Influence of Rare Earth Metals on the phase prepitation and modification of non-metallic inclusion in low alloy steel

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Abstract：Rare Earth (RE) metals are good phase changers for the remaining non-metallic inclusions in steel and have a great influence on the properties of low alloy steel after thermomechanical processing. This paper presents the results of new research and development on the experimental effects of RE on the phase precipitation of the phase change, formation, morphology and distribution of RE non-metallic inclusions in low alloy steel.

The results showed that The free energy of the formation of single RE inclusions can be used for both complex RE inclusions (Al, Si)⋯ Inclusions are nucleated homogeneously. With the increase of RE in steel and alloy, the percentage of solid phase with inclusions decreases, but with the high RE in steel and alloy, complex inclusions of RE and deformed silicon will appear. The phase precipitation factor is established to vary between from 2.5 to 3.2.

The addition of RE significantly slows down the inclusion phase precipitation by reducing the grain boundary energy and carbon diffusion rate. Four different types of RE inclusions in terms of proportion have been studied and discovered in low alloy steel products are as RES, RE2O2S, REO2, REAlO2S, RESiO2S. After adding RE to steel, the main evolution of inclusions will take place from type II scattered on grain boundaries to type I spherical, increasing RE addition will convert type III polygonal Al2O3 to type IIIb which is durable at high temperatures, but when increased too much, it will convert type IV small spherical RES aggregates, when the optimal amount of RE added will transform inclusions to type Ib spherical with RE2O2S in center covered with RES, and when the amount of RE is excessive (~0.06 wt.%RE) will convert brittle inclusions (RE)Al11O18.

When RE is added to the alloy at about 0.01 to 0.02%, the remaining inclusions are in the form of small, smooth spheres, with the core being RE2O2S and surrounded by RES. These are inclusions that do not deform after forging and rolling. These are the optimal inclusions after being modified by RE.

The amount of RE in steel and alloys from 0.02 to 0.05%RE will achieve the least elongation for oxide inclusions (from 2.2 to 3.2μm), the total elongation per mm2 (from 90 to 99μm/mm2) for oxides and sulphides.

The amount of inclusions in steel and alloys is reduced to a minimum of 0.0268% of the surface after refining 0.1 kg/t MishmetalRE compared to CaSi, the lowest reduction is 0.0411% of the surface.

Keywords: Rare earth metals, RE Inclusion, Phase precipitation, Modification, Inclusion types, Distribution, Microstructure, Low alloy steel,

1 Introduction

The cleanliness of steel is influenced by the low total oxygen and sulfur content in steel to the low content of oxide and sulfide inclusions. In low alloy steel, oxide inclusions are usually formed from Al_2O_3, CaO, MgO, SiO_2, and sulfide inclusions are from MnS, FeS [1].

The harmful effects of oxide and sulfide inclusions can be reduced by removing and modifying the remaining amount in steel with rare earth metals (RE) [2].

The secondary phases can be removed by appropriate solid solution heat treatment. The addition of RE with a content of 0.01%RE [3] can effectively slow down the phase precipitation process, which will inhibit the degradation of mechanical properties.

When the RE content exceeds 0.05%RE [3,4], RE-rich particles are formed, resulting in low RE concentrations in the matrix, leading to deterioration of mechanical properties, which can reduce the precipitation in low alloy steels.

RE modifiers form strong bonds with oxygen and sulfur [2,3] to form oxy-sulphites, sulfites and RE oxides, which are capable of modifying the original inclusions. Four different types of RE inclusions (according to the Sim-Dahle classification) in terms of proportion have been detected in low alloy steel products: (Mn,Fe)S[II]→$RESiO_2S$[I]→$REAlO_2S$+RES[IIIb]→RES[IV]→RE_2O_2S+RES [Ib] and when the RE content is excessive (~0.055 wt.%RE) $(RE)Al_{11}O_{18}$ is also present[5].

The result of the interaction between RE with oxygen and sulfur is the formation of complex, often dispersed oxysulphite inclusions with low plastic deformation sensitivity during thermomechanical processing.

Considering the high chemical affinity of RE for oxygen and sulfur and the high melting point of their compounds, they are formed immediately after the introduction of these elements into the liquid steel. However, due to their high density (g/cm^3), their removal from the liquid metal is difficult [6]. The ratio of rare earth elements to sulfur required to completely change the shape of the inclusions must be higher, RE inclusions are characterized by increased dispersion - especially in low alloy steels where the grains will be very small, approaching the nanometer scale - which can positively influence the formation of the microstructure of the steel and inhibit the grain growth of austenite in low carbon steel [4,7].

With the optimal addition of RE, fine spherical RE inclusions can be obtained, which improves the continuity of the steel microstructure and reduces the adverse effects of inclusions on the properties of the steel [7].

The objective of this paper is to determine the effectiveness of the modification of non-metallic inclusions with rare earth metals in low-alloy steels.

