QUANTITATIVE PHASE ANALYSIS USING X-RAY DIFFRACTION OF FERRITE AND AUSTENITE IN DUPLEX STAINLESS STEEL SUBJECTED TO VARIOUS HEAT TREATMENTS

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Abstract

The duplex stainless steel is characterized by having in its microstructure the austenitic and ferritic phases. It combines the best characteristics of austenitic and ferritic steels, which are very good corrosion resistance, high strength, good toughness, excellent resistance to stress corrosion cracking and corrosion fatigue. Due to this superior properties, the duplex stainless steel has been increasing used in structures and in manufacturing tubes in the petroleum industry. In this work we investigate the variation of the volumetric fractions of the austenitic and ferritic phases with the cooling rate after solution annealing. Samples of duplex stainless steel were heated up to 1300°C and then cooled at different rates: (i) water, (ii) oil, (iii) forced air and (iv) oven. The amounts of the austenitic and ferritic phases were obtained by x-ray diffraction.

INTRODUCTION

The duplex stainless steels are widely used in many industries, including chemical, petrochemical, cellulose and nuclear plants. Because of their fine austenitic-ferritic microstructure they provide an excellent combination of mechanical and corrosion resistance properties. The growing use of the duplex stainless steels in the petroleum industry has promoted an more intense necessity to study the mechanical properties of this steel. The performance of the duplex stainless steel is affected by the content of the austenite and ferrite phases, so a possible method to measure this volume fraction is x-ray diffraction. However, the direct treatment used for polycrystalline samples is not satisfactory, because the presence of texture in this steels, an different approach has to be used (Cheary & Ma-Sorrell[3]). In this work we produce duplex stainless steels with different contents of austenitic and ferritic phases by means of heat treatments and measure this volume fractions using x-ray diffraction.

THEORY

The integrated intensity of a \( hkl \) reflection of a given phase in a polycrystalline sample can be written as

\[
I_x^{hkl} = \frac{V_x LP(\theta_x) m_x^{hkl} e^{2\pi}}{v_x^2} F_x^2
\]

where \( V_x \) is the volume fraction of phase \( x \), \( LP(\theta_x) \) is the Lorentz-Polarization factor \( \left( \frac{1 + \cos^2 \theta}{\sin \theta \cos \theta} \right) \), \( B_x \) is the Debye-Waller factor of the \( hkl \) line, \( v_x \) is the cell volume, \( m_x^{hkl} \) is the multiplicity factor and \( F_x \) is the structure factor.
In a completely random oriented two phase material the volume fraction of the phases can be obtained by the following ratio.

\[
\frac{f_{\text{Fe}}^{\text{hkl}}}{f_{\text{A}}^{\text{hkl}}} = \frac{V_L P(\theta_h) m_{\text{Fe}}^{\text{hkl}} e^{-\frac{\theta}{3\lambda}} F_{\text{Fe}}^{2} v_{\text{Fe}}^{2}}{(1-V_L) P(\theta_h) m_{\text{A}}^{\text{hkl}} e^{-\frac{\theta}{3\lambda}} F_{\text{A}}^{2} v_{\text{A}}^{2}}
\] (2)

In principle, we just have to measure the integrated intensity of one reflection of each phase and apply equation (2) where all the other factors but the volume fraction can be calculated from the structure of the phases. The samples used in this work however, exhibit strong texture along the [100] direction for ferrite and [110] for austenite, so the direct use of equation (2) would not give an accepted result, and a large correction for preferred orientation has to be used.

The procedure adopted here to correct integrated intensities for preferred orientation is explained in detail in reference 3. The method consists basically on being able to determine the preferred orientation distributions of the ferrite and austenite phases. This is achieved carrying out asymmetric diffraction so that crystals with their planes oriented at an angle \(\psi\) to the surface normal come into the diffraction condition, as shown in Fig. 1. The samples are always kept spinning around an axis perpendicular to the surface in the case where the preferred orientation distribution depends only on the angle \(\psi\).

\[
I_{X}^{\text{hkl}}(\psi) = I_{X}^{\text{hkl}}(1 + \tan \psi \cot \theta)
\] (3)

where \(I_{X}^{\text{hkl}}\) is the integrated intensity obtained under symmetric reflection for the \(hkl\) plane. The variation with \(\psi\) comes from changes in x-ray absorption and beam spread across the sample surface. In the present case the crystallites are not randomly oriented, thus equation (3) has to be corrected for

\[
I_{X}(\psi) = P_{X}^{\psi}(\psi) I_{X}^{\text{hkl}}(1 + \tan \psi \cot \theta)
\] (4)

In the present work it was measured the integrated intensities of the 200 ferrite \(k_{\text{Fe}}^{200}\) and 220 austenite \(k_{\text{A}}^{220}\) line as a function of the angle \(\psi\). An example of the diffraction profiles of one of the samples used here are shown in Fig. 2, with the range of the angle \(\psi\) from 0° up to 25°.

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\[
I_{X}(\psi) = P_{X}^{\psi}(\psi) I_{X}^{\text{hkl}}(1 + \tan \psi \cot \theta)
\] (4)
where \( P_X(y) \) is the ratio of the number of crystallites oriented in a given direction relative to the random crystal model.

