Thermodynamic analysis of X80 pipeline steel after calcium treatment

Pengbiao Wang[1, a], Qichun Peng[1, b] and Jinling Yang[1,b]

[1] Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan 430081, China;

[a]wangpengbiao@outlook.com, [b]pengqichun1964@163.com

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Abstract. Based on thermodynamic calculation, analysis the inclusions and thermodynamics of X80 before and after calcium treatment on the sample of a steel production. Results show that the effect of Al_2O_3 inclusions degeneration is good and S would exist in a dissolved state so that avoids the CaS inclusion precipitation when the ω[Als] is 0.04%, ω[O] is adjusted to $0.7\times10^{-4}\%\sim18\times10^{-4}\%$, ω[Ca] is adjusted to $6\times10^{-4}\%\sim24\times10^{-4}\%$, in the meanwhile control of ω[S] below 0.009% at 1873K; Al_2O_3 inclusions in steel is effectively modified into calcium aluminate, the number and the size of inclusions were reduced, most of them below 5μm, and the shape more regular.

1. Introduction

X80 as high-level pipeline is used in complex geographical environment, climatic conditions and low cold corrosive with oil and gas, and it called for that the steel has high strength and high toughness, with anti-corrosive hydrogen induced cracking (SCC and HIC) and has good weldability, etc. [1] Calcium teratment is putting calcium lines in the liquid steel,we use calcium deoxidation than aluminum deoxidation ability of this feature,make the Al_2O_3 inclusions which is hige melting point denaturation, control the inclusion morphology and composition within the proper range,ultimately make it into low melting calcium-aluminate mixture,in order to improve casting nozzle clogging phenomenon and lower smelting cost[2,3]. In this paper, we analysis X80 inclusion morphology before and after calcium treatment,explore the inclusion of transgender characters,and evaluate the effect of calcium treatment,so that we can provide a reference for future production.

2. Experimental methods

Experiments is done in a steel site,we produce X80 through KR-BOF-Ar-LF-RH-CC process. Feed calcium line during the refining process, keep smoke micro positive pressure in the process, [Ca]/[Als] is controlled between 0.10~0.12, and argon gas flow is controlled at 500 L/min.We take samples before and after calcium treatment,process the samples into15mm×15mm×10mm metallographic specimen. After coarse grinding, fine grinding, polishing, we use an optical microscope at 100 times 20 consecutive field to observe the inclusions in steel, count the number and size of inclusions.The inclusions in metallographic sample composition analyzed by scanning electron microscopy (SEM) and energy disperses spectroscopy (EDS).Finally, we do thermodynamic calculations according to the key element of the content of calcium treatment.

3. Thermodynamic analysis

3.1 The basic data thermodynamic calculation

Results of experiments of chemical composition is seen in table 1,we search the elements interaction coefficient in the steel by literature[4], According to the literature [5], we use formulas to calculate the main elements activity coefficient in steel at 1873K: $f_{Al}=1.018$, $f_{Ca}=0.486$, $f_S=0.940$, $f_O=0.216$.

Table 1 Chemical composition of X80（mass fraction）

C	Si	Mn	P	S	Al_s	Ca	Nb	Ti	Mo	Cr
0.050	0.217	1.671	0.012	0.0026	0.040	0.002	0.065	0.013	0.215	0.254

3.2 Thermodynamic analysis and calculation

According to the CaO-Al_2O_3 binary phase diagram, in the process of calcium treatment after alu-minum deoxidation there might be Al_2O_3,CaO,CaS,CaO•6Al_2O_3(C•6A),CaO•2Al_2O_3(C•2A),CaO•A-l_2O_3(C•A),12CaO•7Al_2O_3(12C•7A)、3CaO•Al_2O_3(3C•A)， etc. With the increase of calcium,the inclus-ions change by Al_2O_3→CaO•6Al_2O_3→CaO•2Al_2O_3→CaO•Al_2O_3→12CaO•7Al_2O_3→3CaO•Al_2O_3→CaO.Among them,the 12C•7A and the 3C•A is liquid in steel liquid;the melting point of C•A is 1878K, generally considered the L/C •A balance start in forming liquid aluminate. Therefore,the objective of calcium treatment is totransform the Al_2O_3 into 12C•7A or L/C •A.

The activity CaO and Al_2O_3 inclusion changes by inclusion composition,so many scholars had measured the oxides activity in the CaO-Al_2O_3 system, the activity values are shown in table2[6].