2 Experimental Procedure

2.1 Experimental Materials

The study included the chemical composition of low alloy steel for thermomechanical processing. The studied steel blocks weighed 1 kg, and were carried out in the VIF-2 vacuum induction furnace of the VAST Institute of Materials Science laboratory (see Figure 1). The amount of fuel fed into the furnace is set from materials with known chemical compositions. The basic chemical composition includes ARMCO 04JA iron and additional alloys, mainly in the form of pure metal and ferro alloys (FeSi, FeMn, FeNb …). To remove and modify non-metallic inclusions, mishmetal (~55% Ce, ~45% La, …) was used (see Table 1).

Table 1, Chemical composition of feed steel and rare earth

Element	C	Si	S	P	Mn	Al	Nb	Ti	La+Ce	O
Steel	0,05	0,15	0,003	0.003	1,50	0,025	0,025	0,010	0,015	0,0045
RE-Mishmetal	0,10	0,18	0,001	0,006	1,53	0,023	0,014	0,014	~ 55%Ce,~ 45%La	0,0011

-Ferrosilicon with Fe content 23.59%; Si 74.09%; C 0.05%; Si 0.60%; P≤0.10%.

-Low carbon FerroManganese with Fe content 24.00%; Mn75.00%; C 0.05%; Si 0.60%; P≤0.10%.

-Low carbon FerroNiobium with Fe content 30%; Nb 65%; P≤0.05%; S≤0.015%; Al≤0.1%; Si0.25%

After charging, the furnace is closed and the vacuum pumps, which create a vacuum in the furnace chamber, are turned on. When the pressure in the furnace reaches 10÷20 Pa, the furnace heating process is started. After starting the furnace fuel melting process, the next process is carried out in an argon atmosphere, with the vacuum pumps turned off.

The metal bath gassing is carried out after the furnace fuel has been completely melted and the appropriate temperature of the molten steel is automatically measured by a Pt-RhPt probe. After the degassing process is completed, argon at a pressure of ~30 kPa is introduced into the furnace chamber and the final deoxidation of the furnace bath is carried out using aluminium. The remaining alloy (after the analysis results) is then introduced into the furnace bath and stirred. The reduction and modification of non-metallic inclusions is carried out using mischmetal in the amount of 0.1 to 5.5 g per 1 kg of steel, which is carried out in the final addition. The casting process is carried out in an argon environment into cast iron molds with heat-resistant coatings with dimensions according to the requirements of thermomechanical processing.

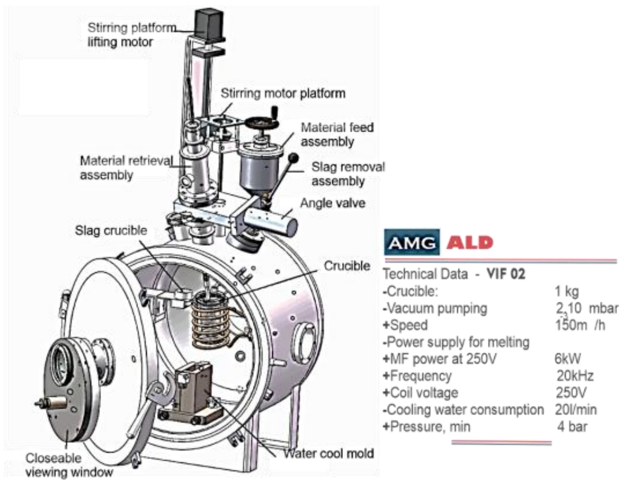


Figure 1, Vacuum induction furnace VIF-2 of the Institute of Materials Science laboratory

2.2 Experimental Equipment

The sample bars after thermomechanical processing are forged by high-speed hydraulic pressing, applying a force of 300 MN, the ingots are annealed at a forging temperature of 1200÷900°C, avoiding the temperature of the material falling below 900°C. The forging process is carried out on ingot bodies with the ends removed during the forging process. The forged products are sampled for analysis and measurement. The assessment of the cleanliness of non-metallic inclusions of steel is carried out based on the determination of their phase, type, size and morphological shape. Measurements are carried out on longitudinal metallographic samples taken from flat bars. The chemical composition analysis of non-metallic inclusions modified by RE is carried out on a JOEL JCXA 733 X-ray analyzer. Local analyses and observations of the distribution of individual elements forming non-metallic inclusions have been studied and carried out. Determination of the cleanliness of the studied steels with non-metallic inclusions and evaluation of the stereometric parameters of the inclusions were carried out on un-etched metallographic samples with an average area of 220 mm^2. For this purpose, a LEICA Qwin automatic image analyzer combined with an AXIOVERT 405M optical microscope was used. The analysis of the contamination level of steels with non-metallic inclusions was carried out based on the measurement of the surface area and surface involvement of the non-metallic inclusions as well as the anisotropy-strain ratio calculated as the ratio between their length and thickness. To determine the amount of particles and distribution of oxide inclusions (CaO-Al_2O_3-SiO_2) in RE-modified steel, the study used a JEOL 35CF scanning electron microscope and a LINK 860/II ED microanalyzer.

