Sensitization of type 430 ferritic stainless steel during continuous annealing

by P.C. Pistorius* and M. Coetzee*

Synopsis

The possibility that type 430 stainless steel can become sensitized during annealing after hot-rolling was studied by simulated cycles of continuous-annealing heat treatments, and by calculation of the carbon solubility. It was found that the lower-carbon steel could be sensitized at lower annealing temperatures than the higher-carbon steel, which is in line with plant experience. The difference in sensitization behaviour is ascribed to the lower rate of recovery of the lower-carbon steel during cooling, since recovery is sensitive to the grain size. At practical heat-treatment temperatures, austenite formation does not play a role.

Introduction

'Gold dusting' is a surface defect that is sometimes observed on cold-rolled AISI type 430 stainless steel. Gold dusting is characterized by a sparkling appearance, which results from small flakes of metal on the cold-rolled surface. Figure 1(a): the flakes are mostly elongated in the rolling direction. When such a surface is etched to reveal the underlying grain structure, Figure 1(b), it is apparent that the size and orientation of the flakes bear no relationship to the grain structure of the cold-rolled metal. These observations indicate that gold dusting is caused by a processing step prior to cold rolling. The previous processing steps include continuous casting, hot rolling, continuous annealing, and pickling. One possibility is that the flakes of metal are grains that had been undercut by intergranular corrosion; such intergranular corrosion may occur during pickling after the annealing step (which itself follows hot rolling). If intergranular corrosion does occur during this pickling step, the intergranular cavities would be elongated by subsequent cold rolling, this can account for the observed morphology of gold dusting.

If the steel has been sensitized, intergranular corrosion may occur during pickling. Pickling is commonly carried out by electrolytic descaling in a neutral sodium sulphate solution, followed by immersion in a nitric acid/hydrofluoric acid bath. The present authors have found in laboratory investigations that sensitized type 430 stainless steel does, indeed, suffer intergranular corrosion in a nitric acid/hydrofluoric acid bath, while it is largely unaffected during electrolytic pickling. Hence, sensitization is a plausible cause of gold dusting. This paper describes an investigation of the possibility that the material is sensitized during annealing after hot rolling.

There is a large body of evidence that supports the theory that the sensitization of ferritic stainless steels—like that of the austenitics—is the result of a local reduction in

Figure 1—Scanning electron photomicrographs of gold dusting on the surface of cold-rolled type 430 stainless steel. The rolling direction is vertical.

(a) Surface of cold-rolled sheet.

(b) Surface after etching to reveal grain boundaries.

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chromium content in those regions of the alloy adjoining chromium-rich grain-boundary carbides. The observed differences between the sensitization behaviour of ferritic steels and that of austenitics stem from the much more rapid diffusion of both carbon and chromium in ferrite. Because of this rapid diffusion, the precipitation of carbides (and the associated sensitization) in commercial ferritic stainless steels can generally not be prevented even by water quenching from the temperature range where carbon is soluble in the metal matrix. However, this effect is mitigated by the rapid recovery of the alloy, which restores the corrosion resistance by diffusion of chromium into the chromium-depleted areas adjacent to the grain boundaries. Once the alloy is in the recovered state, it is no longer sensitized, and it can be re-sensitized only if it is re-heated to the temperature range where the carbides re-dissolve; it is generally stated that the carbides dissolve above about 950°C, although this temperature is expected to depend on the amounts of both chromium and carbon in the alloy.

Sensitization testing showed that, subsequent to hot rolling, type 430 stainless steel is in the recovered condition. Hence, sensitization during annealing is possible only if the chromium carbides are re-dissolved. The typical annealing temperature is 880°C, which appears too low for the dissolution of carbide in the light of the results cited above. The present investigation aimed to show whether sensitizing below 950°C can dissolve sufficient carbon for sensitization to occur. The approach involved the use of experimental annealing cycles, and the calculation of the carbon solubility from thermodynamic data.

Experimental

Annealing cycles

Two AISI type 430 steels were tested in the hot-rolled condition; the compositions are given in Table I. The major difference between the steels concerned the carbon content. Plant experience suggested that gold dusting is much less frequent on steels with a higher carbon content (around 0.04 per cent C) than on those with less carbon (around 0.015 per cent C).

