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Design, Selection and Application of High Efficient Complex Alloys

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Abstract: The design, selection and application principles of complex alloys according to the requirements of making low-alloy steels are discussed. The designed complex alloys containing calcium, barium, magnesium, strontium, rare earth elements, etc. should not only be able to deoxidize, desulphurize and refine liquid steel, but also alloy it. The application principles of alloys are as follows: using Si-Mn or Si-Mn-Al alloys for pre-deoxidizing, Si-Al-Ba or Si-Al-Ca-Ba alloys for final deoxidizing and Si-Ca-Ba-Mg(Sr) alloys for refining.

Key words: deoxidization; desulphurization; inclusion; complex alloy

For steelmaking, the most important thing is to select high efficient alloys to deoxidize, desulphurize and refine liquid steel when oxygen blowing finishes. High efficient alloys can not only deoxidize, desulphurize and refine liquid steel, but also alloy it to reduce the amount of deoxidization products, control their shape and modify them. Currently, many new developed complex alloys containing magnesium, alkaline earth and rare earth metals are good deoxidizing, desulphurizing and refining reagents.

The development and application of all kinds of refining equipment bring high efficiency during alloying for complex alloys. If complex alloys consisting of calcium, barium, magnesium, strontium and rhenium are combined with refining process, the efficiency and function of the complex alloys will be evidently improved.

1 Design and Selection Principles of alloys

Low-alloy steel mainly belongs to killed steel. When designing and selecting alloys to refine the steel, silicon and aluminum should be the main constituents to control dissolved oxygen in steel to the allowed level. At the same time, the amount of silica and alumina in liquid metal should be controlled and attention should be paid to modify them.

1.1 Design principles of alloys

(1) Ferroalloys with low Si or without Si, and also with low Al or without Al should be designed and developed according to the urgent requirement while some other elements with high deoxidizing effect should be added into these ferroalloys instead of silicon and aluminum to deoxidize, desulphurize and clean liquid steel.

(2) The ferroalloys should have superior ability to deoxidize, desulphurize and degasify the liquid steel. They should also have the ability to control the amount of deoxidization and desulphurization products and modify the inclusions formed.

Therefore, calcium, barium, magnesium, strontium and rhenium are used for making ferroalloys. Calcium and barium have excellent deoxidizing and desulphurizing ability and excellent function to modify inclusions. Magnesium is both strong deoxidizer and desulphurizer. Strontium makes the sulfide into spherical shape both in cast and in rolled metal. Rhenium has high desulphurizing ability.

(3) To ensure the removal of non-metallic inclusions from steel, the melting points and the densities of the deoxidization products, the interphase tension between inclusions and metal, the liquid metal's wettablity and permeation to inclusions should be considered. The complex alloys with calcium, barium, magnesium etc. can control the physical properties of inclusions and adjust the components of steel when needed.

(4) When some specific elements are needed to produce special steels, V, Ti, Zr, Ni, Cr, Mn, Mg or other elements are added into the Si-Ca-Ba based alloy to form a complex alloy so as to increase the recovery ratio of the elements.

1.2 Selection of alloys

The amount of oxygen and sulfur in low-alloy steels is commonly required to be low. The total content of di-

ssolved oxygen and sulfur should be less than 50×10^{-6}. Therefore, the fundamental rules of deoxidizing liquid steel are as follows:

(1) Pre-deoxidization stage: the dissolved oxygen content should be controlled to be less than 150×10^{-6} at this stage.

Traditionally, ferromanganese is firstly added to deoxidize and then ferrosilicon is added. The deoxidizing ability of ferromanganese is weak. For example, when dissolved manganese content is 0.5%, the equilibrium dissolved oxygen content is only 0.070% at 1 873 K. When ferrosilicon is used, the shape of silica should be controlled because solid silica is so small in size that it is difficult to be removed. When the dissolved silicon content is 0.4%, the equilibrium dissolved oxygen content can be reduced to 0.008% at 1 873 K. Its deoxidizing ability is only slightly less than that of carbon.

