EFFECT OF RARE EARTH METALS ON SULPHIDE INCLUSION IN PIPELINE STEEL

To Duy Ca* National Metallurgical Laboratory- Jamshedpur 831 007-India

The effects of rare earth metal injection treatment on sulphide inclusions of pipeline steel have been studied in the industrial trials. The melt was stirred by nitrogen from the bottom of the ladle. As a result of addition of RE at the rate of 0.05 kg/t improved desulphurization and reduction of sulphur content from 0.03% to 0.012% took place. When RE addition was done from 0.1 to 0.2 kg/t the sulphides and oxysulphides of type Ib were formed. Addition of 0.1 kg/t of RE resulted in refinement of inclusion size of $1.45.10^{-2}$%area below 4μm and only $0.04.10^{-2}$%area over 10 μm. The lowest reduction of sulphide quantity in steel (0.63.10%area) and the elongation ratio of sulphides below 7 was obtained after addition of RE of 0.03kg/t. The small-smooth globular inclusions of type Ib were undeformed during rolling pipe.

KEY WORDS: Rare earth metal, desulphurization, inclusions , morphology, elongated ratio.

1. INTRODUCTION

The ladle injection treatment has been developed as a major tool for desulphurization and improvement of mechanical properties of most aluminum killed steels[1-7]. The recently studies of rare earth metals (RE), calcium injection treatments have shown successes on removal of Al_2O_3 clusters, manganese sulphide and modification of inclusions[8-18]. The factor that the strongest influences on the technical characteristics and the workability of steel is the presence of sulphur. The REs are elements with a lower standard free energy of sulphide formation than iron [19,20] therefore desulphurization can be achieved by ladle treatment. The RE addition modified inclusions in steel resulting in high strength, low temperature toughness, rollability and weldability of steel.

This work describes the effect of RE injection treatment on formation and modification of sulphide inclusions in pipeline steel.

2. EXPERIMENTAL METHOD

Industrial trials were performed on 9 melts with steel containing 0.015%C, 0.35%Si, 0.030%Mn, 0.03%P, 0.03%S, 0.03%Al, 0.04 %O_2 (total), 0.009%N_2 and this steel was melted in a 45t electric arc furnace. The bath after addition of FeMn, FeSi, Al was tapped into the ladle. Then the ladle was taken to the RE in injection station . The RE wire (ϕ d = 12 mm of composition as follows 45,2%Si, 21,6%RE, 4,3%Ca, 0.9%Mg, 7,2%Al, ~ 21%Fe) were injected into the ladle top with speed from 2 m/sec and nitrogen was used as a carrier stirring gas at a pressure of 6-atmThe temperature was measured automatically. The steel samples were taken at predetermined stages, before and after addition of RE and stirring by gas. Samples from the rolled products were also taken.. Complete chemical analysis was done for selected samples.

Ph.D, Manager, on leave from Institute of Materials Science Hanoi-Vietnam

Samples from each heat were examined metalographically and with a microprobe analyzer for quantitative determination of inclusion in steel by QTM 360, and by SEM (JEOL-35CF) and EDX (LINK 860/II). The samples taken from the rolled steels were subjected to the standard test for determining deformability of inclusions in the steel products.

3. RESULTS AND DISCUSSIONS

The industrial experimental results of desulphurization by RE addition and gas stirring are shown in **figure 1.**

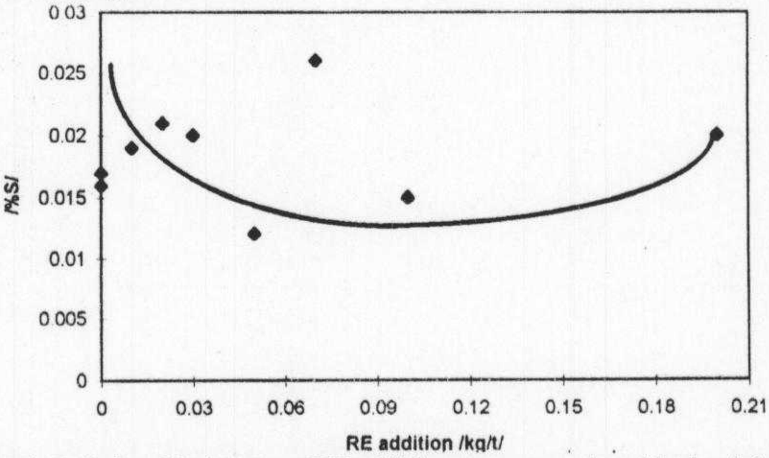

Figure 1. Relationship between RE addition amount and residual sulphur content in steel

