

EFFECT OF CaO-MgO-RE-CaF₂ SYNTHETIC POWDER ON DESULPHURIZATION OF 12Cr20Ni38Mo5 ALLOY

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ABSTRACT

The desulphurization and the control of sulphides by treatment of CaO-MgO-RE-CaF₂ synthetic powder in liquid alloy is used with success in ladle for many alloy products. The results indicated that the synthetic powder ladle treatment is possible to reduce sulphur from 0.035% to 0.009% S by employing agents amounting 14kg/t liquid metal.

The results also show that treated CaO-MgO-RE-CaF₂ powder positively affect the globular type I morphology, small-smooth size and distribution of the remaining inclusions in the 12Cr20Ni38Mo5 alloy. The powder CaO-MgO-RE with increasing MgO shows better efficiency than powder with increasing CaO. Some calculated values have been compared with those reported in literature.

KEYWORDS: synthetic powder, alloy, desulphurization

INTRODUCTION

The problem of ladle refining of steel and alloy is overcome by a very promising method of treating liquid alloy^[1-12] by CaO-MgO-RE-CaF₂ synthetic powder. The effective deoxidation, desulphurization and elimination of non-metallic inclusions in steels and alloys are very important to improve product quality^[13-22]. of late, considerable efforts are being made to improve steel and alloy quality through inclusion shape and composition control^[23-30]. The works on improving cleanliness of steel and alloy by removal of oxide and sulphide cluster and/or through modification of inclusions morphology have been reported in literature^[31-48].

The present work has been done as a co-operative research project of Vietnam KC-05^[47]. This work describes the effect of synthetic powders containing CaO-MgO-RE (with increased CaO or MgO percentage. When CaO is in excess, it is called CaO-RE powder and when MgO is in excess; it is called MgO-RE powder on desulphurization, formation and distribution of sulphide inclusions and improving cleanliness of 12Cr20Ni38Mo5 alloy.

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EXPERIMENTAL METHOD

Experiments were carried out in the lab scale in magnesite open bath induction furnace of capacity 50kg and electric power 130kW. The 12Cr20Ni38Mo5 alloy of the composition given in table 1 was charged into the furnace bath.

Table 1. Analysis of 12Cr20Ni38Mo5 alloy (wt%)

C	Si	Mn	P	S	Al	Cu	Cr	Ni	Mo	Ti
0.12	1.28	1.35	0.040	0.035	0.03	2.80	18.20	38.00	5.40	0.004

The 12Cr20Ni38Mo5 alloy was melted in furnace to all melting and temperature of the melted bath varied from 1600°C to 1650°C then melt was first deoxidized by FeMn (2 kg/t), FeSi (2.5 kg/t), and aluminum wire (0.3 kg/t). The molten bath was stabilised for about 10 minutes and the temperature adjusted to 1660 - 1680°C. In the meantime the heated ladle was prepared heated rare earth metals - RE (2 kg/t mischmetal shows table 2), the synthetic powder (>6 kg/t) (shows table 3) and fluorspar (2 kg/t).

Table 2. Composition mischmetal for adding with synthetic powder (wt%)

La	Ce	Nd	Pr	Fe	Mg	Al	Si	other
50	40	1.7	4.4	2.7	0.4	0.03	-	-

Table 3. Composition rate of CaO-MgO-RE-Al₂O₃ synthetic powder

No	1	2	3	4	5	6	7	8	9	10	11	12	13
CaO	6.0	6.5	7.0	7.5	8.0	8.5	9.0	6.0	6.0	6.0	6.0	6.0	6.0
MgO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.5	2.0	2.5	3.0	3.5	4.0

Ladle addition of the synthetic powder was done in two instalments. At first 2/3rd of the total amount was added to melt. After pouring 1/2 the amount of ladle into the mould, the remaining 1/3rd fraction of powder was added. The melt was stirred by a graphite plunger. Samples of both the slag and the alloy were taken before and after addition of powder for comparison. Complete chemical analysis was done. Scanning electron microprobe analysis by JEOL - 35CF, LINK 860/II (EDX) was done on selected samples for the determination of inclusions.

RESULTS AND DISCUSSIONS

The results of chemical analysis of alloys and slags are shown in table 4 and 5.

Table 4. Chemical analysis of alloy samples (wt%)

C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	Ce	Ti
0.12	1.26	1.52	0.03	0.009	18.10	37.20	4.72	1.78	0.02	0.018	0.009
0.20	2.10	2.00	0.035	0.030	21.30	40.80	6.00	2.02	0.03	0.020	0.012

Desulphurization

The aim of the treatment of liquid alloy by synthetic powder was mainly for desulphurization, or control of the sulphur content and shape control of sulphide inclusions. Effect on desulphurization of liquid alloy is expressed in literature of Richardson^[49], according to which desulphurization can best be achieved by using RE (Ce,La...) and alkaline earth metals (Ca,Mg...).