Complex Si-Mn or Si-Mn-Al alloys are very nice in pre-deoxidization. The deoxidization product of Si–Mn alloy belongs to FeO-MnO-SiO_2 system, which is large in size, low in melting point and easy to float out from steel. When the contents of dissolved silicon and manganese are 0.15% and 0.4% respectively, the equilibrium dissolved oxygen content is 0.02%–0.025%. The ratio of dissolved Si/Mn can be adjusted differently to control the amount of dissolved oxygen according to the steel grade made. The deoxidization product of Si-Mn-Al alloy is FeO-SiO_2-MnO-Al_2O_3 system. When dissolved silicon and manganese contents are kept constant,oxygen activity in liquid metal changes with the change of dissolved aluminum content.

As a result, it is better to use Si-Mn or Si-Mn-Al alloys to deoxidize than ferromanganese or ferrosilicon at pre-deoxidization stage.

(2) Final deoxidization stage: the dissolved oxygen content should be less than 50×10^{-6} at this stage.

The equilibrium oxygen contents of normal deoxidizing elements at 1 873 K are obtained through thermodynamic calculation as follows: Mn, 0.175%; Si, 0.020%; Al, 0.001%; C, 0.020%. It shows that aluminum has the strongest deoxidizing ability and silicon is next to it. The deoxidization level of steel depends mainly on aluminum, and secondly on silicon. For commonly used Si-Al alloys, the deoxidization product is SiO_2-Al_2O_3-$3Al_2O_3\cdot2SiO_2$. Si-Al deoxidizers are effective only when the deoxidizing product is $3Al_2O_3\cdot2SiO_2$. Otherwise the deoxidization products are solid SiO_2 and solid Al_2O_3, the same as the products when silicon and aluminum are used alone.

In order to control the amount of deoxidizing products such as SiO_2 and Al_2O_3 and to modify Al_2O_3 inclusions, Si-Al-Ba alloy is used [1, 2]. Because some silicon and aluminum are replaced by barium, the amount of SiO_2 and Al_2O_3 generated in liquid steel is reduced. The amount of SiO_2 inclusions decreased 26.3%, and that of total inclusions 59.4% [2]. At the same time, Al_2O_3 inclusions are modified and inclusion particles are easy to float out from steel.

For some steel grades such as tube or plate, which require calcium treatment, it is better to use Si-Al-Ca, Si-Ba-Al or Si-Al-Ca-Ba alloys. When the dissolved sulfur content in steel needs to be strictly controlled, Mn-Mg-Al alloy is the best deoxidizer at this stage.

(3) Refining stage: liquid steel is deeply deoxidized, desulphurized and inclusions are separated from it at this stage.

Si-Ca alloy has been widely used at this stage. When the Ca/Al ratio in liquid steel is no less than 0.09, alumina inclusions can expectably be modified into calcium aluminate phases. Moreover, with the increasing of Ca/Al ratio in liquid steel, the Ca/Al ratio in calcium aluminate inclusions linearly increases [3].

Deoxidation experiments were done to compare alloy Si-Ca, Al, RE with alloy Ca-Al-Mg-Si-Ba when making 8WRH6ZA steel. The result showed that the steel deoxidized by alloy Ca-Al-Mg-Si-Ba can reach higher cleanliness than that by Si-Ca, Al or RE. The variations of total oxygen content of steel after deoxidization are shown in **figure 1** [4] when different alloys are used to deoxidize.

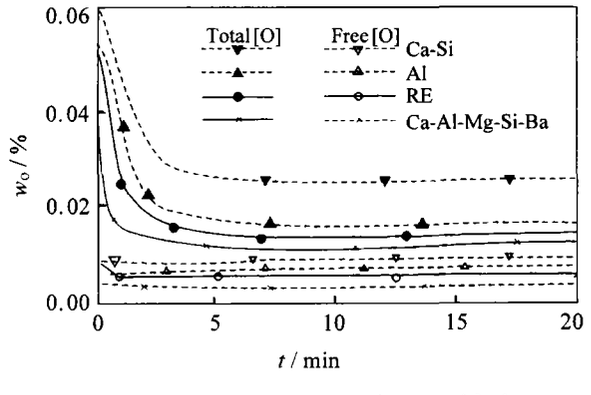

Figure 1 Total oxygen content change with time.

