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Effect of FeO on the formation of spinel phases and chromium distribution in the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system

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Abstract: Synthetic slag samples of the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system were obtained to clarify the effect of FeO on the formation of spinel phases and Cr distribution. X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS), as well as the thermodynamic software FactSage 6.2, were used for sample characterization. The results show that the addition of FeO can decrease the viscosity of molten slag and the precipitation temperatures of melilite and merwinite. The solidus temperature significantly decreases from 1400 to 1250°C with the increase of FeO content from 0wt% to 6wt%. The addition of FeO could enhance the content of Cr in spinel phases and reduce the content of Cr in soluble minerals, such as merwinite, melilite, and dicalcium silicate. Hence, the addition of FeO is conducive to decreasing Cr leaching.

Keywords: stainless steel; slags; spinel phase; chromium; leaching; ferrous oxide

1. Introduction

The electric arc furnace (EAF) process is used for melting scraps and alloys to provide molten steel for subsequent refining by argon oxygen decarburization or vacuum oxygen decarburization processes in many stainless steel plants. Chromium (Cr) is an essential alloying element in stainless steel and has a greater affinity with oxygen than iron. An oxygen injection is often practiced in the EAF process to enhance the melting speed and productivity, and also leads to an oxidization of small amount of Cr [1]. The slag tapped from the EAF process, the EAF slag, contains Cr oxides of several percent. After leaving the EAF process, the slag is cooled and stored for other utilizations. It has been found by some studies [2-5] that hexavalent Cr can be generated from Cr oxides in the EAF slag in the period of slag processing and storage. Hexavalent Cr is toxic and easily leachable from the slag, leading to water pollution and some economic and ecologic issues. In fear of Cr leaching, utilizations of EAF slag and other slags from stainless steelmaking are severely circumscribed.

The leachability of Cr mainly depends on the Cr distribution among the minerals existing in the stainless steel slag. Cr could be present in many different mineral phases due to the conditions of nonequilibrium cooling. Numerous mineralogical species present in the slags are soluble in aqueous media, such as merwinite, periclase, dicalcium silicate, and lime, although there are other phases, such as wustite, spinel, and glass, being considered as resistant to water dissolution [6-7]. The investigation of García-Ramos *et al.* [8] also showed that the Cr leachability has been suppressed by the presence of MgO or Al_2O_3 in the slag system of CaO-SiO_2-Cr_2O_3, with the efficiency of MgO for the leaching suppression higher than that of Al_2O_3, due to the stable binding for Cr in $MgCr_2O_4$. In addition, the mineralogical and microstructural analyses performed by Tossavainen *et al.* [9] and Engström *et al.* [10] have shown that merwinite ($Ca_3MgSi_2O_8$), akermanite ($Ca_2MgSi_2O_7$),

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gehlenite ($Ca_2Al_2SiO_7$), and spinels were major phases in the EAF slag. Jelkina *et al.* [11] found that the amount and purity of mineralogical phases present in the synthetic slags of the CaO-MgO-SiO_2-Cr_2O_3-Al_2O_3 system were highly dependent on the slag composition and heat treatment history.

As one of the components of stainless steel slag, FeO is an oxidizing agent and a spinel-forming compound and has quite low melting point (1369°C). Therefore, the change of FeO content may affect the mineral composition and the distribution of Cr. Researchers from Institut für Baustoff-Forschung e.V. performed laboratory experiments to decrease the leaching of Cr, and they found that the influence of iron(II) and alumina was most successful [12]. The present experimental work was performed for a better understanding of FeO effects on the spinel formation and Cr distribution in EAF slag from stainless steelmaking. Synthetic slag samples of the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system were prepared for characterization. Thermodynamic calculations were also carried out using FactSage 6.2 to aid discussion on results from the experiments.

2. Experimental

Fine powder of reagents, CaO, MgO, Al_2O_3, SiO_2, and Cr_2O_3, of analytical grade were used to prepare synthetic slag samples with the compositions close to the EAF slag generated from stainless steelmaking, as shown in Table 1. The amount of FeO added in samples S1-S3 was 0wt%, 3wt%, and 6wt%, respectively. CaF_2 of approximately 3wt% was used to decrease the melting point of the slag samples.

