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Invited Review

Review on desulfurization in electroslag remelting

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Abstract: Electroslag remelting (ESR) gives a combination of liquid metal refining and solidification structure control. One of the typical aspects of liquid metal refining during ESR for the advanced steel and alloy production is desulfurization. It involves two patterns, i.e., slag–metal reaction and gas–slag reaction (gasifying desulfurization). In this paper, the advances in desulfurization practices of ESR are reviewed. The effects of processing parameters, including the initial sulfur level of consumable electrode, remelting atmosphere, deoxidation schemes of ESR, slag composition, melting rate, and electrical parameters on the desulfurization in ESR are assessed. The interrelation between desulfurization and sulfide inclusion evolution during ESR is discussed, and advancements in the production of sulfur-bearing steel at a high-sulfur level during ESR are described. The remaining challenges for future work are also proposed.

Keywords: electroslag remelting; desulfurization; sulfide inclusions; sulfur-bearing steel; gasifying desulfurization; desulfurization mechanism

1. Introduction

Electroslag remelting (ESR) is widely used to produce some varieties of special steels and alloys mainly because of its ability to simultaneously provide an excellent solidification structure and extreme cleanliness in terms of deoxidation, desulfurization, and non-metallic inclusion and tramp element removal. The role of the processing parameters of ESR, as the last processing stage of liquid metal refining, in the refining efficiency has been extensively explored. The detriments of sulfur to the properties of steel and alloy have been widely recognized. For example, an increase in sulfur content deteriorates the fracture toughness and hot ductility of steel [1–2], lowers the endurance strength of superalloy [3], and leads to the initiation of sulfide-induced stress corrosion crack in steel [4]. The desulfurization capacity of ESR is affected by various factors, such as oxygen levels of liquid metal [5], slag chemistry [6–7], remelting atmosphere [8–9], and sulfide inclusions [10–11].

ESR has a strong desulfurization ability through which the sulfur content is reduced by 50%–80% from an electrode to a remelted ingot generally [12–15]. Although studies on desulfurization by ESR are not as many as those on deoxidation and inclusions in ESR, great efforts have been devoted to lowering the sulfur contents of steel and alloy during ESR. Increasing demands for more excellent properties of steel have urged manufacturers to further improve steel and alloy cleanliness. Therefore, the desulfurization fundamentals of ESR should be fully elucidated.

Targeting a low sulfur content is an important aspect of clean steel and alloy production. In addition, maintaining a high-sulfur content is required for some steel grades, such as free-cutting steel and some high-speed steels. For example, sulfur can act as a free-cutting element to improve the cutting performance of steel and increase the abrasive resistance of high-speed steel [16–17]. However, there are technological difficulties for sulfur-bearing steel production by ESR. In this process, the sulfur contents always vary greatly [17].

In the present work, the desulfurization fundamentals and underlying mechanisms of ESR are assessed. The main factors that influence the desulfurization capacity of ESR are discussed. The interrelation between desulfurization and sulfide inclusion evolution during ESR is also evaluated. The key points of sulfur level maintenance for sulfur-bearing steel production by ESR are presented. A general concluding remark and perspectives for future work are proposed.

2. Desulfurization basis of ESR

ESR is generally operated using high frequencies (50 or 60 Hz) of an alternating current (AC) power supply in production practices worldwide. The ESR described in this article is in an AC mode unless otherwise specified. Steel and alloy produced by ESR usually require a low or ultralow-sul-

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fur content. However, for some steel grades, such as crankshaft steel, a high-sulfur content is required. Desulfurization during ESR occurs in two ways.

(1) Slag–metal reaction involves the removal of sulfur from liquid metal to molten slag. It is expressed as follows:

$$[\mathrm{S}]+(\mathrm{O}^{2-})=(\mathrm{S}^{2-})+[\mathrm{O}] \tag{1}$$

(2) Gas–slag reaction occurs via the oxidation of sulfur ions at the atmosphere/slag interface as a result of their diffusion from molten slag layer to the atmosphere/slag interface and the exposition of the slag surface to atmospheric oxygen. This reaction is described as follows:

$$(\mathrm{S}^{2-})+3/2\{\mathrm{O}_2\}=\{\mathrm{SO}_2\}+(\mathrm{O}^{2-}) \tag{2}$$

where [ ], ( ), and { } refer to a species in liquid metal, slag, and gas phases, respectively.

The equilibrium constant of reaction (1) is expressed as

$$K=\frac{a_{(\mathrm{S}^{2-})}\cdot a_{[\mathrm{O}]}}{a_{[\mathrm{S}]}\cdot a_{(\mathrm{O}^{2-})}} \tag{3}$$

where K is equilibrium constant, $a_{(\mathrm{S}^{2-})}$ and $a_{(\mathrm{O}^{2-})}$ are the activities of sulfur ion and oxygen ion in molten slag, respectively. $a_{[\mathrm{O}]}$ and $a_{[\mathrm{S}]}$ are the activities of soluble oxygen and sulfur in liquid metal, respectively.

Eq. (3) can be rewritten as

$$\frac{a_{(\mathrm{S}^{2-})}}{a_{[\mathrm{S}]}}=K\cdot\frac{a_{(\mathrm{O}^{2-})}}{a_{[\mathrm{O}]}} \tag{4}$$

This deduction suggests that the transfer of sulfur from metal to slag is promoted by a higher basicity of slag and a lower content of soluble oxygen in liquid metal.

The equilibrium constant of reaction (2) is expressed as:

$$K=\frac{p_{\{\mathrm{SO}_2\}}\cdot a_{(\mathrm{O}^{2-})}}{p_{\{\mathrm{O}_2\}}^{3/2}\cdot a_{(\mathrm{S}^{2-})}} \tag{5}$$

$$\frac{p_{\{\mathrm{SO}_2\}}}{a_{(\mathrm{S}^{2-})}}=K\cdot\frac{p_{\{\mathrm{O}_2\}}^{3/2}}{a_{(\mathrm{O}^{2-})}} \tag{6}$$

where p is partial pressure of gaseous component.

According to Eq. (6), gasifying desulfurization is enhanced by a higher partial pressure of oxygen in the atmosphere and a lower basicity of slag. SO_2 generated through gasifying desulfurization (the desulfurization by gas–slag reaction) is diluted in open air atmosphere of ESR. The dilution of SO_2 consequently contributes a lower partial pressure of SO_2 in the atmosphere, which provides a favorable condition for desulfurization during ESR.

