An Investigation of the Sensitization Behavior of Fe-Mn-Cr Austenitic Steels*

G. E. C. Bell, P. F. Tortorelli, and E. A. Kenik

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Oak Ridge National Laboratory

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Oak Ridge, Tennessee 37831

U. S. A.

Abstract

Standard chemical immersion (modified Strauss) tests and analytical electron microscopy (AEM) showed that reduced activation austenitic steels based on Fe-20Mn-12Cr-0.25C (wt %) are extremely prone to thermal sensitization and intergranular corrosion because of their high carbon contents and low chromium concentrations. This susceptibility to sensitization after thermal aging, fabrication, or irradiation makes their use in aqueous and other certain environments problematical. Excellent correlation between intergranular corrosion induced by immersion in the acidified CuSO_4 solution and the presence of narrow chromium-depleted zones around grain boundaries, as determined by AEM, was found. Due to the need to meet reduced activation requirements, the opportunities to increase the sensitization resistance of fully austenitic Fe-Mn-Cr steels by alloy design are limited.

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Introduction

In order to help minimize the the safety and environmental risks of future fusion reactors, the development of "reduced activation" materials has been a focus of fusion programs throughout the world.[1] To that end, a series of fully austenitic Fe-Mn-Cr alloys, which have better tensile properties than standard Fe-Ni-Cr stainless steels and meet current U.S. activation guidelines for shallow land burial after 10 to 100 years has been defined.[2,3] Low chromium concentrations and high carbon levels (as compared to 300-series stainless steels) were necessary to maintain full austenitic stability because manganese is not as strong an austenitic stabilizing element as nickel.[3] Those compositions are normally not consistent with resistance to sensitization which can occur when chromium is depleted locally in the matrix due to nucleation and growth of chromium-rich carbides (normally at grain boundaries) by heating at intermediate temperatures (500-700°C). Sensitization can also be caused by radiation-induced segregation.[4,5] In aqueous environments, sensitized stainless steel can be quite susceptible to intergranular stress corrosion cracking. Prior work[6] has shown that such cracking of high-Mn steels can occur for certain compositions. The present study was undertaken to assess the sensitization behavior of this new class of Fe-Mn-Cr steels.

Experimental Procedures

Small ingots of several Fe-Mn-Cr compositions were melted for this sensitization study. Their compositions are listed in Table 1. Except for 10Mn-16Cr, all alloys were within the austenite phase stability range determined for this system.[2] The details of the thermomechanical processing are described elsewhere.[3] Susceptibility to sensitization and intergranular corrosion was evaluated for these alloys and standard types 304L, 304, and 316L stainless steels using the modified CuSO₄ (Strauss) Test, as defined per ASTM Standard Practice A262E.[7] The test environment was a boiling acidified CuSO₄ solution, which accelerated intergranular corrosion of sensitized austenitic stainless steels. This type of corrosive attack is normally revealed by the cracking that occurs upon bending after exposure.[7] The dimensions of the specimens used for these exposures were 65 x 14 x 0.8 mm. For this specimen thickness, the bending radius (1 cm) was such that strain was approximately 4%.[7] Selected Fe-Mn-Cr steels were thinned for examination by analytical electron microscopy (AEM) using a Phillips 400T-FEG. The Fe-Mn-Cr alloys and standard stainless steels were exposed in two conditions: annealed (1150°C, 1 h in argon, water quenched) and "aged" (annealing followed by 650°C, 2 h in vacuum, water quenched). During a test, two specimens (one annealed and one aged) of the same composition

were individually wrapped in copper wire and embedded in copper shot (per standard practice) and then simultaneously exposed in the same solution.

Results

Chemical Tests

The CuSO_4 exposures were divided into two sequential parts. In the first series, specimens were exposed for 48 h (which is typical for the standard practice[7]). Types 304 and 304L stainless steel and all of the Fe-Mn-Cr compositions listed in Table 1 were examined. The aged Fe-Mn-Cr steels were extensively attacked: the specimens sagged under their own weight and easily crumbled when touched. An example of this condition is shown in Fig. 1. Within 1 h of the start of immersion of all the Fe-Mn-Cr alloys, the light blue CuSO_4 solution turned a dark green indicative of the presence of Cr^{6+} in the liquid. All aged specimens of the Fe-Mn-Cr alloys were plated with copper due to the large galvanic current in the sensitized regions. In contrast, the aged type 304 stainless steel became embrittled, but retained integrity. It cracked (intergranularly) only when stress (albeit small) was applied. The aged type 304L stainless steel showed only a small amount of cracking when a greater stress was applied by bending. Little change in the color of the solution was noted for the types 304L and 304 stainless steel tests. For every composition, the postimmersion integrity of the annealed specimens was not affected (Fig. 1).

