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# Modified Fe-Mn-Si-Al Alloys for High Temperature Oxidation

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Development of corrosion resistant alloys has been investigated by the Bureau of Mines to identify substitutes for stainless steels that could be used in case of disruption in chromium supplies. Since the major chromium supplier to the United States is experiencing political unrest, there is renewed interest in developing chromium-free alloys. To substitute for chromium, aluminum and/or silicon were added because they are readily available, inexpensive elements whose oxides are stable, protective, and adherent to the base metal.(1-4) There has been a great deal of interest in Fe-Mn-Al alloys because these alloys contain no chromium.(5-9) For high temperature oxidation resistance, generally 8 to 10 wt pct aluminum is needed in Fe-Mn-Al alloys to form a continuous protective aluminum oxide layer.(6,7) Consequently, high concentrations of manganese are required to stabilize the austenitic structure because aluminum stabilizes the ferritic structure. The high concentrations of aluminum and manganese result in the formation of the brittle beta-Mn phase which degrades mechanical properties.(8) Although some Fe-Mn-Al alloys have good oxidation resistance to 1,000° C, a fully austenitic microstructure could not be obtained by heat treatment.(9) Many previous Fe-Mn-Al oxidation experiments were conducted under isothermal conditions, but spalling became evident during thermal cycling.(8) After spalling occurred, the alloys oxidized rapidly. On the other hand, the Fe-Mn-Si alloys have shown somewhat higher oxidation rates than does 304 stainless steel, but these alloys did not form the beta-Mn phase.(10,11) Small additions of aluminum further improved the oxidation resistance of these high silicon alloys.(10)

In this brief communication, modified Fe-Mn-Si-Al alloys containing higher concentrations of silicon than aluminum were tested in air and compared to data on Fe-Mn-Al-Si alloys containing higher concentrations of aluminum than silicon. Two alloys were prepared from electrolytic grades of iron, manganese, silicon, and high-purity aluminum.

The materials, weighing 5 lb, were induction-melted, cast, homogenized for 20 h at 1,200° C in vacuum, and hot-rolled at 1,050° C with 20-pct reduction in thickness per pass. Specimens were cut from the rolled coupons, polished to 600 grit, ultrasonically cleaned, and degreased. Alloy compositions are presented in Table 1.

Table I. Alloy Composition

Alloy	Mn	Si	Al	C	P	S
A	31.5	4.73	2.56	0.01	0.003	0.01
B	28.7	3.85	1.87	.77	.002	.01
C*	28.6	2.68	8.63	.69	.05	.02
D*	24.0	2.06	7.25	1.01	.05	.02

\*C and D are from Garcia et al. (7)

Figure 1 shows the microstructure of alloy A after quenching from 1,050° C to room temperature. The microstructure is fully austenitic. Figure 2 exhibits the reaction kinetics of the alloys at 700° C in comparison to two Fe-Mn-Al-Si alloys from Garcia et al. (7), which also are austenitic at room temperature, and 304 stainless steel. Although alloys A and B show somewhat higher oxidation rates than 304 ss, they have much lower oxidation rates than alloys C and D of Garcia et al. These results indicate that the modified alloys showed better oxidation resistance than high-aluminum, low-silicon alloys.

All the alloys obey the parabolic rate law, which means that diffusion is the rate-controlling process. Alloys A and B were thermally cycled several times at 600° C and 700° C, as shown in figure 3. Each triangle and circle represents a time when the specimens were cooled to room temperature, weighed, then placed back into the furnace. The reaction kinetics were not affected by the thermal cycling, which indicates that the oxide scale formed on the base metal was protective and did not spall off.

The oxidized specimens were analyzed by X-ray diffraction to identify the oxides. Manganese oxide ( $Mn_2O_3$ ) was the primary

oxide; a trace amount of iron-manganese spinel and aluminum oxide also were observed. A thin layer containing silicon was formed at the oxide-metal interface to reduce inward and outward diffusion of metal and oxygen ions. A manganese depleted region was observed near the surface of the base metal when the specimens were cross-sectioned. This depletion was due to selective oxidation of manganese from the base metal.(11, 12)

This investigation has shown that modified high-silicon, low-aluminum Fe-Mn-Si-Al alloys have the following advantages over high-aluminum, low-silicon Fe-Mn-Al-Si alloys: 1) lower oxidation rates, 2) no spalling during thermal cyclings, and 3) no beta-Mn phase formation. In these alloys, the manganese concentration might be reduced to stabilize the austenite because lower concentrations of silicon and aluminum are needed for reasonable oxidation resistance. Therefore, modified Fe-Mn-Si-Al alloys that are higher in silicon than aluminum have potential for use as chromium free substitutes for stainless steels.

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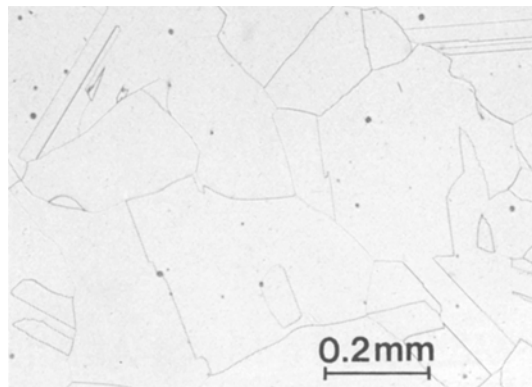


FIGURE 1.- Optical micrograph of alloy A after quenching to room temperature.

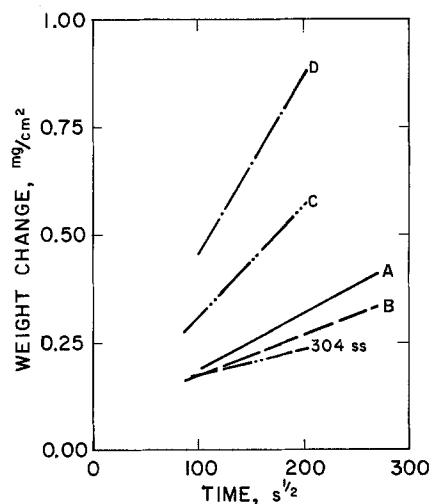


FIGURE 2.- Reaction kinetics of alloys at 700° C.

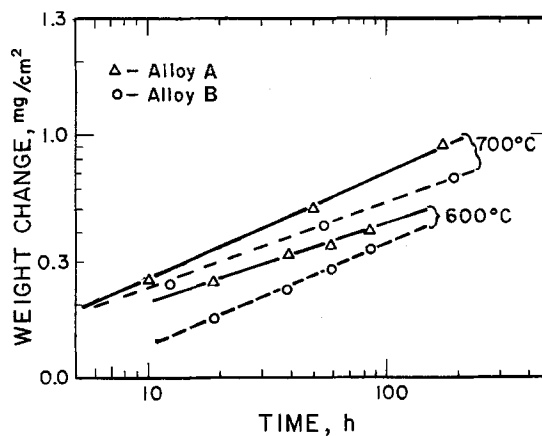


FIGURE 3.- Reaction kinetics of alloys with several thermal cycling at 600° C and 700° C.