Refining of 18%Cr-8%Ni Steel with Ca-CaF₂ Solution*

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Synopsis

Ca-CaF₂ solution was used as an electro-flux in electroslag remelting processing to study the refining power of calcium metal dissolved in CaF₂ melt for various elements contained in 18%Cr-8%Ni steel. The experimental results showed that this metal solution removes all elements of group V-b in the Periodic Table (N, P, As, Sb and Bi) as well as those of VI-b group (O, S, Se and Te) to low levels. Sn and Pb were also found to be reduced by Ca-CaF₂ solution. No substantial changes in the concentrations of metals (Cu, Zn, Al, Ni, Cr and Mn) and semi-metallic elements (C and Si) were observed. This effectiveness of Ca metal solution as a refining reagent is expected to give a new way to the production of steel with extremely low levels of impurities that is not obtainable by conventional refining methods.

I. Introduction

The purpose of the present work is to show an experimental evidence that calcium metal dissolved in CaF₂ melt has an excellent power for eliminating various impurities, such as N, P, S and Pb, from liquid 18%Cr-8%Ni-Fe steel in Ar atmosphere of 1 atm pressure. Ca metal is well known to remove simultaneously O and S from liquid steel to extremely low levels. The reaction products are calcium oxide and sulfide. Compiled data¹⁾ for the heat of formation at 298°K show that calcium nitride, phosphide and arsenide as well as calcium oxide and sulfide are stable compounds. Thus, N, P and As dissolved in liquid steel are expected to be removed with Ca metal.

However, little observation of simultaneous removal of N, P and As by the use of Ca metal and its alloys have been reported. One of the causes is considered to be the ineffective contact between Ca metal and liquid steel owing to the low boiling point (1 497°C), the limited solubility in liquid iron (about 0.032% at 1 600°C), and the low density of Ca metal (1.5 g/cm³). If liquid Ca metal is kept in good contact with liquid steel even above the boiling point under non-oxidizing atmospheres, the efficiency of reaction would be considerably improved, and therefore the expected refining power of Ca metal would be realized. A possible method to obtain liquid Ca metal is the use of CaF₂ melt.

Ca metal is completely miscible with CaF₂ melt at temperatures higher than the melting point of CaF₂ (1 360°C).²⁾ The vapour pressure of Ca metal for Ca-CaF₂ solution can be depressed by decreasing Ca metal concentration. Accordingly, a dilute solution of Ca metal may be kept in contact with liquid steel for a long time with no explosive loss of Ca metal.

We, thus, undertook an experimental study of the refining of 18%Cr-8%Ni-Fe alloy with Ca-CaF₂ solution to extend the knowledge for the usefulness of Ca metal in steel-making processes. This metal solution, however, is remarkably reactive with crucible materials such as magnesia and alumina. Hence, the experiment of electroslag remelting (ESR) was made in which a mixture of Ca metal and CaF₂ powder was used as an electro-flux.

II. Experimental

1. Remelting

An ESR equipment used consisted of a remelting furnace, an electrical power source (50 kVA, 50 Hz), a device for feeding an electrode, a power controller, a rotary pump, and Ar gas supplier. These parts were the same as those reported in the previous work.³⁾ The lower part of the remelting furnace was a water-cooled mold of 70 mm in diameter and 400 mm in length. The upper part was a box covering the mold, which was equipped with a feeder of electro-flux and an electrode-holder. An electrode of 40 mm in diameter and about 1 000 mm in length was vertically clamped inside the box with the electrode-holder which was movable by a motor set outside the furnace. The whole system of the remelting furnace was made air-tight so that an atmosphere within the furnace could be pumped off to 0.1 Torr.

The flux used was composed of mixture of granular Ca metal of more than 99% purity and CaF₂ powder of chemical reagent purity (less than 0.01%P). CaF₂ powder was heated at 900°C for 5 hr and stored in a desiccator until it was mixed with Ca metal just before the experiment. Four remelting experiments were made:

Heat 1: The 18%Cr-8%Ni-Fe alloy containing various elements was treated with Ca-CaF₂ solution to study the refining power of Ca metal.

Heat 2: The same alloy was treated with CaF₂ melt alone to clarify the effect of CaF₂ on the elements studied in Heat 1.

Heats 3 and 4: Commercial steel of SUS 304 grade (18-8 stainless steel) was treated with Ca-CaF₂ solution to examine the case of P and N contents higher than those in the case of Heat 1.