In an attempt to obtain a greater differentiation between different alloy compositions, the immersion time in the CuSO_4 solution was reduced to 8 h for a second series of exposures of most of the Fe-Mn-Cr alloys and types 304, 304L, and 316L stainless steel. Under this condition, all the standard austenitic stainless steels "passed" (no visible signs of cracking after immersion and bending), while the aged Fe-Mn-Cr steels (the first five listed in Table 1) all failed in a similar manner to that described above for the first set of experiments. As before, none of the annealed specimens exhibited any cracking tendency after exposure to the solution.

Analytical Electron Microscopy

The Fe-Mn-Cr steels designated as 20Mn-12Cr, 20Mn-12Cr-1W, 20Mn-12Cr-0.3Ti, and 20Mn-12Cr-1W-0.3Ti (Table 1) were examined by transmission electron microscopy with associated energy dispersive x-ray analysis. For 20Mn-12Cr, some grain boundary M_{23}C_6 carbides were

found to exist even in the annealed condition. Upon aging for 2 h at 650°C, an almost continuous chain of these carbides was observed at some grain boundaries (see Fig. 2). Annealed 20Mn-12Cr-1W also had some $M_{23}C_6$ grain boundary carbides, but none were observed for 20Mn-12Cr-0.3Ti and 20Mn-12Cr-1W-0.3Ti. However, large MC carbides were observed at the grain boundaries of 20Mn-12Cr-0.3Ti and 20Mn-12Cr-1W-0.3Ti in both conditions. After aging at 650°C, $M_{23}C_6$ carbides were also present in these two alloys (see Fig. 3). X-ray analyses revealed significant depletion of chromium around grain boundaries of aged material regardless of the composition of these Fe-Mn-Cr steels. Figure 4 shows composition profiles for 20Mn-12Cr and 20Mn-12Cr-1W-0.3Ti. The concentrations of Cr and Mn are plotted as a function of distance from a grain boundary at a region between carbides. Effective "widths" (full width at half maximum) of the chromium-depleted zones were 20 to 40 nm. As also shown in Fig. 4, the Mn concentration was unchanged near the boundary. (There was an enrichment in iron corresponding to the depletion in chromium.) Similar analyses for Fe-Mn-Cr steels in the annealed condition showed little tendency for chromium (or manganese) depletion.

Discussion

The results from the $CuSO_4$ chemical tests indicate that the Fe-Mn-Cr steels used in the present study are prone to sensitization and are significantly more susceptible than standard (300-series) austenitic stainless steels. This relatively poor sensitization resistance of the Fe-Mn-Cr steels is not unexpected because of the high carbon concentration (and low chromium content) necessary to stabilize the austenitic structure when manganese is substituted for nickel,[3] and the results are in agreement with previous work on sensitization and resulting stress corrosion cracking of Fe-Mn-Cr-(C,N) steels.[6] Using the chromium equivalence approach of Fullman[8] (which was established for Ni-stabilized stainless steels), all of the Fe-Mn-Cr steels listed in Table 1 are predicted to be quite inferior to types 316L, 304, and 304L in their resistance to intergranular corrosion. This is in agreement with the 8 h chemical immersion tests described above. Upon appropriate aging, the high carbon activity of the Fe-Mn-Cr steels provides the driving force for the formation of $M_{23}C_6$, which depletes the surrounding matrix of chromium to below the level necessary for effective corrosion resistance (normally about 12%). This is clearly shown from the results of microanalysis near grain boundaries in the aged Fe-Mn-Cr steels (Fig. 4). The chromium concentration in regions surrounding the grain boundaries (6-7 wt %) is insufficient to prevent the intergranular corrosion observed after exposure to the $CuSO_4$ solution. While the aging treatment of 2 h at 650°C is quite severe, all the 300-series stainless steels heat treated under these conditions passed the 8 h immersion tests.