Typical reactions are given below^[50-55]:

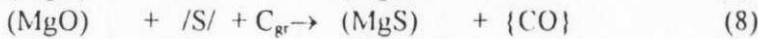
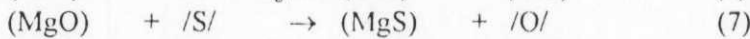
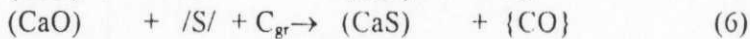
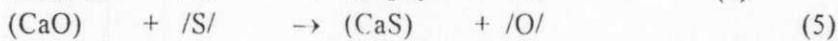
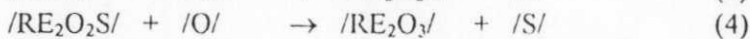


RE were unable to react with carbon at temperature 1873°K by equation (2).

Table 5. Chemical analysis of slag samples and sulphur in alloy (wt%)

sample No	CaO	MgO	SiO ₂	Al ₂ O ₃	CaF ₂	FeO _t	S
1	31.82	3.40	15.00	47.69	0.09	2.00	0.035
2	33.60	3.12	15.51	45.79	0.08	1.90	0.027
3	34.05	3.21	15.05	45.78	0.05	1.86	0.018
4	35.18	3.00	15.03	44.84	0.05	1.90	0.016
5	35.89	3.10	14.90	45.17	0.04	1.80	0.015
6	36.45	3.29	14.98	43.32	0.04	1.92	0.014
7	36.82	3.41	15.12	42.75	0.10	1.80	0.013
8	30.90	3.74	14.57	49.09	0.10	1.60	0.025
9	31.00	3.91	14.13	49.15	0.09	1.72	0.018
10	31.50	4.01	13.95	48.77	0.07	1.70	0.013
11	31.00	4.51	13.91	48.73	0.05	1.80	0.011
12	31.90	6.65	15.15	45.44	0.02	1.74	0.010
13	31.85	10.41	16.65	39.47	0.02	1.60	0.009

The successive reactions are:



The slag basicity for desulphurization can be described as follows [15]:

$$B = \frac{(CaO + 1.4MgO)}{SiO_2} \quad (10)$$

The analysed and calculated slag basicity effecting desulphurization is shown in figure. 1.

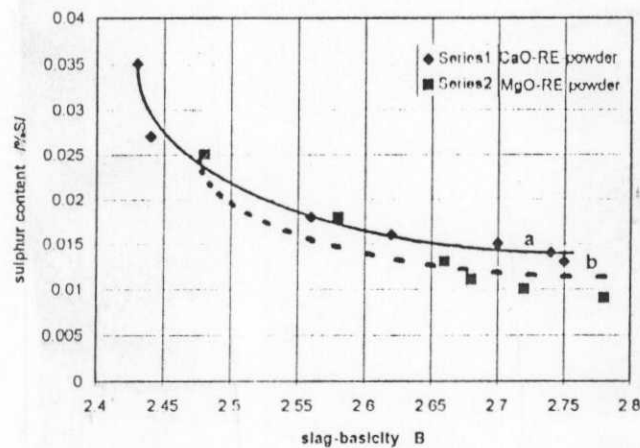


Figure 1. The relationship between slag-basicty during use of synthetic powders and sulphur content in 12Cr20Ni38Mo5 alloy

Figure 1 shows desulphurization level of 12Cr20Ni38Mo5 alloy due to addition of powder. The influence of CaO-RE powder via slag-basicty is clearly visible. The slag-basicty of 2 to 2.7 reduced the sulphur content of alloy rapidly, but when it was higher than 2.7 the

desulphurization of alloy was subdued and may not be varied (figure 1a). The maximum residual sulphur content in alloy was 0.013%S. The figure 1b shows that MgO-RE powder reduced sulphur content of the alloy to 0.009%S (minimum) thus its desulphurization ability was better than CaO-RE powder. The desulphurization of MgO-RE powder has occurred unabated throughout the experiments compared to CaO-RE powder. Owing to the use of RE as shown by reactions from (1) to (4) therefore the reaction (8) can be attained intense. The residual sulphur content in alloy was the lowest. Thus comparable order of desulphurization level between MgO-RE powder and CaO-RE powder was obtained. The results has shown that desulphurization efficiency of MgO-RE powder is higher than that of CaO-RE powder. The same efficacy of desulphurization was obtained at much lower amount of MgO-RE than that of CaO-RE. The reduction of sulphur by MgO-RE is from 0.035 to 0.009%S.

