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EFFECT OF SULPHUR ON WETTABILITY OF LIQUID FE-0.45%C WITH ALUMINA

VPLIV ŽVEPLA NA OMOČLJIVOST TALINE ZLITINE FE-0.45% C Z ALUMINIJEVIM OKSIDOM

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Non-metallic inclusions, particularly alumina (Al_2O_3), pose significant challenges in steelmaking. Their behaviour in molten steel is largely governed by wettability. This study investigates the effect of sulphur, a surface-active element, on the wettability between liquid Fe-0.45%C and alumina substrates, to improve the understanding of alumina non-metallic inclusion formation in medium carbon steel. Experiments were conducted using the sessile drop method in a high-temperature melting microscope. Three Fe-0.45%C samples with varying sulphur contents (0.0020, 0.0120, and 0.0340 *w*/%) were placed on polished single-crystal alumina substrates and heated to 1600 °C in a purified argon atmosphere. Results show that increasing sulphur content in the Fe-0.45%C melt decreases the contact angle with alumina substrates from 106.5° (0.0020 *w*/% S) to 102.0° (0.0340 *w*/% S). Furthermore, sulphur addition increases the influence of temperature leading to a clearer trend of decreasing contact angle values as temperature rises. This implies an increased risk of solid alumina non-metallic inclusion formation if the sulphur content is elevated.

Keywords: wettability, contact angle, non-metallic inclusions, surface-active elements

Nekovinski vključki, zlasti aluminijev oksid (Al_2O_3), predstavljajo velik izziv v jeklarstvu. Njihovo obnašanje v talini jekla je v veliki meri odvisno od omočljivosti. Ta študija preiskuje vpliv žvepla, površinsko aktivnega elementa, na omočljivost med talino zlitine Fe-0,45%C in podlago iz Al_2O_3, z namenom izboljšati razumevanje nastajanja nekovinskih vključkov alumina v srednjeogljičnem jeklu. Eksperimenti so bili izvedeni z metodo sesilne kapljice v visokotemperaturnem talilnem mikroskopu. Trije vzorci zlitine Fe-0,45%C z različnimi vsebnostmi žvepla (0,0020 *w*/%, 0,0120 *w*/% in 0,0340 *w*/% S) so bili postavljeni na polirane monokristalne podlage iz aluminijevega oksida in segreti na 1600 °C v zaščitni atmosferi argona. Rezultati kažejo, da naraščajoča vsebnost žvepla v talini Fe-0,45%C zmanjšuje kot omočenja s podlagami Al_2O_3, in sicer s 106,5° (pri 0,0020 *w*/% S) na 102,0° (pri 0,0340 *w*/% S). Poleg tega dodatek žvepla poveča vpliv temperature, kar vodi do izrazitejšega trenda zmanjševanja vrednosti kota omočenja z naraščajočo temperaturo. To pomeni povečano tveganje za nastanek trdnih nekovinskih vključkov aluminijevega oksida pri povišani vsebnosti žvepla.

Ključne besede: omočljivost, kot omočenja, nekovinski vključki, površinsko aktivni elementi

1 INTRODUCTION

Alumina (Al_2O_3) is one of the most common non-metallic inclusions in steel. It forms during Al deoxidation of a steel melt. Alumina non-metallic inclusions have high liquidus temperatures and are solid during the steelmaking process. They cause numerous problems during casting and hot forming, and they affect the final mechanical properties.[1–3]

Non-metallic inclusion control is essential for the production of high-quality steels, i.e., clean steel production. Wettability is one of the most overlooked non-metallic inclusion properties; it has a profound effect on the critical radius for the formation of a non-metallic inclusion, as well as on its behaviour in a steel melt, such as attachment to gas bubbles and to the walls of the refractory lining.

Wettability between two phases is determined by the contact angle.[4] The contact angle Θ represents the ratio of phase forces in the mechanical equilibrium of liquids in the horizontal direction. **Figure 1** schematically shows

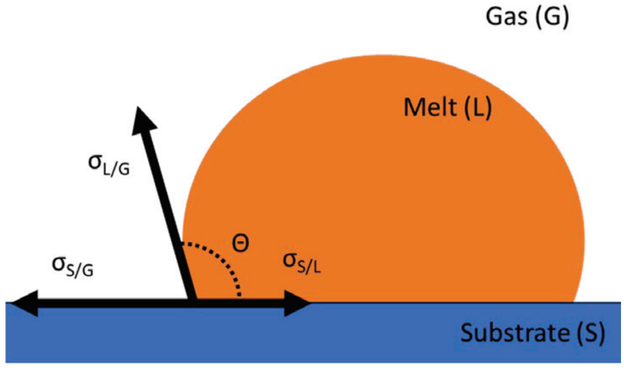

Figure 1: Young's model of mechanical equilibrium of a three-phase system, derived from Young[4]

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Young's model of the mechanical equilibrium between a melt droplet, a solid substrate, and the surrounding gas. The vector sum of interfacial tensions in the equilibrium state determines the contact angle.

