

## INFLUENCE OF RARE EARTH METALS ON NON-METALLIC INCLUSIONS IN CAST ALLOY STEELS

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### ABSTRACT

The chromium and silicon steels usually have defects leading to lower fatigue and toughness characteristics and cracking in the use. A study of Cr27 and silicon Si3 steels has shown that they contain coarse aluminates and silicates which possess high elongation.

Two series of heats were prepared with 0.5 kg/t to 2 kg/t rare earth metals (RE) to study their influence on these defects. Experiments were carried out in induction furnace (160 kW). The results showed that oxygen and sulphur contents in silicon steels reduced from 0.0021% to 0.0028% and 0.001% respectively. The inclusion level was the lowest (0.0188 area %), when RE added into steel was 0.5 kg/t. The optimal residual RE content in chromium steel was 0.013%, and 92.68% inclusions had smaller size than 4µm. The samples did not have inclusions of size over 10 µm. The inclusions morphology was small-smooth globular of type Ib. The composition of inclusions corresponded to RE oxysulphides and complex oxysulphides.

### 1. INTRODUCTION

The rare earth metals are used effectively in steelmaking in recent years with cast qualitative steels /1-15/. The chromium, silicon and manganese alloy steels containing of RE have shown improved surface oxidation resistance, mechanical properties and abrasion resistance /16-22/. However, the role of chemistry of inclusions, quantity, size and morphology in these steels is not well established /23-33/.

In the present work two series of experiments on chromium and silicon cast steels containing RE were conducted to study the effect of RE on inclusion composition, quantity, size, morphology and distribution.

### 2. EXPERIMENTAL

60 kg experimental heats were made in a induction furnace of type 160kW, GV-160., with chemical composition given in table 1.

The RE addition was in the form of FeSiRE containing 25%RE (10%Ce and 7-8%La), 25%Si, 3%Ca and balance Fe. The RE addition was varied from 0.5 kg/t to 2.0 kg/t., and 0.78 kg/t to 0.98 kg/t aluminium was used for deoxidation.

The temperature of the melt was 1600-1620°C and was deoxidized by aluminum wire. The melt was poured into ladle having RE addition in the bottom. The molten steel in the ladle was continuously stirred by wood stick. After three minutes the melt was sampled (C<sub>1-3</sub> and S<sub>1-3</sub>) into small copper moulds for chemical compositions and inclusions study.

**Table 1.** Chemical compositions of chromium and silicon steels

steels	chemical content (wt.%)									
	C	Mn	Si	P	S	Al <sub>l</sub>	O <sub>2l</sub>	N <sub>2</sub>	Cr	Mo
Chromium steel C <sub>0</sub>	0.13	0.83	0.52	0.041	0.024	0.019	0.018	0.0807	23.46	0.10
Silicon steel S <sub>0</sub>	0.029	0.20	2.78	0.010	0.012	0.175	0.00834	0.0095	-	-

The oxygen, nitrogen and oxide phases were analyzed using LECO TC 436. The SEM and EDX were done in JEOL-35CF and LINK 860/II. The inclusion types were analyzed by DX-5000.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Chemical composition of steels

The results of composition in steel are shown in table 2.

