

High-temperature oxidation behaviour of Fe-Mn-Al-Si-C alloys in thermal cycling tests

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Abstract

A study was made of the behaviour under thermal cycling in air of a series of Fe-Mn-Al-Si-C alloys which had shown good resistance to isothermal oxidation tests. Alumina based oxides are formed interspersed with spinels more or less rich in manganese. These spinels undergo microspalling during the cycling, with a continuous loss of materials contained, within acceptable values up to a temperature of 750°C. The role of silicon is particularly important in supporting the formation of the alumina film and in promoting the diffusion of manganese instead of iron in the formation of the spinels, which result in higher resistance to thermal shocks.

Riassunto

Comportamento all'ossidazione ad alta temperatura di leghe Fe-Mn-Al-Si-C in prove di ciclaggio termico

È stato studiato il comportamento al ciclaggio termico in aria di una serie di leghe Fe-Mn-Al-Si-C che avevano manifestato una buona resistenza a prove di ossidazione isotermica. Si formano degli ossidi a base di allumina, interrotti da spinelli più o meno ricchi in manganese. Questi spinelli sono soggetti a microspalling durante il ciclaggio, con una perdita continua di materiale contenuta entro valori accettabili fino alla temperatura di 750 °C. È particolarmente importante il ruolo del silicio nel sostenere la formazione del film di allumina e nel favorire la diffusione del manganese invece del ferro nella formazione degli spinelli che risultano più resistenti ai continui shock termici.

Introduction

This work was undertaken to compare the oxidation behaviours of Fe-Mn-Al-Si-C alloys in thermal cycling tests in air with that already demonstrated in a first work on the same alloys subjected to isothermal oxidation (1).

Particular attention was paid to the reaction mechanism and the influence on it of silicon which, in the isothermal tests, had promoted a filtering function for the iron, allowing the formation of protective oxides rich in aluminium and spinels rich in manganese. In particular, it was interesting to verify such mechanisms in the presence of the thermal stresses induced by repeated cooling cycles.

Materials and methods

The compositions of the investigated steels are given in Table 1. For the operating parameters and preparation technology, see Ref. 1 and 2.

The thermal cycling tests were carried out in air with two different treatment times. In the first case, every cycle required 15 minutes holding time in the furnace and 5 minutes at ambient temperature from a minimum

of 1200 cycles (300 hours total stay in furnace), up to a maximum of 2600 cycles (650 hours). Testing temperatures were chosen according to the isothermal tests behaviour (1, 2), i.e., respectively, 700°C for alloy D, 700, 750 and 800°C for alloy G and 750, 800 and 950°C for alloy H. The samples were weighted at regular intervals. In the second case, cycling involved only samples G and H, with furnace holding times of 24 hours and 15 minutes at ambient temperature. The weights of the samples were recorded continuously with the thermal balance throughout the duration of the tests.

This second methodology allows continuous evaluation of the behaviour of the sample, both with the oxide growth in furnace, and during descaling and successive reconstruction of the oxide. The results of this test are more significant than those of the first, because during the thermal transients heavier layers of oxide and greater stress are involved.

After oxidation, the specimens were subjected to morphological examination (SEM) and EDS analysis.

Results

Figs. 1-3 give the results of the short-time cycling tests.

TABLE 1 - Composition of the alloys

Alloys	C	Mn	Al	Si
D	0.76	32.5	10.2	—
G	0.98	19.8	6.1	1.7
H	0.92	27.9	7.9	2.4

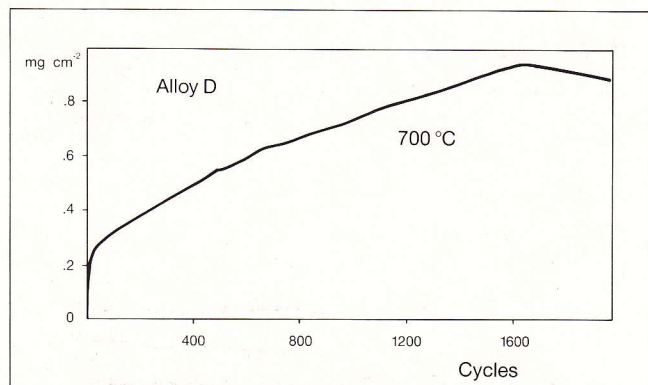


Fig. 1 - Curve of increase in mass per unit area in cyclic tests, for sample D.

