Abstract

Super 304H is an austenitic steel, which is mainly used for boilers in thermal power plants and the energy sector. Strength at high temperatures has become one of the most important attributes in the design of boiler tubes. The differences in material properties, especially in its creep resistance compared to other austenitic steels of similar composition, are mainly achieved by the addition of about 3 wt.-% of copper. The formation of fine Cu-rich precipitates during manufacture leads to an increased creep strength during the process of precipitation hardening. The impact of the welding cycle on the grain coarseness in the heat-affected zone (HAZ) for S304H steel will be demonstrated in this paper. The options and procedures for predicting grain size by mathematical modeling of welding and heat treatment will also be shown here. The method of acquiring the input data for the mathematical models, which predict the grain size, will also be described.

Introduction

The continuous trend of operational parameters to increase their energy and chemical conditions also requires the development of new materials, which are able to operate under such conditions. Heat-resistant steels can undoubtedly be classed as one of these materials. They have to fulfill many requirements, which are often contradictory. The main requirement lies in its enhanced resistance against long term loading under high temperatures. No less important is sufficient resistance against corrosion, which forms an oxide layer on the steel surface. [1]

Applications of such new materials and the inclusion of the technological processes for joining them together are often accompanied by the use of welding simulations and heat treatment computations. These computations can largely eliminate the risks, which are connected with the occurrence of unacceptable defects, or they can lead to the elimination of inner stresses caused by the process. The Sysweld program is one of the most commonly used programs for this type of computation.
When predicting the structure and resulting properties of the welded joints area, it is important to know not only the grain size in the initial state, but also during the welding process. For this reason, this paper describes the methodical procedures and the experimental results, which lead to the definition of a computational model. This model then enables the prediction of the austenitic grain size of the weldments made by S304H steel, especially in the heat-affected zone, but not in the weld area.

1 The Characteristics and Uses of S304H Steel

Generally speaking, austenitic steels have good mechanical properties and excellent corrosion resistance even at high temperatures, varying from 650-700°C. However, this advantage is countered by their unfavourable thermal-physical properties such as low thermal conductivity and high thermal expansivity. Another major drawback is the possible damage to the material through thermal fatigue, especially when these steels are used in power stations where they are working in cyclic thermal modes. The cost of these steels prohibits their use on a larger scale. [6] Currently austenitic heat resistant steels grade 304, are used in Europe, USA and Japan. Recently, S304H, which is a new type of austenitic stainless steel containing 3% copper, is being adopted for the production of super-heater /re-heater tubes of 600°C USC power plant boilers. [2]

The strength of this material at high temperatures is elevated and particularly its creep properties are improved by adding about 3 wt.-% of copper, increasing the carbon content and adding certain amounts of niobium and nitrogen. The addition of nitrogen leads to a solid solution heat strengthening of the material. This increases the tensile stress resistance. The stress resistance under creep conditions is mainly increased by the precipitation of a Cu-rich phase in the matrix. [4] The Cu-rich phase is mainly composed of Cu and also a part of Fe, Cr and Ni. The content of Cu in the Cu-rich phase is lower than 20 at pct at early stage of precipitation after 1 hour aging, and then it is increasing continually with aging time and reaches almost 90 at pct at centre when aging for 500 hours. These results represent that Cu atoms gradually concentrate to Cu-rich particles and the other elements (such as Fe, Cr, Ni etc.) diffuse away from Cu-rich particles to matrix with the increasing of aging time at ± 650°C. It is reasonable to suggest that Cu will be the only main composition in Cu-rich phase when aging for very long time. [11]

During manufacture, this Cu-rich phase and a niobium carbonitride phase precipitate simultaneously. S304H is characterized by an excellent precipitation hardening effect. It reaches peak hardness (246 HV) at 1000 h and maintains almost the same level till 8000 h at 650°C. [3]

The diffusion of chromium to the surface is accelerated and the formation of an adherent and dense chromium oxide (Cr2O3) layer is enhanced. This protective layer reduces further oxidation to a minimum.

Tubes of the material (ø 38 mm, wall thickness 6.3 mm) were used for grain size prediction. Its chemical composition analysis is shown in Table 1. Figure 1 shows the initial state microstructure of the tested material.