3 Results and evaluation of results

3.1 Process of formation and secretion of inclusions

1. Process of secretion of inclusions [4,7]

The process of secretion of inclusions is a process in which the energy ΔGo of the reaction is converted:

$$/mM/_{xz} + /nI/_{xz} \rightarrow M_mI_n \qquad \Delta G_1^o \qquad (3.1)$$

where: M is the metals that are depurinated. I is the interstitial element (O,S) that is depurinated. X is the dissolved base metal such as Fe . m, n is the number of atoms of the element in the reaction. / /xz is the solid state symbol.

When forming a standard (clean) compound, the depurination reaction is as follows:

$$mM_z + nI \rightarrow M_mI_n \qquad \Delta G_2^o \qquad (3.2)$$

The transition of phase-deposited elements from liquid solution to standard state is as follows:

$$/mM/_{xz} \rightarrow mM \qquad \Delta G_3^o \qquad (3.3)$$

$$\text{and} \quad /nI/_{xz} \rightarrow nI \qquad \Delta G_4^o \qquad (3.4)$$

The energy conversion of the phase separation process is calculated as the sum of the free enthalpy changes of the fractions.

$$\Delta G_1^o = \Delta G_2^o + \Delta G_3^o + \Delta G_4^o \qquad (3.5)$$

Thanks to the Van't Hoft isotherm equation, the conversion enthalpy can be expressed as follows:

$$\Delta G_1^o = -RT \ln \frac{a_{MmI_n}}{a_M{}^m . a^n{}_I} \qquad (3.6)$$

T…. is the temperature, /°K/
R…. is the gas constant, 8.3144.103 /J.K^{-1}.kmol^{-1}/
a_M and a_I is the activity of the M elements, I
a_{MmIn} is the activity of the released inclusions

The thermodynamic equilibrium constant is expressed as follows:

$$K = e^{\frac{-\Delta G_1^o}{RT}} = \frac{a_{MmI_n}}{a_M{}^m . a^n{}_I} \qquad (3.7)$$

The relationship between activity and composition is expressed as follows:

$$a_M = f_M \ . \ /\%M/ \qquad (3.8)$$

Here: f_M is the activity coefficient of element M
/%M/ is the composition of element M, /%/

Because with RE the interaction coefficient is not known in advance, the works have given the activity coefficients f_M, f_I and a_{MmIn} equal to 1 [1] which can be determined:

$$\frac{-\Delta G_1^o}{4{,}575T} = -\log/\%M/^m - \log/\%I/^n \qquad (3.9)$$

With the transformation of expression (3.9) to obtain the necessary inclusion phase conditions [7,8]:

$$\frac{\dfrac{-\Delta G_1^o}{4{,}575T}}{-\log/\%M/^m - \log/\%I/^n} \geq 1 \qquad (3.10)$$

That is, no inclusion is secreted until the left side of expression (3.10) approaches 1. According to Scheil's differential formula [9], we have:

$$C^L = C^o . (1 - f_S)^{-1+ko} \qquad (3.11)$$

Here: C^L is the concentration of liquid inclusions, /%/
C^o is the average concentration of the initial inclusions, /%/f_S is the % solid phase, /%/ko is the equilibrium coefficient between the solid and liquid phases.

Elements such as S, O have high diffusion coefficients denoted by E, which are established by Scheil as follows;

$$E^L = E^O . (1 - f_S + f_S.k_O) \qquad (3.12)$$

Substituting (3.11) and (3.12) into expression (3.10) establishes the phase separation conditions for the formed inclusions:

$$\frac{\dfrac{-\Delta G^o_{MmIn}}{4{,}575T}}{-\log/ C^o(1-f_s)^{-1+k_o^C} /^m - \log/ E^o.(1-f_s)+f_s.k_o^E /^n} \geq 1 \qquad (3.13)$$

$$\frac{\dfrac{-\Delta G^o_{MmIn}}{4{,}575T}}{-\log/ C^o(1-f_s)^{-1+k_o^C} /^m - \log/ E^o.(1-f_s(1-k_o^E)/^n} \geq 1 \qquad (3.14)$$

To reduce the specific inclusion M_{mIn}, according to the average composition of the elements, the condition of the right side of expression (3.13) must be multiplied by a reduction factor, that is:

$$\frac{\dfrac{-\Delta G^o_{MmIn}}{4{,}575T}}{-\log/ C^o(1-f_s)^{-1+k_o^C} /^m - \log/ E^o.(1-f_s(1-k_o^E)/^n} \geq 1 \cdot Q_{M_m I_n} \qquad (3.15)$$

2. Determination of inclusion phase of metal oxides and sulphides RE [11-14]

The determination of values for different types of inclusions such as oxides and sulphides RE is based on the experiment of To Duy Phuong's scientific group, comparing with the works [10-12] that have specifically established for Ce_2O_3 and Ce_2O_2S, we have: , and according to the work [11], we have 0.36, 0.03.

