Effect of rare earth for solute distribution of Cr-Mn-N stainless steel by directional solidification

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Abstract. We prepared Cr-Mn-N stainless steel sample by directional solidification technique, analyzing solid-liquid interface solute distribution of different composition and the pull-speed quantitatively with Energy Disperse Spectroscopy. The experimental results indicate that Cr element equilibrium distribution ratio of the sample without the addition of rare earth is less than 1, Mn and Ni elements close to 1. When the withdrawal rate is 12 μm/s, the distribution ratio of Cr element increases and Mn and Ni elements equilibrium distribution coefficient decreases with the increase of Ce. When sample is not added rare earth, Cr element enriches in the solid-liquid interface, Mn element shows a decreasing trend, small change in Ni element. When the rare earth content is 0.002%, Cr element gathers in solid-liquid interface, Mn element reduces, the change of Ni element is not great. When the rare earth content increases to 0.067%, Cr element reduces in the solid-liquid interface, Mn and Ni elements increase.

Introduction

The application of Cr-Mn-Ni stainless steel is very wide in different industrial ranges, the quality requirements of Cr-Mn-N stainless steel are also more stringent. Cr-Mn-N stainless steel is a complex multi-component alloy, the distribution of Cr, Ni, Mn and other elements will change during solidification process with the different solidification rate and composition. Solidification process determines the distribution of solute solidification microstructure morphology, the phase distribution and uniformity of the organization affect the quality and performance of the material ultimately. The solute distribution coefficient of equilibrium solidification process is the ratio of the solid solute content \(c_s\) to the liquid solute content \(c_l\) on both sides of solid-liquid interface, as a constant \(k=c_s/c_l\). When \(k<1\), the solute enriches in the liquid phase, whereas when \(k>1\), the solute gathers in the solid phase. In this study, Cr-Mn-N stainless steel specimens was prepared by directional solidification technique. when the solidification rate was 12 μm/s, the disciplines of solute distribution of stainless steel containing different amounts of rare earth Ce were analyzed during directional solidification.

Preparation and Experience Method of Test Steel

As raw material, the experiment Cr-Mn-N stainless steel firstly used ZG-0.03A vacuum induction melting furnace to smelt, and adding different content of rare earth Ce. After forging billet, taking Ф6.8mm×70mm directional solidification samples on forging billet. the surface of obtained sample was polished with sandpaper and cleaned, then putting it into the induction furnace for directional solidification. Preparation process: the sample was heated to 1600°C, maintaining 10min, pulled with 12μm/s rate. when it was pulled up to 35mm, It is urgent to quenched into coolant to obtain a sample. Components test of steel were shown in Table 1.

The samples with the different components and pull-speed were cut by Molybdenum wire cutting machine along longitudinal midline, then analyzing solute distribution by EDS. As shown in Fig. 1, each sample was hit a number of points from the initial interface to the solid-liquid interface.
in the longitudinal cross-section to get its solute distribution measured by EDS\textsuperscript{[3]}, the ratio of the measured distance from the initial interface to the total length of the fully solidified specimen is the solidification fraction ($f_s$) and to measure solute content ($c_s^*$) in solid phase and the solute content ($c_l^*$) in the liquid phase on both sides of the solid-liquid interface less than 1 microns distance. At the forefront 2mm of the solid-liquid interface could get average liquid solute content ($c_l$).

\begin{table}[h]
\centering
\begin{tabular}{ccccccc}
\hline
Number & Ce & C & Cr & Mn & Ni & N \\
\hline
1# & - & 0.092 & 14.00 & 11.18 & 1.00 & 0.10 \\
2# & 0.002 & 0.098 & 13.20 & 10.40 & 1.00 & 0.096 \\
3# & 0.067 & 0.089 & 13.47 & 10.44 & 1.00 & 0.089 \\
\hline
\end{tabular}
\caption{Test steel composition (wt %)}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{solute_distribution_diagram.png}
\caption{Solute distribution diagram hitting a number of points to measure it by EDS}
\end{figure}

**Results and Analysis**

According to Eq. 1, $k_i$ is the solute partition coefficient of $i$ element, $c_s^*$ and $c_l^*$ are the solid and liquid solute content on both sides of solid-liquid interface. Figure 2(a) represents solute distribution when $k_i < 1$, Figure 2(b) is solute distribution while $k_i > 1$. $c_0$ and $c_l$ are the initial composition of the sample and the average solute content in the liquid phase respectively. The initial point of solidification is $f_s = 0$, the solute content of the liquid phase ($c_l^0$) is $k_i c_0$. The initial distribution of solute concentration at the interface is shown in Fig. 3, the solute distribution coefficient $k_i^0$ can be obtained at the initial position. When there is convection in the liquid phase, the flow will affect redistribution of solutes, so it is critical to use the effective solute partition coefficient $k_e$ to indicate the distribution of solutes.