Tab. 1: Chemical composition of tested material

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>0.090</td>
<td>0.873</td>
<td>0.243</td>
<td>0.005</td>
<td>0.015</td>
<td>18.8</td>
<td>8.449</td>
<td>0.508</td>
<td>3.515</td>
</tr>
</tbody>
</table>

Source: Own
The reduction of Gibbs surface free energy acts as the thermodynamic driving mechanism for grain growth. The grain growing process results in the reduction of the grain surface boundary and thus to a decrease in free energy. Grain size is important in two respects. It is important with regard to the mechanical properties of the material (e.g. brittleness), but also with respect to the influence on the transformation processes. The first models, which were built on the physical basis, were developed at the beginning of 1950s. In 1980, a new approach based on mathematical modelling was introduced. On the basis of computed simulations it was also possible to monitor the processes, which were previously difficult to observe, for example the volume change rate of the individual grains. Currently, the most commonly used simulation method is the “Monte Carlo Potts Model” method. A description of this method is given as an example in [5, 7]. An ideal rule for grain growth is given by equation (1). [8]

\[
D^a - D_0^a = C \cdot e^{\frac{Q}{R \cdot T} \cdot t}
\]  

(1)

D – grain diameter (mm),
\(D_0\) – initial grain size (mm),
C – material constant (mm\(^a\)·s\(^{-1}\)),
Q – activation energy (J·mol\(^{-1}\)),
R – gas constant (J·K\(^{-1}\)·mol\(^{-1}\)),
t – time (s),
a – coefficient (-).

It was established by experiments that coefficient values vary between 2 and 5. Value a=2 applies if the growing process is solely controlled by diffusion. Value a=4 is determined in the case where there is precipitation and diffusion along the grain boundary. Grain growing is, however, influenced by other factors, for example, heating rate and grain growth barriers. The computation of grain size proceeds in the Sysweld simulation program based on equation (2) which expresses the growing rate of the grain size.

\[
\dot{D}^a = C \cdot \exp\left( -\frac{Q}{R \cdot T} \right)
\]

(2)
Constant C is usually $0.4948 \cdot 10^{14}$ mm$^3$.s$^{-1}$. This computational equation is designed for cases when the amount of austenite is constant or is decreasing. If the amount of austenite increases, two developments are observed:

- Existing grains increase in size.
- New grains are generated with zero initial grain size.

By generalizing the conventional equation in order to determine the grain size, we arrive at the following equation (3).

$$\dot{D}^a = C \cdot \exp \left( - \frac{Q}{R \cdot T} \right) - \frac{\dot{\lambda}}{\lambda} \cdot D^a$$

In this equation, the $\lambda$ value expresses the austenite proportion while the value $\dot{\lambda}$ shows the transformation rate of this phase. For $\dot{\lambda} > 0$ the austenite is created. If the austenite is not created, i.e. $\dot{\lambda} \leq 0$ then is the grain size expressed by the equation (2).

3 Experimental determination of grain size

For numerical analysis in Sysweld, it is important to know the input conditions defining the grain size changes, which depend on time and thermal exposure of the material. The test samples were 12 mm long rings cut from the given tube (ø 38 mm, wall thickness 6.3 mm). Since it concerned the moulding product, the specimens were measured longitudinally and transversely, because of the fact that the grains could be deformed during the moulding process. The specimens were thermally exposed in an oven at 1000°C, 1100°C for 4 and 8 hours and were subsequently cooled in water. While heating up to the test temperature the heating rate for all specimens was 420°C/hour.

Specimens for validating the structure were prepared according to a standard metallographic procedure. To accentuate the grain boundaries the specimens were cauterized in solution (80 ml HCl; 13 ml HF; 7 ml HNO$_3$). This solution had to be used because cauterization agents like Villela Bain or Vogel, which are commonly used for alloy materials, do not work with the used material. The grain size was evaluated according to CSN EN ISO 643 standard. The evaluation of the grain size was expressed by the intersection method and by the planimetric method. Based on these measurements, the average number of sections to one millimetre of measured line $N_L$ was determined using the intersection method. Then, data such as the average length of linear sector $l$, the grain size number $G_1$ and the number of grains in one mm$^2$ marked $m$ were also determined. For the planimetric method it is important to determine the grain size number, $G_2$ (based on this data it is possible to determine the average grain diameter $\bar{d}$ and the average grain surface area $\bar{a}$). From this, the real average grain surface area $\bar{a}$, the real average grain diameter $\bar{d}$ and the number of grains in one mm$^2$ can also be computed. [9] The determined values of the grain size for each set of experimental conditions for the intersection and planimetric method are shown in table 2.
### Tab. 2: Determined values of grain size

<table>
<thead>
<tr>
<th>Specimens S 304H</th>
<th>The data determined by help of intersectional method</th>
<th>The data determined by help of planimetric method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N_l</td>
<td>1</td>
</tr>
<tr>
<td>Initial state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LD</td>
<td>52.326</td>
<td>0.01911</td>
</tr>
<tr>
<td>TD</td>
<td>47.007</td>
<td>0.02127</td>
</tr>
<tr>
<td>1000 °C 4 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LD</td>
<td>40.716</td>
<td>0.02456</td>
</tr>
<tr>
<td>TD</td>
<td>53.353</td>
<td>0.01874</td>
</tr>
<tr>
<td>1000 °C 8 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LD</td>
<td>45.857</td>
<td>0.02181</td>
</tr>
<tr>
<td>TD</td>
<td>67.634</td>
<td>0.01479</td>
</tr>
<tr>
<td>1100 °C 4 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LD</td>
<td>41.222</td>
<td>0.02426</td>
</tr>
<tr>
<td>TD</td>
<td>35.911</td>
<td>0.02785</td>
</tr>
<tr>
<td>1100 °C 8 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LD</td>
<td>45.880</td>
<td>0.02180</td>
</tr>
<tr>
<td>TD</td>
<td>51.672</td>
<td>0.01935</td>
</tr>
<tr>
<td>Source: [9]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N_l – average number of grains gripped to the line unit length, 1 – average length of linear sector, G1 – grain size number evaluated with intersectional method, G2 – grain size number evaluated with planimetric method, LD – longitudinal direction, TD – transversal direction