Newly designed Si-Ca-Ba-Mg wire was fed to refine SS400. Compared with Si-Ca wire, it had better deoxidizing and desulphurizing abilities, and the total inclusion amount reduced 37.1%. The amount of both aluminate and sulfide inclusions decreased, and that of spherical or elliptoid inclusions increased [5].

Si-Ca-Ba-Mg-(RE, Sr) alloy can be selected when limited content of dissolved aluminum in steel is requi-

red. Otherwise Ca-Al-Mg-Si-Ba-(RE, Sr) alloy can be used. Both are the best alloys to deeply deoxidize and desulphurize liquid steel and modify the shapes of inclusions so as to be easily removed.

2 Behavior of Complex Alloys with Alkaline-earth Metals

Physical and chemical properties of alkaline-earth metals are shown in **table 1**. In order to improve the deoxidizing and desulphurizing abilities of calcium and magnesium and improve the modification of inclusions, barium must be incorporated to the alloys. Calcium, barium and magnesium can dissolve with each other. Barium can reduce the vapor pressure of calcium and magnesium so as to reduce their oxidizing and evaporating losses and improve their yield. As a result, reaction time of alloys containing calcium, magnesium and barium is extended and their deoxidizing and desulphurizing abilities are improved.

Table 1 Physical and chemical properties of Ca, Ba, Mg and Sr

Element	r / nm	T_m / K	T_b / K	H_b / kJ·kg^{-1}	P_{1873K} / MPa	γ_{1873K} / %
Mg	0.162	923	1 380	357	1.952	0.106
Ca	0.197	1 125	1 125	216	0.185	0.032
Sr	0.215	1 043	1 043	960	0.367	0.026
Ba	0.220	983	1 913	129	0.034	0.020

Note: r—atom radius; T_m—melting point; T_b—boiling point; H_b—melting heat; P_{1873K}—vapour pressure; γ_{1873K}—solubility in liquid iron.

Calcium, barium, magnesium and strontium have a high affinity for oxygen and sulfur. And calcium, barium and magnesium have very high deoxidizing and desulphurizing ability. When the partial pressure of calcium, barium and magnesium are kept appropriate, the amount of oxygen and sulfur can be reduced to a very low level. Calcium is the most effective deoxidizing and desulphurizing alkaline-earth metal. If calcium, barium and magnesium dissolve with each other at high temperature, the amount of oxygen and sulfur can be reduced to even lower level.

Calcium, barium, magnesium and strontium have a high affinity for silicon and aluminum and they can dissolve with each other at high temperature, so their solubilities in liquid steel are greatly improved. The influence of aluminum, nickel and silicon on the solubility of calcium at 1 600 ℃ is shown in **figure 2** [6]. Therefore, the deoxidizing and desulphurizing abilities of each element are higher when it is used as alloy than when it is used alone. For example, in the alloy containing barium, deoxidizing ability of silicon is as high as that of aluminum and deoxidizing ability of barium is two exponents higher than that of aluminum [7].

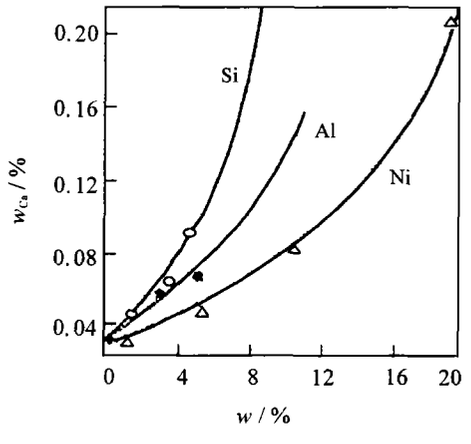

Figure 2 Effect of Si, Al, Ni on the solubility of calcium at 1 600 ℃.