The schematic of an ESR apparatus is shown in Fig. 1. Desulfurization of liquid metal takes place at four reaction sites during ESR: ① electrode tip/slag interface, ② metal droplet/slag interface, ③ liquid metal pool/slag interface, and ④ atmosphere/slag interface. The reaction sites of desulfurization during ESR is schematically presented in Fig. 2. The desulfurization of slag–metal reactions occurs at reaction sites ①, ②, and ③, and the gas–slag reaction takes place at reaction site ④. These reaction sites contribute, more or less, to the overall desulfurization during ESR. Among these reaction sites, reaction site ① is the phase boundary with the largest refining potential for desulfurization by ESR. In this site, desulfurization occurs predominantly during the formation of a liquid metal film at the electrode tip [18–20]. It is attributed to more preferable kinetic conditions, namely, long chemical reaction time and high surface-to-volume ratio between a liquid metal film at the electrode tip and slag [20–22]. Reaction site ② is of a little importance as a desulfurization site because of the very short residence time of metal droplets passing through the slag pool (virtually 0.01–0.1 s [20,23]). Desulfurization at the liquid metal pool/slag interface makes little contribution to the desulfurization during ESR because of reaction time limitation [24].

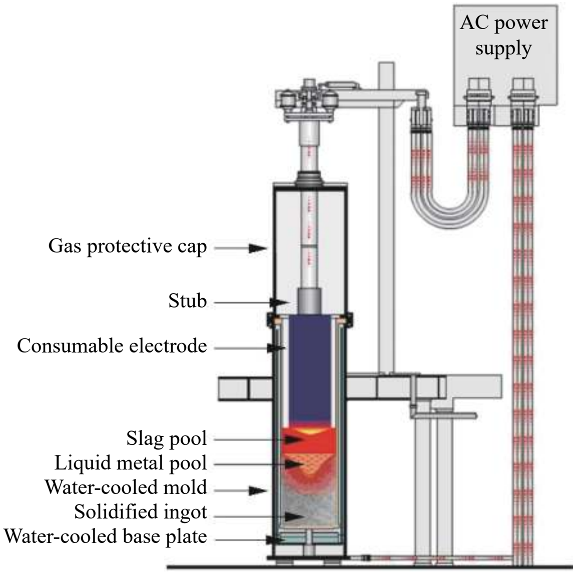

Fig. 1. Schematic of an ESR apparatus.

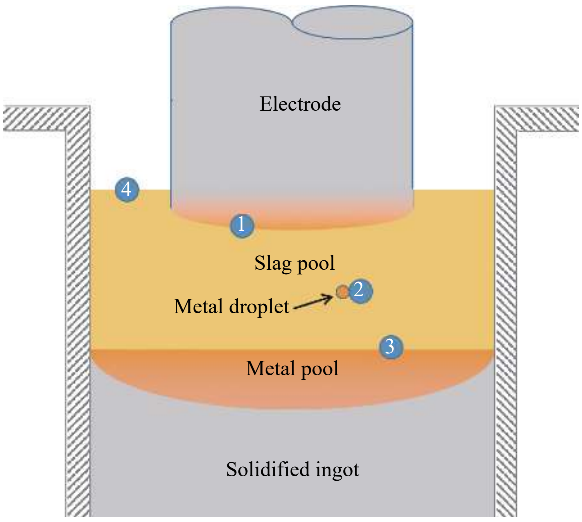

Fig. 2. Desulfurization reaction sites of ESR. ① electrode tip/slag, ② metal droplet/slag, ③ metal pool/slag, and ④ atmosphere/slag.

Desulfurization by ESR includes chemical reactions and mass transfer of components in liquid metal, molten slag, and gas phases. Using a kinetic model developed based on the penetration and film theories for the ESR of 1Cr21Ni5Ti stainless steel, Hou *et al*. [25] proposed that remelted steel has a minimum sulfur content because of kinetics limitation at a given sulfur content of steel electrode, such a low sulfur content cannot be further reduced even though increasing the sulfur distribution ratio between metal and slag phases or decreasing the sulfur content of the slag.

Desulfurization of liquid steel during ESR is determined by one or several factors, such as slag compositions, remelting atmosphere, melting rate of ESR, and oxygen content of liquid steel. For a specific ESR process, some of these factors make a negligible contribution, but one of them controls desulfurization.

3. Dependence of desulfurization on the processing parameters of ESR

3.1. Initial sulfur content of consumable electrode

For low-sulfur steel production, a low-sulfur electrode should be prepared for ESR. This condition has been verified with the experimental data of open air atmosphere ESR, as shown in Figs. 3 and 4. The sulfur content of remelted steel is reduced to an average of 0.007wt% after remelting of the steel electrode with 0.015wt% sulfur (see Fig. 3), whereas increasing the sulfur content of the consumable electrode to 0.025wt% results in a relatively higher sulfur content of remelted ingots (0.008wt% to 0.012wt%), in which the sulfur contents are dependent on the differences in the slag compositions [26].

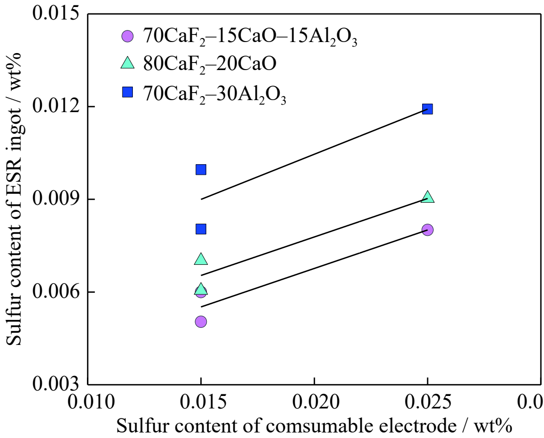

Fig. 3. Effect of initial sulfur content in consumable electrode on the sulfur content in the ingot when using different slag systems in ESR process [26]. The chemical composition of slag is presented in mass fraction.