### 4 Mathematical computation of grain size using Sysweld

The experimentally determined values of grain size (see table 2) were used as input data for the grain size calculation in the Sysweld simulation program. The computations of this program are based on equations (2) and (3). The value of the activation energy, Q, can be set in the definition of the computation model by using a positive power constant, a, and the constant, C.

In the first phase, the input data leads to a computed grain size, which corresponds to the experimentally determined grain size. Based on experience, it can be said that the main parameter for predicting grain size by mathematical simulation is the activation energy, Q. Constant C remain unchanged, C=0,4948·10^{14} mm^4.s^{-1} and the power constant, a, usually matches a=4 (the case of precipitation and diffusion along the grain boundary). Based on these results, the activation energy Q or the ratio Q/R is then determined. In the case of S304H steel it is optimal to keep the ratio Q/R=73400 for a temperature of 1000°C and Q/R=74800 for a temperature of 1100°C. [10]
This validated model is consequently used for the calculation of the grain size based on non-stationary temperature fields appearing during welding. Figure 2 depicts a 3D simulation model of a weld made up of three weld beads as well as the weld’s basic geometry. All the weld beads on the simulation model are only created by using an additional material. However, the simulation model the of heat source correspond with melting boundaries to the real weld geometry of individual weld beads.

Figure 2: 3D simulation model of the weld with three weld beads and the weld geometry

Figure 3 shows the results of computing the grain size in HAZ for the weld made on S304H steel tube ø 38, wall thickness 6.3 mm. The weld was made by an automated machine using GTAW method. Three weld beads were made with a preheating temperature of 180°C, an interpass temperature of 290 °C and using additional material Thermanit MTS 616. The edges of the individual weld beads were reciprocally shifted by 120° while the welding directions of the successive beads were reversed. None of the weld beads was finished immediately after 360°, they all overlapped their edges at least by 10 mm. Experimental welds were made in Vitkovice Steel company and the welding parameters are their know-how. The asymetricity of the austenite grain distribution in HAZ in rotary symmetrical model (fig.3) occurs in the areas where the ends of original beads were rewelded by about 10 mm.

Figure 4 displays the details of grain coarseness in HAZ on the boundary of the second and third weld bead.
Following the real-life welding experiment, the computed data of the grain size and the real-life grain size formed in HAZ were compared. Specifically points 0.5; 1; 1.5; 2; 2.5; 3 and 5 mm from the melting boundary (MB) were compared. Table 3 shows the comparison of the grain size results computed numerically and formed experimentally.

Source: Own

**Fig. 3:** The results of computing grain size in HAZ after welding (S304H)

Source: [10]

**Fig. 4:** Detail Details of grain coarseness in HAZ after welding on the boundary of the second and third weld bead (S304H)
**Conclusion**

The computational program module for the determination of grain size using the Sysweld program was developed as a marginal module, mainly meant for public purposes. However, we can now see an increasing demand for this type of simulation computation. That is why one of the aims of the TA02010992 project is the validation and, if necessary, the modification of this program module, thus the predicted values of austenitic grain size after welding or heat treatment correspond to the real situation. The most important aspect is the optimization of the HAZ results, because the processes are very dynamic there and thus we can expect intensive grain growth in that area.

From Table 3 it is evident that the prediction of austenitic grain size using mathematical models reflects the reality very well. This close agreement is especially evident at 1.5 mm from the melting boundary. In the area with the highest thermal gradients to the area 1.5 mm from the melting boundary, the grains predicted by simulations (G5) are smaller than those determined experimentally (G4). This discrepancy is probably caused by the computational program module design, which, at present, makes it impossible to insert the input data in the form of temperature dependency. This particular inaccuracy could also be caused by the grain size determination method according to CSN EN ISO 643 standard.

According to this norm, the grain size is determined at the defined surface. There is irregular temperature distribution in the HAZ of the weld and the grain size decreases as the distance of the melting boundary increases. However, there are no standard instructions for predicting grain size in the HAZ and thus the selected method provides the most relevant results.

**Acknowledgements**

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**Literature**


Vliv svařování na tepelně ovlivněnou oblast trubek ze stahovaného austenitického nerezového oceli S304H se zaměřením na predikci velikosti zrna pomocí numerických simulací