Table 1. Compositions of synthetic slag samples of the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system wt%

No.	CaO	SiO_2	MgO	Al_2O_3	Cr_2O_3	FeO	CaF_2
S1	45.00	32.00	8.00	6.00	6.00	0	3.00
S2	43.65	31.04	7.76	5.82	5.82	3	2.91
S3	42.30	30.08	7.52	5.64	5.64	6	2.82

The reagent powders for each of the slag samples, after thoroughly homogenizing, were placed in an Al_2O_3 crucible, which was placed in a graphite crucible inside an induction furnace to heat slowly for sample melting. After the melt temperature reaching 1600°C, a special procedure of furnace operation was employed to obtain a cooling condition not only for a better crystallization of some slag phases but also for a closer simulation of industry practices for slag cooling. The furnace temperature was measured with an S-type thermocouple. A high-quality argon gas was supplied in the furnace to protect the synthesized slag samples at high temperature. The cooling operation started by first maintaining the melt temperature of 1600°C for 30 min followed by decreasing the temperature to 1450°C, which was held for 30 min. Then, the temperature declined again and was kept at 1300°C for 60 min. After these cooling operations, the slags remained inside the furnace to cool down to room temperature naturally.

The synthetic slag samples were separated from the Al_2O_3 crucibles. About 30 g samples from each of the slags were prepared for characterization. The mineral compositions were determined by powder X-ray diffraction (XRD) analysis (M21x, MAC), with a measuring range of 10°-90° in a step of 0.02°. Microstructural properties of the samples were analyzed using scanning electron microscopy (SEM; Jeol 6480LV) equipped with a Thermo Electron NSS energy-dispersive spectrometer (EDS). Thermodynamic calculations of mineral phases were performed by FactSage 6.2 [13-14]. The compounds of ideal gas and pure solids were included. The databases selected were Fact53, FToxid, FToxid-slagA, FToxid-Mel, and FToxid-spinA. Fact53 was suppressed by FToxid to exclude the duplication in the data set. Input data for the slag compositions are from Table 1. The temperature range was 900-1800°C with a step of 10°C and the system pressure was set as a constant of 1.013×10^5 Pa for the calculations.

3. Results

The microstructures of solidified synthetic slags of the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system with different FeO contents are shown in Fig. 1. Elemental compositions, based on results from SEM-EDS analysis, of phases identified in Figs. 1(a)-1(c) are presented in Tables 2-4, respectively.

Sample S1 without FeO addition consists of four major phases: merwinite ($Ca_3MgSi_2O_8$), melilite, Ca_2SiO_4 (C_2S), and spinels (Fig. 1(a) and Table 2). Melilite, C_2S, and spinels are solid solutions. Melilite is formed mainly by akermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$) [15-17]. MgO may dissolve into the crystal lattice of Ca_2SiO_4 (C_2S) through, probably, isomorphous replacement, giving an Mg content of 3.89at% in the phase. The existence of two types of spinels is observed, with phase 4 rich in chromium (Cr 23.27at%) and phase 5 rich in aluminum (Al 24.02at%). Data in Table 2 reveal also the Cr existence in silicates, with merwinite and C_2S with a Cr content of 0.09at% and 0.10at%, respectively.

There are also four mineral phases observed in sample S2 with the FeO content of 3wt%, similar to the sample without FeO addition. However, Cr is measured only in the spinel of phase 9 with the content of 23.09at% and the three silicates are free from Cr, as seen in Fig. 1(b) and Table 3. Compared with samples S1 and S2, there are more minerals in sample S3 with 6wt% FeO. The three spinel phases, phases 12-14, are solid solutions with different contents of Cr, Al, Mg, and Fe elements, as shown in Fig. 1(c) and Table 4. The two silicates and the MeO phase, phases 10, 11, and 15, are also Cr free, the same as the three silicates in sample S2 with the FeO of 3wt%.