Table 2 Activity of CaO and Al_2O_3 in different states at 1873 K

铝酸钙	a_{CaO}	$a_{Al_2O_3}$
C/L	1.000	0.017
12C•7A	0.340	0.064
L/C•A	0.150	0.275
C•A/C•2A	0.100	0.414
C•2A/C•6A	0.043	0.637
C•6A/A	0.003	1.000

3.2.1 Al-O balance curve

Al and O have the following relation before calcium treatment:[7]

$$2[Al]+3[O]=Al_2O_3(s) \qquad (1)$$

$$\lg K = \lg\frac{a_{Al_2O_3}}{a_{Al}^2 a_O^3} = \frac{61304}{T} - 20.3 \qquad (2)$$

Put the f_{Al}、f_O and $a_{Al_2O_3}$ in table 2 in equation (2) to calculate ,make the Al-O balance curve in different balance at 1873K what we can see in the figure 1.We can see that when ω[Al] is 0.04% and ω[O] is controlled between 7×10^{-4}%~18×10^{-4}% ,the calcium aluminum inclusions is liquid form, the inclusion degeneration is good.

And from the figure 1, when we control ω[Als]=0.04%,ω[Ca]=0.0024% the Al_2O_3 inclusions change into 12C•7A, the denaturation effect is optimal and increase liquidity to reduce nodulation in water intake.

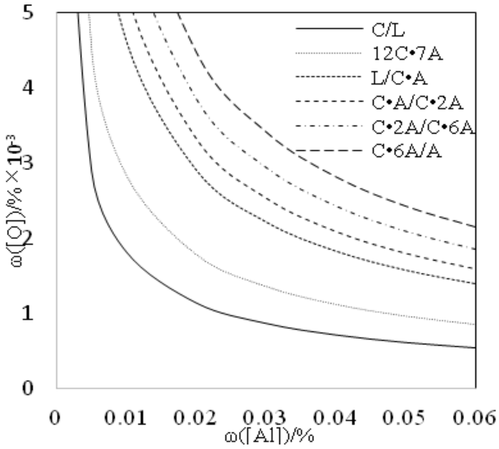

Fig1 Al-O equilibrium curve in different inclusions at 1873 K

3.2.2 Ca and Al balance curve

Ca and Al have the following relation before calcium treatment: [7]

$$3[Ca]+Al_2O_3=3CaO+2[Al] \quad (3)$$

$$\lg K=\lg\frac{a_{Al}^2 a_{CaO}^3}{a_{Ca}^3 a_{Al_2O_3}}=\frac{15661}{T}-2.58 \quad (4)$$

Put the f_{Ca}、f_{Al} and $a_{Al_2O_3}$ a_{CaO} in table 2 in equation (4) to calculate ,make the Ca-Al balance curve in different balance at 1873K what we can see in the figure 2.The figure2 shows that,we only need trace amounts of calcium make the Al_2O_3 inclusions change. When ω[Al]=0.04% and ω[Ca] is controlled between$6\times10^{-4}\%\sim24\times10^{-4}\%$,the calcium aluminum inclusions is liquid.After calcium treatment the content of calcium in X80 is 0.002%,thus the liquid calcium aluminate exists.In the actual production, when we control ω[Als]=0.04%,ω[Ca]=0.0024% the Al_2O_3 inclusions change into 12C•7A, the denaturation effect is optimal and increase liquidity to reduce nodulation in water intake.

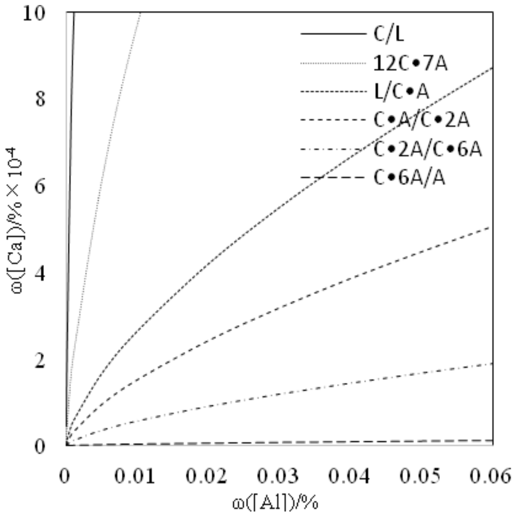

Fig.2 Al-Ca equilibrium curve in different inclusions at 1873 K

3.2.3 Al and S balance curve

Al and S have the following relation before calcium treatment: [7]

$$3CaO+3[S]+2[Al]=3CaS+Al_2O_3 \quad (5)$$

$$\lg K=\lg\frac{a_{Al_2O_3} a_{CaS}^3}{a_{Al}^2 a_S^3 a_{CaO}^3}=\frac{44279}{T}-15.05 \quad (6)$$