Therefore, to deduce the Ce_2O_3 phase, it is necessary to:

$$\frac{25{,}86}{-2\log/\ Ce(1-f_S)^{-0{,}64} /-2\log/\ O.(1-0{,}95 f_S)/} \geq Q_{Ce_2O_3} \qquad (3.16)$$

and Ce_2O_2S needs:

$$\frac{24{,}93}{-2\log/ Ce(1-f_S)^{-0{,}64} /-2\log/ O.(1-0{,}95 f_S)/-\log/ S(1-0{,}97 f_S)/} \geq Q_{Ce_2O_2S} \qquad (3.17)$$

Conditions for Ce_2O_3 phase precipitation require:

$$\frac{25{,}86}{-2\log/\ Ce(1-f_S)^{-0{,}64} /-2\log/\ O.(1-0{,}95 f_S)/} \geq Q_{Ce_2O_3} \qquad (3.18)$$

and Ce_2O_2S needs:

$$\frac{24{,}93}{-2\log/ Ce(1-f_S)^{-0{,}64} /-2\log/ O.(1-0{,}95 f_S)/-\log/ S(1-0{,}97 f_S)/} \geq Q_{Ce_2O_2S} \qquad (3.19)$$

The phase depletion coefficient and are established according to the prediction shift in the range from 2.5 to 3.2. The inclusion particle size decreases with the increase in the inclusion phase depletion percentage f_S [24].

Thus, the relations from (3.9) to (3.11) are established based on thermodynamics, microscopic segregation and inclusion crystallization nucleation starting from simplifying the parameters as follows [21]:

1. Let all the activities of the inclusion phase be equal to 1 .

2. Let all the activity coefficients of the inclusion phase be equal to 1 .

3. The free energy of the formation of single inclusions RE can be used for complex inclusions RE(Al,Si).

4. The inclusions are nucleated homogeneously.

5. Elements that form inclusion segregation follow simple segregation formulas.

Because of the simplification of the calculation of the phase loss coefficient, there may be errors, the calculation results are only approximate and qualitative, the deviation coefficient needs to be taken into account. Some deviations may be due to the analyzer, and also due to the heterogeneous distribution of inclusions in the sample. The QTMB quantimeter actually only gives qualitative inclusion particle sizes. Research results from works [13, 14] show that with the increase of RE in steel and alloys, the percentage of solid phase loss of inclusions decreases, but with high RE in steel and alloys, complex inclusions of RE and deformed silicon will appear.

The phase loss factor and is determined to vary between 2.5 and 3.2 (see Figure 2) [15].

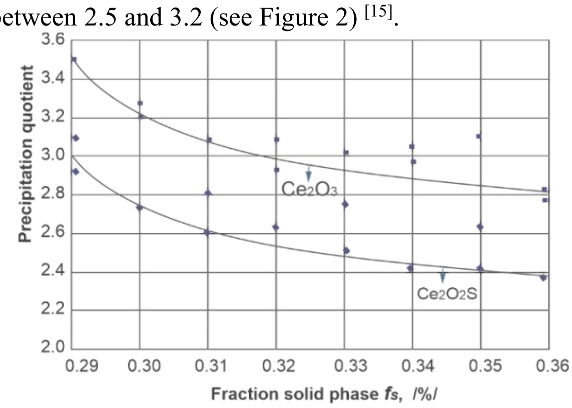


Figure 2. Relationship between the inclusion phase loss factor and the percentage of solid phase lost to inclusions

3.2 Inclusions

(1) Inclusion morphology

Classification of inclusion morphology [16-18] The inclusion morphology process is divided into 4 types according to Sims and Dahl [11]:

Type I: Scattered spherical inclusions, the main component is MnS .

Type II: Eutectic inclusions scattered on grain boundaries, the main component is FeS .

Type III: Scattered polygonal inclusions, the main component is Al_2O_3 .

Type IV: Clustered fine inclusions, the main component is sulfides in the form of MeS or (Me,Fe)S

Type Ib: Fine, uniform spherical inclusions, the main component is RE sulfide oxides in the form of RE_2O_2S

Type Ib inclusions are inclusions with a core of RE sulfide oxides and an outer shell of RES sulfides. These are stable, durable inclusions that do not deform during forging and rolling (see Figure 3) [18].

(2) Formation and Morphological process of inclusions [19-21]

Morphological MnS inclusions in the form of long, thin strips on the entire cross-section of the alloy sample. The morphological classification is not only for oxide inclusions but also for oxides and sulphides, the results established are shown in Figure 4.a. The two-part inclusions; two gray, dark, round, strip-shaped or flat (Figure 4a) inclusions are MnS [15]. These are deformable inclusions and can crack when rolling.