**Table 2.** Chemical composition of chromium and silicon steels containing RE

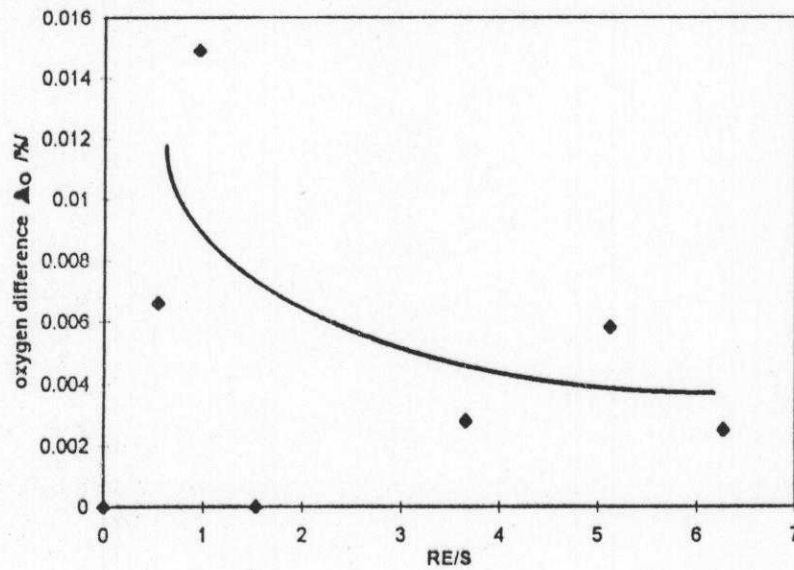
sample	chemical content (wt%)													
	C	Mn	Si	P	S	Al <sub>r</sub>	Al <sub>l</sub>	O <sub>2l</sub>	Ce	La	RE	N <sub>2</sub>	Cr	Mo
S <sub>1</sub>	0.026	0.13	2.94	0.010	0.011	0.060	0.072	0.00619	0.010	0.007	0.017	0.00804	-	-
S <sub>2</sub>	0.051	0.19	3.06	0.011	0.012	0.090	0.093	0.00550	0.028	0.010	0.010	0.00842	-	-
S <sub>3</sub>	0.036	0.13	3.40	0.011	0.011	0.064	0.065	0.00576	0.040	0.029	0.069	0.00842	-	-
C <sub>1</sub>	0.130	0.52	0.73	0.036	0.024	0.090	0.010	0.01140	0.008	0.005	0.013	0.08950	23.70	0.09
C <sub>2</sub>	0.130	0.53	0.73	0.023	0.022	0.003	0.019	0.00300	0.012	0.009	0.021	0.07160	23.11	0.09
C <sub>3</sub>	0.110	1.03	0.91	0.038	0.016	0.080	0.087	0.01220	0.050	0.032	0.082	0.05920	22.54	0.10

Table 2 shows the following <sup>i)</sup>RE contents in steel remained 0.013% to 0.082%. <sup>ii)</sup>Melt samples S<sub>1</sub> and S<sub>3</sub> have reduced sulphur contents the lowest is 0.011%. <sup>iii)</sup>Melt samples C<sub>2</sub> and C<sub>3</sub> also show reduced sulphur content of 0.016%. <sup>iv)</sup> remain oxygen content is reduced substantially <sup>v)</sup>. Aluminum content 0.02% to 0.10%. <sup>vi)</sup> Aluminum influences reduction of sulphur content in samples C<sub>2</sub> and C<sub>3</sub> with increasing RE additions. <sup>vii)</sup> RE dissolves more in chromium steel than in silicon steel. <sup>viii)</sup> RE influences on oxygen and sulphur depending on ratio of RE/S, Al+Si/RE and the original oxygen and sulphur contents( table 3).

Table 3 shows that with ratio of RE/S less than 2 oxygen content is reduced and higher than 4 the reduction is very slow (figure 1.). This result agrees with previous work /34/. The correlation has also shown that when sulphur content is lower than 0.012%, oxygen content (in samples C<sub>1</sub> to C<sub>3</sub>) is reduced slowly.

**Table 3.** Relationship between RE, O<sub>2</sub>, S and Al + Si / RE in steels

sample	RE add. /kg/t	RE /‰	S /‰	$\Delta_S$ /‰	RE/S -	O <sub>2</sub> /‰	$\Delta_O$ /‰	S/O -	Al /‰	Si /‰	Al+Si/RE -
S <sub>0</sub>	0	0	0.012	0	0	0.0083	0	1.4	0.092	2.78	-
S <sub>1</sub>	0.5	0.017	0.011	0.001	1.54	0.0062	0.0021	1.7	0.072	2.94	174.0
S <sub>2</sub>	1.0	0.044	0.012	0	3.66	0.0055	0.0028	2.2	0.093	3.06	71.0
S <sub>3</sub>	2.0	0.069	0.011	0.001	6.27	0.0057	0.0025	1.9	0.065	3.40	50.0
C <sub>0</sub>	0	0	0.021	0	0	0.0180	0	1.1	0.018	0.52	-
C <sub>1</sub>	0.5	0.013	0.024	-0.003	0.54	0.1140	0.0066	2.1	0.010	0.73	57.0
C <sub>2</sub>	1.0	0.021	0.022	-0.001	0.95	0.0030	0.0149	7.3	0.019	0.73	35.0
C <sub>3</sub>	2.0	0.082	0.016	0.005	5.12	0.0122	0.0058	1.3	0.087	0.91	12.0



**Figure 1.** Relationship between oxygen difference  $\Delta_O$  and RE/S ratio in steels

In these samples RE metals have modification effect. It can be concluded that the more the initial sulphur lower, is the reduced final oxygen content in chromium steel. The final oxygen content in steel also depended Al+Si/RE. This result is seen in figure 2.