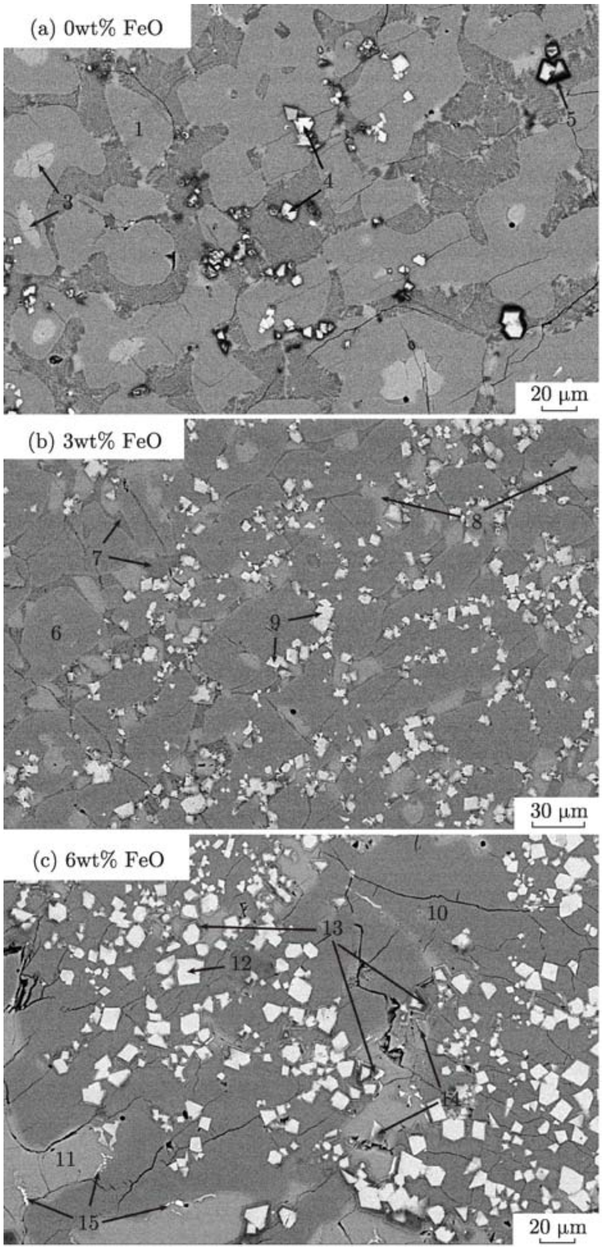

Fig. 1. SEM images of samples S1 (a), S2 (b), and S3 (c).

Table 2. Elemental compositions of mineral phases in sample S1 shown in Fig. 1(a) at%

No.	Phase	O	Mg	Al	Si	Ca	Cr
1	Merwinite	52.22	7.84	0.42	16.66	22.77	0.09
2	Melilite	53.37	3.22	6.90	15.21	21.20	—
3	C_2S	52.08	3.89	1.20	16.83	25.90	0.10
4	Cr-spinel	53.12	15.71	7.15	0.26	0.49	23.27
5	Al-spinel	50.95	15.31	24.02	1.32	1.13	7.27

Table 3. Elemental compositions of mineral phases in sample S2 shown in Fig. 1(b) at%

No.	Phase	O	Mg	Al	Si	Ca	Cr	Fe
6	Merwinite	54.16	7.30	0.47	16.26	21.64	—	0.20
7	Melilite	57.19	1.54	11.14	13.87	14.72	—	1.56
8	C_2S	53.72	0.49	0.47	16.44	28.89	—	—
9	Spinel	54.99	13.48	5.74	0.43	0.53	23.09	1.75

Table 4. Elemental compositions of mineral phases in sample S3 shown in Fig. 1(c) at%

No.	Phase	O	Mg	Al	Si	Ca	Cr	Fe
10	Merwinite	52.41	7.94	0.38	16.86	22.35	—	0.07
11	C_2S	52.13	0.75	0.49	16.86	29.79	—	—
12	Cr-spinel	53.64	14.56	2.74	0.15	0.38	27.21	1.32
13	Al-spinel	52.85	11.02	16.61	4.84	4.83	4.37	5.48
14	Spinel	56.79	11.29	19.45	1.37	2.92	1.15	7.04
15	MeO*	50.60	15.31	1.30	3.08	3.91	—	25.75

Note: *Me presents metal elements, such as Mg and Fe.