The contact angle (θ) is defined as:[4]

$$\cos(\theta) = (\sigma_{S/G} - \sigma_{S/L}) / \sigma_{L/G} \quad (1)$$

where $\sigma_{S/G}$, $\sigma_{S/L}$, and $\sigma_{L/G}$ are the interfacial surface energies between the substrate and the gaseous phase, between the substrate and the melt, and between the melt and the gaseous phase, respectively. In this context, the substrate represents a non-metallic inclusion, and when the contact angle between the melt and the non-metallic inclusion is between 90 and 180°, this indicates relatively poor wettability. Poor wettability of non-metallic inclusions is a consequence of higher surface energy between the inclusion and the melt compared to the surface energy between the inclusion and the gaseous phase.[5–7] Equation (2) gives the expression for the adhesion work W_a, introduced by Dupre,[8] which describes the thermodynamic work for the separation of a non-metallic inclusion from the melt. The higher the angle, the more easily the non-metallic inclusion separates.

$$W_a = \sigma_{L/G} \cdot (1 + \cos(\theta)) \quad (2)$$

Generally, non-metallic inclusions have poor wettability ($\theta > 90°$) with the steel melt and are less dense than steel.[3,7,9–22] Poor wettability also indicates larger critical radii for the formation of new inclusions. This means larger inclusions. According to Stokes' law, the speed of non-metallic inclusion flotation increases with their size; thus, larger inclusions float faster and are easier to remove from the steel melt.[23,24]

Sulphur is a surface-active element, meaning it reduces the surface tension of the steel melt.[6,7,15,25–28] A reduction in the surface tension in molten steel affects the contact angle between the melt and solid non-metallic inclusions. Theoretically, the addition of sulphur at the final stage of steel melt preparation, just before casting, could reduce the critical radius for nucleation of non-metallic inclusions and promote the formation of a large number of smaller alumina inclusions. This can cause additional difficulties, such as submerged entry nozzle clogging during continuous casting.[3,29]

The effect of sulphur on the contact angle between liquid Fe-0.45%C and alumina was investigated. The results will contribute to a better understanding of alumina non-metallic inclusion formation in medium carbon steel.

2 EXPERIMENTAL PART

The chemical compositions of three samples derived from Fe-0.45%C, with different sulphur contents, are given in **Table 1**. They were prepared by melting electrolytic iron, carbon, and sulphur in a vacuum induction melting furnace, cast into 8 kg ingots and hot forged into rods. Cylindrical samples with a diameter of 4 mm and a height of 8 mm were machined from the rods. The samples were ultrasonically cleaned in ethanol before the contact angle experiments. The sulphur and carbon contents were determined with an ELTRA CS800 combustion mass spectrometer (ELTRA GmbH, Germany), and the content of oxygen was determined with an ELTRA ON900 analyser (ELTRA GmbH, Germany). Each sample was placed on a single-crystal alumina substrate with the (0001) orientation. The single-crystal alumina substrate dimensions were (15 × 15 × 1) mm and the substrates had polished surfaces with average roughness R_a < 0.5 nm. These substrates were also ultrasonically cleaned in ethanol just before use. Contact angle measurements were conducted using the sessile drop method in a high-temperature melting microscope, Dataphysics OCA25-HTV1800. Once a sample was placed in the furnace, the chamber was evacuated and refilled with high-purity argon three times. Before introducing argon to the chamber, the gas passed through a deoxygenation and dehydration unit to remove residual oxygen and moisture. Finally, the chamber was filled with purified argon, and the sample was heated to 1600 °C at a rate of 5 °C/min. After being held for 20 minutes at this temperature, the samples were cooled to RT in an inert atmosphere. The contact angle was determined via an ellipse fitting procedure using the software that was installed with the equipment.

Table 1: Chemical compositions of analysed steel samples (*w*/%)

Sample name	C	S	O	Fe
Fe-0.45%C-0.0020%S	0.44	0.0020	0.0026	bal.
Fe-0.45%C-0.0120%S	0.44	0.0120	0.0034	bal.
Fe-0.45%C-0.0340%S	0.46	0.0340	0.0021	bal.