In spite of the fact that rare earth metals do not react with carbon, but ones transformed into deoxidation zone desulphurization reactions (6) and (8) ^[57] occur.

The desulphurization efficiency as expressed above is explicit. It is customary now to correlate the percentage drop in sulphur with weight of the reagent. Now the effect on desulphurization efficiency the modification of inclusion in alloy will be discussed.

Inclusions and cleanliness of alloy

Normally, inclusions in the alloy produced by straight aluminium addition are Al_2O_3 - clusters and manganese sulphides which is shown in figure 2.



4665 VV X500

A $\rightarrow Al_2O_3$

B $\rightarrow Al_2O_3SiO_2$

Figure 2. Typical inclusions in cast alloy made by straight Al-addition

Before treatment with synthetic powder, the samples taken from the furnace, contained mainly large randomly distributed angular type III inclusions. After treatment, both CaO-RE and MgO-RE synthetic powders had changed Al_2O_3 clusters and manganese inclusions into low melting calcium and magnesium aluminates and small-smooth RE-Mn complex inclusions (figure 3). The RE reacts with the dissolved sulphur following reaction (1) and by reductants CaO and MgO together agitating carbon plunger following reaction (3) and precipitates RE-oxysulphide (figure 5). The primary inclusions act as nucleus for the precipitation of RE-oxysulphide with the result that the RE_2O_2S phase is confined to the outer surface and commonly very small-smooth globular. The secondary inclusions precipitated during the solidification process from dissolved Ca, Mg with remaining RE the alloy. The covering primary RE-oxysulphide is shown in figure 4.

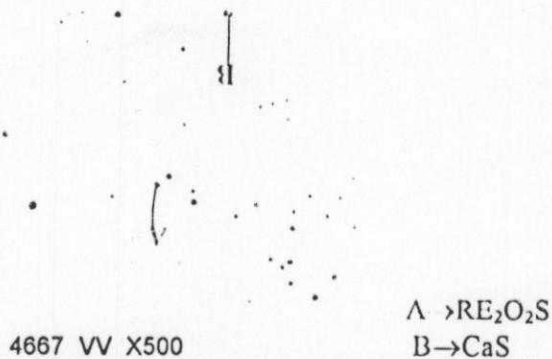


Figure 3. Typical inclusions by using 8.5CaO-RE powder (sample No.6)

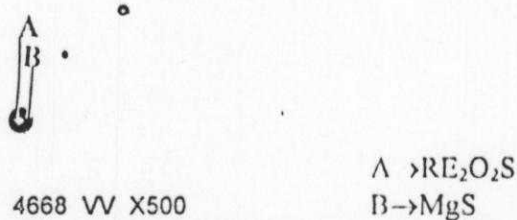


Figure 4. Typical inclusions by using 3.5MgO-RE powder (sample No.12)

For comparison, sulphides appearing in alloy by treating with CaO-RE and MgO-RE powder are shown in figure 5. They are in accordance with desulphurization principle.

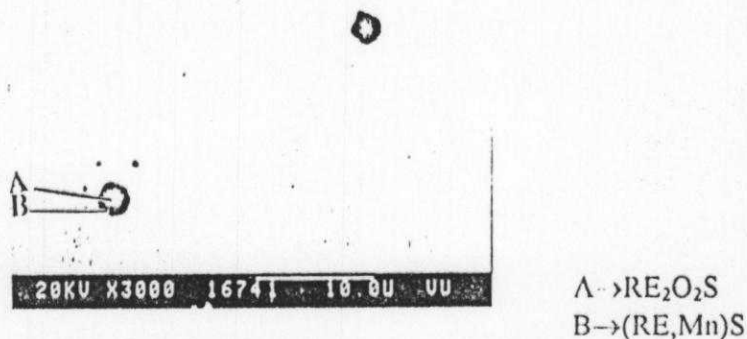


Figure 5. Typical oxide-sulphide inclusions by using 7.5CaO-RE powder (sample No. 4)

The sulphides in alloy of figure 5 treated with the 7.5CaO-RE based powder were of duplex type containing CaS and RES. In fact difference of the influence of synthetic powder on both inclusion compositions and morphologies were comparable. It can be seen from figures 4 and figure 5 that the number of inclusions was more with 8.5CaO-RE powder than with 3.5MgO-RE powder.

Figure 6 also shows composition of inclusion in alloy, with treatment 4.MgO-RE powder and may be explained for inclusion structure with reference to figure 4.