The contents of Cr in spinel phases are approximately 23at% in samples S1 and S2, as seen in Tables 2 and 3, respectively. The Cr content increases to a higher value (27.21at%; Table 4) in one of the spinel phases (phase 3) in sample S3 with the FeO content higher than the two samples. A comparison of slag microstructures in Fig. 1 reveals a clear trend that the amount and size of spinel minerals increase with an increase of FeO content in the samples.

XRD patterns of the three slag samples are shown in Fig. 2. The peaks of merwinite ($Ca_3MgSi_2O_8$) are rather high, indicating that it is a major mineral phase in these samples. Chromite ($MgCr_2O_4$) and $MgAl_2O_4$ also appear in all samples. Another spinel mineral, donathite ($(Fe,Mg)(Cr,Fe)_2O_4$), is identified in the samples containing 3wt%-6wt% FeO.

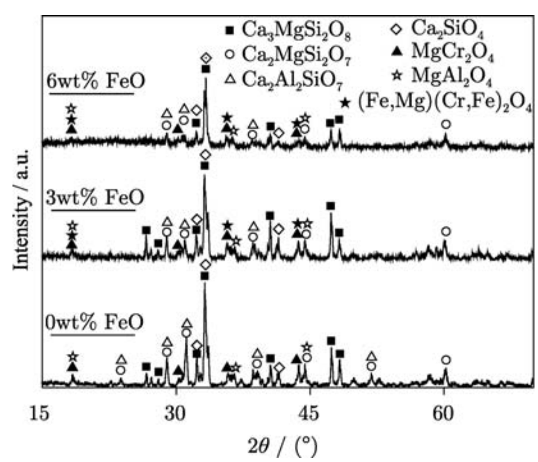

Fig. 2. XRD patterns of slag samples S1, S2, and S3 containing the FeO contents of 0wt%, 3wt%, and 6wt%, respectively.

Fig. 3 shows that the mass fractions of merwinite, $Ca_3MgSi_2O_8$, calculated by FactSage 6.2, range from 44% to 57% in the three slag samples S1-S3. The calculation indicates also that the mass fractions of spinel minerals are 41.8% and 70.2% higher in samples S2 and S3 containing FeO of 3wt% and 6wt%, respectively, compared with the spinel fraction in sample S1 without FeO addition, due to the formation of a new spinel mineral, $FeCr_2O_4$. These calculation results agree rather well with SEM and XRD results in Figs. 1 and 2. Results in Fig. 3 also demonstrate that, compared with sample S1, the precipitation temperatures of merwinite and melilite for samples S2 and S3 are lower, as well as the solidus temperature calculated for the two samples.