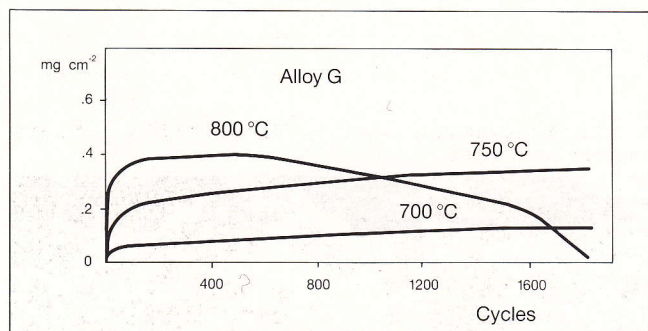


Fig. 2 - Curves of increase in mass per unit area in cyclic tests, for sample G.

In Fig. 1 is plotted the curve for the growth per unit of surface of alloy D at 700°C, for which we have a progression rising up to 0.93 mg cm^{-2} in about 1600 cycles, and subsequent reversal.

Fig. 2 gives analogous curves for alloy G up to a maximum of 800°C, by that temperature there is a reversal of the curve at 0.4 mg cm^{-2} in 600 cycles; for alloy H, curves in Fig. 3 show a reversal at 950°C after 100 cycles and 0.3 mg cm^{-2} . Fig. 4 gives the results of long-term cycling tests at 750°C both for sample G (408 hours total holding in furnace) and for sample H (216 hours). Both samples show weight losses on cooling, above all in the initial cycles; for sample G these losses are more massive and stabilize the final weight of the sample at values practically equal to that at the start.

Fig. 5 shows the surface morphology of alloy D, oxidised at 700°C for 1800 cycles. The oxide layer consists of a base of Fe-Mn spinels with excrescences of spinels richer in manganese.

The morphology and EDS analysis of the surfaces of alloy G, oxidised at 700°C for 1800 cycles (Fig. 6), show the behaviour of the alloys containing silicon. In this case a dense film appears, based on Al (alumina) interspersed with oxides based on Fe-Mn corresponding to individual points or fractures of the

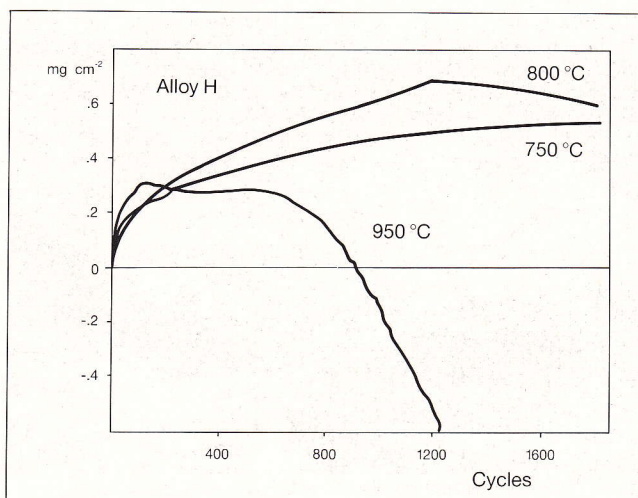


Fig. 3 - Curves of increase in mass per unit area in cyclic tests, for sample H.