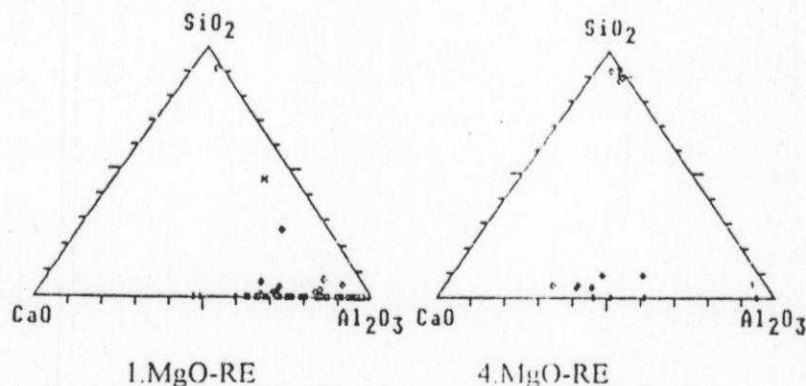


Figure 6. Transformation of Al_2O_3 - cluster in alloy by 4. MgO-RE synthetic powder (sample No 13)

The RE addition in such an alloy did not appreciably reduce the total inclusion level. Rare earth metal treatment usually results in several oxides (La_2O_3 , Ce_2O_3), oxysulphides (La_2O_2S , Ce_2O_2S) and sulphides (LaS , CeS). Their inclusions are relatively heavier and therefore probably remain in the bottom of the the melt and may contain relatively higher amount of inclusions in the alloy. Therefore use of synthetic powder containing combination CaO-RE and MgO-RE for desulphurization and inclusion morphology are beneficial.

CONCLUSIONS

Results of experiments concluded to study the effect of treatment synthetic powders CaO-MgO-RE- Al_2O_3 on desulphurization and inclusions in 12Cr20Ni38Mo5 alloy using 50 kg induction furnace are presented below:

1. The rare earth metals reduced sulphur content in the 12Cr20Ni38Mo5 alloy owing to the reductants CaO and MgO together of graphitic carbon.
2. The desulphurization could be achieved by MgO-RE powder better than CaO-RE powder and the maximum sulphur distribution coefficient L_s of 75.11 in slag is attained, whilst the lowest sulphur content of 0.009% S obtained by MgO-RE powder.

The effective on desulphurization was obtained at much lower amount of MgO-RE than that of CaO-RE.

4. The ladle treatment by CaO-RE and MgO-RE powder modified angular type II of aluminium cluster into globular type I of small-smooth oxysulphides morphology in the alloy. In this regard also the MgO-RE powder shows better results than CaO-RE powder.

5. The synthetic powder ladle treatment improved cleanliness of alloy explicitly.

6. Although enough development has been observed in this R & D work with MgO-RE powder, there is further scope of development for which continued research work is envisaged.