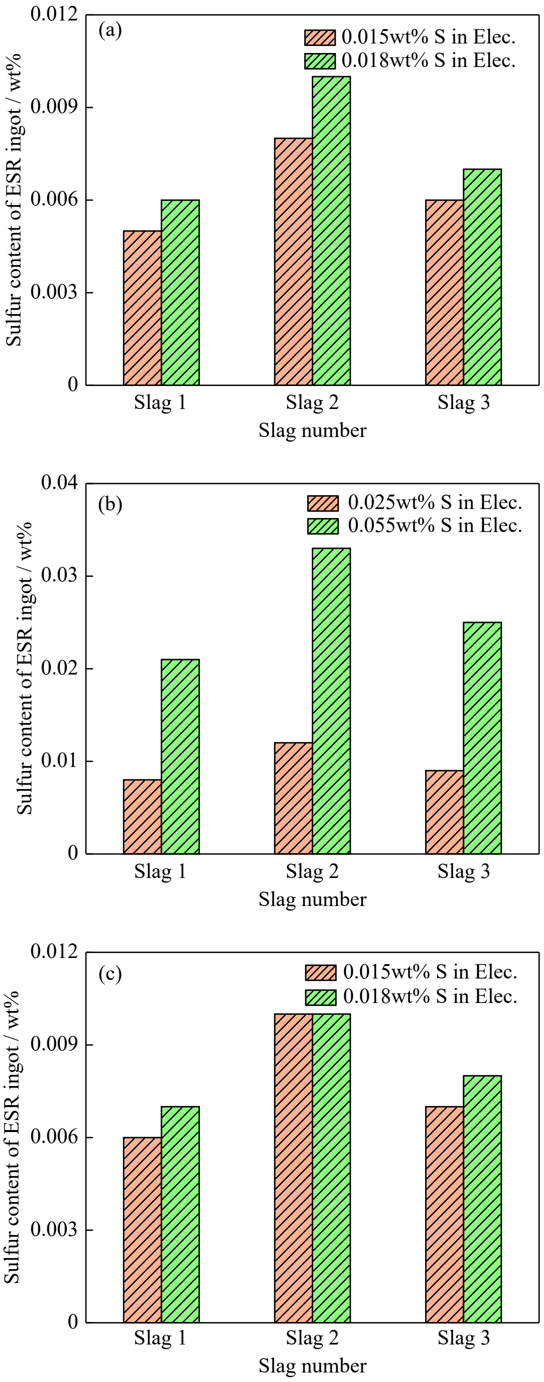

Fig. 4. Sulfur content in the ingot produced by using different slag systems and with different initial sulfur contents in the steel electrode for ESR of (a) tool steel D3, (b) tool steel L6, and (c) high speed steel M2. Elec. represents steel electrode. Adapted from published data [27].

It is learned from Fig. 4 that, for refining three different grades of tool steel (namely, D3, L6, and M2), the sulfur content of the ESR ingot is lower in the case of electroslag remelting of the electrode with a lower sulfur content [27]. It is more pronounced in the ESR of the electrodes with high original sulfur contents (0.025wt% and 0.055wt%) than in the ESR of electrodes with low original sulfur contents, as presented in Fig. 4(b). The chemical composition of the slag used in ESR trials is shown in Table 1 [27]. For the ESR of the tool steel D3 and the high-speed steel M2 electrodes with identical initial sulfur contents, differences in the sulfur contents of ingots are expected to originate from variations in steel electrode compositions, especially oxygen contents, but the data of oxygen contents are not presented in the reference [27]. As a result, these differences lead to various activities of soluble oxygen and activity coefficients of sulfur in liquid steel. However, Padki *et al.* [28] showed that the sulfur contents of all remelted ingots range from 0.017wt% to 0.019wt% irrespective of the initial sulfur contents of steel electrode (0.02wt% to 0.38wt%) in which 70wt%CaF_2–30wt%Al_2O_3 slag is used in the ESR trials.

Table 1. Chemical composition of the slags used in ESR trials. Adapted from published data [27] wt%

Slag	CaF_2	CaO	Al_2O_3
Slag 1	50 ± 2.5	20 ± 2.5	30 ± 2.5
Slag 2	55 ± 2.5	20 ± 2.5	25 ± 2.5
Slag 3	50 ± 2.5	5 ± 2.5	45 ± 2.5

A low sulfur level of a consumable electrode generally gives a low sulfur content of remelted ingots, but this condition is not always the case. This low sulfur level of remelted ingots also depends on slag composition and oxygen content [29–31]. The ESR of a steel electrode with a high-sulfur level (hundreds of parts per million or more) has been described in references [26–28]. With advances in steelmaking technologies, the sulfur content of steel electrode can be lowered to a low level (a few parts per million) during the secondary refining of liquid steel for electrode production. For low- or ultralow-sulfur steel and alloy production, the sulfur content of low-sulfur electrodes should still be further reduced through ESR. Laboratory-scale open air atmosphere ESR trials with a mold diameter of 165 mm and a low frequency of 4.5 Hz of an AC power supply show that the sulfur content of steel is reduced to 0.0004wt%–0.0008wt% despite a very low initial sulfur level (0.0013wt%) in electrodes [32], in which the variations in the sulfur content of ESR ingots are dependent on the slag composition as shown in Table 2. More work is needed to study the desulfurization of electrodes with low sulfur content in large-scale ESR trials and at a high frequency of the AC in ESR, which are the usual modes of ESR production practices.

Table 2. Chemical composition of the slags used in ESR trials [32] wt%

Slag	CaF_2	CaO	Al_2O_3	MgO	SiO_2
3C3A	31.5	29.5	33.5	3	1.5
3C3A1S	29	27	30.5	3	10
4C4A	14.5	37.5	41.5	4	1.5
3A	68	—	30	—	2

3.2. Remelting atmosphere

The previous studies on the desulfurization in different remelting atmospheres of ESR are summarized in Table 3 [9,12–13,23,26,32–39]. The oxygen partial pressure of remelting atmosphere influences the removal of sulfur from molten slag to gas phase during ESR. Gasifying desulfurization also helps enhance the overall desulfurization capacity of ESR, as verified by open air atmosphere ESR trials [6,9,12,26,33] and the desulfurization in protective argon atmosphere ESR trials [12,23]. The study by Schneider *et al.* [32] shows that the desulfurization capacity of ESR is less pronounced under a protective nitrogen atmosphere, in comparison with that in open air atmosphere ESR.

In direct-current ESR, the desulfurization ratio is low under a low oxygen partial pressure in ESR, and a high desulfurization ratio is obtained in open air atmosphere ESR [23]. In ESR with an AC power supply of M41 steel, up to 64% of the initial sulfur content of the charge is removed by gas–slag reaction [9]. Hlineny and Buzek [8] indicated that most of the sulfur that removed from liquid metal enters the gas phase of open air atmosphere ESR.

As oxidative desulfurization at the atmosphere/slag interface is restrained by the protective inert atmosphere of ESR, sulfur ions as the desulfurization products of slag–metal reactions constantly accumulate in molten slag with the progress of the desulfurization during ESR, which can cause a decrease in the desulfurization ability or an increase in the sulfur content of remelted ingots [12,23,40]. Kang *et al.* [39] reported that the desulfurization ratio (34%) contributed by ESR in open air atmosphere is higher than that (27%) by the remelting in a nitrogen atmosphere under a slight overpressure. This higher desulfurization degree (the ratio of the difference between the sulfur content of electrode and the sulfur content of ingot to the sulfur content of electrode) is attributed to gasifying desulfurization in ESR, which results in a lower degree of sulfur ion accumulation in molten slag, consequently increasing the desulfurization of the molten slag indirectly.