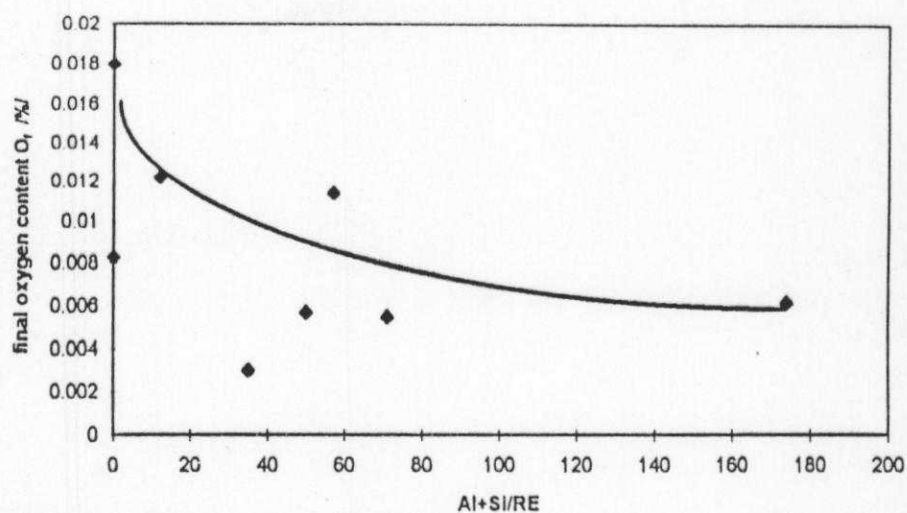


Figure 2. Relationship between Al+Si/RE ratio and final oxygen content  $O_f$  in chromium steels.

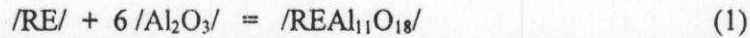
### 3.2. Chemical composition of inclusions

The chemical compositions of inclusions are shown in table 4.

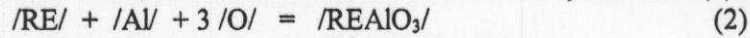
Table 4. Chemical composition of inclusions in steels

type	sample	chemical content (wt%)								
		Al	Si	Ca	S	Mn	Ti	Cr	Ni	RE
oxide	S <sub>0</sub>	59	16	5	11	10				0
	S <sub>1</sub>	45	20	6	7	0				23
	S <sub>2</sub>	15	5	5	3	0				71
	S <sub>3</sub>	6	77	3	2	0				12
	C <sub>0</sub>	32	2	19	1	19	1	21	0	5
	C <sub>1</sub>	32	15	16	1	11	1	23	0	11
	C <sub>2</sub>	34	9	10	1	10	1	18	0	17
	C <sub>3</sub>	2	11	5	1	3	1	31	18	26
sulphide	S <sub>0</sub>	20	5	3	36	35				
	S <sub>1</sub>	6	2	2	23	2				65
	S <sub>2</sub>	1	2	2	18	1				77
	S <sub>3</sub>	0	6	3	18	0				74
	C <sub>0</sub>	2	2	37	0	37	1	17	0	0
	C <sub>1</sub>	3	2	31	1	19	2	18	0	25
	C <sub>2</sub>	3	2	37	1	34	0	19	0	4
	C <sub>3</sub>	2	1	16	1	6	3	9	7	55