Figure 1 shows that residual sulphur content in the steel reduced to 0.012%S and then increased . The cause can be described as follows by reactions [4, 17, 21] :

$$2\,/RES/ + 2\,/O/ \rightarrow /RE_2O_2S/ + /S/ \quad (1)$$

$$/RE_2O_2S/ + /O/ \rightarrow /RE_2O_3/ + /S/ \quad (2)$$

The reactions cited above are typical of reoxidation reactions and sulphur content to the molten steel, therefore in the curve of figure 1 the is increased part. The oxygen of the reactions describing above can come from from atmospheric air entrained by the ladle stream during casting [22-23]

Thus RE treatment usually resulted in several oxysulphides, according to the prediction[24,25] as follows: (Ce_2O_2S, La_2O_2S...), oxides (Ce_2O_3, La_2O_3...) and sulphides (CeS, LaS..). These inclusions were relatively heavy and therefore probably remain in suspension in the melt.

The reduction of sulphide inclusions obtained after RE addition is shown in figure 2

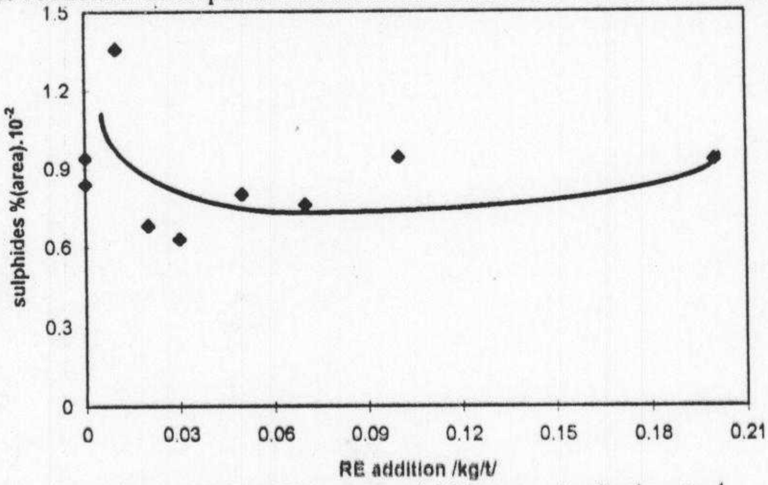

Figure 2. Affect of RE addition on sulphide quantity in the steel. 2

The sulphide inclusions reduced to minimum of 0.63.10%area after RE addition of 0.03 kg/t and then again increased (shows figure 2). It can be explained that the RE addition affect transformation of sulphide inclusion in steel from larger to more smaller (figure 3)

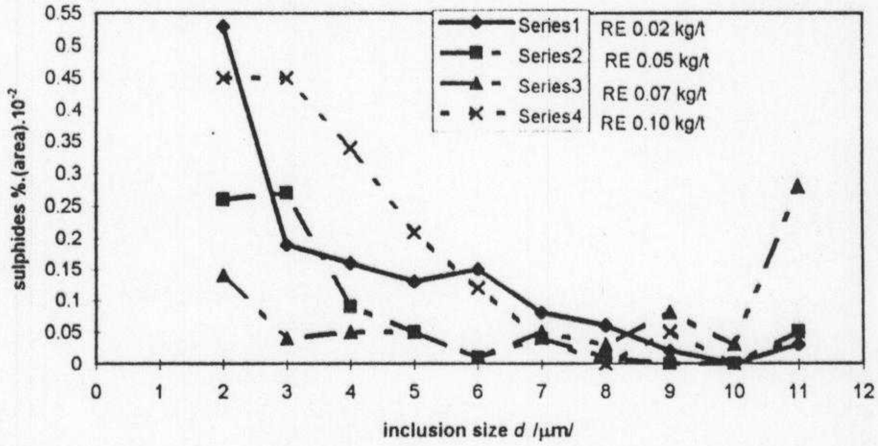

Figure 3. Relationship between sulphide sizes and sulphide amounts in steel products on RE amount additions