Experimental conditions were summarized in Table 1. The detail of the remelting procedure was as fol-

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1. Heat 1

The 18%Cr-8%Ni-Fe alloy examined was made by vacuum induction melting. Several elements concerned were added during the melting of the alloy: Mn, Cu, C, Si, Sn, Pb, As, Sb, Bi, Se and Te. The concentrations of these elements as well as N, P, O and S are shown in Table 2. Ca-CaF₂ mixture of 350 g was charged on the bottom of the mold. Then, air within the furnace was pumped off and replaced by Ar to avoid the oxidations of Ca metal and the electrode. Ar gas of commercial high-purity (nomi-

nal purity 99.999%) was used without further purification. The flow rate of Ar stream was 5 l/min. After the initially charged flux had been completely melted down by arc-heating, the electrode tip was immersed into Ca-CaF₂ solution. The electric potential difference between the electrode holder and the mold bottom was kept at a given value by the adjustment of the depth of the electrode tip in the solution during the remelting procedure. The electrode tip was melted and the ingot grew layer by layer in the mold. The remelting rate of the electrode was held at a given value throughout the run by manual control of electric current. During the remelting the mixture of Ca metal and CaF₂ powder was continuously fed to the mold in a manner shown in Table 1. When the ingot grew to some length (240 mm in this case), the power was turned off and immediately the electrode tip was detached from the Ca-CaF₂ solution.

2. Heat 2

The same alloy used in Heat 1 was remelted by using CaF₂ powder alone as an electro-flux. The procedure and the remelting rate were similar to those in Heat 1. However, no continuous feeding of CaF₂ powder was made.

3. Heat 3

The commercial steel of SUS 304 grade was treated with Ca-CaF₂ solution. The contents of N, P, As, S and O in the steel were shown in Table 3. The experimental conditions and procedure were almost similar to those conducted in Heat 1, as shown in Table 1.

4. Heat 4

Ca-CaF₂ treatment was made for the commercial

Table 1. Experimental conditions

		Heat 1	Heat 2	Heat 3	Heat 4
Voltage (V)		12	20	11.5	12
Current† (A)		2 450	1 000	2 450	2 250
Remelting rate (g/min)		163	158	173	128
Ingot height (mm)		240	229	197	196
Flux					
Initially charged					
Ca (g)		14	0	14	24
CaF ₂ (g)		336	400	336	376
Continuously fed					
Ca (g/min)		1.0*		1.67**	
		0.3		0.3	
CaF ₂ (g/min)		5.0*		8.3**	
		5.0		5.0	

† Average

* For 10 min from the start of remelting

** For 6 min from the start of remelting

Table 2. Results of Heats 1 and 2

Element	Position* (mm)	Transition element			I-b	II-b	III-b	IV-b group			
		Cr (%)	Mn (%)	Ni (%)	Cu (ppm)	Zn (ppm)	Al (ppm)	C (%)	Si (%)	Sn (ppm)	Pb (ppm)
Electrode		17.03	1.30	7.80	770	84	20	0.051	0.39	220	152
Heat 1	30	—	—	—	710	80	70	—	—	73	35
	120	—	—	—	710	77	<20	—	—	55	35
	210	17.08	1.30	7.74	710	78	<20	0.053	0.43	78	35
Heat 2	30	—	—	—	730	79	40	—	—	250	143
	120	—	—	—	770	80	<20	—	—	250	146
	210	17.08	1.25	7.78	710	73	<20	0.054	0.42	250	143
Element	Position* (mm)	V-b group					VI-b group				II-a
		N (ppm)	P (ppm)	As (ppm)	Sb (ppm)	Bi (ppm)	O (ppm)	S (ppm)	Se (ppm)	Te (ppm)	Ca (ppm)
Electrode		76	30	52	20	160	211	130	110	86	25
Heat 1	30	26	10	<20	<5	3	36	<50	40	12	80
	120	33	5	<20	<5	4	40	<50	40	11	110
	210	56	10	<20	<5	4	34	<50	<30	10	150
Heat 2	30	81	45	52	5	81	87	90	30	75	10
	120	80	35	52	5	78	83	130	80	74	10
	210	77	35	56	5	90	76	130	90	78	10

* Distance measured from the ingot bottom

steel. The contents of impurities were shown in Table 3. Initially charged mixture of Ca metal and CaF_2 powder was by 50 g more than that in Heat 3. How-

Table 3. Results of Heats 3 and 4

	Position* (mm)	Element (ppm)					
		N	P	As	O	S	Ca
Heat 3	Electrode	356	240	80	75	80	30
	20	87	20	<20	—	14	—
	50	166	40	—	—	—	—
	80	149	30	<20	—	15	—
	110	134	30	—	—	—	—
	140	173	45	<20	—	19	—
	180	234	70	20	—	19	—
Heat 4	Electrode	361	240	80	60	90	10
	20	29	<10	<20	7	17	361
	50	80	15	—	—	—	—
	80	148	25	<20	—	14	100
	110	218	45	—	—	—	—
	140	299	90	—	—	20	116
	180	346	125	<20	10	14	110

* Distance measured from the ingot bottom

ever, continuous feeding was not performed.