The quantity \( P_X(y)I_{hkl}^{\text{IN}} \) is known as the texture function \( \Gamma_X(y) \). So starting from the measured integrated intensities we can determine the texture function.

The main objective of this work is to determine the ratio \( (I_{200}^{\text{F}}/I_{220}^{A}) \), as if the material did not present texture. It can be done determining the average of the texture function in all directions. The samples are kept spinning thus an average around the normal to the sample surface is achieved so it is only necessary to perform a measurement varying the angle \( y \). The orientation distribution function for these samples are characterized by a peak around \( y = 0^\circ \) and decays rapidly to zero within a few degrees. Then the procedure is to measure the texture function in a given interval, with this result to perform a fit and extrapolate the fitted result to 180\(^\circ\). Finally average in all space which gives the mean value of the texture function. This is equal to the integrated intensity of the \( hkl \) reflection divide by the multiplicity factor as if the material did not present preferred orientation. The result is divided by the multiplicity factor because in a strong oriented material not all the members of the family planes contribute to the intensity.

EXPERIMENTAL

All the x-ray measurements were carried out using a powder diffractometer PHILIPS, model X’Pert Pro, in step scan mode with step size of 0.02° and time per step of 2s. It was used CoKa (1.79010Å) radiation with 40KV and 40mA. In order to keep the beam completely on the sample for low incident angles it was used a divergence slit of 1/2°. The chemical analysis was performed in a scanning electron microscope PHILIPS, model XL30.

The samples used in this paper were duplex stainless steel UNS S31803 which has the average composition 22% Cr, 5% Ni, 2.5% Mo, 0.03% C and 0.14% N. They were cut in parallelepipeds, then they were heated up to 1300\(^\circ\)C and then cooled in three different ways, (a) water, (b) oil, (c) air, (d) oven (in fact the sample type b was cooled in the oven until 1000\(^\circ\)C and then put in water to prevent phase sigma).
RESULTS AND DISCUSSION

The atomic scattering factor used to determine the structure factor for calculating the volume fraction from equation 2 were obtained from the International Tables for Crystallography Volume C\(^2\). The alloying elements in the samples were supposed to be randomly oriented so the scattering factor can be written as a combination of them. Starting from the chemical analysis we write the atomic scattering factor for ferrite as 
f = 0.66f_{Fe} + 0.23f_{Cr} + 0.05f_{Ni} + 0.06f_{Mo} \text{ and for austenite } f = 0.69f_{Fe} + 0.21f_{Cr} + 0.07f_{Ni} + 0.03f_{Mo}.

It was assumed that the temperature parameters \(B_F = B_A\) and that these values will be \(\approx 0.35\) Å, the same as Fe at room temperature. The lattice parameters used to calculate the cell volume were obtained directly from the diffraction peak, \(a_F = 2.878\) Å and \(a_A = 3.609\) Å. The fitting procedure of the texture functions and the numerical calculations were done using the software package ORIGIN 5.0.

The x-ray diffraction patterns for the four samples are shown in Fig 2. The sample cooled in water clearly presents only the peaks related to the ferritic phase what lead us to conclude that the duplex stainless steel became an ferritic stainless steel. Similar thing happens with the sample cooled in the oven, in this case the sample became almost completely an austenitic stainless steel. In these two cases the x-ray diffraction patterns are very conclusive and the procedure described here is not needed.

![Figure 3. X-ray diffraction patterns for the four different samples showing the different intensities of the peaks related of ferritic and austenitic structures.](image)

The samples cooled in oil and air presents peaks corresponding to both austenitic and ferritic structures as can be seen in Fig 2. In this case, the intensities of these peaks varies when you compare the two samples, this means that the volume fractions of these phases are different in the two samples. Due to the texture presented in this material the procedure described before was used to determine this volume fraction.
Table 1. Results obtained for the breaths of the texture functions of each sample and each phase, the fractional volume corrected for texture and the fractional volume using the integrated intensity measured at $\Psi = 0^\circ$.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>$H_F$</th>
<th>$H_A$</th>
<th>$V_F$ (Corrected)</th>
<th>$V_F$ (Uncorrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>3.3</td>
<td>3.3</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Oil</td>
<td>4.8</td>
<td>3.6</td>
<td>91%</td>
<td>89%</td>
</tr>
<tr>
<td>Air</td>
<td>4.8</td>
<td>3.6</td>
<td>35%</td>
<td>37%</td>
</tr>
<tr>
<td>Oven</td>
<td>-</td>
<td>-</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

The texture functions $\Gamma_F(\psi)$ and $\Gamma_A(\psi)$ obtained for the samples cooled in the oil and in forced air as a function of $\Psi$ angle going from $0^\circ$ to $12^\circ$ are shown in Fig. 4. The results of the calculated volume fraction $V_F$ of ferrite, the breaths, $H_F$ and $H_A$, of the functions $\Gamma_F(\psi)$ and $\Gamma_A(\psi)$, and a different result for $V_F$ are present in Table I. The term $H$ is the angle in which the fitted texture function reach half of its value The texture has almost the same behavior for both phases, the difference in the $H$ value is minimal. The volume fraction termed non corrected are obtained from the integrated intensities of the peaks at $\Psi = 0^\circ$. The difference of only 2% between the corrected and non corrected volume fractions may be due to the fact that the texture functions of the austenitic and ferritic phases has almost the same behavior.

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REFERENCES

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