Figure 3 shows that the quantity of large inclusions reduced very considerably. The larger sulphide sizes than 10µm are negligible. The sulphide inclusions only observed in steel are from $0.03.10^{-2}$% to $0.09.10^{-2}$ area. The smaler sulphide sizes than 4µm increased. In fact, the sulphide inclusions having smaller sizes than 4µm in steel are from $0.14.10^{-2}$ to $0.53.10^{-2}$%area. Addition of 0.1 kg/t of RE to steel produced small inclusion size; about $1.45.10^{-2}$% area sulphide inclusions are smaller than 4µm. The inclusions of over 10µm only were less than $0.04.10^{-2}$%area. The sulphides having smaller size than 4µm are less elongated in the pipe steels (shows figure 4).

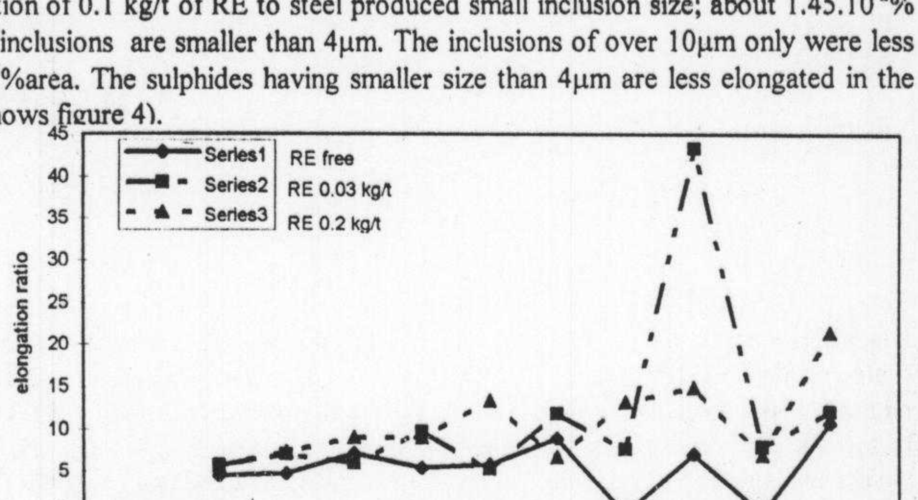

Figure 4. Effect of RE addition on elongation ratio of sulphides in pipe steel

Figure 4 shows that the elongation of smaller sulphides than 4µm is relatively neligible. Figure 4 also proved that the RE addition into steel had positive effects on the elongation of the remaining sulphide inclusions in this steel. The elongation ratio of the small sulphides (below 4µm) is lower than 9, while the elongation ratio of large sulphides (over 10 µm) is higher than 10. When the RE is added about 0.03 kg/t, the elongation of sulphides is lowest (below 7). In figure 4 there is one higher point, which might be errorof analysis.

Normally, in the steel there are Al_2O_3-clusters by aluminum addition (figure 5) and manganese sulphides of type II, which form stringers and long, flat ribbons during hot-rolling process.

Figure 5. Optical micrograph of inclusions in steel before addition of RE, x500

The RE addition had changed prolong manganese sulphides of type II into globular oxysulphide of type Ib. Here the dissolved RE in the melt reacts with the dissolved sulphur and precipitats RE sulphides. These primary RE sulphide inclusions act as nuclei for the precipitation of RE-oxysulphides with the result that the RE oxysulphide phase is formed in the core. The complex RE sulphide inclusions are probably the secondary inclusion precipitated during the solidification process from dissolved RE and aluminum, sulphur, oxygen in the steel. This secondary inclusion formed peels surrounding primary core (show figure 6)