Put the f_{Al}、f_S and $a_{Al_2O_3}$ a_{CaO} in table 2 in equation (6) to calculate,and take a_{CaS} =0.75[8],make the Ca-Al balance curve in different balance at 1873K what we can see in the figure 3. CaS has a melting point at 2773K, is solid inclusions in the steel,and high content while also causing nozzle clogging in the continuous casting process, so we must avoid generation of CaS. The figure 3 shows that, when ω[Als]=0.04% and ω[S]>0.009%,the single CaS inclusions will be generated. In the actual production, when we control ω[Als]=0.04%,ω[S]=0.0026%.Thus, CaS inclusion doesn't precipitate at 1873K, sulphur in steel liquid would exist in a dissolved State.

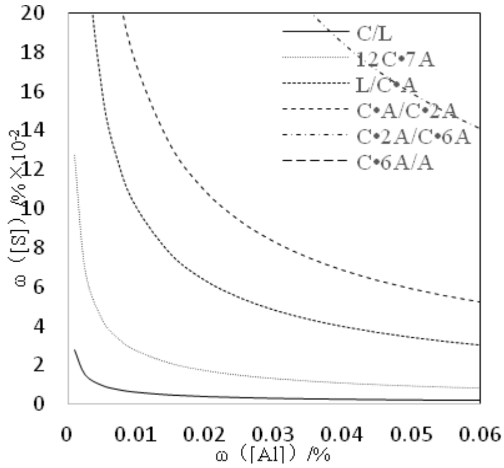

Fig.3 Al-S equilibrium curve in different inclusions at 1873 K

3.2.4 Ca and S balance curve

Ca and S have the following relation before calcium treatment: [7]

$$[Ca]+[S]=CaS(s) \qquad (7)$$

$$\lg K = \lg \frac{a_{CaS}}{a_{Ca} a_S} = \frac{19980}{T} - 5.90 \qquad (8)$$

Put the data in table 2 and take a_{CaS} =0.75 in equation (8) to calculate, make the Ca-S balance curves at 1773K and 1873K what we can see in the figure 4.When ω[Ca]=0.002% ,ω[S] should be higher than under the 0.009% at 1873K or ω[S] should be higher than under the 0.0023% at 1773K so that the CaS can exist. We see that, ω[S]=0.0026%,CaS cann't exist at 1873K, but in the steel solidification process is likely to react with sulfur in CaS.

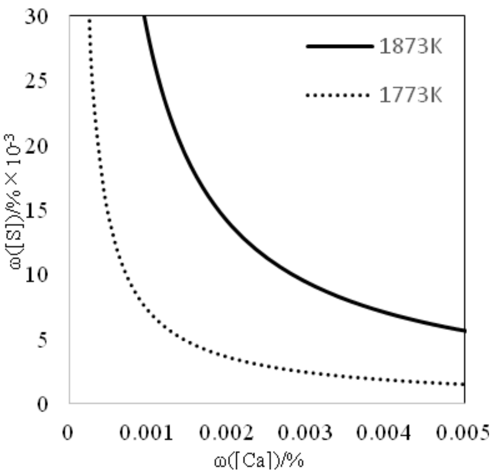

Fig.4 Ca-S equilibrium curve at 1873 K and 1773 K

4. Summary

(1)Before calcium treatment,the inclusions in steel are mainly Al_2O_3, CaO-MgO-Al_2O_3 inclusions and a few MnS, After calcium treated, the inclusions is mainly calcium aluminate, inclusions are effectively degeneration, calcium treatment with good results.

(2)When the ω[Als] is 0.04%，ω[O] is adjusted to 0.7×10^{-4}%~18×10^{-4}%，ω[Ca] is adjusted to 6×10^{-4}%~24×10^{-4}%,in the meanwhile control of ω[S] below 0.009% at 1873K,the effect of Al_2O_3 inclusions degeneration is good and S would exist in a dissolved state so that avoids the CaS inclusion precipitation.

(3)After calcium treatment,the inclusions reduce at 6.99个/mm^2, the percentage of large granular inclusions discrease and the percentage of small granular inclusions increase; most of the inclusions below 5μm.

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