3 RESULTS AND DISCUSSION

Figure 2 shows sessile droplets of the molten steel samples on the polished single-crystal alumina substrates at a temperature of 1600 °C. Steel samples Fe-0.45%C-0.0020%S, Fe-0.45%C-0.0120%S, and Fe-0.45%C-0.0340%S exhibit average contact angles of 106.5°, 103.3°, and 102.0°, respectively. The average contact angles were determined during a 20-minute holding period of the molten droplet at 1600 °C. As the sulphur content in the melt increases, the wettability of the steel melt with the alumina substrate slightly improves.

The results of the contact angle measurements in the temperature range of 1585–1600 °C for the three different chemical compositions are shown in **Figure 3**. The sample with 0.0020 *w*/% S exhibits only a slightly decreasing trend of the contact angle with increasing temperature. However, with the addition of sulphur, the 0.0120 *w*/% S and 0.0340 *w*/% S samples show a clearer trend of decreasing contact angle values as the temperature rises. The following equations for contact angles were derived from the measurement points:

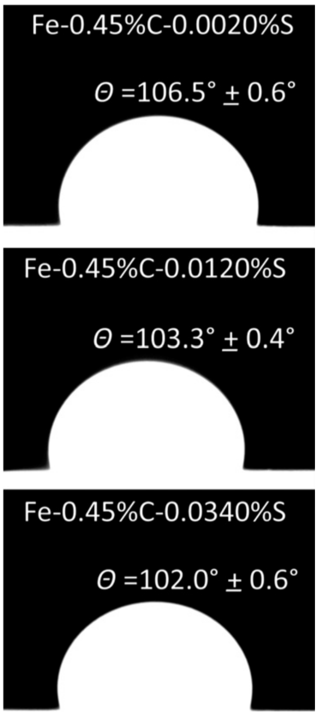

Figure 2: Sessile drops of liquid Fe-0.45%C with different S contents on polished single-crystal alumina substrate at 1600 °C

Fe-0.45%C-0.0020%S: = – 0.0112 · T [K] + 127.4

Fe-0.45%C-0.0120%S: = – 0.1366 · T [K] + 358.8

Fe-0.45%C-0.0340%S: = – 0.1634 · T [K] + 408.1

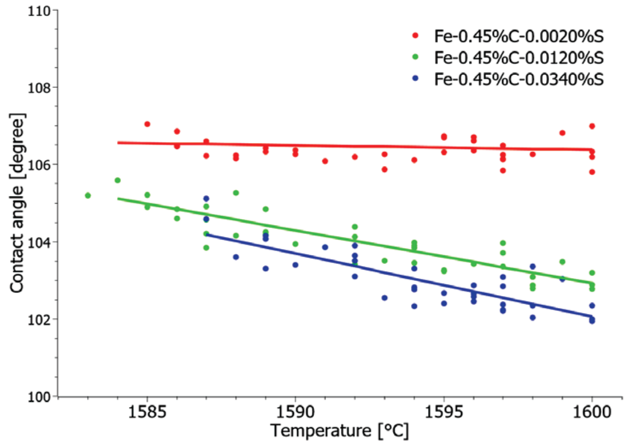

Figure 3: Contact angle during heating of sessile droplets

The addition of sulphur lowers the contact angle and increases the temperature sensitivity of the wettability between non-metallic inclusions and liquid Fe-0.45%C. Based on the results, it can be deduced that the addition of sulphur to the Fe-0.45%S system improves the wettability between alumina and the melt, thus decreasing the critical radius of the non-metallic inclusions. This, in turn, increases the number of stable solid alumina non-metallic inclusions in the liquid steel by increasing the sulphur content.

A decrease in the temperature causes higher contact angles, which in turn require a higher critical radius for the formation of alumina non-metallic inclusions. However, the Gibbs free energy for the formation of non-me-

Table 2: Summary of contact angle values of liquid iron/steel on alumina substrates