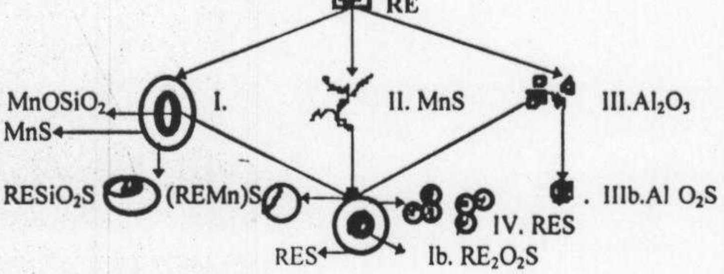

Figure 6. Schematic of modification of the inclusions in steel containing RE

Figure 6 shows that the peel of inclusion is RE sulphide when the sulphur content is low and the RE addition is optimal. The RE-manganese sulphides are formed when sulphur content is high. Whe the RE addition exceeds optimal amount, the cluster sulphide of type IV can be formed (figure 7). The complex sulphides $REAlO_2S$ and $RESiO_2S$ form when quantities of Al_2O_3 and $MnOSiO_2$ in steel are high. Steel sample taken from the ladle contained mainly complex globular distributed inclusion, see figure 7. The oxide is rather complex containing the RE aluminate and calcium phases together with sulphide phase (figure 7a-g). In contrast to the alumina stringers, which are found in figure 5, the oxides in the RE treated steel are globular and equal distributed. As can be seen from the figures, the sulphides in the steel containing RE are oxysulphides and sulphides of calcium and aluminum. These sulphides are not deformed during the rolling process. The reason is probably that during rolling process small and uniformly distributed inclusions are not so severely affected as the large inclusions. The RE addition increases hardness of the manganese phase [26], thereby hindering its elongation during the rolling process.