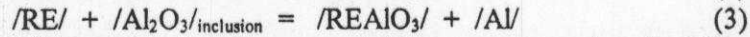
Table 4 shows that without RE additions the inclusions are aluminates, silicates and manganese sulphides. With RE additions fast reduction of sulphides occurs. The complex aluminates and silicates reduced substantially in the all samples of silicon steels with RE. The chromium oxides are reduced obviously in chromium steel containing RE. This results can be explained as follows: With RE addition of 0.5 kg/t and ratio of Al+Si/RE higher than one complex oxides form on the basis of RE and aluminum, reduction of aluminates occurs by reactions /4,25,26,35,36/:



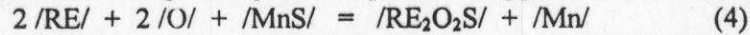
When RE content is about 0.02%, oxides are formed on the basis of by reactions (2) and (3):



and



With increase of RE addition to 2 kg/t manganese sulphides are appeared as the following reaction:



Thus mainly oxysulphide inclusions of type like RE<sub>2</sub>O<sub>2</sub>S form and nearly all manganese sulphides disappear. This result agrees with the conclusion of recent work /4/.

### 3.3. Quantity and size of inclusions

The results on quantity and size of inclusions are shown in table 5.

**Table 5.** Influence of RE additions on inclusion quantity and size

sample	total quantity		oxide		sulphide		inclusion size		
	number /cm <sup>-2</sup> /	area /%/	number /cm <sup>-2</sup> /	/%/	number /cm <sup>-2</sup> /	/%/	1-4μm /%/	4-10μm /%/	over 10μm /%/
S <sub>0</sub>	9982	0.0561	9945	99.62	38	0.38	92.48	6.39	1.13
S <sub>1</sub>	1576	0.0188	1216	77.15	360	22.84	72.90	26.45	0.69
S <sub>2</sub>	4747	0.0404	1145	24.12	3603	75.90	79.43	20.16	0.40
S <sub>3</sub>	7065	0.0636	4194	59.36	2871	40.63	87.87	17.14	1.98
C <sub>0</sub>	9264	0.0803	8556	92.35	708	7.64	83.33	14.23	2.42
C <sub>1</sub>	6505	0.0293	3703	56.92	2802	43.07	92.68	7.30	-
C <sub>2</sub>	13150	0.1029	12654	96.22	495	3.76	88.76	8.90	2.05
C <sub>3</sub>	18989	0.0821	6830	35.90	12159	64.03	96.05	3.94	-

Inclusion observed on surface of the samples was the lowest in silicon steel sample S<sub>1</sub> (RE addition to 0.5 kg/t) i.e.: 0.0188 area% ( 1576 incl./cm<sup>-2</sup>, ( figure 3).

Figure 4 shows that sulphide quantity remaining in steel sample S<sub>1</sub> is negligible, ( 360 inclusions per cm<sup>-2</sup>).

In chromium steel sample adding 0.5 kg/t of RE into steel shows that the lowest inclusion number is 6505 incl./cm<sup>-2</sup>, ( figure 5 and 6).

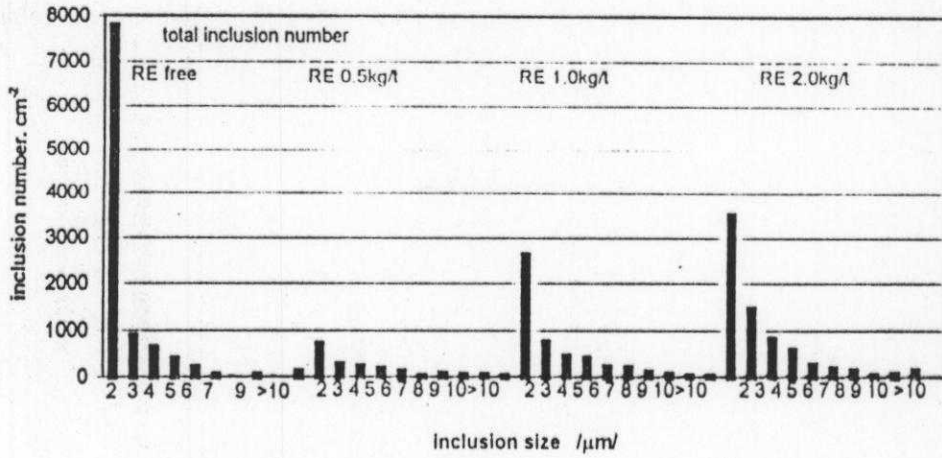


Figure 3. Effect of RE additions into silicon steel on quantity and size of inclusions