The ESR of GH4169 superalloy shows that the desulfurization degree in argon atmosphere is lower than that in open air atmosphere. However, the desulfurization degree in ESR in an argon atmosphere combined with calcium addition is higher than that in the open air atmosphere, as shown in Fig. 5 [35]. The sulfur content of GH4169 superalloy decreases as the calcium content of the superalloy increases [35]. The change in the sulfur content of slag against the height of remelted ingots is shown in Fig. 6.

Even though the sulfur content of the slag is apparently higher in protective argon atmosphere ESR combined with calcium addition than that in open air atmosphere ESR, the desulfurization degree in the former case, in which gasifying desulfurization is absent, is indeed higher than that in the latter case (see Figs. 5 and 6). The high desulfurization ratio in the case of calcium addition during ESR is attributed to the chemical reaction between soluble calcium and sulfur in li-

Table 3. Previous studies on desulfurization in different remelting atmospheres of ESR

Author	Chemical composition of slag (wt%)	Sulfur content in electrode / wt%	Sulfur content of ingot in different atmospheres / wt%			Year
			Air	Argon	Nitrogen	
Cooper and Kay [33]	$100CaF_2$	0.13	0.070–0.142	Same result as the remelting in air atmosphere	—	1970
	$95CaF_2–5CaO$		0.065–0.126		—	
	$90CaF_2–10CaO$		0.040–0.047		—	
	$80CaF_2–20CaO$		0.015–0.025		—	
	$70CaF_2–30CaO$		0.008–0.023		—	
Narita *et al.* [12]	$54.2CaF_2–19.5CaO–24.6Al_2O_3–0.8MgO–1.1SiO_2–0.11T.Fe$	0.018	0.0032	0.0032–0.0068	—	1978
Kato *et al.* [23]	$69.0CaF_2–29.8Al_2O_3–0.06SiO_2–0.4CaCO_3$	0.095	0.033–0.062	0.078–0.079 0.074–0.076*	—	1983
Eissa andEI-Mohammadi [26]	$70CaF_2–15CaO–15Al_2O_3$	0.015	0.005–0.006	—	—	1998
		0.025	0.008	—	—	
	$80CaF_2–20CaO$	0.015	0.006–0.007	—	—	
		0.025	0.009	—	—	
	$70CaF_2–30Al_2O_3$	0.015	0.008–0.010	—	—	
		0.025	0.012	—	—	
Mattar *et al.* [9]	$65CaF_2–15CaO–20Al_2O_3$	0.012	0.009	—	—	2008
	$75CaF_2–15CaO–10Al_2O_3$		0.007	—	—	
	$55CaF_2–30CaO–15Al_2O_3$		0.005	—	—	
Ahmadi *et al.* [34]	$33.3CaF_2–33.3CaO–33.3Al_2O_3$	0.019	0.004–0.005	—	—	2009
Chen *et al.* [35]	$60CaF_2–20CaO–20Al_2O_3$	0.0018	0.0004–0.0006	0.0005–0.0009	—	2012
Shi *et al.* [13]	$60CaF_2–20CaO–20Al_2O_3$	0.0180	0.0020–0.0052	0.0020–0.0047	—	2012
Chang *et al.* [36]	$(48–52)CaF_2–(18–22)Al_2O_3–(18–22)CaO–(4–6)MgO–(4–6)SiO_2$	0.0018	0.0012	0.0012	—	2014
Radwitz *et al.* [37]	Slag S1 (Table 4)	0.0078	—	0.0050–0.0079	—	2015
	Slag S2 (Table 4)		—	0.0014–0.0035	—	
	Slag S3 and S4 (Table 4)		—	0.0009–0.0018	—	
	Slag S5 (Table 4)		—	0.0010–0.0016	—	
	Slag S6 (Table 4)		—	0.0016–0.0022	—	
Radwitz *et al.* [38]	See Table 5	0.0070	—	0.0012–0.0016	—	2015
Kang *et al.* [39]	$40CaF_2–30CaO–30Al_2O_3$	0.005	0.0029–0.0033	—	0.0029–0.0037	2018
Schneider *et al.* [32]	3C3A (Table 2)	0.0013	0.0004	—	—	2018
	3C3A (Table 2)		—	—	0.0009	

Note: T.Fe represents total Fe content under slag. * ESR under $Ar–5vol\%O_2$ atmosphere.

quid metal [35], as expressed in the following reaction:

$$[Ca] + [S] = (CaS) \tag{7}$$

This finding is a progress in the desulfurization by protective argon atmosphere ESR. However, the chemical analysis of the sulfur content in the ingots at such low sulfur contents is associated with some uncertainties. More work is needed to assess the thermodynamics and kinetics of the chemical reactions between soluble calcium and sulfur in ESR.

The abovementioned studies [12,35,39] have shown that protective atmosphere of ESR lowers the desulfurization ability of ESR because gasifying desulfurization is prevented. This phenomenon is different from the desulfurization in open air atmosphere ESR. However, Shi *et al.* [13], Cooper and Kay [33], and Chang *et al.* [36] demonstrated that an argon atmosphere does not reduce the desulfurization degree of ESR compared with that in open air atmosphere. An experimental work has been conducted to compare the effects of the open air atmosphere and argon atmosphere of ESR on the sulfur content of tool steel (0.39C–0.26Si–0.43Mn–13.37Cr–0.10Ni–0.21Mo–0.34V–0.079Al–0.0089O–0.020P–0.018S, wt%) [13]. Its results have demonstrated that sulfur content is substantially reduced from 0.0180wt% in an electrode to 0.0020wt%–0.0047wt% in the ingots produced by protective argon atmosphere ESR, and 0.0020wt%–0.0052wt% in the ingots in the case of open air atmosphere ESR. These results are evidence of the comparable desulfurization efficiency in these two cases.

For the ESR of the steel with low sulfur and oxygen contents (0.0018wt% S and 0.0006wt% O), the sulfur content of the remelted ingots produced by both protective argon atmosphere ESR and open air atmosphere ESR is 0.0012wt% [36]. It indicates that remelting atmospheres exert no effect on the desulfurization degree of low-sulfur steel. More work is needed to establish the relationship between the remelting atmosphere and the desulfurization of low-sulfur steel by ESR when using other slag systems.