The ingot thus made and the flux used were cooled in the furnace after the power was turned off. The ingot was vertically sectioned. No micro-pore and hair-crack on the cross section were observed. The size of non-metallic inclusions was less than $10\text{ }\mu\text{m}$. Several samples for chemical analysis were taken along the vertical central axis of the ingot to determine the axial variation of the composition of the ingot. The results were shown in Table 2 for Heats 1 and 2 and Table 3 for Heats 3 and 4.

2. Gas Evolution from the Used Flux

A small portion of the Ca-CaF_2 flux remaining at the top of the ingot after the experiment was crushed and then treated with water at room temperature. Gaseous mixture with ammoniac and garlicky smell was found to be readily evolved. The gas was collected and then dried with potassium hydroxide. The compounds included in the gas were examined with infra-red spectroscopic method. However, spectra of NH_3 was too intense in the range from 800 to $1\text{ }300\text{ cm}^{-1}$ to clarify other ones to be assigned, as shown in Fig. 1(a). Hence, NH_3 was extracted with a large amount of water. The residual gas was dried and then examined again. The spectra obtained are

(a) Spectra of gaseous mixture produced by treating the used flux with water
(b) Spectra of redidual gas after NH_3 is removed from the gaseous mixture indicated in Fig. 1(a).

Fig. 1. Result of infra-red spectroscopic examination

shown in Fig. 1(b), which reveal that the gas included C_2H_2 , PH_3 , and AsH_3 . In the case of the CaF_2 flux used in Heat 2, gas evolution was not observed by the treatment with water.

III. Results and Discussion

1. V-b Group Element

Table 2 shows the results of Heats 1 and 2 to compare the refining power of $Ca-CaF_2$ solution with that of CaF_2 melt itself for various elements in the alloy studied. Insignificant changes in N, P, and As contents were observed in the case of CaF_2 melt (Heat 2). However, $Ca-CaF_2$ solution (Heat 1) does efficiently remove these elements during the remelting process. N content at the middle position of the ingot was reduced by about 60% of the initial one, P by about 67% and As by more than 60%. Similar reduction of these elements by $Ca-CaF_2$ solution are found in Table 3 which shows the experimental results of Heats 3 and 4. On the other hand, Sb and Bi were removed by both $Ca-CaF_2$ solution and CaF_2 melt. However, the degree of Bi removal by $Ca-CaF_2$ solution (97%) was far higher than that by CaF_2 melt (50%). Conclusively, efficient and simultaneous removal of Vb group elements in the Periodical Table (N, P, As, Sb and Bi) observed in Heat 1 may be due to the presence of Ca dissolved in CaF_2 melt.

As seen in Table 3, axial variations of N and P concentrations were observed for Heat 4 the remelting of which was made without continuous feeding of $Ca-CaF_2$ mixture. At the earlier stage of the remelting (corresponding to the bottom side of the ingot), the degree of N removal was highest. As the ingot grew progressively, N content remaining in the ingot increased gradually and approached that in the electrode. Similar tendency was observed in P behaviour. During this course, the concentrations of N and P in $Ca-CaF_2$ solution are expected to increase progressively, because the removed elements would be accumulated in the Ca metal solution. Accordingly, the efficiencies of N and P removals might be determined by the contents of N and P dissolved in $Ca-CaF_2$ solution. For Heat 3, the concentration variations of N and P were found to be relatively small when compared with those for Heat 4. This uniformity would result from the continuous feeding of $Ca-CaF_2$ mixture that keeps the concentrations of N and P in $Ca-CaF_2$ solution at a relatively low level throughout the run.

2. VI-b Group Element

$Ca-CaF_2$ solution removed O, S, Se and Te (VI-b group) to extremely low levels, as shown in Table 2. On the other hand, CaF_2 melt reduced oxygen by about 50% of the content in the electrode remelted, whereas slight decreases in S, Se and Te contents were observed. Ca metal in CaF_2 melt, therefore, is

regarded as a powerful reagent for eliminating Se and Te as well as O and S. Table 3 shows that sulfur concentration (14~20 ppm) is uniform along the ingot axis, irrespective of the amount of Ca metal charged.

