



NON-METALLIC INCLUSIONS IN STEEL PROCESSED WITH MODIFIERS

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Annotation

At present, rare earth metals (REM) are widely used in steel production, which have a high affinity for oxygen, sulfur, nitrogen, non-ferrous metals and other impurities. The effect of rare-earth metals is manifested both in a decrease in the content of these impurities in steel and in their transfer from active forms to passive ones, which contributes to the purification of grain boundaries and ensures the formation of a finely dispersed dendritic structure. Purifying steel from harmful impurities, REMs improve its casting properties, fluidity, feeding conditions and crack resistance of castings, and also reduce the anisotropy of the mechanical characteristics of steel. The high efficiency of the influence of REM on the properties of steel is due to their favorable effect on the composition, type, shape, quantity and uniformity of the distribution of the resulting non-metallic inclusions (NI), a significant improvement in the macro- and microstructure of the workpiece, a decrease in its physical and chemical heterogeneity, providing increased density and dispersion of crystalline structures in all areas of the cast billet, including small sections.





Keywords Rare earth metals, oxygen, sulfur, nitrogen, non-ferrous metals, non-metallic inclusions

Introduction

Studies of free energy for various REM compounds make it possible to make some assumptions about the interaction of REM with oxygen and sulfur. Most of the results agree with the theoretical premises, while others do not, and finally, it is sometimes difficult to explain the detected inclusions on the basis of thermodynamic parameters. For the effective use of REM, it is necessary to have a clearer understanding of the conditions for the formation of certain compounds, the types of REM inclusions and the sequence of their formation.

Rare earth elements (REM, or R) - cerium, lanthanum, neodymium and others have a high affinity for oxygen (greater than that of aluminum) and sulfur; form refractory oxides and sulfides: Ce_2O_3 , CeO_2 , CeS , Ce_3S_4 , Ce_2S_3 . REM is introduced into steel in the form of mischmetal, which contains approximately 50% Ce, or in the form of ferrocerium.

Thermodynamic analysis of the interaction of REM with oxygen and sulfur in steel showed that the formation of oxides, oxysulfides and sulfides depends on the ratio $[O]/[S]$. If this ratio is about unity, an oxide is formed R_2O_3 ; at $[O]/[S] < 0,1$ possible release of oxysulfides R_2O_2S ; only less oxidized ($[O] < 0,01[S]$) sulfide formation is possible R_2S_3 , then R_3S_4 and RS .

In order to save expensive rare-earth metals and reduce the number of non-metallic inclusions, steel is preliminarily deoxidized and reduced $[S] < 0,015\%$.

REMs interact not only with dissolved oxygen, but also with Al_2O_3 oxides, reducing them or forming complex oxides. Detailed studies of the change in the nature of inclusions with an increase in REM additions have shown that already at 0.01% residual REM content in the metal melt, alumina reduction begins, forming oxides of the type $RA_{11}O_{18}$. With an increase in the addition of REM, the amount of Al_2O_3 , formed $(R, Al)_2O_3$. When the REM content is $> 0.02\%$, oxysulfides appear R_2O_2S , surrounded by a shell of sulfide R_xS_y . In steel with $REM > 0.03\%$ alumina is absent, globular two-phase oxysulfides are formed $R_2O_2S \cdot RS$ and sulfides RS . However, some researchers believe that with the addition of 0.06% REM, the steel content Al_2O_3 makes up approximately 10% of the total amount of oxide non-metallic inclusions, and only at 0.12% REM, aluminum oxide is practically absent.

Many works indicate that in steel with a small amount of REM ($[R]/[S] < 3$) complex sulfides are formed $(Mn, Ce)S$ or $(Ce, Mn)S$. Already at a low content of cerium in MnS sulfide, the deformability of the steel decreases significantly; along with single-phase



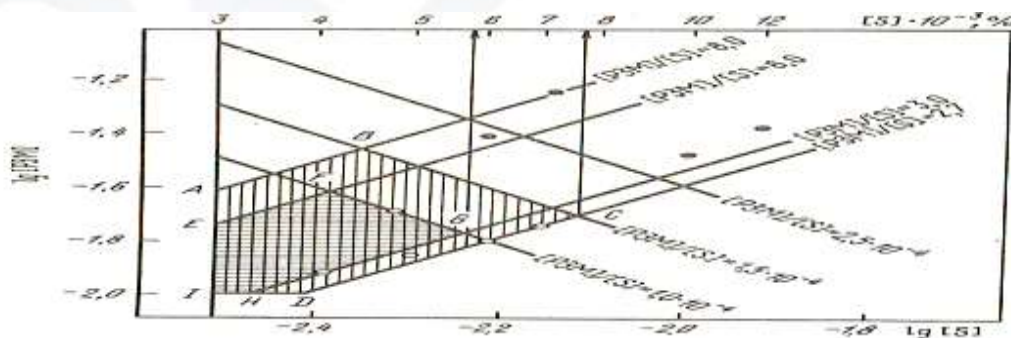


complex sulfides, two-phase sulfides are formed: MnS sulfide with a light shell of cerium sulfide. When the value of $[R]/[S]>3$, alumina crystals are not observed, aluminum is not detected in oxysulfides either; manganese is absent in sulfides, that is, complex sulfides are not formed.