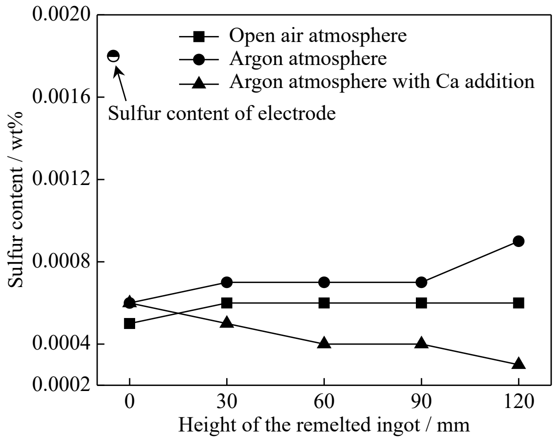

Fig. 5. Change in the sulfur content of remelted ingots against the height of ingots produced under different atmospheres[35].

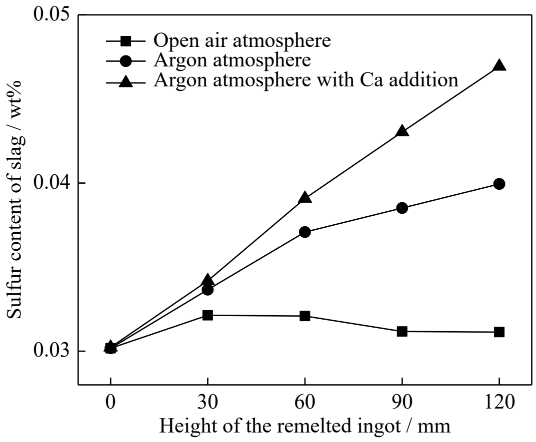

Fig. 6. Change in the sulfur content of slags corresponding to the height of ingots produced under different atmospheres [35].

With increasing demands for the cleanliness of steel and alloy, protective atmosphere remelting has become a standard for new ESR plant installations to lower the oxygen content of remelted ingots and suppress the loss of alloying elements during ESR. Protective atmosphere ESR is generally referred to the remelting in an argon atmosphere. Although gasifying desulfurization is prevented in an inert atmosphere, the desulfurization degree of ESR in a protective argon atmosphere is not reduced compared with that of the remelting in open air atmosphere provided that sulfides in the used molten slag during protective atmosphere ESR are still away from their saturation and the kinetics condition is comparable in these two cases.

The decrease in the desulfurization degree of ESR, which is caused by a protective atmosphere, is highly dependent on the sulfide capacities of slag melts. In a sufficiently high sulfide capacity of slag, slag–metal reactions can already yield a high desulfurization capacity of ESR. On the contrary, gasifying desulfurization is needed to enhance desulfurization in ESR following the desulfurization by slag–metal reactions. In the latter case, the remelting atmosphere plays a significant role in desulfurization during ESR. More work is needed to quantitatively verify the role of protective argon atmosphere in the desulfurization during ESR by using the slag with different compositions.

Pressurized ESR is a promising technology for producing high nitrogen steel [41–43]. In recent years, vacuum ESR has been developed to further improve the cleanliness of steel in terms of oxygen and inclusion contents [44–45]. The nitrogen transfer behavior at different nitrogen partial pressures of pressurized ESR and the deoxidation of vacuum ESR have been studied [43,45–46]. Nevertheless, future work should be performed to reveal the roles of pressurized and vacuum atmospheres in the desulfurization in ESR.

3.3. Slag composition

The chemical composition of slag is the most important concern among the factors affecting the steel cleanliness in terms of the deoxidation, non-metallic inclusion removal, and desulfurization efficiency of ESR [5,32,47–48]. ESR-type slag is generally CaF_2–CaO–Al_2O_3-based system with minor additions of MgO, TiO_2, and SiO_2 to tailor the slag for specific remelting requirements. On the basis of the sulfide capacities of CaF_2–CaO–Al_2O_3 melts, Mattar *et al.* [9] reported that the optimum desulfurization (highest sulfide capacity) for this slag system is attained with 20wt% CaO and 80wt% CaF_2. However, the experimental work supporting this assertion for desulfurization by ESR is lacking.

Slag chemistries not only affect sulfur removal by slag–metal reaction but also influence the elimination of sulfur from molten slag to gas phase via gas–slag reaction. The thermodynamic analysis of slag–metal desulfurization and gas–slag desulfurization, as expressed in Eqs. (4) and (6), shows that high basicity (high $a_{(O^{2-})}$) and low oxygen potential (low $a_{[O]}$) are favorable to the desulfurization by slag–metal reaction, whereas low basicity (low $a_{(O^{2-})}$) and high oxygen partial pressure (high $p_{\{O_2\}}$) are beneficial to the desulfurization by gas–slag reaction. These two desulfurization reactions not only affect each other, but also have inherent contradictions. From the viewpoint of kinetics, the desulfurization rates of slag–metal and gas–slag reactions increase as slag viscosity decreases. The slag viscosity is mainly dependent on slag chemistries. A low slag viscosity causes a strong stirring action, which is mainly caused by electromagnetic forces, and a strong diffusion of sulfur from molten metals through the slag layer and to the atmosphere/slag interface [9]. Consequently, the desulfurization rate of gas–slag reaction increases.

A sufficient amount of CaO should be added to the slag to achieve pronounced desulfurization during ESR. Sulfur removal via slag–metal reaction is enhanced by increasing the CaO/Al_2O_3 mass ratio of the slag because of a high CaO activity in ESR [9]. The ESR of free-cutting steel (0.13wt% S) when using the CaF_2–CaO slag with different CaO contents (0, 5wt%, 10wt%, 20wt%, and 30wt%) shows that the sulfur content of steel apparently decreases as CaO contents increase expectedly in open air atmosphere ESR [33]. The desulfurization degree decreases at the later stage of open air atmosphere ESR because of an increase in the oxygen content of liquid steel through increasing the FeO content of the slag with the progress of the ESR, especially for the case of low-CaO slag [33].

In the protective argon atmosphere ESR of the steel with 0.0029wt% sulfur, the desulfurization degree of ESR decreases as the SiO_2 content in the slag increases [30]. A similar finding is observed in the protective argon atmosphere ESR of the steel with 0.0032wt% sulfur [31]. It is attributed to a decrease in the CaO activity as the SiO_2 content of the slag increases [30–31]. Meanwhile, the desulfurization kinetics of ESR deteriorates because of the increased SiO_2 contents of the slag. The deterioration of the desulfurization kinetics originates from the reduction of the depolymerization degree of molten slag structures and the enhancement of the diffusion resistance of structural units as the SiO_2 content of slag melts increases [49].