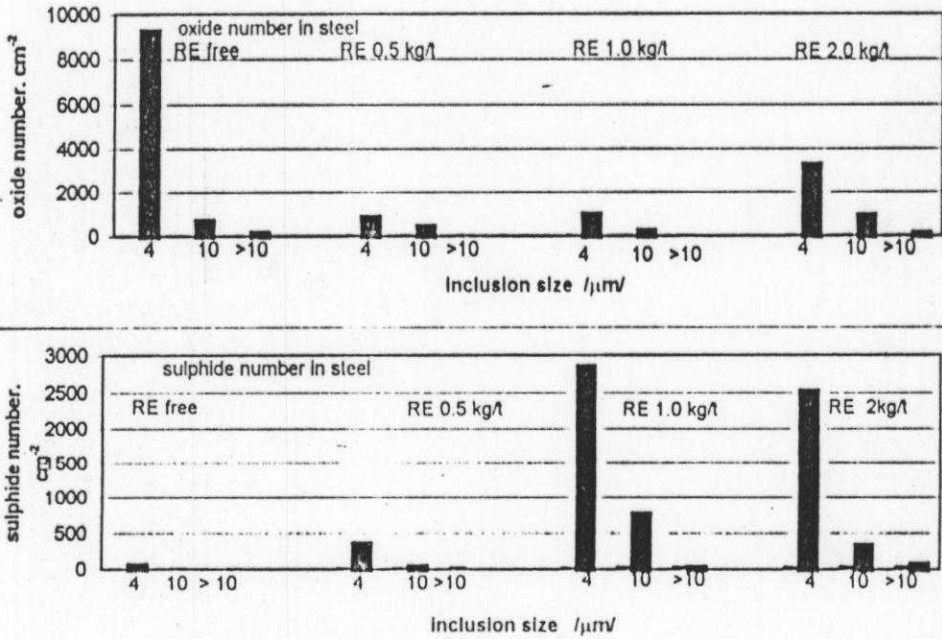


Figure 4. Effect of RE additions into silicon steel on quantity and size of oxides and sulphides

The figures, which given an impression that RE addition increases inclusions. The RE additions in fact refines the coarse silicates and aluminates to smaller than 4μm inclusions (figures 3 - 6) as observed on the surface of samples, these small inclusions improve mechanical properties and quality of steel product.



In high silicon steels RE modifies silicates. These steels reveal smaller complex oxides and oxysulphides containing RE, Al and Si like  $RE(Al,Si)_nO_{1.6}$  or  $RE(Al,Si)O_3$  /37-49/

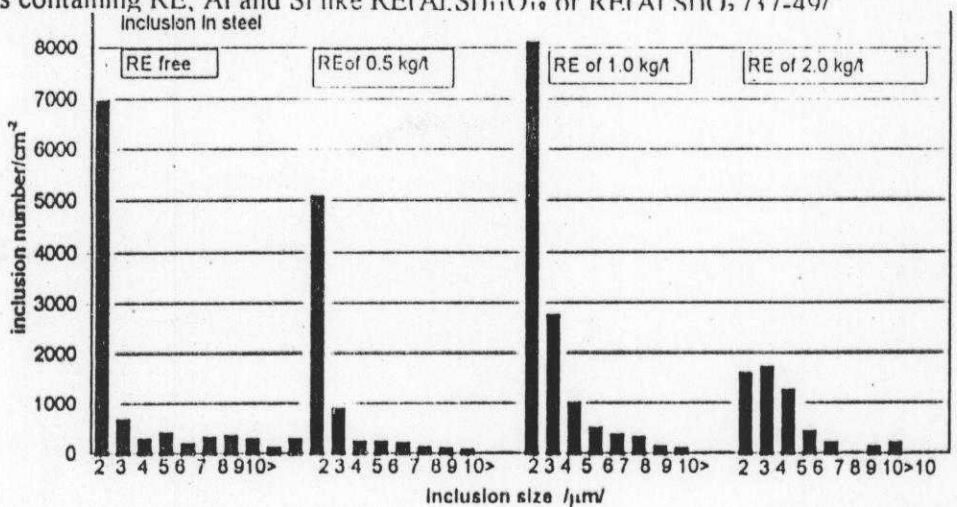


Figure 5. Effect of RE addition into chromium steels on inclusion quantity and size

