Effect of cooling rate on solidification structure and linear contraction of a duplex stainless steel

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Abstract: Cooling rate is a key factor that can drastically affect the phase transformation and thermal stress of duplex stainless steels. Therefore, in this research, different sand moulds were used to explore the influence of cooling rate on the solidification of the 2304 duplex stainless steel (DSS). The macro and micro structures of the 2304 DSS were investigated. Small equiaxed grains are obtained in chromite sand mould sample with a lower pouring temperature and a higher cooling rate, whereas coarse columnar and equiaxed grains are found in silica sand and refractory powder mould samples. The size of austenite phase is significantly increased with decreasing cooling rate, while the ferrite phase content ranging from 51.6% to 53.9% does not change obviously. In addition, the linear contraction of the 2304 DSS decreases from 2.34% to 1.09% when the mean cooling rate above 1,173 K increases from 0.99 K·s\(^{-1}\) to 3.66 K·s\(^{-1}\).

Key words: duplex stainless steel; solidification structure; linear contraction; cooling rate

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1 Experimental procedure

Duplex stainless steel (DSS), which exhibits favorable comprehensive properties, consists of both ferrite and austenite phases with approximately equal amount. The mechanical properties and the corrosion resistance of DSS are better than those of austenitic stainless steels. Moreover, the fabrication of DSS is easier than that of ferritic stainless steels [1]. Most of DSSs contain small additions of Mo, Mn, N, and Cu, which are beneficial to their mechanical and corrosion properties. Owing to their excellent corrosion resistance (Cl\(^-\)) and mechanical properties, DSSs have been extensively applied to many fields recent years, such as the chemical and petrochemical industries, marine construction, nuclear industry and so on [2-4].

In casting process, the cooling rate is a key factor seriously influencing the ratio of phases and thermal stress of the DSS [5]. The high temperature ferrite phase transforms into austenite after solidification. Various analytical models, which are primarily based on the assumption that the diffusion of nitrogen is the controlling mechanism, have been developed to explain this transformation [4, 6-8]. As the ferrite-to-austenite phase transformation during a regular solidification is controlled by diffusion, which is influenced by temperature, the morphology and content of austenite should be affected by the cooling rate. However, there is little research on estimation of this influence.

In addition, the overall dimension and porosity are important indicators for ingots. The solidification shrinkage can induce shrinkage cavities and porosities, whereas the linear contraction is a main factor resulting in thermal stresses, cracks and dimension errors [9]. As the contraction coefficient varies with different phases and temperature ranges in steels, solid phase transformation and the degree of supercooling will influence the linear contraction. Up to now, many works have been done on the thermal expansion coefficient of alloys [10-13], however, little attention was paid on the contraction during continuous cooling process, such as mould casting [5]. Since DSS represents a complicate metallurgical transformation which can take place in the ferrite or austenite phases [14], the solidification contraction may exhibit a different behavior as compared with that in carbon steels [15].

In the present study, the influence of cooling rate on solidification structure and linear contraction of the 2304 DSS has been investigated in mould casting. The correlation of the pouring temperature, cooling rate, solidification structure and the linear contraction has been discussed.

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the 2304 DSS is Fe (balance), 22.93 Cr, 3.96 Ni, 1.47 Mn, 0.44 Si, 0.28 Mo, 0.02 C and 0.14 N. Its liquidus and solidus were calculated to be 1,748 K and 1,663 K, respectively, by software of Thermal-Calc. The raw material was melted in a medium-frequency induction furnace, and then directly poured into the sand moulds. In order to acquire different cooling rates, the moulds were separately made using chromite sand, silica sand and refractory powders. The thermal conductivities of these three materials reduce orderly.

The linear contraction as a function of the temperature was measured by a linear contraction setup [16]. A sketch of the linear contraction setup is shown in Fig. 1, being composed mainly of a sand mould, a displacement sensor and a thermocouple. The thermocouple protected by a 5 mm SiO₂ tube was placed at the 1/4 length of the sample, and inserted 2.5 mm into the sample. The outer dimension of the linear contraction mould was 100 mm × 100 mm × 425 mm, while the sample size was 20 mm × 375 mm. After pouring, the melt attached to a screwed steel rod that was in connection to a displacement sensor. The temperature and linear contraction of samples were recorded with a computer data acquisition system after pouring the melt into the mould, at a frequency of 10 data points per second.