The comparison of the desulfurization degree of the slag with different CaO contents (i.e., 70wt% CaF_2–15wt%CaO–15wt%Al_2O_3, 80wt%CaF_2–20wt%CaO, and 70wt%CaF_2–30wt%Al_2O_3) in the open air atmosphere ESR of three different grades of tool steel shows that 80wt%CaF_2–20wt%CaO slag is the most effective in the desulfurization via gas–slag reaction, and 70wt%CaF_2–15wt%CaO–15wt%Al_2O_3 slag gives the highest degree of desulfurization via slag–metal reaction [26]. Eissa and EI-Mohammadi [26] indicated that these differences in the desulfurization degree are attributed to the variations in the slag viscosity and interfacial tension. However, their explanation did not include the differences in the sulfide capacities of these slag systems and steel compositions, especially the oxygen contents of these three steels for desulfurization. These thermodynamic aspects can make a remarkable difference in the desulfurization degree of ESR.

For the slag without CaO in its initial chemistry, desulfurization also occurs in open air atmosphere ESR [11,50]. The sulfur content decreases from 0.039wt% to 0.0171wt% in NiCrMoV alloy and from 0.011wt% to 0.0017wt% in CrMoV alloy after ESR [11]. Liu *et al.* [11] claimed that CaO is generated through the chemical reaction expressed in Reaction (8), and subsequently reacts with sulfur in liquid steel for desulfurization, and the gasifying desulfurization ratio reaches 92.2%.

$$3(\mathrm{CaF_2}) + (\mathrm{Al_2O_3}) = 3(\mathrm{CaO}) + 2\{\mathrm{AlF_3}\} \tag{8}$$

However, Liu *et al.* [11] pointed out that the amount of CaO formed through the reaction described in reaction (8) is quite small. Therefore, the desulfurization ability of the slag with CaO-free in its initial chemistry is virtually limited.

With respect to the desulfurization by ESR when using the slag without CaO in its initial chemistry, more research is needed to quantify the amount of CaO generated via fluoride evaporation from slag melts and its contribution to the desulfurization. Desulfurization contributed by MnO and FeO, which is an inevitable component in the slag during ESR, should also be considered. The sources of FeO in ESR have been summarized in reference [5].

The desulfurization abilities of the slag with different CaF_2, CaO, and Al_2O_3 contents in the ESR of 21CrMoV5-7 steel in an argon atmosphere at a slight overpressure (0.12 MPa) are compared [37], as shown in Fig. 7. The chemical compositions of the slags are shown in Table 4 [37]. The desulfurization ability of the ESR almost remains unchanged as the CaO content increases from 20wt% to 40wt% and as the CaF_2 content simultaneously decreases from 60wt% to 20wt%. As shown in Fig. 7, 20wt% CaO is sufficient to keep a satisfactory sulfur removal until the end of ESR.

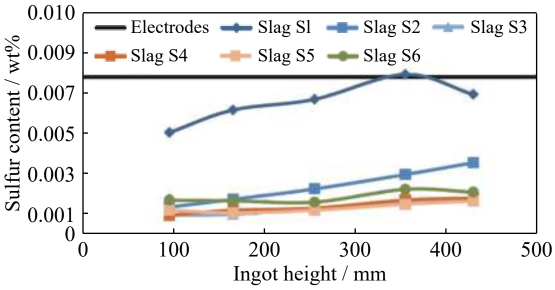

Fig. 7. Variation in the sulfur content of remelted ingots for different slag systems [37].

Table 4. Chemical composition of the slags used in ESR trials [37] wt%

Slag No.	CaF_2	CaO	Al_2O_3	MgO	SiO_2	FeO
S1	98.9	0.35	0.02	0	0.17	0.01
S2	79.12	9.666	9.33	1.016	0.196	0.028
S3	59.34	18.982	18.64	2.032	0.222	0.046
S4	39.56	28.298	27.95	3.048	0.248	0.064
S5	19.78	37.614	37.26	4.064	0.274	0.082
S6	0	46.93	46.57	5.08	0.3	0.1

Increasing the MgO content of the slag from 2wt% to 15wt% and decreasing the CaO content from 19wt% to 12.5wt% do not change the desulfurization ability of protective argon atmosphere ESR because the desulfurization by ESR under this atmosphere is mainly based on CaS formation and slightly based on MgS formation [38]. The sulfur content is decreased from 0.0070wt% in the electrode to 0.0010wt%–0.0018wt% in remelted steel. The chemical compositions of the studied slags in reference [38] are summarized in Table 5. The variation of TiO_2 contents in the slag shows a negligible difference in the desulfurization degree of ESR of the Fe–25Ni–15Cr alloy with an original sulfur content of 0.0070wt% [51]. It is suggested that the activities of slag components should be used to characterize the differences in the desulfurization capacities of slag melts with different chemistries, rather than their contents in slag melts.

Table 5. Chemical composition of the slags used in ESR trial [38] wt%

Slag No.	CaF_2	CaO	Al_2O_3	MgO	SiO_2	FeO
F1	59.34	18.98	18.64	2.03	0.22	0.046
F2	59.34	17.48	17.13	5.07	0.01	0.04
F3	59.34	15.05	14.69	9.98	0.03	0.04
F4	59.34	12.62	12.25	14.89	0.04	0.03

For ESR of a steel electrode with a low sulfur content, slag chemistry virtually slightly affects the desulfurization during ESR. The sulfur content of X37CrMoV5-1 hot work tool steel decreases from 0.0013wt% in the steel electrode to 0.0004wt%–0.0008wt% after ESR in open air atmosphere when the slag with varying CaF_2, CaO, Al_2O_3, and SiO_2 contents is used [32]. The chemical compositions of the slag used in ESR trials are listed in Table 2. In these cases, the initial sulfur content of the steel electrode is very low. Therefore, the differences in the sulfur contents of remelted ingots are subjected to some uncertainties associated with the chemical analysis of the sulfur contents. For ultralow-sulfur steel and alloy production, more studies are needed to reveal the effect of slag compositions on the desulfurization during the ESR of the electrodes with initial low sulfur contents.

3.4. Deoxidation schemes of ESR

Desulfurization of liquid metal is influenced by the soluble oxygen content of liquid metal. The deoxidation of ESR is an indispensable condition to increase the desulfurization degree of liquid metal. This precondition and its related factors have been systematically assessed in reference [5]. The continuous or periodic addition of deoxidizing agents to the slag pool of ESR is widely used for the deoxidation of ESR [13,52–54]. For the ESR of an Fe–Al intermetallic alloy, the presence of a high aluminum content (15wt%) of this alloy lowers the oxygen potential of given system during ESR. Consequently, sulfur content decreases from 0.0120wt% in the electrode to 0.0032wt% in the alloy after ESR [55].