Electron image

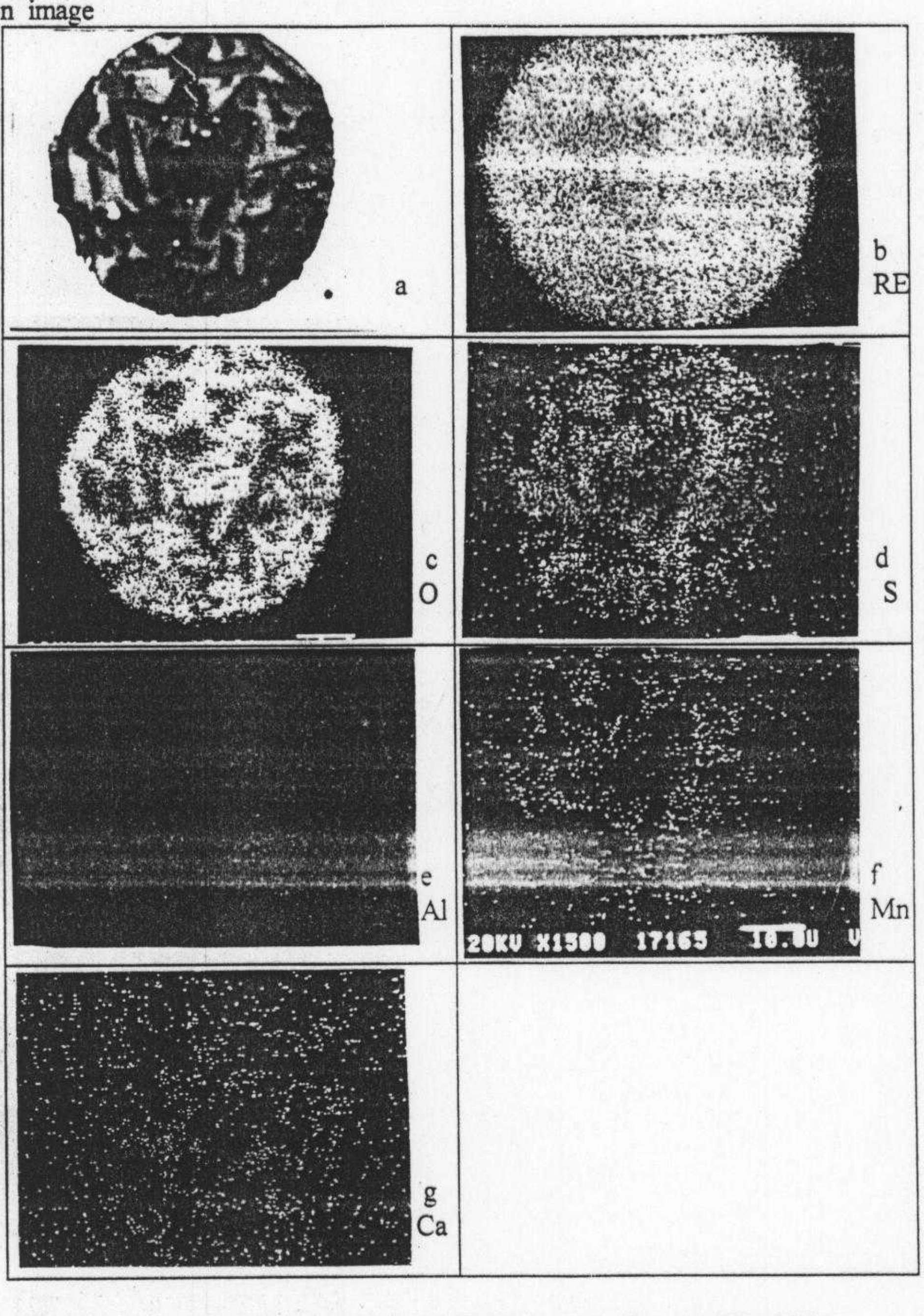

Figure 7. An inclusion typical of those found in steel after the RE addition (with 0.1 kg/t RE treatment)

Typical inclusion appearing in the rolled pipe product is shown in figure 8. As can be seen from the figure the inclusion is small,undeformed and of RE-oxysulphide type. This oxysulphide RE_2O_2S) forms the core and surrounds it with the peel RE, Al and Ca sulphides (figure 8 b-g). The morphology of inclusions (figures 7 and 8) is according to mechanism citing above (show figure 6)