3. IV-b Group Element

The result for IV-b group elements (excluding Ge) are shown in Table 2. Sn and Pb were evidently removed by Ca metal. C and Si contents were found to be unchanged within analytical errors ($\pm 0.003\%$ C, $\pm 0.03\%$ Si).

4. Other Elements

No significant changes in the concentrations of Cr, Mn and Ni (VI-a, VII-a and VIII group) were found, as shown in Table 2. Similarly, Cu (I-b group) and Zn (II-b group) were apparently not removed. Al content (III-b group) in the bottom of the ingot treated with $Ca-CaF_2$ solution (Heat 1) was higher than that in the electrode used. As compared with Al content in the ingot treated by CaF_2 melt (Heat 2), the increase in the Al content appears to be due to the reduction of Al_2O_3 present in CaF_2 powder and a small amount of Al contained in Ca metal used. The behaviour of Al in the middle and top of the ingot, however, is inconclusive owing to low concentration of Al beyond the chemical analysis limit. It should be noted that the liquid alloy absorbs Ca metal during the remelting process, as shown in Tables 2 and 3. The level of Ca metal in the ingot is 0.01 to 0.015%.

5. Reaction Schemes of N and P Removals

The gaseous mixture formed by treating the used flux with water was found to include NH_3 , PH_3 , AsH_3 and C_2H_2 . Therefore, N, P, As and C may be fixed in the used flux as Ca_3N_2 , Ca_3P_2 , Ca_3As_2 and CaC_2 at room temperature, because these compounds are known to produce readily NH_3 , PH_3 , AsH_3 and C_2H_2 with water or water vapour, respectively.⁴⁾ The spectroscopic results for N, P and As are compatible with those of chemical analysis: N, P and As dissolved in the alloy are transferred to $Ca-CaF_2$ solution.* However, the compounds, Ca_3N_2 , Ca_3P_2 and Ca_3As_2 , appear to precipitate on cooling in the ESR furnace. During the remelting, the transferred N and P would be assumed to be dissolved in $Ca-CaF_2$ solution in atomic or ionic form under the present experimental conditions. A possible scheme of the dephosphorization or denitrification reaction occurring at $Ca-CaF_2$ solution/liquid alloy interface may be written:

where, []: a constituent dissolved in the liquid alloy

* On the contrary, chemical analysis of C in the electrode and the ingot shows that C removal by $Ca-CaF_2$ solution is negligibly small. A reason for the discrepancy may be the difference in sensitivity of chemical and spectroscopic analysis to C.

(): a constituent dissolved in Ca-CaF₂ solution.

Unfortunately, the problem, which of the reactions (1) and (2) is real, is left unsolved. However, it should be noted that if the reaction (2) is actual, the existence of CaF₂ is indispensable as a solvent not only for Ca metal but also for the reaction product.

The proposed mechanism of dephosphorization reaction is essentially distinct from that ever reported. In conventional steel-making processes, phosphorus dissolved in liquid steel is oxidized to P₂O₅ and then fixed by lime in basic slags as calcium phosphate.⁵⁾ Dunn, Jr.⁶⁾ studied the dephosphorization reaction of liquid steel with Ca metal under oxidizing conditions. The reaction steps proposed by him is similar to those occurring in conventional processes except that Ca metal is first converted to very reactive lime. As a whole, the established knowledge indicates that the dephosphorization should be achieved under oxidizing conditions by using lime. However, the present result reveals that P can be removed under a reducing condition. In addition, efficient removal of P can be performed even for high-Cr steel which is not dephosphorized by the conventional method because of preferential oxidation of Cr to P.

IV. Conclusion

The experimental work evidences that all elements belonging to V-b and VI-b groups, Sn and Pb in liquid 18%Cr-8%Ni-Fe alloy can be reduced to extremely low levels by Ca metal dissolved in CaF₂ melt. These removed elements are in general regarded as hurtful ones for steel properties. On the other hand, the contents of important and specified elements such as Cr, Mn, Ni, Si and C remain sub-

stantially unchanged by treating the alloy with Ca-CaF₂ solution. Therefore, this metal solution is a suitable and promising reagent for the production of highly clean steels not obtainable by conventional refining methods.

Generally, alkaline-earth metals are known to have strong affinities for N and P. Furthermore, these metals are soluble in their molten halides salts to some extent. Hence, the alkaline-earth metals/their halides solutions would be expected to exhibit similar refining power for liquid iron-alloys to that obtained in the present work. We would like to name the unique refining-method with these metal solutions "MSR" (Metal bearing Solution Refining) in distinct from ordinary ESR.

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