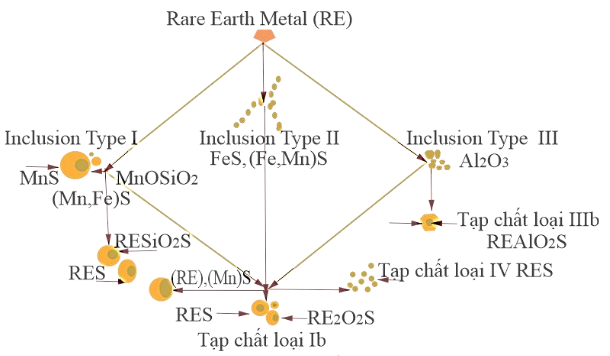


Figure 3. morphological process of rare earth metal inclusions

When transforming low alloy steel with about 0.02%RE, the inclusions RES, $(RE)_2O_2S$, $(RE)AlO_2S$ and $(RE)SiO_2S$ are spherical oxides and sulphides with dark cores surrounded by gray shells. or crack, break when forging, rolling. The $(RE)SiO_2S$ inclusions tend to be larger in grain size than the simple oxides and sulfides.

Inclusions with silicon instead of aluminum are coarser, the deformation is also larger than RE, Al inclusions when the amount of RE in steel is over 0.03%RE (Figure 4.c,d,e).

Inclusions RE_2O_3, $(RE)Al_{11}O_{18}$ and $(RE)AlO_3$ are similar to polygonal Al_2O_3, less deformed, less harmful to the alloy; distributed in a scattered pattern in steel and alloy (Figure 4f,g,h).

Rare earth metals are large surface active substances, which have the effect of increasing the surface tension of the inclusion phase, leading to the formation of round inclusion nuclei and suppressing the growth of these inclusions, making the morphological inclusions mostly in the spherical or near-spherical polygonal state. Many recent research works have explained this problem. This work contributed more favorable results; but clarified more clearly about the strip, flat, spherical and polygonal morphologies [2].

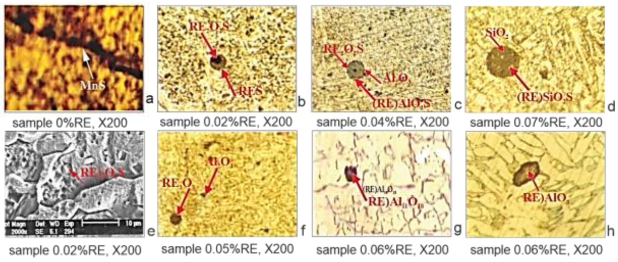


Figure 4. Oxide, sulphite and oxysulphite inclusions RE, Mn, Al, Si in low alloy steel modified with RE with different amounts, x200

(3) Inclusion particle size [19-20]

The inclusion particle size is established and shown in the graph of Figure 5.

Figure 5 shows that the inclusion particle size decreases with increasing f_S inclusion fraction, the sulfite oxide inclusions have larger particle size, while the sulfites and RE oxides have smaller particle size.

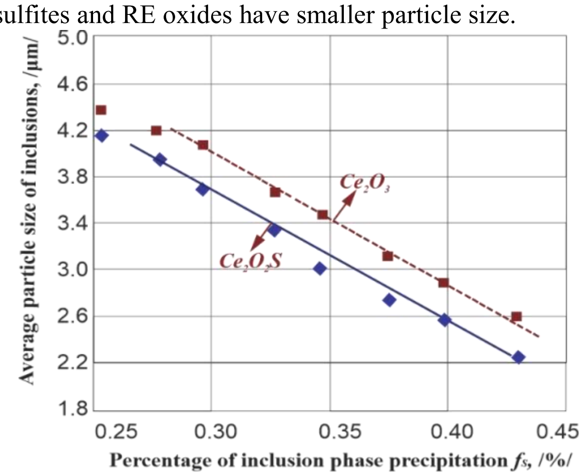


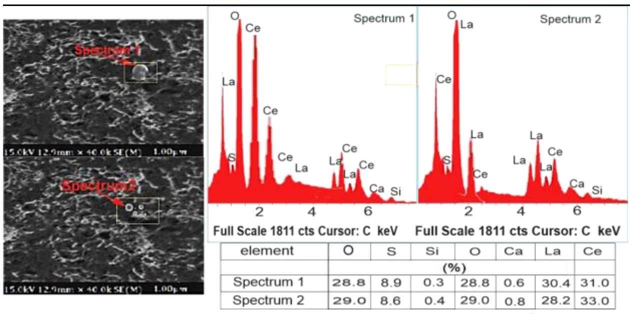
Figure 5, Relationship between inclusion percentage and inclusion particle size [8].

The results of the inclusions obtained are RE_2O_3, $(RE)Al_{11}O_{18}$ or $(RE)AlO_3$, $(RE)_2O_2S$, $(RE)AlO_2S$, and $(RE)SiO_2S$. Inclusions with only RE are spherical, non-deformed inclusions

Single sulfides with large deformations above 4.75μm are harmful to the rolling process; especially cracks and fractures in the direction of rolling the product. Inclusions above 4 μm have a particle count greater than 1.07 particles/mm^2 [22].

RE content in steel and alloys from 0.02 to 0.05% will achieve the least elongation for oxide inclusions (from 2.2 to 3.2 μ m), total elongation per mm^2 (from 90 to 99μm/mm^2) for oxidesulphite inclusions [23].