For the simulated annealing cycles, specimens 2 mm thick, 19 mm wide, and 65 mm long were cut from the hot-rolled steel. The specimens were heated in a welding simulator, spending approximately 120 seconds at the peak temperature. Typical thermal cycles are illustrated in Figure 2. The time at peak temperature and the subsequent cooling rate were selected to be similar to the actual annealing cycle in a plant. Peak temperatures ranged from 745 to 980°C.

Figure 2—Typical thermal cycles to which the hot-rolled specimens were subjected to simulate continuous annealing. The two cycles shown are for the highest and lowest annealing temperatures considered.

Sensitization testing

Potentiostatic etching was used in a test of whether the specimens were sensitized after the annealing cycle. This procedure is based on the effect of chromium content on the passivation potential of iron-chromium alloys in 0.5 M H_2SO_4 as illustrated in Figure 3. If the potential of an alloy is below its passivation potential, the alloy dissolves actively with a high anodic current, whereas the alloy is passive for potentials above the passivation potential, giving a low anodic current. Hence, if the potential is controlled at a given value, E_{etch}, those parts of the microstructure containing less chromium than that which gives a passivation potential of E_{etch} will corrode actively, while parts containing more chromium will be passive. As Figure 3 shows, if the potential is controlled at 0.100 V relative to the saturated calomel electrode, regions with less than approximately 11 per cent Cr (i.e. chromium-depleted regions) are active. In this way, the current density during potentiostatic etching gives a quantitative indication of the presence of chromium-depleted regions. In addition, microscopic investigation after the etching treatment can identify those regions which had dissolved.

For the potentiostatic etching, an area of 1.23 cm² of each specimen was exposed to an electrolyte of 0.5 M H_2SO_4 at 25°C. The potential was maintained at 0.100 V (relative to the saturated calomel electrode) for 300 seconds, recording the current density at the end of this period.

Table I

<table>
<thead>
<tr>
<th>Element</th>
<th>Stainless steel 1 (higher carbon)</th>
<th>Stainless steel 2 (lower carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>16.60</td>
<td>17.00</td>
</tr>
<tr>
<td>C</td>
<td>0.0370</td>
<td>0.0140</td>
</tr>
<tr>
<td>N</td>
<td>0.0171</td>
<td>0.0142</td>
</tr>
<tr>
<td>Si</td>
<td>0.73</td>
<td>0.70</td>
</tr>
<tr>
<td>Mn</td>
<td>0.54</td>
<td>0.42</td>
</tr>
<tr>
<td>Ni</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>Mo</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Ti</td>
<td>0.005</td>
<td>0.006</td>
</tr>
<tr>
<td>V</td>
<td>0.003</td>
<td>0.007</td>
</tr>
<tr>
<td>S</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>P</td>
<td>0.017</td>
<td>0.021</td>
</tr>
<tr>
<td>C</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Co</td>
<td>0.013</td>
<td>0.015</td>
</tr>
<tr>
<td>Al</td>
<td>0.024</td>
<td>0.034</td>
</tr>
<tr>
<td>Nb</td>
<td>0.003</td>
<td>0.005</td>
</tr>
</tbody>
</table>

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300 seconds was found to be sufficiently long to ensure that the measured anodic current density was not due to hydrogen dissolved in the steel, and to allow sufficient dissolution to facilitate subsequent microscopic investigation.