Ref.	Sample	Substrate	Substrate roughness	Temperature [K]	Atmosphere	Contact angle [°]
Present work	Fe-0.45%C-0.0020	single-crystal Al_2O_3	R_a < 1 nm	1873	Ar	106.5
	Fe-0.45%C-0.0120					103.3
	Fe-0.45%C-0.0340					102.0
9	Fe	single-crystal Al_2O_3	R_a ≈ 10 nm	1815	Ar	103
10	Fe-0.20%C	single-crystal Al_2O_3	R_a < 0.5 nm	1821	Ar–10 v/% H_2	110
					Ar–3 v/% H_2	95
					Ar	70
6	Fe-30%Cr-S	sintered Al_2O_3	R_a = 200–300 nm	1823	Ar	80–145
7	Fe-S	sintered Al_2O_3	–	1873	H_2–H_2O and H_2–H_2S	135
11	Fe	single-crystal Al_2O_3	R_a = 0.7 nm	1873	Ar	103
5	Fe-16Cr-O	sintered Al_2O_3	–	1823	Ar–H_2	150
12	Fe	sintered Al_2O_3	–	1823	Ar	136
15	Fe-16%Cr-O	sintered Al_2O_3	–	1823	Ar	130–155
13	Fe-Ti, Fe-P, Fe-Ti-P	sintered Al_2O_3	R_a = 200 nm	1823–1893	Ar	85–135
18	Fe	sintered Al_2O_3	R_a = 78 nm	1873	Ar	114
14	Fe	sintered Al_2O_3	–	1823	Ar, Ar–H_2	90–140, 135
17	Fe	sintered Al_2O_3	–	1873	Ar	124–142
22	Fe	sintered Al_2O_3	–	1823	Ar–5 v/% H_2	126.9
16	Fe	Al_2O_3	–	1873	Ar	98

tallic inclusions is lower with falling temperatures, thus decreasing the critical radius of the non-metallic inclusions.[29] This means that the temperature drop has less of an effect on the formation of non-metallic inclusions when the S content is increased.

Although there is a change in the critical radius, the overall wettability is still relatively poor, meaning that the non-metallic inclusions still tend to agglomerate and stick to refractory surfaces. This means that during continuous casting, there is an increased chance of deposition of solid alumina non-metallic inclusions on the walls of submerged entry nozzles if the sulphur content is increased.

In order to put the data into perspective, our results were compared with those reported in the literature[5–7,9–18,22]. The data on the contact angle measurements of various iron alloy samples on alumina substrates are presented in **Table 2**. The contact angles vary depending on the concentration of surface-active elements in the melt (O, S). The oxygen activity in the atmosphere influences the surface energy of the melt and, consequently, the contact angle. An increase in the oxygen activity in the atmosphere, and thus in the melt, leads to a decrease in the contact angle between the steel melt and the alumina substrate.[5,7,10,14] To minimize the influence of atmospheric oxygen activity, some researchers used a gas mixture of Ar and H_2.[5,7,10,14,22] The substrate surface condition also plays a significant role in wettability.[30,31] As noted by Qi et al.[31] an increase in substrate roughness results in a higher contact angle. The data shows that low-roughness substrates (especially single-crystal Al_2O_3) result in low contact angles between 100° and 115°, while rougher alumina substrates (especially sintered Al_2O_3) result in higher contact angles, up to 145°.

An increased oxygen activity can lead to interfacial reactions. According to the literature, hercynite ($FeO·Al_2O_3$) forms at the interface.[9–11] The lower the oxygen activity in the melt, the thinner the reaction layer between the sessile droplet and the substrate. With increased substrate roughness, the interfacial area between the two phases increases, which in turn enhances the kinetics of the hercynite formation. In the present work, the oxygen activity in the atmosphere was not measured; wettability experiments were conducted in a high-purity Ar atmosphere, and the initial oxygen concentration was low. The observed detachment of the steel droplets from the single-crystal substrates after testing suggests slow interfacial reaction kinetics between the steel samples and the single-crystal alumina substrates.

4 CONCLUSIONS

This study provides valuable insights into the effect of sulphur content on the wettability between liquid Fe-0.45%C and alumina (Al_2O_3) substrates, with significant implications for steelmaking practice and non-metallic inclusion management.

The experimental results demonstrate that sulphur, as a surface-active element, influences the contact angle between molten steel and alumina substrates. Increasing sulphur content in liquid Fe-0.45%C from (0.0020 to 0.0120 and 0.0340) *w*/% improves the wettability with alumina substrates, as evidenced by a decrease in contact angles from 106.5° to 102.0°.

Sulphur addition increases the temperature's influence on the contact angle, which has critical implications for continuous casting, potentially leading to increased inclusion deposition at lower temperatures.

The substrate surface condition significantly impacts wettability; it was found from other published works that increased substrate roughness generally leads to higher contact angles, emphasizing the importance of using low-roughness substrates for accurate contact angle measurements.

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