The compositions of inclusions appearing in samples are shown in table 1

Electron image

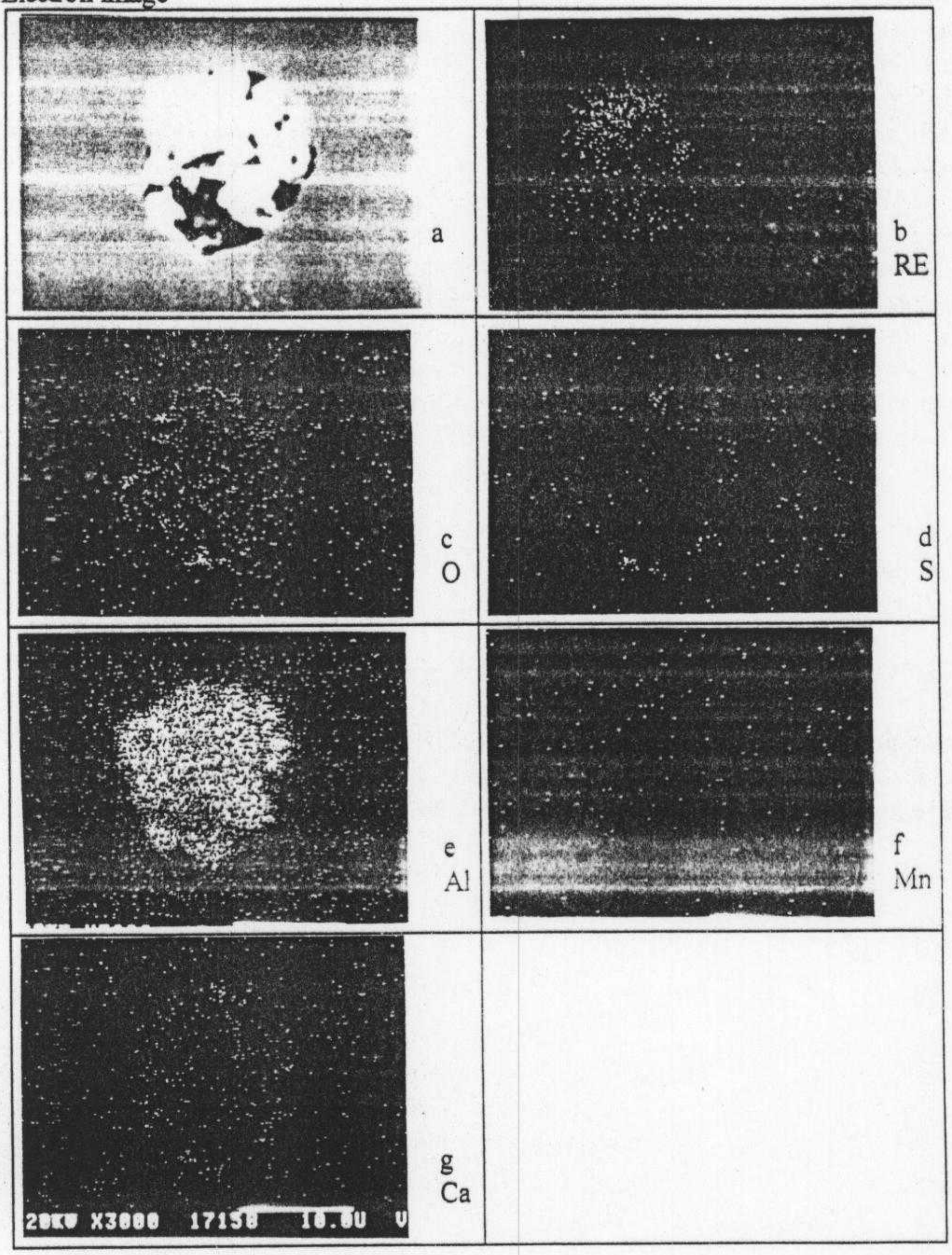

Figure 8. An inclusion typical of those found in steel pipe product (with 0.2 kg/t RE treatment)

Table 1. Effect of RE on composition of sulphide inclusions in pipeline steel

Sample No.	Amount of RE addition /kg/t/	Quantity of inclusion /%.10^{-2} area /	Compositions
1.1808	0.01	1.36	3Al2Ca37S58MnRE
2. 2106	0.02	1.36	3Al1Ca39S50MnRE
3.1815	0.03	1.06	5Al8Si4Ca38S45Mn1RE
4.2107	0.05	0.79	7Al1Si6Ca42S44MnRE
5.3213	0.07	0.76	1Al2Si3Ca44S50MnRE
6.2114	0.10	1.69	7Al6Ca43S45Mn5RE
7.1799	0.20	3.02	17Al6Ca26S25Mn28RE

Table 1 shows that the compositions of sulphide inclusions in the pipeline steel are RE, Al, Ca, Mn, S and O . Table 1 also shows that none of the sample contained pure manganese sulphide or isolated pure calcium and RE sulphide inclusion. The sulphide inclusions always contained RE, calcium and manganese. The prediction of inclusion types are RE_2O_2S, RES, $REAlO_2S$, (RE,Mn)S and a few (RE,Ca)S [27,28]. These sulphide inclusions are undeformed during rolling pipe.The results agreed with previous works[29-33]

4. CONCLUSIONS

The effect of RE on sulphide inclusions in pipeline steel has been studied:

1.The lowest reduction of sulphur content in steel (0.012%S) was obtained after addition of RE of 0.05 kg/t.

2.The lowest reduction of sulphide quantity in steel (to $0.63.10^{-2}$%area) is obtained after RE addition of 0.03 kg/t.

3. Addition of 0.1 kg/t of RE to steel refines $1.45.10^{-2}$%area of sulphides to lower than 4μm size, which are harmless and only $0.04.10^{-2}$%area of sulphides is over 10 μm size.

4. The elongation ratio of sulphides below 7 is obtained after addition of RE of 0.03 kg/t.

5. The optimal amount of RE for globular morphology of sulphides of type Ib are 0.1 to 0.2 kg/t, which is undeformed during rolling process.

ACKNOWLEDGMENT

The author is gratefully to Dr. Oldrich Volny and his colleague for helping and supporting this research. The author is thankful to Professor, P. Ramachandra Rao,Director and CAP Division of National Metallurgical Laboratory-Jamshedpur, India for encouragement and helping in the preparation of manuscript.

