, and I. Vaajamo. *Outotec, The Conference of Metallurgists*, (2015).
2. M.E. Schlesinger, M.J. King, K.C. Sole, and W.G. Davenport, *Extractive metallurgy of copper*, *Elsevier*, ch. 1, 5, and 6., (2011).
3. W.J. Parker, R.J. Jenkins, C.P. Butler, and G.L. Abbott, *J. Appl. Phys.*, *Vol.* 32, 9, 1679 (1961).
4. K. Shinzato, and T. Baba, *J. Therm. Anal. Calorim.,* Vol 64, pp. 413-422. (2001)
5. S. Min, J. Blumm, and A. Lindemann, *Thermochim. Acta*, *455*(1-2), 46 (2007).
6. J. Heimo, A. Jokilaakso, M. Kekkonen, M. Tangstad, M. and A. Støre. Unpublished research. (2019)
7. R. Eriksson and S. Seetharaman, *Metall. Mater Trans B*, *35*(3), 461 (2004)
8. K. Nishioka, T. Maeda, and M. Shimizu, *ISIJ Int*., vol. 46, 427 (2006).
9. F. Grønvold, and E.F. Westrum Jr., *J. Chem. Thermodyn*. 1987, 19, 1183 (1987).
10. J. Duan, C. Zhu, M. Guan, P. Lu, Y. He, Z. Fu, L. Zhang, F. Xu, X. Shi, and L. Chen, *Ceram. Int.*, *44*(11), 13076 (2018).
11. M. Bourgon, G. Derge, and G.M. Pound, *JOM*, *9*(11), 1454 (1957).
12. J.C. Osuwa, and E.C. Mgbaja, E.C., *IOSR J. Appl. Phys.*, *6*(5), 28(2014).
13. G.P. Sorokin, Y.M. Papshev, and P.T. Oush, *Fiz Tverd Tela, USSR*, *7*(7), 1810 (1966).
14. L. Yang, G.M. Pound and G. Derge, *JOM*, *8*(6),783(1956).
15. E. W. Johnson, and R.L. Readal, *Vdi Bericht.*, *3*(2),407(1963).
16. C. Uhlig, E. Guenes, A.S. Schulze, M.T. Elm, P.J. Klar, and S. Schlecht, *J. Electron. Mater.*, *43*(6) 2362 (2014).
17. K.C. Mills, and M. Susa, *NPL Report DMM(A)* Vol. 68, National Physical Laboratory, London (1992).
18. C. Kittel, P. McEuen, and P. McEuen, *Introduction to solid state physics* (Vol. 8, pp. 323-324). New York: Wiley. (1976).
19. Y. Kang, J. Lee, and K. Morita, *ISIJ Int*., 54(9), 2008 (2014).
20. S. Min, J. Blumm, and A. Lindemann. *Thermochim. Acta*, *455*(1-2), 46 (2007).
21. E.L. Thyse, G. Akdogan, P. Taskinen, and J.J. Eksteen, *South African Pyromet.*, *1*, 173 (2011).
22. A. V. Powell, J. Appl. Phys, 126(10),100901 (2019).