To further investigate the microstructure, several slices were cut from the solidified sample along the longitudinal and cross-section at 1/4 length of the sample. After being polished, the slices are etched in a mixture of bluestone (15 g), hydrochloric acid (40 mL) and deionized-distilled water (60 mL). The microstructures of the samples were observed using a Leica DM6000M optical microscope (OM). The volume fraction of the ferrite phase was measured using a FERITSCOPE FMP30 unit based on the principle of electromagnetic induction.

2 Results and discussion

2.1 As-cast structure

Figure 2 shows the macro-structures of the as-cast samples and Table 1 lists the experimental results of the samples fabricated with three different moulds. Different pouring temperatures or moulding materials can result in different grain structures (see Fig. 2). Entire equiaxed grains are observed in chromite sand mould sample, and the mean equiaxed grain size decreases from 1.15 mm to 0.24 mm with decreasing pouring temperature, as shown in Figs. 2(a) to (c). As compared with that of the refractory material mould, the thermal conductivity of the chromite sand mould is much greater (see Table 1). As such, when the melt flows across the running channel in the chromite sand mould, its temperature would be decreased significantly, so a large number of crystals nuclei form and survive in the metal liquid. These survived nuclei grow up and lead to a fully equiaxed grain structure in the chromite sand mould sample despite different pouring temperatures [17]. On the other hand, the high pouring temperature, i.e., the increased superheat, leads to the reduction in quantity of the crystal nucleus, hence coarse equiaxed grains are acquired.

The coarse columnar and equiaxed grains were found in the samples of silica sand and the refractory powder moulds [see
Figs. 2(d) and 2(e)], very different from the complete equiaxed grains in the chromite sand mould [see Figs. 2(a) to (c)]. Due to the smaller thermal capacity and heat conductivity of the refractory powders, a higher superheat during the pouring and filling processes of the metal liquid could be maintained, resulting in the decrease of the nucleation rate and the coarse grains.

It should be noted that in the four solidified samples, a similar phenomenon of shrinkage porosity is observed, as marked in Figs. 2(a) to (d). Due to the rapid cooling rate, the feeding channel is blocked immediately after the filling process, there is little liquid flows from the pouring cup to the samples to feed the solidification shrinkage, thus a shrinkage cavity or porosity should be observed in samples. However, the interval between the liquidus and solidus of 2304 DSS is 85 K, a rather large solidification range. Samples are solidified in the mushy state, and the melt is partitioned by dendritic framework, and consequently, dispersive porosities are formed. This problem can be avoided by using of the refractory powder mould [Fig. 2(e)], because the feeding channel from the pouring cup to sample maintains a longer time due to its low cooling rate.

### Table 1: Results of the experiments with different cooling rates and pouring temperatures

<table>
<thead>
<tr>
<th>No.</th>
<th>Moulding material</th>
<th>Pouring Temperature (K)</th>
<th>Mean cooling rate (&gt;1,173 K) (K·s⁻¹)</th>
<th>Linear contraction rate (%)</th>
<th>Percentage of equiaxed grains (%)</th>
<th>Mean equiaxed grain size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>Chromite sand</td>
<td>1,933</td>
<td>\</td>
<td>1.65</td>
<td>100</td>
<td>1.15</td>
</tr>
<tr>
<td>2#</td>
<td>Chromite sand</td>
<td>1,903</td>
<td>3.87</td>
<td>1.50</td>
<td>100</td>
<td>0.58</td>
</tr>
<tr>
<td>3#</td>
<td>Chromite sand</td>
<td>1,873</td>
<td>3.66</td>
<td>1.09</td>
<td>100</td>
<td>0.24</td>
</tr>
<tr>
<td>4#</td>
<td>Silica sand</td>
<td>1,873</td>
<td>2.51</td>
<td>1.51</td>
<td>66.37</td>
<td>1.19</td>
</tr>
<tr>
<td>5#</td>
<td>Refractory powders</td>
<td>1,873</td>
<td>0.99</td>
<td>2.34</td>
<td>66.37</td>
<td>0.87</td>
</tr>
</tbody>
</table>