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REFERENCES

1. W. Kuntscher, Peter R. Ebeling F. and Schulz H.J. Nueu Hutte 1962, 7 (1), p. 41
2. W.G. Wilson Electr. Furnace conf. 1977, vol. 44,
3. C. To Duy Proc. 1th Inter. seminar on materials science, Hanoi 1.1.1997 p.121
4. R. Peters, F.Ebeling, H.J.Schulz G. Hofferf and O.H. Kumpel Nueu Hutte,1963, 8 (1), p.43
5. J.J.Bosley and J.J.Quavec. Inter. Iron & steel congress, Chicago 16-20 April,1978
6. H. P. Hoastert W. Klapdar and H. Rellermeyer,Inter.magnesium conf.Oslo 23-26 June1979,p.34
7. W. Moore Inter. magnesium conf. Oslo 23-26 June 1979,p.46
8. Y. Katura and D. Oelschlager Stahl und Eisen 1980, 100(1), p.20
9. S.W. Gilby Ironmaking proc. AIME 1973,32. p.133
10. P.J. Koros R.G. Petruska and R.G. Kerlin Steelmaking proc. AIME 1977,60, p.386
11. T. Lehner, and P.Ritakallio, Inter. magnesium conf. Oslo 23-26 June 1979,p.55
12. E.J.Dunn, Proc. conf. 34th electr. furnace St Louis 7-10 Dec. 1976
13. O. Kubaschewski Evans E.L. and C.B. Alcock Metallurgical Thermochemistry 4th Ed. Pergamon press 1967 p.333
14. C. To Duy Heavy Industry Reviews 1992, 3, p. 31
15. E.T. Turkdogan BOF steelmaking AIME NewYork 1975, 2, p.153
16. C.W. Sherman and J. Chipman Trans. AIME 1952,194,p.597
17. C.To Duy, Industrial Reviews 1994 , 6, p. 17
18. C. To Duy and O. Volny, Science and Technology 1995 33 (3), p.39
19. R.D. Pehlke,Proc. steelmaking AIME 1978, 61, p.511
20. G. William Wilson and R.G. Wells, Metal progress Dec. 1973 p.75
21. R.G. Blossey and P.J. Koros P.J. 61th AIME NOH and BOS conf. Chicago 1978 p. 515
22. P. Ritakallio, Proc. inter. conf. on Injection metallurgy Lulea- Sweden 9-10 June 1977
23. H. J.Langhammer H.Abratis and P. Patel, Proc.inter.conf. on Injection metallurgy,Lulea-Sweden9-10 June 1977
24. V.I. Machikin and E.N. Skladovskii, Stal 1977, 9(4), p.1
25. H. Gruner, F.Bardenheuer and H. Schulte, Proc. inter. conf. on Injection metallurgy Lulea-Sweden 9-10 June 1977
26. N.A. Gurov Metallurg 1976, 19, p. 254
27. S. Yamaguchi, Ironmaking and steelmaking 1977, 4(5) p.276
28. L. Holappa and Tahtinen, Proc.inter.conf.on Injection metallurgy Lulea-Sweden 9-10 June 1977
29. S. K. Saxema. and Engh T.A. Scan. J. of Metallurgy 1976, 5, p. 105
30. K. Tahtinen, Vainola R. and Sandholm R. Proc.inter.conf.on Injection metallurgy Lulea-Sweden 9-10 June 1977
31. C. To Duy , J. Science and Technology 1996 , 34 (3) p. 42
32. K. Taguchi, T. Oyano, H. Sato, S. Uchida, T. Kawawa and R. Imai Tetsu To Hagane 1977, 64(4), p.160
33. H. Kosmider Stahl und Eisen 1979, 99, p.1215
34. T. Emi and Y. Habu, 61th AIME NOH and BOS conf. Chicago 1978 p. 525
35. T. Takenouchi and K.Suzuki, Transactions ISIJ 1978, 18, p. 344
36. M. Benda, Sbornik VSB Ostrava 1968, 3, p. 75
37. B. Triveliu and T. Sohlgren, Iron and steelmaker Nov. 1979 p. 38
38. U. Kalla, H.W. Kreutzer and E. Reichenstein, Stahl und Eisen 1977, 97, p. 383
39. H.D. Pflipsen and R.A. Weber, Stahl und Eisen 1978, 98, p. 474
40. R. Bruder,Stahl und Eisen 1980, 100, p. 1074
41. M.M. Nzotta R. Nilson, Du Sichen and S. Sietharaman, Ironmaking and

- steelmaking 1997, 24(4), p.300
42. A. Lucny, Stahl und Eisen 1989, 99, p. 1504
 44. D. P. Wilcox, Whitwood M.M. and D.J. Dyson, Ironmaking and steelmaking 1977, 24(3), p.243
 45. H. Graf Stahl und Eisen 1976, 96, p.117
 46. C. Holden, J.M. Young, P.E. Eldridge and T.W. Deakin, The Iron and Steel Institute London 1972 p.167
 47. C.To Duy Project KC-05-23N4 report (unpublication) Hanoi 1995
 48. R. Kiessling and N.Lange, Non Metallic Inclusions in steel parts I-IV, 2 Ed. The Metals Society Book No. 194, London, 1968
 49. F.D. Richardson and J.H.E. Jeffes, J. Iron Steel Institute 1952, 171, p.165
 50. Z. Buzek Hutnicke aktuality, VUIZ Dobra, 1979, 1-2
 51. C.To Duy, J. Science and Technology 1994, 32(2), p.23
 52. A. McLean and D.A.R. Kay, Microalloy & 5, Proc. vol Union Carbide Corp. 1977 p.215
 53. J.W. Farrell P.J. Bilek and D.C. Hilty, Electr. Furnace conf. proc. AIME 1970 p.64
 54. R. K. Iyengar R. K. and W. O. Philbrook, J. of Metals 1971 2(5A), p. 92
 - 55 C. K. Kim and A. MacLean, Metall. Transactions 1979, 10B(4) p.575
 56. A. McLean C. K. Kim. Metall. Transactions 1979, 10B(4) p.585
 57. C. To Duy Minimum Ostrava 1989 p. 32

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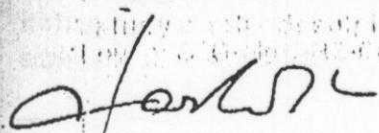
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