The deoxidation of ESR should be performed to keep a low oxygen potential of molten slag (FeO and MnO contents) by adding deoxidizing agents because this practice is a prerequisite to successfully lower the sulfur content ($S \leq 0.0020wt\%$) of 200 t scale ingots, besides increasing the oxidability of the remelting atmosphere [56]. Decreasing the oxygen potential of molten slag by periodically adding aluminum shots (0.1% of the ingot weight) during the ESR of 15CDV6 steel has been verified to increase the desulfurization degree of ESR and eliminate the loss of silicon, manganese, and chromium in the steel [57]. For the ESR of steel with a low oxygen content (0.0018wt%), the addition of different amounts of calcium and Al-based deoxidizing agents in protective atmosphere ESR fails to further reduce the oxygen content of remelted ingots. Consequently, calcium and Al-based deoxidizing agents addition exerts no influence on the sulfur content of remelted ingots (0.0016wt% in all cases) [29].

3.5. Melting rate of ESR

Liquid metal films form on an electrode tip during ESR and thereafter accumulate as liquid metal droplets. This stage plays a predominant role in the desulfurization of liquid metal during ESR. The melting rate of ESR largely determines the thickness of a liquid metal film on electrode tip and the residence time of the liquid metal film and metal droplets at the electrode tip [20,58]. In general, the desulfurization degree of ESR increases as the melting rate of ESR decreases. This observation has been verified in the ESR of Mn18Cr18N steel containing 0.0082wt%–0.0110wt% sulfur using the slag composed of $69wt\%CaF_2–29wt\%Al_2O_3–1wt\%SiO_2–1wt\%FeO$ [59] and the ESR of commercial-grade iron [6]. However, the mechanisms of these findings are not presented in these two studies [6,59]. The present authors claim that the increase in the desulfurization degree originates from the increase in the residence time of liquid metal films at the electrode tip as the melting rate of ESR decreases.

In the case of protective argon atmosphere electroslag rapid remelting (ESRR) of a steel electrode with 0.0008wt% oxygen and 0.0026wt% sulfur, reoxidation of liquid steel takes place during the ESRR, which results in the oxygen contents nearly double (0.0014wt% to 0.0017wt%), and sulfur contents are between 0.0018wt% and 0.0021wt% after ESRR. In these cases, the sulfur contents negligibly differ in the remelted steel produced at different melting rates (350, 400, 450, and 500 kg/h) [10]. This finding is different from those obtained by Mehrabi *et al.* [6] and Tang *et al.* [59]. From the viewpoint of desulfurization kinetics, increasing the melting rate of ESR lowers the residence time of liquid metal films at the electrode tip, and this reduction is unfavorable to the removal of sulfur from the liquid metal. The differences in the sulfur contents of remelted ingots with varying melting rates are negligible because the desulfurization is limited by the thermodynamics of chemical reactions in these cases, including the initial sulfur content and soluble oxygen content of liquid steel.

3.6. Electrical parameters of ESR

At the initial stage of ESR development, direct current (DC), along with AC power supply, is widely used [23,60–62]. However, ESR is generally operated using high frequencies (50 or 60 Hz) of AC in production practices worldwide. ESR with a DC power supply has been studied, but previous studies mainly focused on the deoxidation of liquid steel and non-metallic inclusions during ESR with a DC power supply [23,62–64]. Studies on the desulfurization during ESR with a DC power supply are extremely limited.

The influences of the type and polarity of an electric current on the desulfurization have been studied through laboratory-scale open air atmosphere ESR trials of 30KH13 steel with 70wt%CaF_2–30wt%Al_2O_3 slag [65]. Electric current and voltage are maintained at the same level (I = 0.8 kA, U = 46 V) for all power supply types. The desulfurization degree of ESR with an AC power supply is much higher than that of ESR with a DC of both polarities (see Fig. 8). The reversed polarity contributes a higher desulfurization degree of ESR than the straight polarity does. These results are in agreement with the observations reported by Zhang *et al.* [66] in the ESR of wood alloy with AC, DC of reversed polarity, and DC of straight polarity (see Fig. 9).

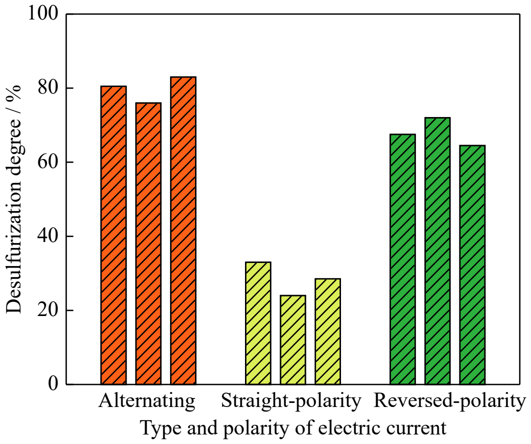

Fig. 8. Influence of the type and polarity of electric current on the desulfurization degree of ESR [65].

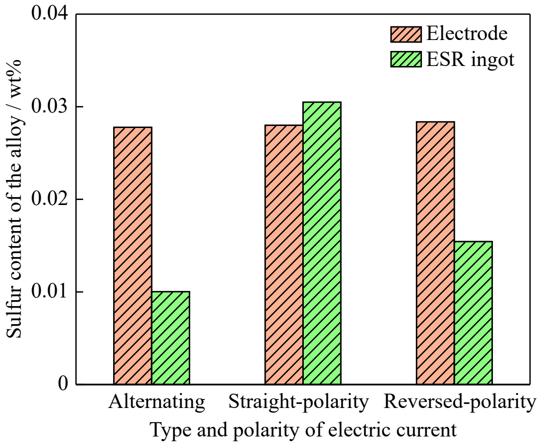

Fig. 9. Influence of the type and polarity of electric current on the sulfur content of ESR ingots [66].

In ESR with direct reversed polarity current, electrons move from a steel electrode (cathode) because of electrolytic processes, and sulfur is removed from liquid steel. However, during ESR with straight-polarity DC, S^{2-} anions are attracted to the electrode (anode). These anions are adsorbed in liquid metal films at the electrode tip and transferred with metal droplets to liquid metal pool, leading to a high-sulfur content. Therefore, the desulfurization degree of ESR operated with straight-polarity DC is much lower than that of ESR with reversed polarity DC. Among these three power supply modes, the desulfurization degree of ESR with an AC power supply is maximal because of an increased area of the slag–metal interface caused by a developed electrocapillary vibration of the molten slag–liquid metal interface during ESR with an AC power supply [65–66].