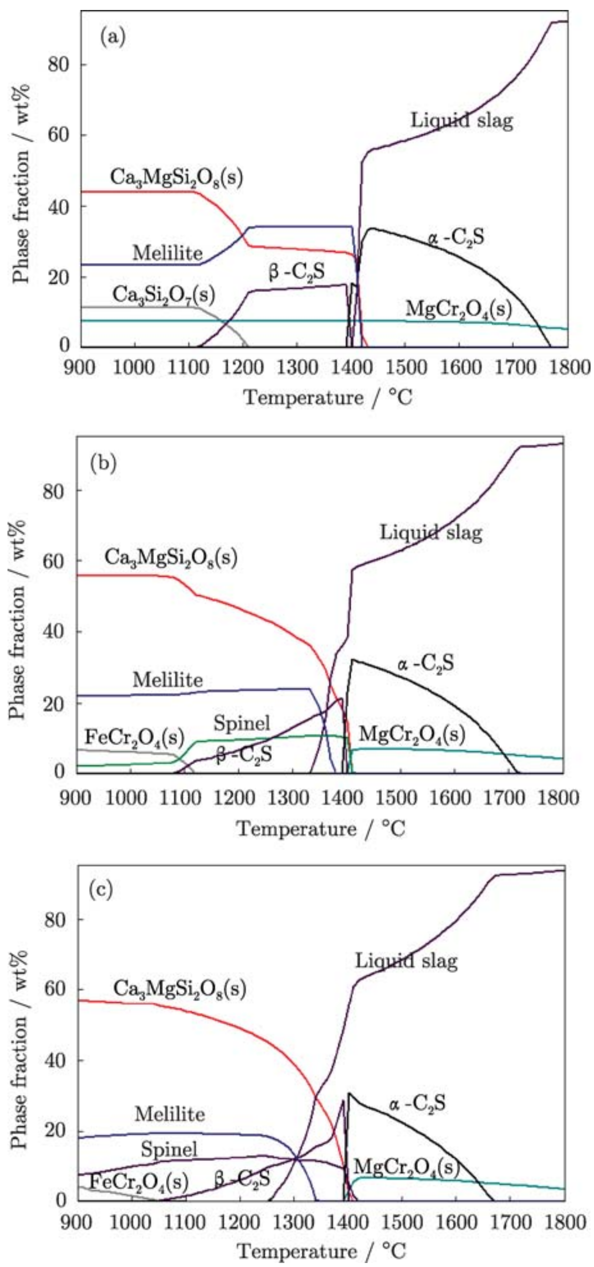

Fig. 3. Mass fractions of mineral phases calculated by FactSage 6.2 for slag samples S1-S3 with the FeO contents of 0wt%, 3wt%, and 6wt%, respectively: (a) S1; (b) S2; (c) S3.

4. Discussion

From the viewpoint of thermodynamics, a solid spinel can be formed via reaction (1) in a simple system of Mg-Cr-O. With Al in the system, it is also possible to form the spinel with reaction (2). For a more complicated case, such as adding FeO in the Mg-Cr-Al-O system, a reasonable prediction on the formation of spinel minerals may not be straightforward only from thermodynamic considerations.

$$MgO(s) + Cr_2O_3(s) = MgCr_2O_4(s) \tag{1}$$

$$\Delta G^{\ominus} = -34462 - 13.857T, \text{ J/mol.}$$

$$(MgO) + (Cr_2O_3) + (Al_2O_3) \rightarrow Mg(Cr,Al)_2O_4(s) \tag{2}$$

$$(MgO) + (FeO) + (Cr_2O_3) + (Al_2O_3) \rightarrow (Mg,Fe)(Cr,Al)_2O_4(s) \tag{3}$$

The concept of isomorphous replacement has been useful for studies in the field of mineralogy. According to this concept, a part of Mg^{2+} cations can be replaced readily by Fe^{2+} cations [18], facilitating spinel formation in the Mg-Cr-Al-O system, which can be described using reaction (3). With FeO addition to promote isomorphous replacement, the formation possibility and quantity of the spinel phases may be enhanced.

Additionally, for the growth of spinel crystals in a slag melt, the conditions of mass transfer for oxides in liquid and solid state should be taken into account [19]. It is reasonable to assume the mass transfer depending mainly on diffusion and to use the Fick's first law (Eq. (4)), which specifies that the diffusion flux is a function of diffusion coefficient D and concentration gradient. The concentration gradient is related closely to the slag composition; according to the Stokes-Einstein equation [20] (Eq. (5)), the diffusion coefficient is a function of temperature, ionic radius, and viscosity.

$$J_A = -D\frac{dC_A}{dx} \tag{4}$$

$$D = \frac{k_B T}{6\pi r\eta} \tag{5}$$

where J_A is the diffusion flux of component A, D refers to the diffusion coefficient, C_A is the concentration of component A, k_B is the Boltzman constant, η is the viscosity, and r represents the ionic radius.

Results listed in Table 5 show that the viscosity values calculated by FactSage 6.2 for samples S2 and S3 with the addition of FeO are lower than the viscosity of sample S1. The results also demonstrate a more pronounced decrease in viscosity at a higher temperature. For instance, the viscosity of sample S1 (without FeO) at 1600°C is 0.141 Pa·s, and that for sample S3 (with 6wt% FeO) is 0.054 Pa·s, about one third of that of sample S1.