SEM-EDS analysis of RE-containing inclusions can be seen from Figure 6 that the addition of RE transforms the large-sized inclusions (Spectrum 1)into fine spherical RE inclusions (Spectrum 2).



element	O	S	Si	O	Ca	La	Ce
	(%)						
Spectrum 1	28.8	8.9	0.3	28.8	0.6	30.4	31.0
Spectrum 2	29.0	8.6	0.4	29.0	0.8	28.2	33.0

Figure 6. Morphology and energy spectrum analysis of typical inclusions in low alloy steel.

Due to the higher affinity of RE elements for S and O [23], the free energy of RE inclusions formed is lower than that of other types of inclusions. RE elements added to steel first react with O and S elements to form oxides, sulphites and oxysulphites. RE elements can also be enriched on the surface of the original inclusions and eventually transform into RE inclusions. RE inclusions have a larger contact angle, low wettability and high surface tension in liquid steel, so RE inclusions are mainly spherical in shape [24].

The inclusions in Spectrum 1 are mainly oxides, their shape is irregular and the size is approximately 4 µm, as shown in spectrum 1. After adding 0.01% RE, the inclusions in spectrum 2 are complete RE_2O_2S, their shape changes to spherical and the size is reduced to ~2 µm, as shown in spectrum 2. When the RE content is up to 0.025%, the inclusions are still RE_2O_2S, finer and spherical, distributed dispersedly. However, when the RE content is increased to 0.04%, the size of RE_2O_2S inclusions increases to 5 µm due to the agglomeration of RE2O2S inclusions and their shape becomes irregular again, as can be seen in spectrum 2. In spectrum 2, the inclusions in steel are mainly RE_2O_2S in the dark core and RES surrounding the fine spherical particles.

(4) Inclusion amount [1,5,23,24]

The amount of inclusions per 1 mm2 was determined on the Quantimet QTMB machine. The size of the inclusion particles was measured on a surface of about 50 mm^2 for each sample for each type of oxide and sulfide inclusion. The measurement results showed that in samples with inclusions larger than 4 µm (measured surface in the rolling direction). The important thing to recognize here is that single sulfides with large deformations above 4.75 µm are harmful to the rolling process; especially cracking and breaking in the rolling direction of the product. Inclusions above 4 µm have a particle count larger than 1.07 particles/mm^2) [24]. The amount of RE in steel and alloys from 0.02 to 0.05% will achieve the least elongation for RE oxide inclusions (from 2.2 to 3.2 µm), total elongation per mm2 (from 90 to 99 µm/mm^2) for RE oxide sulphides, The results of this work are close to the results published in the work of Malm [1,26].

Thus, RE, Al_2O_3 oxides and RE oxide sulphides are spherical, polygonal and undeformed morphologies while Mn sulphides and RE+Si oxide sulphides are coarse, large-grained and deformed morphologies.

RE is a substance with high surface activity and high surface tension [1]. Figure 7 can show that the percentage of surface containing inclusions is significantly reduced after RE modification with nitrogen gas stirring.

The results of determining the amount of inclusions in steel and alloys showed that the amount of inclusions per 1 cm^2 and the percentage of surface containing inclusions decreased after RE refining. Some samples showed a slight increase in the amount of inclusions after RE addition, which could be explained by the fact that RE dissolved the coarse, large inclusions in steel and alloys and created more small, fine inclusions, although the percentage of surface containing inclusions per 1 cm^2 was lower. This is a characteristic of the steel modification process using RE.

The surface percentage containing inclusions decreased significantly after RE refining with nitrogen agitation (except for sample 07.2, it increased to 0.0585% surface). The amount of inclusions in steel and alloys decreased to the lowest of 0.0268% surface (sample 08.2) after refining with 0.1 kg/t mishmetalRE and 13.90 minutes of N_2 agitation, and with CaSi, the amount of inclusions decreased to the lowest of 0.0411% surface (sample 02.2) [1,5].

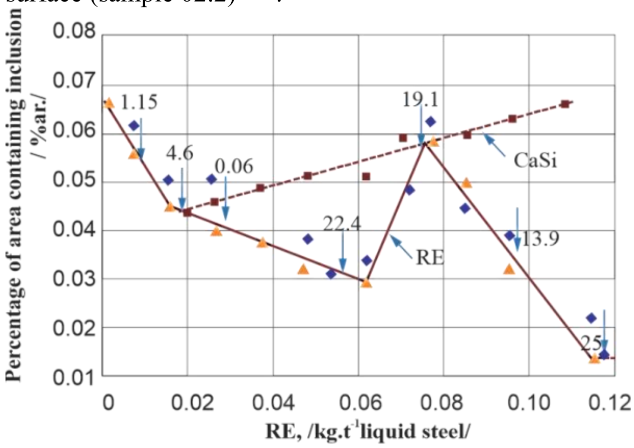


Figure 7. Relationship between RE content and surface percentage containing inclusions in steel and low alloys

The transformation of the amount of inclusions after RE refining are shown in the phase diagram of Figure 8.