Calcium, barium and magnesium are so active that they will form $\{Ca, Ba, Mg\}_{(g)}$ bubbles or bubbles of each element own. The bubbles contact with liquid steel and react with it at the gas-liquid interface. The rates and extents of gas-liquid reactions are dependent on the floating up rates or diffusing rates of the bubbles. In order to increase the reaction extent of the bubbles with impurities in steel and improve kinetic conditions, it is better to stir with argon in the refining equipment such as in ladle furnace. Calcium, barium and magnesium must be added into steel in form of alloys. Hence, manganese, titanium, vanadium, zirconium, strontium and magnesium should be added to Si-Ca-Ba based alloys to form all kinds of high quality complex alloys needed by each steel grade.

3 Effect of Alloys

Deoxidization practice and refining method of each kind of steel are different according to the steel grade made. They will be discussed below.

Piping steel (such as 20 g): piping steel is a kind of low carbon (w_C = 0.18%–0.22%) and high quality steel. Because the steel containing 0.18%–0.22% carbon has low intensity and high contraction ratio at the temperature 1 450 ℃ near solid curve, the billet is liable to crack at the surface or inside crystal interfaces. This steel demands strict control of oxygen. The amount of

aluminum added needs to be strictly controlled. When the amount of aluminum added is too less, it is liable to produce pinholes and crack at the surface of the billet. On the other hand, when the amount of aluminum added is too much, it is liable to bring reoxidization and then the amount of alumina inclusions increases. As a result, it is easy to form nozzle clogging. Therefore, it is necessary to reduce oxygen content before aluminum is added to control the amount of aluminum added (less than 0.5–0.7 kg/t) at the final deoxidizing stage and to control sulfur content to no more than 0.005%. In order to meet these requirements, Si-Ca-Ba or Si-Al-Ca-Ba alloys can be selected, which can not only reduce the amount of aluminum added, but also improve the deoxidizing and desulphurizing abilities and modification function. Experiments were done in Anyang Steel Works in Henan province. The results show that the deoxidizing and desulphurizing ratios increase 30%–50%, 20%–25% respectively. The total amount of inclusions reduces 35%–45% and the amount of oxide inclusions decreases by one third. The plasticity of the steel is improved and the surface defects of the semifinished pipe and the finished products are reduced.

Deep drawing steel: it is a kind of low carbon aluminum-stabilized steel ($w_C \leqslant 0.04\%$, $w_{Si} \leqslant 0.06\%$). The dissolved carbon and sulfur contents require to be low in order to ensure good deep drawing property and flatness. In order to attain good extension ability, the cleanliness of the steel needs to be high enough to ensure that the sizes of inclusions are less than 2.5 μm and the sizes of metallic crystal grains are minute. This steel grade is mainly deoxidized by aluminum. Ca-Al-Mg-Si-Ba alloys with less silicon can be used to make aluminum well distributed in liquid steel and so as to reduce the loss amount of aluminum due to oxidation and control the amount of alumina inclusions. Under the condition that aluminum is the main deoxidizing element, the added elements such as calcium, barium and magnesium can not only improve deoxidizing and desulphurizing abilities, but also modify the alumina inclusions. If refining process is combined, better effects can be attained.

High carbon and high quality killed steel: such as rail steel and wire steel.

Rail steel: there is a strict limit on chain-type alumina inclusions. Si-Ca-V and Si-Ca-Ba-V alloys that contain calcium and barium can improve the morphotype and distribution of oxide inclusions. They were used at Anshan Steel to deoxidize heavy rail steel. The results show that the length of chain-type inclusions is reduced by 25%–28%. Chain-type alumina inclusions are turned to be spherical.

High carbon wire steel: the amount of aluminum added should be strictly controlled. Si-Ca-Ba-Mg alloy that contains low aluminum can be used. If combined with refining process, it becomes more effective.

4 Conclusions

(1) The designed complex alloys containing calcium, barium, magnesium, strontium, rare earth elements, etc. can not only deoxidize, desulphurize, refine and alloy liquid steel, but also modify the inclusions in liquid steel.

(2) The application of alloys is as follows: using Si-Mn or Si-Mn-Al alloys for pre-deoxidizing, Si-Al-Ba or Si-Al-Ca-Ba alloys for final deoxidizing and Si-Ca-Ba-Mg (Sr) alloys for refining.

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