**Calculation of carbon solubility**

For the calculation of the carbon solubility, use was made of thermodynamic data for the Fe-Cr-C system as compiled by Arai et al.\textsuperscript{15}. Comparison with experimentally measured phase distributions is necessary as a test of the validity of the predictions made on the basis of these data. Unfortunately, there is a paucity of experimental data for 17\% Cr alloys in the low-carbon range, which was the range of interest in the present investigation. However, the calculations can be tested by a comparison of the predicted and the measured compositions of the M\textsubscript{23}C\textsubscript{6} carbide, which is responsible for sensitization. The general formula for this carbide is Cr\textsubscript{23}Fe\textsubscript{23}\textsubscript{(1-y)}C\textsubscript{6}. The value of $Y$, the atomic fraction of the metallic component of the carbide that is made up of chromium, depends on the temperature and on the composition of the phase with which the carbide is in equilibrium. Arai et al.\textsuperscript{15} modelled the formation of this carbide by assuming it to be a regular solution of Cr\textsubscript{23}C\textsubscript{6} and the hypothetical carbide Fe\textsubscript{23}C\textsubscript{6}. Based on the data of Arai et al.\textsuperscript{15}, this assumption yields a value for the free energy of formation of the carbide, which can be used to give the equilibrium constant, and hence the activity of carbon in equilibrium with the carbide (with a certain value of $Y$) and with austenite or ferrite of a given composition. The equilibrium value of $Y$ was determined as the value (between 0 and 1) that minimized the free energy of the system. The calculated values of $Y$ are compared with the experimental results of Benz et al.\textsuperscript{16} in Figure 4; it is apparent that the agreement is satisfactory. The positions of the various phase boundaries ($\alpha = \alpha + \gamma$, $\alpha = \alpha + M\textsubscript{23}C\textsubscript{6}$, $\gamma = \gamma + M\textsubscript{23}C\textsubscript{6}$, and $\alpha + \gamma = \alpha + \gamma + M\textsubscript{23}C\textsubscript{6}$) were calculated in a similar manner by imposing the criteria of minimum free energy at equilibrium and equality of activity of carbon and chromium in all the phases that are in equilibrium. The results of these calculations are presented later in this paper in Figure 7.

As another test of the accuracy of the calculations, the calculated temperatures for the appearance of austenite in low-carbon 17\% Cr alloys were compared with the experimental results of Tricot and Castro\textsuperscript{17}; the calculated temperatures (approximately 900°C, depending on the carbon and chromium content) agreed with the results of Tricot and Castro within the 50°C resolution of their experimental data. It thus appears reasonable to assume that the data of Arai et al.\textsuperscript{15} provide a reliable description of the Fe-Cr-C system.

**Results and discussion**

The results from the potentiostatic etching of the two grades of type 430 stainless steel following annealing at different temperatures are presented in Figure 5. In this diagram, current densities below approximately 4 μA/cm\textsuperscript{2} indicate that the alloy is passive (no sensitization). The diagram reveals that some sensitization of the lower-carbon alloy occurs after annealing at 859°C, while sensitization of the higher-carbon alloy requires annealing at 897°C or higher. Investigation of the potentiostatically etched surfaces (by scanning electron microscopy) confirmed that intergranular attack had occurred in these specimens. The results in Figure 5 agree with the plant experience that gold dusting is more likely in the lower-carbon steel, where a lower annealing temperature (within the range used in plant practice) dissolves sufficient carbon to sensitize this steel, while a higher annealing temperature is required to sensitize the higher-carbon steel. It is also apparent that annealing temperatures substantially lower than the quoted value\textsuperscript{5,6,11} of 950°C can result in sensitization.

These results, while in agreement with plant experience, are somewhat paradoxical, in that they seem to indicate that a lower-carbon alloy is more easily sensitized than one of...
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Figure 5—Current density, after 300 seconds of potentiostatic etching at 0.100 V_{OCP} in 0.5 M H_2SO_4 for hot-rolled specimens of the lower-carbon and higher-carbon type 430 stainless steels, after simulated continuous annealing at different peak temperatures. Current densities higher than approximately 4 μA/cm² indicate sensitization. Multiple points were obtained from replicate experiments.

higher carbon content—while carbon in solution is necessary for sensitization. Previous workers have suggested that, for higher-carbon alloys, the formation of austenite at elevated temperatures prevents sensitization by strong partitioning of the carbon to the austenite (which forms martensite upon cooling)\(^7,15\). The validity of this mechanism for the present situation was tested by an examination of the microstructures, and by calculation of the carbon solubility.