2.2 Austenite and ferrite phases

According to the calculated phase diagram, the nucleation and growth of austenite would occur in the temperature range from 1,573 K to 1,173 K. To consider the solid state phase transformation, the mean cooling rates in different moulds are calculated from the peak temperature to 1,173 K and listed in Table 1. The DSS mainly consists of two phases, ferrite (δ(α)) and austenite (γ); and sometimes it may precipitate a number of intermetallic phases, such as σ phase, χ phase and carbide, etc. [18]. The micro and macro structures of the samples solidified in different moulds were observed by an OM as shown in Fig. 3. All five samples contain both isolated and Widmanstatten austenite structure, whereas no evidence of σ phase is observed. Furthermore, the ferrite phase volume fractions were measured at 30 points of each sample by a FMP30 ferrite content measuring instrument, and the average content of ferrite, ranging between 51.6% and 53.9%, does not change significantly with pouring temperature and cooling rate [Fig. 4(a)]. However, the decrease in cooling rate appears to increase the size of the austenite phase. The mean width of island-shaped austenite increases from less than 6.23 μm to 32.86 μm.
as cooling rate above 1,173 K decreases from 3.66 K·s\(^{-1}\) to 0.99 K·s\(^{-1}\) [Fig. 4(b)]. The low cooling rate can also bring out coarse austenite Widmanstatten structure, which grows up from the grain boundaries.

It is suggested that the ferrite/austenite ratio is mainly determined by composition\(^{[1, 6]}\), therefore the appropriate ratio of \(\delta/\gamma\) phase could be easily achieved during DSS casting. However, the size of austenite could be evidently affected by cooling rate. If not taking thermal stress into account, a high cooling rate is allowed to reduce the size of austenite during hot rolling or heat treating.

Generally, coarse austenite phase structure may reduce the mechanical properties and the corrosion resistance of DSS \(^{[1]}\). A part of black spots in Fig. 3 are corrosive pits. Most of them are observed at the interfaces of ferrite and austenite phases (marked by arrows in Fig. 3), and some pits can also be identified in ferrite phase (marked by ellipses in Fig. 3).

### 2.3 Linear contraction

The measured linear contraction rates at different pouring temperatures and different cooling rates (i.e., in different sand moulds) are listed in Table 1. The results suggest that the linear contraction rates increase with the decrease of cooling rates (LCR) could be smaller than those of some other steels, and contracted. As a result, the values of these linear contraction coefficients could not be detected before the tensile strength of the sample becomes stronger than the frictional resistance of the sand mould. However, the sample solidifies with a remarkable temperature gradient in axis direction. This large temperature gradient can result in that the metal under the pouring cup still remains in liquid state while both ends of the sample may have solidified and contracted. As a result, the values of these linear contraction rates (LCR) could be smaller than those of some other steels, which have been measured in a uniform thermal field \(^{[5, 15]}\).

Furthermore, the linear contraction rate below 973 K is plotted as a function of the temperature in Fig. 5(b). The mean thermal linear contraction coefficient below 973 K, calculated by the linear relationship between contraction and temperature, increases from \(16.5 \times 10^{-6}\) to \(23.2 \times 10^{-6}\) K\(^{-1}\) with decreasing cooling rate. These thermal linear contraction coefficient values are very close to that of austenitic stainless steel D9 \(^{[10]}\), but higher than that acquired from product manuals (approximately \(12 \times 10^{-6}\) to \(14 \times 10^{-6}\) K\(^{-1}\)). This result indicates that the linear contraction coefficient is affected by cooling rate during the continuous cooling process.

The LCR of an ingot is not only controlled by thermal contraction coefficient, but also influenced by thermal field and mould resistance. In these experiments, it is obvious that the chrome sand mould has the greatest temperature gradient and mould resistance, so its LCR is smaller than those of the other two. On the other hand, the superheat of melt can change the temperature gradient of the sample, and lead to the increase of LCR with increasing superheat. Therefore, to obtain accurate size of ingots, the mould size should be calculated according to the moulding material, pouring temperature, solid state phase transformation and thermal field, rather than considering only the thermal contraction coefficient. These linear contraction curves could be considered as a reference to mould design.
3 Conclusions

In the present study, the linear contraction rates have been measured and the macro- and micro-structures of the solidification samples have been investigated by varying the pouring temperature and the cooling rate in different moulds. The correlations among the cooling rate, linear contracting rate and the structure have been discussed. Based on the experimental and analytical results, the following conclusions can be drawn:

(1) Full equiaxed grain structure can be obtained in chromite sand mould sample, and the mean equiaxed grain size decreases from 1.15 mm to 0.24 mm with pouring temperature decreasing from 1,933 K to 1,873 K. However, coarse columnar grains can be observed both in silica sand mould and refractory powder mould samples.

(2) The width of austenite phase changes dramatically from less than 20 μm to about 50 μm with decreasing cooling rate, while the ferrite contents of about 52% on average on all samples, do not seem to change obviously with the changing conditions.

(3) The linear contraction rate of the 2304 DSS increases with increasing pouring temperature, and decreases from 2.34% to 1.09% as the mean cooling rate above 1,173 K increases from 0.99 K·s⁻¹ to 3.66 K·s⁻¹.

References


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