Table 5. Viscosity (η) calculated by FactSage 6.2 for slag melts at different temperatures

Sample	FeO content / wt%	η / (Pa·s)		
		1600°C	1450°C	1300°C
S1	0	0.141	0.652	1.350
S2	3	0.098	0.596	1.273
S3	6	0.054	0.539	1.196

Based on the Stokes-Einstein equation (Eq. (5)), with a decrease in viscosity resulting from FeO addition, the diffusion coefficient D is enhanced [21]. The FeO addition also changes slag composition that leads possibly to an increase in concentration gradient for spinel forming oxides. FeO may then be considered effective for increasing both the diffusion coefficient and the concentration gradient, which, according to the Fick's first law (Eq. (4)), may largely increase the diffusion flux or rate for formation and growth of spinel minerals in the slag system containing FeO.

Besides the decrease of viscosity, for sample S3 (with 6wt% FeO), the precipitation temperatures of melilite and merwinite and the solidus temperature reduce by 80, 30, and 150°C, respectively, compared with sample S1 (without FeO), referring to temperature data calculated by FactSage 6.2 in Table 6. Based on the temperature decreases, another FeO effect may be deduced regarding the Cr distribution.

Table 6. Phase precipitation temperatures (T_P) and solidus temperature (T_S) calculated by FactSage 6.2

Sample	FeO Content / wt%	T_P / °C		T_S / °C
		Melilite	Merwinite	
S1	0	1420	1430	1400
S2	3	1380	1411	1330
S3	6	1340	1400	1250

The decreases in precipitation temperature and solidus temperature due to FeO addition can contribute to not only an increase of Cr content in the spinel phase but also a decrease of Cr content in the soluble minerals. If the temperature for these minerals to form or precipitate and the solidus temperature can be decreased to lower values, there may be more time or a larger chance for some of the Cr remaining in the melt to enter the existing, solid spinel minerals by diffusion at a higher temperature. As a result, since melilite and merwinite start to precipitate at a lower temperature, there may be a very little or no Cr left, consequently making these soluble minerals free of Cr.

For suppressing Cr leaching, it is necessary to minimize a Cr distribution in the slag minerals, which are easily soluble [11]. It may be difficult to avoid the formation of the minerals, such as melilite and merwinite, in the EAF slag [9-10], but the addition of FeO reduces the content of Cr in these minerals. Therefore, FeO could be considered as an effective additive for a positive Cr distribution in the slag, by which Cr is bonded largely in stable spinel minerals and the dissolution of Cr-free silicates does not cause Cr leaching.

The discussion of the present results may imply positive effects of FeO on the prevention of Cr leaching from the EAF slag within the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system. However, any contact of FeO with the stainless steel melt must be avoided due to the risk of Cr oxidation by the Fe oxides at high temperature [22].

5. Conclusions

The influences of FeO addition on the formation of spinel phases and Cr distribution in synthetic slag samples of the CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 system were investigated using XRD, SEM-EDS, and thermodynamic software FactSage 6.2. The following results can be obtained.

(1) The amount and size of spinel minerals increase with an increase in FeO content in the samples. The content of Cr in the spinel phases are approximately 23at% in the samples containing 0wt%-3wt% FeO. When the FeO content increases to 6wt%, the content of Cr in the spinel phases increases to a higher value (27.21at%).

(2) Cr exists in merwinite and C_2S with the contents of 0.09at% and 0.10at%, respectively, in the sample without FeO. The silicates become Cr free with the addition of 3wt%-6wt% FeO in the samples.

(3) The viscosity becomes lower for the samples with an addition of FeO. At 1600°C, the viscosity for the sample without FeO is 0.141 Pa·s and that for the sample with 6wt% FeO is 0.054 Pa·s. The FeO added largely increases the diffusion flux or rate for formation and growth of spinel minerals in the slag samples due to a reduction of viscosity.

(4) For the sample with 6wt% FeO, the precipitation temperatures of melilite and merwinite and the solidus temperature decrease by 80, 30, and 150°C, respectively, compared with the sample without FeO. By decreasing the temperature, the FeO addition can contribute to not only an increase of Cr content in the spinel phase but also a decrease of Cr content in the soluble minerals. This may effectively prevent Cr leaching from the EAF slag.

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