Figure 6 contains representative optical micrographs. In most cases, two micrographs are presented for each structure: one gives the appearance after etching with Ralph’s etchant\(^18\), and the other after electrolytic etching in oxalic acid\(^18\). The former etchant reveals the general structure, while the latter preferentially etches the carbides. After hot rolling, both steels had a deformed, unrecrystallized grain structure, Figure 6(a) and (b). Annealing at 745°C resulted in recrystallization, Figure 6(c) and (d): the two steels have similar grain sizes after this annealing process, while the carbide distribution is unchanged from that in the as-hot-rolled structure, Figure 6(e) and (f). Evidently, the carbide distribution is quite non-uniform and bears no relation to the grain structure at this stage, but does appear to be elongated in the rolling direction. Annealing at a higher temperature (859°C) results in little grain growth in the higher-carbon steel, Figure 6(g), while significant grain growth occurs in the lower-carbon steel, especially in the regions where the grain boundaries are not pinned by carbides, Figure 6(h): for these two microstructures, the average grain diameter (determined by the linear intercept method) is 84±12 μm for the lower-carbon steel and 27±2 μm for the higher-carbon steel. Carbides are present on the grain boundaries of both steels after this annealing process, Figure 6(i) and (j).

No martensite was present following the 745°C or 859°C heat treatment; the lowest annealing temperature for which martensite was observed was 914°C, Figure 6(k). This temperature of austenite formation is slightly lower than that predicted by the thermodynamic calculations (Figure 7), which is not surprising given that the effects of elements other than Fe, Cr, and C were neglected in the calculations. However, the correspondence is close enough to give some
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Figure 6—Optical micrographs of hot-rolled and heat-treated specimens of type 430 stainless steel. The rolling direction is vertical in (a) to (k), i.e. all the micrographs
(a) Higher-carbon steel as hot-rolled (Ralph's etch)
(b) Lower-carbon steel as hot-rolled (Ralph's etch)
(c) Higher-carbon steel annealed at 745°C (Ralph's etch)
(d) Lower-carbon steel annealed at 745°C (Ralph's etch)
(e) Higher-carbon steel annealed at 745°C (oxalic acid etch)
(f) Lower-carbon steel annealed at 745°C (oxalic acid etch)
(g) Higher-carbon steel annealed at 859°C (Ralph's etch)
(h) Lower-carbon steel annealed at 859°C (Ralph's etch)
(i) Higher-carbon steel annealed at 859°C (oxalic acid etch)
(j) Lower-carbon steel annealed at 859°C (oxalic acid etch)
(k) Higher-carbon steel annealed at 914°C (Ralph's etch)
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Confidence in the predictions of the calculations. The calculated phase diagrams in Figure 7 predict little difference in the carbon solubility in the two steels up to the temperature of austenite formation.

In summary, the results show that the lower-carbon steel is more susceptible to sensitization (Figure 5), despite the facts that the carbon solubility in the two steels is identical in the temperature range where the sensitization difference arises (Figure 7), that no martensite forms in this temperature range (Figure 6) and Figure 7), and that grain-boundary carbides form in both steels (Figure 6(i) and (j)). It is thought that the difference in intergranular corrosion behaviour can be explained, not by the carbide precipitation step, but by the recovery step. In principle, three requirements can be stated for the sensitization of a ferritic steel: firstly, sufficient carbon must be brought into solution during annealing to allow subsequent grain-boundary precipitation; secondly, grain-boundary carbide precipitation must occur during cooling; and, lastly, recovery must not take place. From the presence of grain-boundary carbides, Figure 6(i) and (j), it is evident that the first two requirements are met by both steels. It is therefore concluded that the difference between the two steels lies in their recovery behaviour: the higher-carbon steel is not susceptible to intergranular corrosion after annealing at 859°C, despite the presence of grain-boundary carbides. This indicates that this steel recovered during cooling. It is not unexpected that recovery plays a prominent role in determining whether ferritic stainless steel is susceptible to intergranular corrosion given the rapidity of carbide precipitation, which, as mentioned in the introduction, cannot be suppressed by water quenching.

