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Precipitation in the 15-5 PH alloy by anomalous small angle X-ray scattering

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Abstract . - The precipitation of A type partially coherent precipitates occurring in the first step of the structural hardening of the 15-5 PH martensitic stainless alloy was studied by anomalous small angle X-ray scattering at four absorption edges (KCr, KFe, KNi and KCu). An important anomalous effect was clearly observed at the KFe and KCu absorption edges. The precipitation occurs according to the two-phase model. Considering our alloy as a pseudo-ternary one (Cr+Ni, Fe, Cu), it has been possible to determine the slope of the tie-line corresponding to the precipitation taking place at 500°C.

I - Introduction

The precipitation hardening (PH) martensitic stainless steels are very used in the nuclear and aeronautical fields. In the 15-5 PH, having the chemical composition (in at %) as follows: 76.40-16.07Cr-4.68Ni-2.85Cu, the precipitation occurs in two steps as a function of increasing temperature, [1]. A structural hardening is associated with each step. The maximum of hardening takes place during the first step in the temperature range 400-550°C. This step was studied both by transmission electron microscopy and anomalous small angle X-ray scattering at four absorption edges (KCr, KFe, KNi and KCu).

The precipitates formed at 500°C were A type showing either a double-lobe strain contrast or a striated contrast as the one associated to 2-3 fine stacking faults. They give rise to streaks across the b.c.c. matrix diffraction spots and to maxima of intensity on these streaks about the position where a f.c.c. diffraction spot \{111\} will be observed when the precipitates will become f.c.c. (in accordance with the Kurdjumov and Sachs orientation relationship between f.c.c. and b.c.c. structure).

II - Bases of the ASAXS method

According to D. de Fontaine [2], the I(q,E) intensity scattered by a ternary alloy is a linear combination of the three independent partial structure functions (PSF) referred to as Sij(q). At small angles, the q dependence of the atomic scattering factor fi can be neglected, so I(q,E) can be expressed as follows:

\[ I(q,E) = F_1(E)^2S11(q) + 2F_1(E)F_2(E)\cos\Phi(q)S12(q) + F_2(E)^2S22(q) \]  

where : - q is the reciprocal vector = 4\pi\sin\theta/\lambda, E is the photon energy of wavelength \lambda and \theta is the Bragg angle,
- \( F_1 = |f_i-f_0| \) and \( F_2 = |f_j-f_0| \) are the modulus of the contrast and \( \cos\Phi(q,E) \) is the cosine of the angle between \( F_1 \) and \( F_2 \); i and j are the indexes of the solute elements and 0 is the reference element,
- \( f_i \) is the atomic scattering factor of element i and is equal to:
\[ Z_i + f_i' + f_i'' \]  

At least three experiments are necessary, but the three independent PSF can be determined by inversion of the overdimensioned system of linear equations after recording ASAXS intensity at different energies in the
neighbourhood of different absorption edges [3]. The PSF obey to the following relations:

\[ S_{ii}(q) > 0, \quad \forall q \]  \hspace{1cm} (3)

\[ S_{ij}(q)^2 < S_{ii}(q)S_{jj}(q) \quad \forall q \]  \hspace{1cm} (4)

From ref[3], in the case of proportional concentration profiles and when the interfaces between precipitates and matrix are sharp, the PSF are proportional to the same function \( \text{Spm}(q) \):

\[ S_{ij}(q) = \Delta C_i \Delta C_j \text{Spm}(q) \]  \hspace{1cm} (5)

where \( \Delta C_i \) is the difference of the solute \( i \) concentration between the precipitate \( p \) and the matrix \( m \) and \( \text{Spm}(q) \) the structure factor of the two-phase model.

### III - Results and discussion

In Figure 1 is shown one of the microstructures analysed by ASAXS.

![Figure 1 - Dark field electron micrograph of the 15-5 PH aged at 500°C for 2 h. The precipitates present a double lobe or a striated contrast which can be related to fine twinnings; their average size is about 15 nm.](image)

The atomic scattering contrasts are indicated in Table 1.