In the equilibrium solidification conditions, the distribution coefficient of solute is:

$$k_i = \frac{c_s^*}{c_l^*}$$  \hspace{1cm} (1)

**Effective Solute Partition Coefficient Definition:**

$$k_e = \frac{c_s^*}{c_l^*}$$  \hspace{1cm} (2)

From the Eq. 2, the ratio of the average solute distribution content of the solid phase to liquid...
phase in solid-liquid interface is defined as active solute distribution coefficient.

![Fig. 2 solute content distribution diagram in the solid phase after the solute allocation process](image)

Table 2 respectively shows measured solid phase, the solid at the original interface, liquid phases on both sides of solid-liquid interface and the solute content in the distance ahead of the interface of #1-#3 sample, when pull-rate is 12μm/s. The left dashed line represents the initial solidification interface, the right is the solid-liquid interface. From table 2 dates, we can calculate the initial distribution coefficients $k_i^0$, the equilibrium distribution coefficient $k_i$ and an effective partition coefficient $k_e$ respectively. As can be seen from Table 2, the distribution ratio of Cr element of rare earth-free sample #1 is less than 1, Mn and Ni elements distribution ratio close to 1, which could indicate Ni and Mn elements solute distribution is very uniform. Equilibrium distribution coefficient of Cr element of #2 and #3 specimens adding rare earth Ce decreases, which could indicating that Cr element enriches in the solid-liquid interface, Mn and Ni elements equilibrium distribution coefficient decrease. This is because that the rare earth Ce in the liquid phase of the solid-liquid interface area is more enrichment and it could increase supercooling of composition, relatively reducing the content of other solute elements in liquid solidification interface area.

Table 2 solute element content and solute distribution coefficient when pulling speed of directional solidification is 12 μm/s

| Number | element | $c_o$ | $c_o^s$ | $c_i^s$ | $c_i^* | c_i | k_i^0 | k_i | k_e |
|--------|---------|-------|---------|---------|-------|        |       |       |      |
| 1      | Cr      | 16.79 | 15.06   | 15.21   | 15.35 | 15.88  | 0.90  | 0.99  | 0.96 |
| 1      | Mn      | 10.93 | 11.45   | 11.27   | 11.24 | 11.44  | 1.05  | 1.003 | 0.99 |
| 1      | Ni      | 0.82  | 0.94    | 1.03    | 1.10  | 1.07   | 1.15  | 0.94  | 0.96 |
| 2      | Cr      | 15.15 | 15.45   | 15.50   | 16.23 | 15.34  | 1.02  | 0.96  | 1.01 |
| 2      | Mn      | 11.47 | 11.60   | 10.71   | 11.20 | 11.59  | 1.01  | 0.96  | 0.92 |
| 2      | Ni      | 1.17  | 1.21    | 0.91    | 1.06  | 1.10   | 1.03  | 0.86  | 0.82 |
| 3      | Cr      | 14.76 | 15.59   | 14.83   | 15.33 | 15.35  | 1.06  | 0.97  | 0.97 |
| 3      | Ni      | 0.93  | 1.07    | 0.29    | 1.45  | 1.22   | 1.15  | 0.89  | 1.06 |

From Fig.3, solute content of Cr-Mn-Ni stainless steel along the longitudinal in the directional solidification process with the different the solidification fraction can be seen, the solid phase constantly changes with the different solid fraction of solute concentration. In the rare earth-free sample #1, the Cr element enriches at solid-liquid interface, Mn element shows a downward trend, a small change in Ni element. With 0.002% rare earth-containing sample #2, rare
earth Ce tends to aggregation in solid-liquid interface, Cr element also enriches at the solid-liquid interface and the Cr content increases in the liquid phase during solidification, Mn element content decreases, Ni element content changes small. When the rare earth content increases to 0.067%, Cr content of 3# sample decreases in the solid-liquid interface, Mn and Ni element contents of 3# sample decrease, rare earth Ce is enrichment in solid-liquid interface. This is because that the atomic radius of the rare earth Ce is relatively large, which tends to enrichment during solidification in the solid-liquid interface. The results match the solute partition coefficient calculated in Table 2.

Fig. 3 Variation of solute content with solidification fraction along longitudinal of Cr-Mn-Ni stainless steel during directional solidification

Conclusions

(1) when the withdrawal rate is $12\mu m/s$, the distribution ratio of Cr is less than 1 of the sample without the addition of rare earth, the equilibrium distribution coefficient of Mn and Ni elements close to 1. With the increase of Ce element, the distribution ratio of Cr element increases, while Mn and Ni elements equilibrium distribution coefficient decrease.

(2) Cr element tends to aggregation in the solid-liquid interface of samples without the addition of rare earth. Mn shows a decreasing trend, small change in Ni. When the rare earth Ce content is 0.002%, Cr element enriches in solid-liquid interface, Mn element reduces and the change of Ni is not great. When the rare earth Ce content increases to 0.067%, Cr element content decreases in the solid-liquid interface, the Mn and Ni elements increase.

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Literature References