In this light, the differences in the susceptibility of the two steels to intergranular corrosion after annealing can be explained by different rates of recovery. The rate of recovery depends on the distance over which chromium must diffuse to replenish the chromium-depleted zones; this distance is proportional to the width of the chromium-depleted zone. Since the M23C6 carbide forms at an approximately stoichiometric ratio of chromium to carbon (with θ around 0.7, Figure 4), a thicker grain-boundary carbide 'film' will result in a wider chromium-depleted zone. If one assumes that carbide precipitation occurs to an equal extent on all grain boundaries (which is approximately so, as indicated in Figure 6(i) and (j)), then the thickness of the carbide film is proportional to the amount of carbon that precipitates from solution, and inversely proportional to the ratio of the grain-boundary area to the grain volume. These arguments have been quantified by Stawstrom and Hillert19, who arrived at the following approximate expression for the time for recovery (that is, the time required to increase the chromium content adjacent to the carbide to above the minimum value for passivity):

\[
t = \left(\frac{h_{Cr}}{x_{Cr} - 0.13}\right)^2 \frac{D}{D}
\]

In equation [1], the expression between brackets is proportional to the chromium-diffusion distance, with \(h\) the ratio of the grain volume to the grain-boundary area (which approximates to \(d/6\), where \(d\) is the average grain diameter); \(x_{Cr}\) the molar fraction of carbon in solution, which precipitates out as a carbide film; \(x_{Cr}\) the molar fraction of chromium in the alloy; 0.13 the minimum molar fraction of chromium in the solid solution that is assumed to be required for passivity; and \(D\) the diffusion coefficient of chromium.

From equation [1] it is apparent why the time for recovery will be longer for the lower-carbon alloy. Consider, for example, the situation after annealing at 859°C. While both alloys have 0.002 per cent C in solid solution (Figure 7), and thus \(x_{Cr} = 1.0 \times 10^{-4}\), the average grain diameter of the lower-carbon alloy is approximately three times that of the higher-carbon alloy (Figure 6(g) and (h)), resulting in a recovery time that is nearly an order of magnitude larger. For example, if one considers recovery at a constant temperature of 700°C, where the diffusion coefficient of chromium is approximately \(5.1 \times 10^{-16} \text{m}^2/\text{s}\), and uses average grain diameters of 84 μm and 27 μm for the lower-carbon and higher-carbon steels respectively, the recovery times are calculated as 25 seconds and 2.6 seconds respectively. This difference appears to be sufficient to explain why the lower-carbon alloy does not recover during the particular cooling cycle that was employed here (Figure 2), while the higher-carbon alloy does recover. (It is not thought that sensitization-free carbide precipitation, such as that which occurs in austenitic stainless steels19, plays a role here. The reason for this is that the chromium concentration in equilibrium with M23C6 and carbon in solution is strongly temperature-dependent. For example, it has been calculated that the chromium concentration—in ferrite—in equilibrium with 0.002 per cent C in solution drops from 17 per cent at 850°C to 10 per cent at 830°C, and to 6 per cent at 800°C.)

Differences in the rate of recovery can also be used to explain the observed effect of increased sensitization with increased annealing temperature (Figure 5). Higher annealing temperatures bring more carbon into solution (Figure 7), as well as causing grain growth; as expressed by

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equation [1], both factors promote a wider chromium-depleted zone, for which the recovery time is longer. In this way, more sensitization is retained after the alloy has cooled to room temperature from a higher annealing temperature.

Conclusion

The lower-carbon type 430 stainless steel can be sensitized by continuous annealing below 880°C (the annealing temperature used during production), while the higher-carbon steel is sensitized only at annealing temperatures of 897°C or higher. The differences in sensitization behaviour appear to be explicable by differences in the rate of recovery during cooling after annealing; less recovery takes place in the lower-carbon steel because of its larger grains, which result in wider chromium-depleted zones. The lower-carbon steel appears to be inherently more susceptible to grain growth because of less grain-boundary pinning by carbides. From these results, it appears plausible that the gold-dusting defect is caused by sensitization during continuous annealing. The results also suggest practical measures that can be taken to prevent sensitization. These include a limiting of the annealing temperature to 840°C (which is still sufficient for recrystallization), a lowering of the cooling rate after annealing (by the use of batch annealing, for example), and a limiting of grain growth.

Acknowledgements

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References