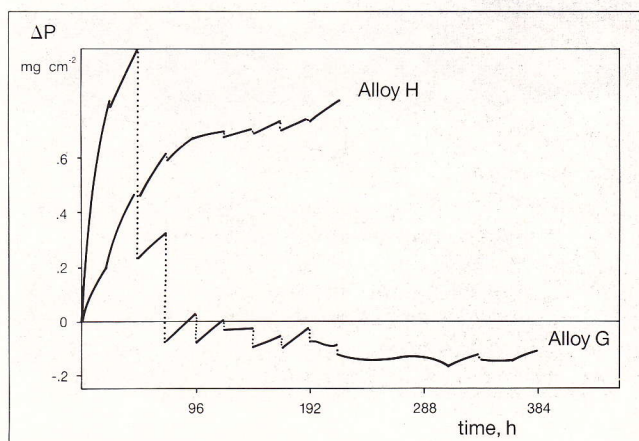


Fig. 4 - Curves of increase in mass per unit area in long-term cyclic tests, at 750°C for alloys G and H.

Fig. 5 - Surface appearance of alloy D after 1800 cycles at 700°C.



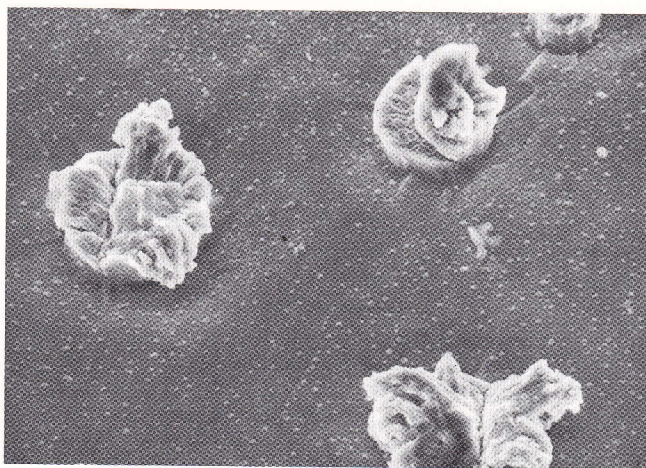


Fig. 6 - Surface appearance of alloy G after 1800 cycles at 700°C.

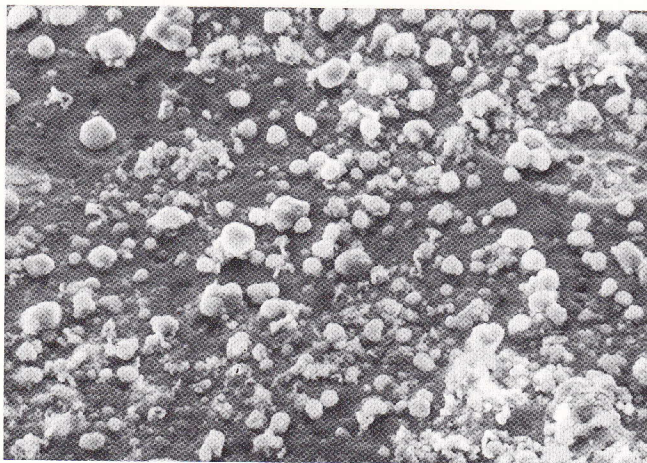


Fig. 7 - As in Fig. 6 but at 750°C.

film. With increase in the testing temperature the number of Fe-Mn spinels increases (Fig. 7), on a base always rich in alumina. At 800°C there is evidence of spalling phenomena, particularly concerning the spinels previously formed. EDS linear analysis of metallographic sections reveals an outside layer rich in Fe-Mn and an inside one rich in Al, in agreement with the results previously obtained (1,2). Close to this double layer of oxide, the profile of the manganese in the metal shows a diminution compared with the inner layer (Fig. 8), revealing a concentration gradient. At the test temperatures silicon in the surfaces is not confirmed, which agrees with the thesis already developed in the case of isothermal tests, for which the silicon exerts a sub-scale filtering action for iron. In Figs. 9 and 10 are given the morphologies of the oxides formed after 1800 cycles for alloy H; it shows a film of alumina covered with filamentary spinels grown through outward oxidation whose composition is close to 100% Mn.

Fig. 8 - EDS profile of concentration of Fe, Mn, Al, Si in scale and in metal in a section of Fig. 7 sample. The analyses of Si were carried out with a lower background scale.