4. Desulfurization associated with sulfide inclusion evolution during ESR

Sulfide inclusion (single-phased or sulfide phase in an oxide-sulfide complex inclusion) removal during ESR is achieved on the basis of the good desulfurization capability of ESR [63,67]. The present authors' previous study [31] shows that CaO–Al_2O_3–SiO_2–MgO inclusion acts as formation site for patch-type (Ca,Mn)S inclusion in consumable steel electrode. No sulfide inclusions are present in liquid metal pool, and all (Ca,Mn)S inclusions in the steel electrode are removed before liquid metal droplets collect in liquid metal pool during ESR. In addition, CaS inclusions adhering to CaO–Al_2O_3–MgO inclusions, together with isolated CaS-only inclusions, dissociate into liquid steel as soluble calcium and sulfur during liquid metal film formation and subsequent collection into droplets at the electrode tip during ESR [10]. This phenomenon is in accordance with the findings regarding the removal of (Mn,Cr)S and MnS inclusions during ESR [11,13−14,29]. It is the trajectory that the original CaS, (Mn,Cr)S, and MnS inclusions in consumable steel electrodes are fully removed during ESR.

The soluble sulfur in liquid steel that dissociates from original sulfide inclusions is removed by desulfurization, as expressed in Reaction (1), during ESR. Therefore, the desulfurization during ESR is closely associated with the removal of original sulfide inclusions. The factors that affect the removal of original sulfide inclusions influence the desulfurization of liquid steel during ESR. Furthermore, the desulfurization degree of ESR influences the generation of fresh sulfide inclusions during liquid steel solidification in ESR, as verified by Qi *et al.* [68] In this process, a high desulfurization efficiency of ESR suppresses the generation of fresh sulfide inclusions.

5. ESR for sulfur-bearing steel production

A high level of sulfur content is expected for some kinds of steel grades, such as freecutting steel, and some crankshaft steel. The uniformity of sulfur in these sulfur-bearing remelted steels can hardly be successfully kept. Low-CaO or CaO-free slag, which has a low sulfide capacity, is usually used for ESR to prevent the loss of sulfur during ESR and ensure the uniformity of sulfur in remelted ingots. The optimized slag system for the ESR of sulfur-bearing 34CrNiMo6 steel is composed of 60wt%CaF_2–30wr%Al_2O_3–5wt%MgO–5wt%SiO_2, which gives a uniform distribution of sulfur in ESR ingots (610 mm in diameter) [69]. A certain amount of FeS addition in slag is also one of the effective countermeasures to produce sulfur-bearing remelted steel in ESR practice. However, the inhomogeneity of sulfur in steel should be noted in this operation, and further studies should be conducted on related topics, such as sulfur transfer between molten slag and liquid steel and the role of slag compositions in sulfur transfer.

In open air atmosphere ESR of the steel with 0.09wt% sulfur when using the slag composed of 50wt%CaF_2–30wt%Al_2O_3–20wt%SiO_2, the sulfur contents of remelted ingots range from 0.066wt% to 0.075wt%, which meets the requirement of the sulfur contents of AS136 steel (0.05wt% to 0.1wt%). However, alumina and silicate inclusions in the steel are beyond the requirement of inclusion evaluated criterion [50]. By contrast, a uniform distribution of sulfur (0.05wt% to 0.061wt%) in remelted ingots, an improved inclusion distribution and size are achieved when using the slag composed of 70wt%CaF_2–28wt%Al_2O_3–2wt%MgO in combination with the continuous addition of 4.5wt% MgO to the molten slag pool during ESR to maintain a constant sulfur distribution ratio between liquid steel and molten slag [50]. This result indicates that CaO-free slag largely suppresses the decrease in the sulfur content during the ESR of sulfur-bearing steel, and SiO_2 addition in CaO-free slag can further suppress the desulfurization ability of ESR.

A ternary CaF_2–Al_2O_3–CaS system as the initial slag chemistry in combination with periodic CaS addition to molten slag pool during protective argon atmosphere ESR prevents the loss of sulfur in crankshaft steel [70]. The slag composed of 60wt%CaF_2–15wt%Al_2O_3–5wt%CaO–20wt%SiO_2 slag with intentionally added 2.5wt% CaS exhibits an excellent performance in open air atmosphere ESR to prevent the sulfur loss of sulfur-containing high-speed M35 steel (0.015wt%–0.030wt% sulfur) during ESR in open air atmosphere [17]. Sulfur contents at the different positions of remelted ingots remain nearly constant, and only a quite small amount of sulfur is lost in remelted ingots. For the slag without intentionally added CaS, a significant amount of sulfur is lost from the steel after open air atmosphere ESR [17]. CaO-free slag with intentionally added CaS has an excellent performance in producing sulfur-bearing remelted steel because of the limited desulfurization capability of ESR. For sulfur-bearing steel production, the uniformity of sulfur in the remelted ingots remain a challenge, especially in producing heavy remelted ingots.

6. Concluding remarks

A low initial sulfur level generally gives a low sulfur content of the remelted ingots, but this is not always the case. Low sulfur levels of the remelted ingots also depend on the slag compositions and the oxygen contents. Gasifying desulfurization remarkably contributes to the desulfurization by ESR. The reduction of the desulfurization caused by protective atmosphere is highly dependent on the sulfide capacities of slag. Deoxidation during ESR is a prerequisite for improving the desulfurization.

Slag–metal and gas–slag reactions for the desulfurization during ESR not only affect each other but also have inherent contradictions. The desulfurization rates of slag–metal and gas–slag reactions are enhanced with the reduction of slag viscosity. The activity of CaO in slag is the main factor of the remarkable desulfurization by ESR. CaO-free slag in its initial chemistry can exhibit apparent desulfurization in the ESR. More work is needed to quantify the amount of CaO generated through fluoride evaporation from slag melts and its contribution to the desulfurization. Slag chemistry exerts only a slight effect on the desulfurization capacity of the ESR of the electrode with a low initial sulfur content.

The desulfurization capability of ESR increases as the melting rates of ESR decrease except when desulfurization is determined by reaction thermodynamics. The desulfurization degree of ESR with an AC power supply is much higher than that in the case of the DC of straight and reversed polarities. The desulfurization degree of ESR with straight-polarity DC is minimal. Desulfurization during ESR is associated with the elimination of sulfide inclusions and the generation of fresh sulfide inclusions. CaO-free slag with intentionally added CaS shows an excellent performance in producing sulfur-bearing remelted steel.

Significant progress has been made in the desulfurization and a high-sulfur target for sulfur-bearing steel in ESR. However, the desulfurization by ESR at various partial pressures in different remelting atmospheres for an ultralow-sulfur target and achieving an accurate sulfur level in ESR for sulfur-bearing steel production are still in their infancies. Future work is needed to study the roles of different remelting atmospheres on the desulfurization by ESR when using the slag with different compositions and on the desulfurization capacity of ESR of low-sulfur electrodes. For sulfur-bearing steel production, the uniformity of sulfur in remelted ingots remains a challenge, especially heavy remelted ingots.

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