Figure 8 shows that after refining RE, the form of inclusions has changed; removing and reducing the amount of silicate inclusions in samples 05.10.1. Here it can be explained that in the initial smelting batch, the amount of oxygen in the inclusions was not known, so it could be higher and the oxidation process of inclusions was not complete, so the oxide inclusions existed in the steel and alloy. Sample 05.2 (0.03 kg/tRE) although not stirred with nitrogen, still had a reduction in the amount of inclusions to 0.0395% of the surface, here it is explained that because the process of strongly discharging RE into the alloy caused the stirring like stirring with gas [27,29].

The important thing to recognize here is that RE has transformed and reduced the amount of silicate and formed aluminates with higher temperature stability.

The results in Figure 8 show that similar to the experimental results, the amount of inclusions in sample 08.2 has the lowest amount of inclusions at the Al_2O_3 peak.

(1) The amount of inclusions in steel and alloys is reduced to the lowest 0.0268% of the surface after refining 0.1 kg/t mishmetalRE compared to CaSi, the lowest amount is 0.0411% of the surface.

(2) After refining RE has changed the form of inclusions; removed and reduced the amount of silicate inclusions in steel and alloys to about 50%, while CaSi is only about 8.8%.

(3) RE has acted to form aluminates in steel and alloys, increasing stability at high temperatures

(4) RE has significantly increased the cleanliness and quality of steel and alloys.

3.3. Inclusion deformation process

The deformation of inclusions in steel and alloys after forging and rolling is the cause of harmful defects and even scrap steel and alloys. Dangerous harmful inclusions are cracks and flaking on the working surface of steel and alloys. Inclusions causing cracks and flaking depend on the morphogical form of the inclusion before deformation as shown in Figure 9 [22,23].

When the aluminum content in steel and alloys is below 0.005%, complex type I oxide sulfide inclusions are formed (Figure 9, a1.). These inclusions contain the elements O, S, Al, Mn and Si. These inclusions do not deform or deform slightly after forging and rolling (Figure 9, a2), but are stable at low temperatures, and therefore this type of inclusion is not required in rolled steel and alloys (tubes). In some cases, when rolling tubes, these inclusions will deform and form ripples [28].

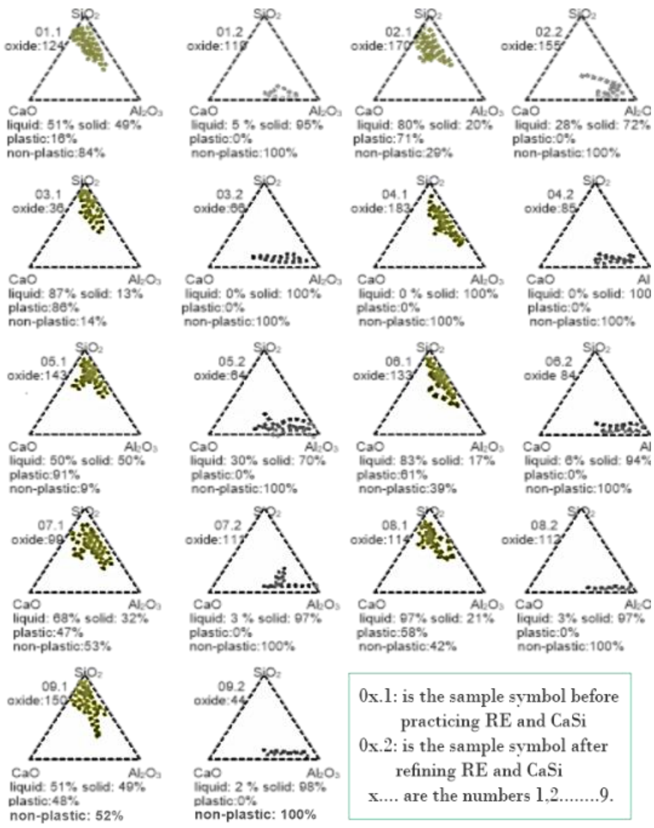


Figure 8. Phase diagram of the SiO2-CaO-Al_2O_3 system

With aluminum content in steel and alloys from 0.005 to 0.02%, typical inclusions exist in the form of eutectic sulfide, band on the grain boundary of type II (Figure 9, b1). These inclusions strongly deform after rolling (Figure 9, b2), reducing the mechanical properties of the alloy, often leading to waste products such as cracks, breaks, and broken rolled products.

When the aluminum content in steel and alloy is about 0.02 to 0.05%, the inclusions formed are polyhedral type III (Figure 9, c1), this is the type of inclusion that is stable at high temperatures and has little deformation after rolling (Figure 9, c2), but is coarser than type I.