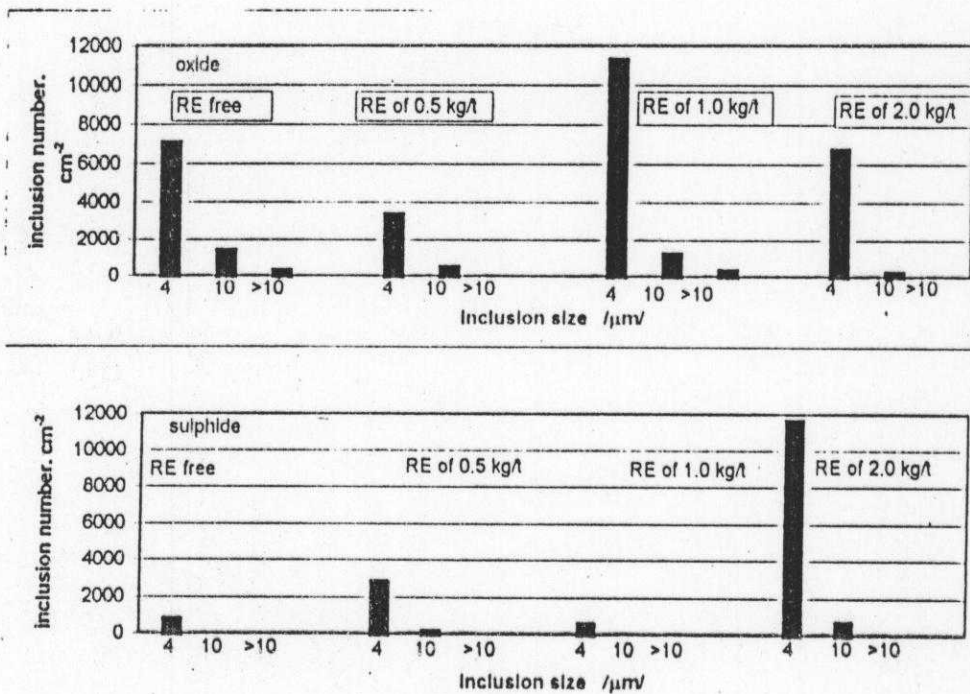


Figure 6. Effect of RE addition into chromium steels on quantity and size of oxides and sulphides

Addition of 2 kg/t of RE to silicon steels produced; about small inclusion size 96.05% inclusions are smaller than 4 $\mu\text{m}$ . The inclusion of over 10 $\mu\text{m}$  were not present. The residual RE was found and be 0.082% (0.05%Ce).

In general steels containing RE had 86-96% inclusions of size than 4 $\mu\text{m}$  and only about 1% over 10 $\mu\text{m}$ , while the RE-free steel had about 4.5% inclusions of over 10 $\mu\text{m}$ . From these results it can be emphasized that RE minimizes surface activity of manganese sulphide, and coarse inclusions are not found. The RE oxides and sulphides are more thermodynamically stable. The surface tension of RE inclusions are very high, and do not been grow in inclusion coarse. Figure 7 is a plot of inclusion size and number which shows that less is the size more is the number of inclusions.

