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APPLICATIONS OF A.E.M. TO RAPIDLY SOLIDIFIED MATERIALS

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Abstract - We describe (a) a STEM analysis of centrifugally-atomised powders of high-phosphorous steels, and (b) a study of the oxide scale formed on wrought or rapidly solidified stainless steels during high-temperature oxidation.

It is now well established that rapid solidification of alloys holds considerable advantage over conventional processing because of the fuller potential for microstructural control realizable through rapid solidification. With this new emphasis on microstructural control via rapid solidification processing has come the need for detailed microstructural analysis. Also, with the reduction in size of characteristic microstructural entities that occurs on rapid solidification, there developed a need for new experimental techniques that could probe both structure and composition with much higher resolution than was previously available. Fortunately, the advent of scanning transmission electron microscopy (STEM) occurred virtually simultaneously with the developments of rapid solidification technologies. With STEM, the capability for compositional analysis by X-ray fluorescence spectroscopy with a spatial resolution on the order of 5 nm in electron transparent sections has been realized. In this paper we present two examples drawn from research involving microstructural characterization of rapidly solidified steels.

The field emission STEM used in this work is a V.G. Microscopes HB5 instrument fitted with an energy-dispersive X-ray analysis system and an electron energy loss spectrometer. The electron source is a cold tungsten field emitter. There is a two-lens electron probe forming system, by which typically 2 nA of 100 kV electrons can be formed into a probe approximately 1.6 nm diameter on the specimen. The vacuum in the specimen chamber is \( \approx 2 \times 10^{-9} \) torr, which minimizes any problems of specimen contamination. The X-ray detector is a Kevex Si (Li) detector in the ultra-thin window (UTW) configuration coupled to a Kevex 7000 multichannel analyser and microcomputer system for spectral manipulation.

Of particular importance in this research has been the construction of composition profiles across solidification-related microstructural features. Where grain boundaries or cell walls have been analyzed the analysis was performed by orienting the grain boundaries parallel to the electron beam and then manually stepping the electron probe along a line perpendicular to the boundary. After each point has been analyzed, the boundary was examined to ensure that no specimen drift had occurred before repositioning the probe at the next data point. Whenever possible, boundaries were selected that were perpendicular to the edge of the foil so that the step scan occurred in a region of uniform...
thickness. Additionally, the line of the step scan was oriented perpendicular to the line between the specimen and the X-ray detector.

**STEM Analyses of High-Phosphorus Steel Powders**

Steel powders with a composition of Fe-16Cr-10Ni-0.4P (wt. pct.) were produced via centrifugal atomization. The average cooling rate for these powders is ~10^5°C/sec. Powders were "sandwiched" in a Ni electroplate and prepared as thin sections for electron microscopy by standard techniques. Observations of these powders revealed that their microstructure was composed of crystalline dendrites or cells surrounded by an intercrystalline (or intercellular) amorphous phase. By means of quantitative X-ray analysis the composition of the amorphous phase was found to be Fe-36Cr-7Ni-8P (at. pct.).

In Figure 1 is presented the data which supports the observation and analysis of the amorphous phase in this alloy. The convergent beam patterns across the dendrites in the image show a definite amorphous character, through the diffuse halo, for the intercellular phase. The composition profile substantiates the segregation of Cr and P to this phase. In addition to these observations it has been found that ~5% of the powder is ferromagnetic (i.e., bcc) while the remainder of the powder is the expected fcc phase. The bcc powders predominate at the smaller sizes and are present as a result of the nucleation dependent phenomenon of alternative phase formation in isolated liquid droplets. Additional observations of this type have also been made in 303 stainless steel.

**Analysis of the Oxide Layer Formed on Stainless Steel**

In stainless steels, a layer of silica is formed between the metal and the chromium oxide during high-temperature oxidation. This silica can grow down the grain boundaries of the underlying metal, possibly providing a "pegging" effect (1). In some cases, it has been reported that the silica can form an essentially continuous layer (2,3). We are investigating the effects of rapid solidification processing upon the oxidation characteristics as we would expect (a) an increase in the chromium transport to the surface by grain boundary migration, and (b) possibly an increase in silicon migration by the same mechanism, both of which should improve the oxidation performance of the material.