REFERENCES

[1]. Forster E., Klapdar W., Richter H.,. Rommerswinkel H. W, Spetzer E. and Wendorff J. *Stahl und Eisen* **94,** (1974), 474

[2]. Haastert H.P., Maas H. and Richter H., Proc. of 2nd Int. Conf. on Injection Metallurgy Lulea Sweden (1980)

[3]. Bruder R., Schulz E. and Richter H. *Stahl und Eisen* **100,** (1980), 1074

[4]. Wilson W.G. Proc.of Electric Furnace Conf. **44,** (1977)

[5]. Brosley J.J. and Qravec J.J., Int. Iron and Steel Cong. Chicago 16-20, April (1978)

[6]. Haida O. Proc. of 95th ISI Meeting (1978), 94

[7]. Emi T., Proc. of NOH BOS Conf. AIME Chicago 16-20, April (1978)

[8]. Schoop J. and Aschendorff K.K., *Radex-Rundschau* **2,** (1969), 495

[9]. Emi T., Habu Y., Physico Chemie et Siderurgie, Versailles (1978)

[10]. Takenouchi T., Suzuki K., *Trans. ISIJ* **18,** (1978), 344

[11]. Ritakallio P. Proc. of Int. Conf. on Injection Metallurgy Lulea Sweden (1977), 13:1

[12]. Lehner T., Proc. of Int. Conf. on Injection Metallurgy Lulea Sweden (1977), 11:1

[13]. Haastert H.P., W. Kladar and H. Rellermeyer, Proc. World Magnesium Conf. Oslo 23-26 June (1979), 34

[14]. Moore W., Proc. World Magnesium Conf. Oslo 23-26 June (1979), 46

[15]. Lehner T. and Ritakallio P. Proc.World Magnesium Conf.Oslo 23-26 June (1979), 55

[16]. Kubaschewski O. , Evans E.L. and Alcock C.B., Metallurgical Thermochemistry 4th Ed. Pergramon press (1967), 333

[17]. Luyckx L., *Metall. Trans.* **1,** (1970), 3341

[18]. Brawnring A. and Chambers F.M., *J. Iron and Steel Institute* **209,** (1970), 1078

[19]. Richardson F.D. and Jeffes J. H.E. , *J. Iron and Steel Institute* **171,** (1952) 165

[20]. Buzek Z., *Hutnicke Aktuality* VUHZ, Dobra c 1&2 (1979)

[21]. To Duy C., Kandidatska Discrtacni Prace Ostrava 1991

[22]. Kim C.K. and McLean A., *Metall. Trans.* **10B,** (1979), 4, 575

[23]. McLean A. and Kim C.K , ***Metall. Trans.*** **10B,** (1979), 4, 585

[24]. Kiessling R., Lange N., Non-Metallic Inclusions in Steel, P.I to P.IV, 2 Ed. The Metals Society Book No.194, London (1978)

[25]. Rowntree G., Weiner R.T. and Mickelthwaite B., *J.Iron and Steel Institute, (1973), 1*

[26]. Wilson W.G. and Wells R.G. *Metal. Progress Dec. (1973), 75*

[27]. Schindlerova V. and Buzek Z., *Hutnicke listy* (1970), 5, 316

[28]. Cizner J., Premunt P. and Svejcar J., *Slevarenstvi* **27,** (1979), 6, 230

[29]. Kepka M., *Hutnik* **23,** (1973), 10, 370

[30]. Premunt P. *Slevarenstvi,* **32, (1984), 1, 11**

[31]. To Duy C., Heavy Industry Reviews (1992), 3, 31

[32]. To Duy C., and Volny O. *Science and Technology,* **33,** (1995), 3, 39

[33]. Wilson W.G., and Wells R.G., *Metaal. progress* Dec. (1973), 75

[34]. Little J.H. and Henderson W.J., Effect of Secon-phase particles on the Mechanical properties of Steel, The Iron and Steel Institute, London (1971), 182

The Iron and Steel Institute of Japan
Keidanren Kaikan 3rd Floor
1-9-4, Otemachi, Chiyoda-ku,
Tokyo, 100-0004 JAPAN
Phone: +81-3-3279-6022
Fax:+81-3-3245-1355

98EI3023
May 29, 1998

Dr. To Duy Ca
National Metallurgical Laboratory
Jamshedpur 831 007, India

Dear Dr. To Duy Ca:

This is to acknowledge receipt of your paper titled "Effect of rare earth metals on sulphide inclusion in steel rolling pipe"(Receipt No.:98-305) for publication in ***ISIJ International***. You will be advised in due course of the acceptability for publication in the journal.

With best regards.

Sincerely yours,

H. Suito

Hideaki SUITO
Editor-in-Chief,
Editorial Board of ***ISIJ International***
(Professor, Tohoku University)

HS/YK/st