An anomalous effect was clearly observed at the three absorption edges \( K_{Cr} \), \( K_{Fe} \) and \( K_{Cu} \). It is the higher at the \( K_{Fe} \) (see Figure 2) and \( K_{Cu} \) edges and smaller at the \( K_{Cr} \) edge. It reveals an important difference in composition in particular in \( Fe \) and \( Cu \) between the matrix and the precipitates. At the \( K_{Ni} \) absorption edge, the effect was not noticeable.

We considered the 15-5 PH alloy as a pseudo-ternary one as follows: (Cr+Ni)-Fe-Cu.

In this alloy, the precipitation occurs according to the two-phase model because first, \( \Delta C_i / \Delta C_j \) determined from data obtained near one edge \( i \) are the same that the one determined near the other edge \( j \); secondly the relation \( S_{ij}(q)^2 - S_{ii}(q)S_{jj}(q) = 0 \) is fulfilled; in consequence, there is only one independent function \( \text{Spm}(q) \) which is the structure function of the precipitates, all \( S_{ij}(q) \) being proportional with related ratios.
Table 1 - Atomic scattering contrasts $F_1$ and $F_2$

<table>
<thead>
<tr>
<th>E(eV)</th>
<th>$F_1 = ‖f_{Fe} - f_{Cu}‖$</th>
<th>$F_2 = ‖f_{(Cr+Ni)} - f_{Cu}‖$</th>
<th>$\cos(F_1,F_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5840</td>
<td>3.67</td>
<td>6.276</td>
<td>0.9996</td>
</tr>
<tr>
<td>5920</td>
<td>3.70</td>
<td>6.719</td>
<td>0.9995</td>
</tr>
<tr>
<td>5955</td>
<td>3.71</td>
<td>7.275</td>
<td>0.9993</td>
</tr>
<tr>
<td>5972</td>
<td>3.72</td>
<td>7.864</td>
<td>0.9992</td>
</tr>
<tr>
<td>5980</td>
<td>3.73</td>
<td>8.422</td>
<td>0.9990</td>
</tr>
<tr>
<td><strong>K Cr absorption edge (5988 eV)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6875</td>
<td>4.81</td>
<td>4.354</td>
<td>0.8829</td>
</tr>
<tr>
<td>6990</td>
<td>5.43</td>
<td>4.210</td>
<td>0.8850</td>
</tr>
<tr>
<td>7056</td>
<td>6.28</td>
<td>4.132</td>
<td>0.8873</td>
</tr>
<tr>
<td>7090</td>
<td>7.20</td>
<td>4.092</td>
<td>0.8897</td>
</tr>
<tr>
<td>7104</td>
<td>8.36</td>
<td>4.077</td>
<td>0.8920</td>
</tr>
<tr>
<td><strong>K Fe absorption edge (7112 eV)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8880</td>
<td>2.35</td>
<td>1.917</td>
<td>0.8963</td>
</tr>
<tr>
<td>8940</td>
<td>2.79</td>
<td>2.000</td>
<td>0.9538</td>
</tr>
<tr>
<td>8960</td>
<td>2.93</td>
<td>2.398</td>
<td>0.9846</td>
</tr>
<tr>
<td>8973</td>
<td>3.41</td>
<td>3.453</td>
<td>0.9982</td>
</tr>
<tr>
<td><strong>K Cu absorption edge (8980 eV)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The tie-line slope $ΔC_{Fe}/ΔC_{(Cr+Ni)}$ deduced from ASAXS data near the absorption edges Cr and Fe edges, in the case of the alloy aged at 500°C for 2 h., was found equal to 3.50
Figure 2 - Corrected experimental ASAXS intensity curves versus q for the 15-5 PH alloy aged at 500°C for 2 h., near the KFe absorption edge.

The calculated partial structure functions $S_{ij}(q)$ are shown in Figure 3. The SCu-Cu is the highest.

Figure 3 - Calculated partial structure function $S_{ij}(q)$ in the case of the 15-5 PH alloy aged at 500°C for 2 h.

IV - Conclusion

In the 15-5 PH alloy, we have shown by ASAXS that the A type precipitates are very enriched in Cu. Such a result was recently confirmed by X microanalysis on extracted replica in which the $\Delta C_{Fe}/\Delta C_{(Cr+Ni)}$ was found to be identical [4].

References