An important finding of this study was that significant chromium-depleted zones did exist around grain boundaries in aged Fe-Mn-Cr steels and that there was an excellent correlation between their existence and negative results from the immersion tests. Chromium-depletion widths of only 20 to 40 nm were sufficient to cause extensive intergranular corrosion upon specimen exposure to the CuSO_4 solution. These observations suggest that the width of a chromium-depleted zone is not the major factor in the corrosion process since these relatively narrow regions still caused catastrophic failure. The results also validate the use of a rather simple chemical procedure to detect sensitization and to determine the influence of composition on a Fe-Mn-Cr steel's resistance to this phenomenon. In general, improvement in sensitization resistance can be obtained by reduction of a steel's carbon content and an increase in its chromium concentration. However, in order to be effective in the present case, these compositional changes would cause a loss of full austenitic stability. This would result in a more complex duplex structure, which is less desirable for control of radiation effects. A concomitant increase in austenite-stabilizing elements such as nickel and/or nitrogen would result in a Fe-Mn-Cr steel that does not meet shallow land burial requirements. At concentrations up to 0.3 and 1 wt %, respectively, the addition of elements such as Ti and/or W to form MC at the expense of M_{23}C_6 was not sufficient to avoid chromium depletion (see Fig. 4). Increasing the concentration of these elements will lead to loss of a fully austenitic structure and/or the formation of a brittle intermetallic phase. Therefore, unless guidelines for reduced activation austenitic steels are revised, it appears that opportunities to increase the sensitization resistance of these Fe-Mn-Cr steels by alloy design are quite limited. This sensitization susceptibility would probably then bar the use of such steels in aqueous and certain other (for example, lithium and hydrogen) environments. However, these steels might still find application with Pb-17 at. % Li, in which they exhibit corrosion rates similar to those measured for standard austenitic stainless steels.[9,10]

Conclusions

Results from chemical tests and analytical electron microscopy showed that reduced activation austenitic Fe-Mn-Cr steels are very prone to thermal sensitization and resulting intergranular corrosion because of their high carbon contents and low chromium concentrations. Therefore, their susceptibility to intergranular stress corrosion cracking after appropriate thermal aging, or possibly irradiation, makes their use in aqueous environments problematical.

There was an excellent correlation between intergranular corrosion induced by immersion in the acidified CuSO₄ solution and the presence of narrow chromium-depleted zones near grain boundaries.

If all the reduced activation requirements are to be met, the opportunities to increase the aqueous corrosion resistance of fully austenitic Fe-Mn-Cr steels by alloy design appear to be limited.

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Figure Captions

1. Fe-10Mn-16Cr steel after immersion in acidified CuSO_4 solution for 48 h.
2. Transmission electron micrograph of Fe-20Mn-12Cr steel after annealing and aging at 650°C for 2 h.
3. Transmission electron micrographs of Fe-20Mn-12Cr-0.3Ti and Fe-20Mn-12Cr-1W-0.3Ti steels after annealing and aging at 650°C for 2 h.
4. Concentrations of chromium and manganese as a function of distance from grain boundary. (a) Fe-20Mn-12Cr steel. (b) Fe-20Mn-12Cr-1W-0.3Ti steel..

Table 1. Compositions of Fe-Mn-Cr steels used for sensitization study

<u>Steel</u>	<u>Concentration (wt %)</u>			
	<u>Mn</u>	<u>Cr</u>	<u>C</u>	<u>Other</u>
20Mn-12Cr	20	12	0.25	
20Mn-12Cr-1W	20	12	0.25	1W
20Mn-12Cr-0.3Ti	20	12	0.25	0.3Ti
20Mn-12Cr-1W-0.3Ti	20	12	0.25	1W, 0.3Ti
20Mn-16Cr-4Ni	20	16	0.25	4Ni
10Mn-16Cr	10	16	0.25	

Fe-10Mn-16Cr-O.25C Exposed To Strauss Solution

Sensitized

Solution Annealed

Fig. 1

03 5276
5 013000

625221

G 35724

File 3

(a)

(b)

Fig. 4