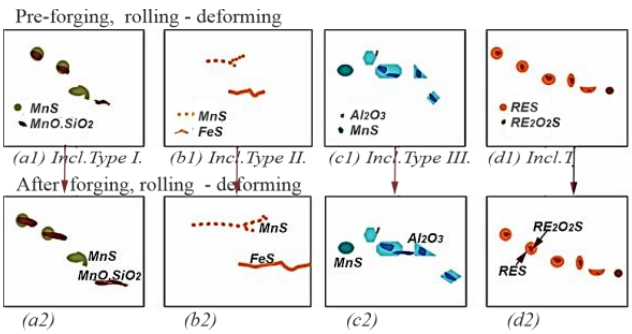


Figure 9. Typical types of deformation of inclusions in steel and alloys.

From Figure 9, it can be seen that when RE is added to the alloy at about 0.01 to 0.02%, the remaining inclusions are in the form of small, smooth spheres, with the core being RE_2O_2S sulfide oxides surrounded by RES.

These are non-deformed inclusions after rolling (Figure 9, d2). This is the optimal inclusion after RE modification [1].

Elongation of inclusions in steel and alloys [23,25]

During the rolling of steel and alloys, most inclusions will deform along the rolling direction. Elongation of inclusions exceeding the specified level will cause defects in the rolled product. Silicate inclusions are stable at low temperatures and deform during rolling and mechanical and thermal processing. Inclusions transformed to Al_2O_3 will increase stability at high temperatures. After RE refining, the amount of silicate inclusions can be reduced by up to 50% as in samples 04.2 and 05.2 compared to CaSi modification (sample 01.2 is only 4.4% and sample 02.2 is only up to 8.8%) [1].

The elongation (oval) of inclusions was determined on the JEOL 35CF and EDX-Link860/II machines. The ovality was determined by the ratio of the length (l) to the width (d) of the inclusions. The highest ratio was 1 for the rolled state. To determine the elongation of inclusions, each sample was scanned at 200 points with a surface of about 5 to 9 mm^2.

The experimental results from the work of To Duy Phuong [1] show that the sulfides have a stronger elongation than the oxides after rolling. Here it can be explained that the elongation of inclusions is determined by the ratio l/d, which means that these inclusions are initially bean-shaped as shown in Figure 9.d1. Here the length of the inclusions is 2 times larger than the width, so the elongation in the rolling direction is very small.

The lowest elongation strain of the sulfides after rolling was 4.89 (sample 08.2). The lowest elongation strain of the polygonal and very spherical oxides after rolling was 1.56 (sample 09.2).

These results can be supplemented with the recently published works [1,24,25].

1. The optimal RE content for modification in terms of inclusion fineness is from 0.05 to 0.1 kg/t.

2. The lowest sulfide content with fineness from 4 to 10 μm is 0.0022% surface, when the RE content is 0.2 kg/t and the highest sulfide content is about 0.0145% surface with the RE content is 0.07 kg/t.

3. The amount of sulfide with fineness > 10 μm is negligible, about 0.0006% of the surface when the RE modification amount is 0.2 kg/t

4. The lowest elongation – oval deformation of sulfide inclusions after rolling is about 4.89 when the RE modification amount is 0.1 kg/t.

5. Polygonal and spherical oxides are very little deformed after rolling and the lowest elongation – oval deformation after rolling is 1.56 when the RE modification amount is 0.2 kg/t.

Conclusion

- The free energy of the formation of single RE inclusions can be used for complex RE inclusions (Al, Si)… The inclusions are nucleated homogeneously.

- With increasing RE content in steel and alloys, the percentage of solid phase inclusions is reduced, but with high RE content in steel and alloys, complex inclusions of RE and deformed silicon will appear.

The phase removal coefficient $Q_{Ce_2O_3}$ and $Q_{Ce_2O_2S}$ is established to shift between 2.5 and 3.2

- The addition of RE significantly slows down the phase precipitation process of inclusions by reducing the grain boundary energy and carbon diffusion rate.

-Four different types of RE inclusions in terms of proportion have been studied and discovered in low alloy steel products: RES, RE2O2S, REO2, REAlO2S, RESiO2S

-After adding RE to steel, the main evolution of inclusions will take place from type II scattered on grain boundaries to type I spherical, increasing RE addition will convert type III polyhedral Al2O3 to type IIIb which is durable at high temperatures, but when increased too much, it will convert type IV small spherical aggregates RES when the optimal amount of RE added will transform inclusions to type Ib spherical with oxide sulphite center RE_2O_2S covered with RES, and when the amount of RE is too much (~0.06 wt.%RE) will convert brittle inclusions $(RE)Al_{11}O_{18}$.

RE_2O_2S covered with RES. These are non-deformable inclusions after forging and rolling. This is the optimal inclusion after being modified by RE.

-The amount of RE in steel and alloys from 0.02 to 0.05% will achieve the least elongation for oxide inclusions (from 2.2 to 3.2µm), total elongation per mm^2 (from 90 to 99$\mu m/mm^2$) for oxidesulphite inclusions.

-The amount of inclusions in steel and alloys is reduced to a minimum of 0.0268% of the surface after refining 0.1 kg/t mishmetalRE compared to CaSi, the lowest reduction is 0.0411% of the surface.

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