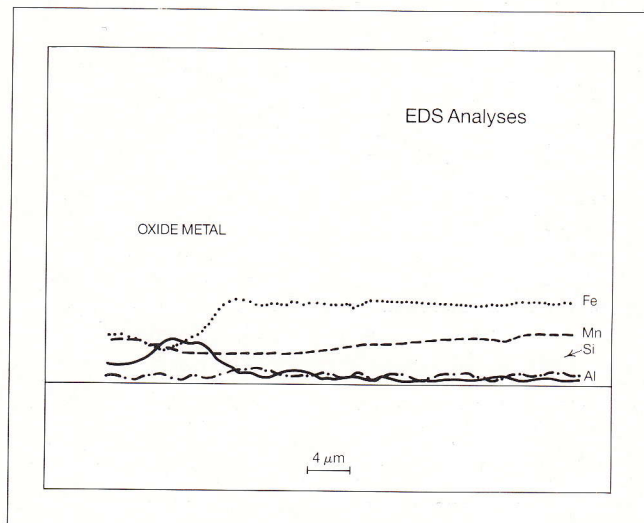


Fig. 9 - Surface appearance of alloy H after 1800 cycles at 800°C. Formation of manganese based spinels.

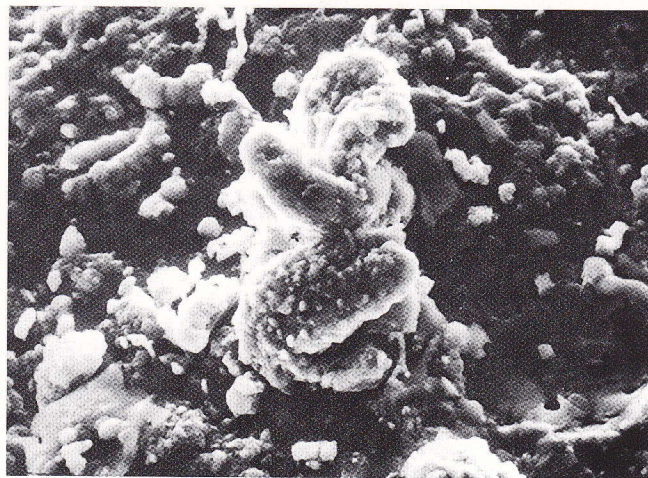
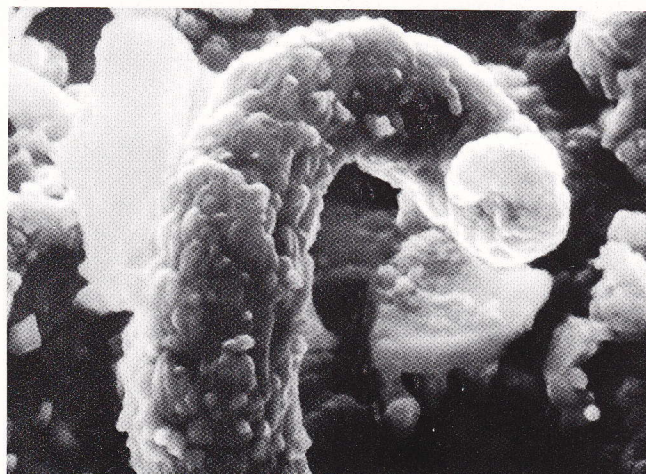


Fig. 10 - Detail of a zone of Fig. 9 sample with filamentary spinel.