We studied a wrought (W) 310 stainless steel, and a rapidly solidified (RS) 303 steel prepared from centrifugally atomized powder. The compositions are given in Table 1. The silicon content is somewhat above half of the optimum content found by Evans et al. (2) to minimize the parabolic rate constant for oxidation. Average grain sizes were 45μm and 5.6μm for the W-310 and RS-303 respectively.

It has been shown by Yurek et al. (1) that in cyclic oxidation experiments performed at 900°C the RS-303 performed very much better than the W-310, the weight gain of the RS 303 being lower, and spallation on this steel being virtually non-existent.

We prepared transverse slices of the oxide layer by a process essentially as developed by M. Tinker (private communication). Briefly, the process was as follows: Specimens were prepared for oxidation in the form of small bars, 2.0mm x 5mm x ~15 mm. After oxidation, a thin nickel layer was deposited by vacuum evaporation on each face of the bar. Approximately 0.5mm of nickel was electrodeposited on the sample, the cross-section now being 3.0mm x 1.5mm. Slices approx. 0.5mm thick were cut from the bar with a diamond slitting wheel. The slices were thinned on silicon carbide paper followed by diamond polish to a thickness of ~50μ. The final thinning was performed by ion-milling.

Figure 2 shows an annular dark field image of the W-310, oxidized at 1000°C for 100 hours in dry oxygen, with a sketch indicating the composition of the different regions. Figure 3 is another dark field region of the same specimen, with the corresponding silicon pulse map, showing three areas of silica, two at the oxide/metal interface, one within the metal.
In Figure 4 is seen an area of the oxide/metal region of the RS 303 which has undergone a similar oxidation treatment. The metal/oxide interface is seen to be very convoluted, and structures are seen growing back into the metal. Energy-dispersive X-ray analysis shows these to be composed only of silicon and oxygen, and microdiffraction shows them to be vitreous. At high magnifications, a silica layer can sometimes be seen between the oxide and the metal, (Fig. 5), and sometimes it can be seen that no such layer exists.

No significant differences were noticed in the outer oxide layers of the two steels. Thus it appears that the improvement in oxidation resistance of the rapidly solidified steel is due at least in part to the promotion of the formation of a vitreous intergranular film of silica at and near the metal/oxide interface in this steel. It is possible that further improvements in performance could be obtained if this layer became continuous, although it has been shown (2) that increases in silicon content above about 0.9% cause degradation in the oxidation characteristics.

Fig. 1 - Bright field STEM image from a 90 μm diameter high-phosphorous steel powder. The microdiffraction patterns and composition profile traverse the intercellular region between two crystalline dendrites as indicated.
References

TABLE I - Compositions of Steels (wt. %)

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Co</th>
<th>S</th>
<th>P</th>
<th>Mo</th>
<th>Cu</th>
<th>C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-310</td>
<td>24.1</td>
<td>19.5</td>
<td>1.6</td>
<td>.53</td>
<td>--</td>
<td>.008</td>
<td>.002</td>
<td>.2</td>
<td>--</td>
<td>.033</td>
<td>bal.</td>
</tr>
<tr>
<td>RS-303</td>
<td>17.31</td>
<td>8.68</td>
<td>1.60</td>
<td>.62</td>
<td>.15</td>
<td>.34</td>
<td>.028</td>
<td>.37</td>
<td>.78</td>
<td>.059</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Fig. 2. Annular dark-field (ADF) image of scale formed on W-310. In the sketch (right) regions marked 1 are spinel (Cr$_2$MnO$_4$), the region marked 2 is a fine-grained Cr$_2$O$_3$ with Fe and Mn dissolved in varying amounts, regions marked 3 are complex regions including silica. Fig. 3. ADF image (left) and corresponding silicon map (right) of scale/metal region on the W-310. Three areas of silica are seen. Fig. 4. ADF image of scale/metal interface region of RS 303 steel, showing structures (determined to be silica) growing along the grain boundaries of the metal. Fig. 5. ADF image of silica layer (bright band) growing between Cr$_2$O$_3$ (above) and metal (below) in RS-303.