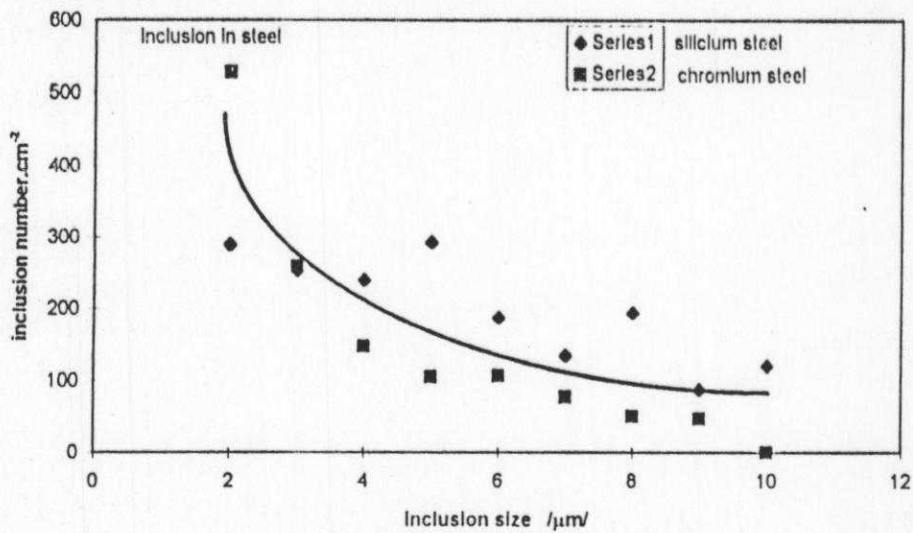


Figure 7. Relationship between inclusion number and inclusion size in steels containing RE

### 3.4. Morphology and distribution of inclusions in steels

Mechanism of formation and morphology of inclusions have been studied recently /40/ and described in figure 8.

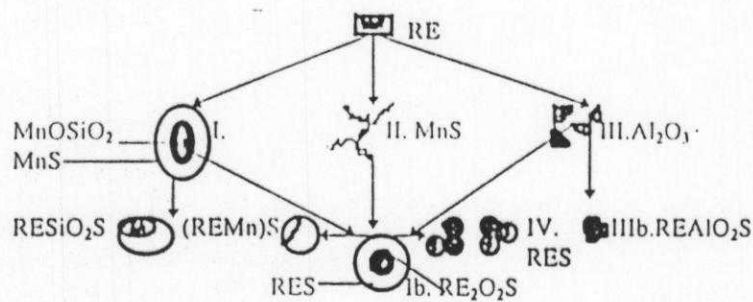
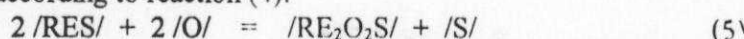


Figure 8. Schematic of formation and morphology of inclusion type in steel.

It can be seen that without RE addition commonly globular manganese oxysulphides of type I, manganese sulphide of type II and cluster angular aluminates of type III are observed. The RE



addition changes manganese sulphides of type II into globular oxysulphide of type Ib. The explanation is as follows: The dissolved RE reacts with the dissolved sulphur and precipitates RE sulphides. These primary RE sulphide inclusions act as nuclei for the precipitation of RE-oxysulphides according to reaction (4):



These primary oxysulphide phases are confined to the outer surface. The secondary RE sulphide and complex sulphides are probably precipitated during the solidification of steel, are formed surrounding the primary cores. Figure 8 also shows that these RE sulphides, have low sulphur content. Manganese sulphides form when sulphur content is higher. With RE addition high the cluster sulphide inclusions of type IV form. The heterogeneous angular sulphides (RE  $\text{AlO}_2\text{S}$  and  $\text{RESiO}_2\text{S}$  of type IIIb) are formed, when quantity of  $\text{Al}_2\text{O}_3$  and  $\text{MnOSiO}_2$  are presented in high amount.

### 3. CONCLUSIONS

The following observation can be made from the present work:

i) The RE additions of 0.5 kg/t formed heterogeneous oxysulphide inclusions of RE and Al according to reactions from (1) to (3) and they reduced the quantity of aluminates. The RE additions of 1 kg/t formed globular oxysulphides according to reaction (4) and (5).

ii) The influences of RE addition is reduced inclusion number in silicon steel and the lowest with residual RE content of 0.017%. The optimal residual RE content for chromium steel is 0.013%.for minimum inclusions

iii) The RE refines 82-96% of inclusions to lower than  $4\mu\text{m}$  size which are harmless.

iv) The optimal residual RE for globular morphology of inclusions of type Ib are 0.013% to 0.021%, for angular inclusions of type IIIb from 0.021% to 0.038% and for cluster inclusions of type IV 0.069% to 0.083%. The residual RE of 0.069% is the over limit of level

v) The of RE inclusions may float in silicon steels.

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