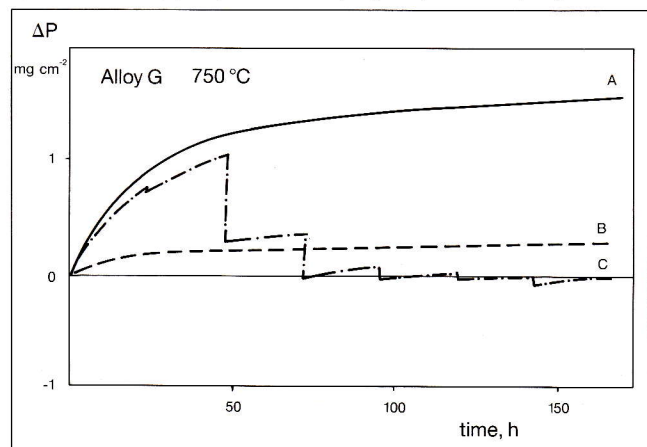
Discussion

The presence of silicon in this family of Fe-Mn-Al-C alloys is a necessary condition for the development of a film of alumina based oxides (1-3). The silicon, because of its low diffusivity in oxides (4), concentrates in a thin layer underneath the alumina scale. Because of the low diffusivity of iron in layers of silicon oxide, in surfaces where the alumina film is interrupted, predominantly manganese arrives to form oxides more protective than those rich in iron. This is evident in the silicon free alloy D for which a notable increase in weight per unit of surface is recorded as a consequence of the formation of an oxide free from alumina, despite the higher percentage of such element in this alloy than in the other two. Alloys G and H, containing silicon, form the alumina film and have kinetics of oxidation much slower. With increase in the testing temperature, the content of iron in the oxides diminishes steadily. In Figs. 11 and 12 are plotted the curves for isothermal oxidation (1) and those for cycling, calculated under the same temperature holding conditions for a comparison with the behaviour of the first 150 hours at 750°C. For alloy G the 15 minutes cycling curves result in values lower than the isothermal ones; the difference is attributable to a continuous microspalling, with the loss of a very fine powder consisting of spinels.

The curves for long-term cycling with continuous recording of the weight confirm these phenomena of weight losses on cooling. In the first hours we noticed a weight increase comparable with that in the isothermal tests, as long as spalling did not intervene to depress the curves and, therefore, to stabilize them at gradients exactly similar to those of the 15 minutes cycling tests. The surface oxide is characterized by a film of alumina

Fig. 11 - Comparison between oxidation curves at 750°C for alloy G, for equal holding time in furnace:

A) Isothermal test (1); B) 15 minutes cycling; C) 24 hours cycling.



interspersed with Fe-Mn spinels. Alloy H shows a more homogeneous behaviour in the three treatments: the 15 minutes cycled sample is, on the whole, similar to the sample oxidised isothermally, while a slight increase in weight in the long-term cycled sample is noticed only after the first 24 hours of the test. This last test is by far the most severe, because the thermal shocks on cooling act on the heavier oxides; the alloy, however, shows less scaling than alloy G and excellent capacity for reconstitution of the surface layer, consisting of alumina and filamentary spinels very rich in manganese.

For alloy G and H, therefore, the mechanism of oxidation outlined in Fig. 13 is proposed. A film of alumina, which comes out in the first stages of oxidation, is not able to cover the whole surface of the sample and is interrupted by spinel excrescences at points characterized by metallurgical peculiarities (grain boundaries, inclusions, surface inhomogeneities in composition...) as well as geometrics (polishing lines, sharp edges...), as indicated in Fig. 13A. In the isothermal test (Fig. 13B), there is a further development of both the oxides with the different kinetics that are entailed, higher for the spinels and

Fig. 12 - Comparison between oxidation curves at 750°C for alloy H, for equal holding time in furnace:

A) Isothermal test; B) 15 minutes cycling; C) 24 hours cycling.