Most researchers argue that REMs are steel desulfurizers, and that their addition leads to a significant decrease in the sulfur content. Other researchers believe that sulfur and REM are stored for a long time in liquid steel after the introduction of REM. This may be due to rare-earth sulfides that did not have time to float up; flocculent accumulations of inclusions in the surface zone of the ingots can serve as evidence of this; however, apparently, a significant part of the introduced REM remains for some time in liquid steel in a dissolved state.

In steel ingots with REM, there is often a significant inhomogeneity in the distribution of sulfur and REM along the height: a small content in the upper part and a very high content in the lower, in the deposition cone. The appearance of a sedimentation cone depends on the sulfur content and the amount of REM introduced, namely, on the value of the $[R]/[S]$ ratio. Many studies have shown that at $[R]/[S]>3$, MnS sulfides and Al_2O_3 oxides are not formed in steel. All the resulting inclusions are globular sulfides and oxysulfides of REM, uniformly distributed over the cross section of the ingot. However, if this ratio becomes > 6 , a significant chemical inhomogeneity is created in the ingot: a deposition cone with a large accumulation of non-metallic inclusions - oxides and oxysulfides of rare-earth metals is formed in the lower part. Flaky accumulations of REM-containing inclusions in the surface layer of an ingot and a continuously cast billet are also observed when small amounts of REM are added. This inhomogeneity in the distribution of inclusions leads to a significant reduction in the properties of the cast steel.

Some works show that the condition $[R]/[S]=3...6$ is necessary but not sufficient for uniform distribution of REM sulfides in the ingot; for this it is also necessary that $[R] \cdot [S] \leq (1,0 \dots 1,5) \cdot 10^{-4}$. These two conditions are graphically represented in Figure 1.

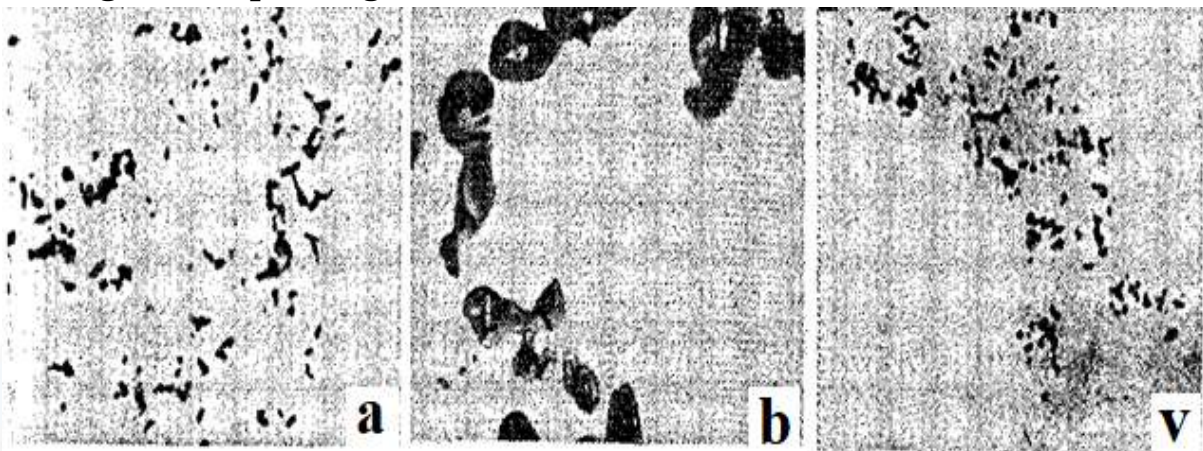


Picture 1 - "Zone of REM" for low carbon steel



As can be seen from Figure 1, these conditions determine the range of steel compositions for REM and sulfur, in the ingot of which no cone of precipitation of inclusions is formed, and globular sulfides and oxysulfides of REM are evenly distributed over the entire cross section of the ingot. However, this area is defined for steels with a low sulfur content, $<0.01\%$. In the case of high sulfur contents, the sedimentation cone, apparently, also forms at the ratio $[R]/[S] < 3$.

A large accumulation of sulfides and oxysulfides of rare-earth metals in the cone of sedimentation was observed by many researchers. These inclusions are oval and of various irregular shapes (Figure 2).



Picture 2 - The shape of non-metallic inclusions (NI) in the ingot deposition cone:

a – $\times 100$ и b – $\times 600$ not etched; v – $\times 200$ etched with sodium picrate

As can be seen from Figure 2, often NI are combined into branched formations (Figure 2, a). At high magnification, it can be seen that the inclusions are, as a rule, two-phase: they consist of a gray core and a dark or orange (with increased REM additions) shell (Figure 2, b). It is very important that the accumulations of inclusions in the sedimentation cone are located between the branches of the austenite dendrites. At low magnifications, this is clearly visible both on unetched sections and clearly after etching with sodium picrate (Figure 2, v).

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