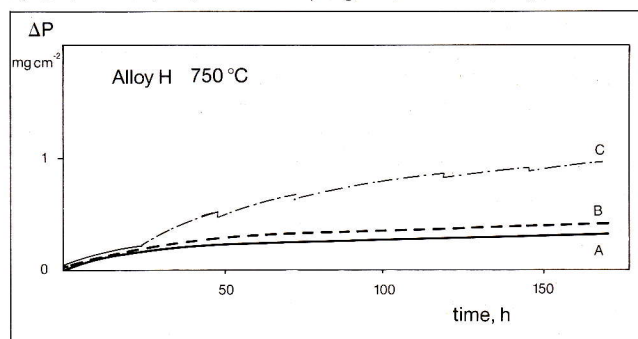
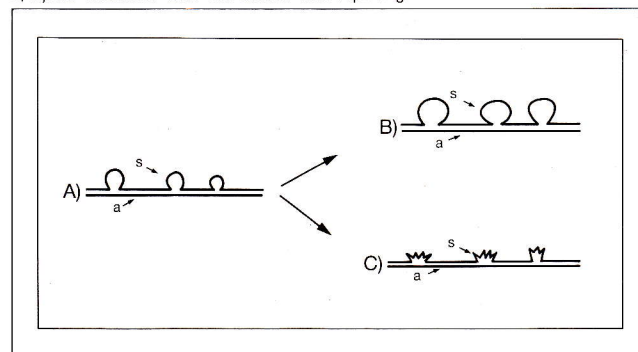


Fig. 13 - Model of oxidation in the presence of spinels (s) and of compact film of alumina (a):

A) First stages of oxidation; B) Isothermal oxidation, in absence of thermal shocks; C) Cyclic oxidation with continuous microspalling.



much lower for the alumina. In the 15 minutes cycling tests, on the other hand, we have a continuous microfracture of spinels (Fig. 7) due to thermal shocks and the consequent creation of preferential sites of oxidation, which localize the weight increase in their continuous growth (Fig. 13). From the balance between weight loss by rupture and weight acquisition by oxidation, alloy G records a total increase apparently less for the cycled than for the isothermally treated samples (Fig. 11). With increase in the testing temperature, this phenomenon becomes more marked and the difference between the two families of curves increases (1). For long times (Figs. 2 and 3), a macroscopic breakaway occurs when the total thickness of the oxide layer promotes massive ruptures that cannot be compensated immediately by the reforming mechanism of the oxide. This is also shown up by the results of the first cycles of the 24 hours cycling tests.

For material H the difference between the cycling and isothermal curves is slight, because of the better resistance of the oxides formed. The greater contents of manganese and silicon in the alloy facilitate the growth of spinels consisting almost exclusively of manganese oxides. These spinels appear very well preserved (Figs. 9 and 10) and suggest a greater resistance to thermal shocks compared with those of material G which are much richer in iron. According to the proposed model, this involves a slight loss of weight by microspalling of the spinels and therefore a more elevated kinetic of oxidation for H compared with G, at the same temperature level and number of cycles; in fact, this applies only to apparent increments in mass, in one case being measured and not in the other. It can be seen, therefore, that the thermal weighting method for evaluation of the oxidizing kinetics is completely valid only in the absence of spalling, which constitutes a limit to it. When macroscopic scaling intervenes, alloy H behaves, as expected from the results of the isothermal tests, better than alloy G, inasmuch as, at the same temperature level, a tougher layer of oxide forms which breaks after a greater number of cycles. This underlines the interest in completing the picture of the applicable behaviour of the material, supporting cycling tests that show only the effects of thermal transients. The continuous thermal weighting techniques in isothermal tests are, however, able to demonstrate microspalling phenomena given the elevated sensitivity of the thermal balance; for the materials of this work we can exclude an isothermal microspalling in the times adopted for the tests (170 hours).

At the end of the isothermal test, moreover, massive scaling on cooling occurs for alloy D at 700°C, for alloy G at 750°C and for alloy H at 1000°C.

Conclusions

The Fe-Mn-Al-Si-C alloys examined in this work have good hot cycling oxidation behaviour in air up to 750°C. An oxide scale forms, based predominantly on alumina, spaced with spinel excrescences. There is evidence of microspalling phenomena on cooling on the spinels, which keep the weight gain curves low.

The Fe-Mn spinels are richer in manganese at increasing test temperatures and with increasing content of alloying silicon; the spinels richer in manganese come out tougher than those rich in iron, and are therefore less susceptible to fracture under thermal shock.

For a further improvement in the hot oxidation behaviour of these alloys, we should consider both silicon and aluminium, but both these elements are ferritising agents and worsen the workability of the alloys; therefore they presuppose an increase in the content of austenitising elements like manganese.

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