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The Effects of Reactive Elements on the Oxidation of Alumina-Forming Iron-Chromium-Aluminium Alloys at High Temperature

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Abstract. A study is being undertaken into the influence of sulphur and reactive elements on the growth and adhesion of alumina scales on iron-chromium-base alloys during thermal cycling in air from 1300°C. A low-sulphur (< 10 ppm) containing alloy has shown considerable improvements in scale adhesion compared with an alloy containing a higher concentration of sulphur. Additions of reactive elements to the low sulphur-containing alloy had little further effect on scale adhesion, although second-phase precipitates facilitated preferential inward growth of the scale and the development of a very irregular scale/alloy interface. All the alloys showed evidence for stress development during scale growth, but this was often relieved by flow of the weak alloy. Although not extensive, all the low sulphur-containing alloys exhibited some scale failure, involving both a decohesion, buckling and tensile cracking route and a shear cracking and wedging route.

1. INTRODUCTION

Many alloys for use at temperatures to 1300°C are based on iron, nickel or cobalt and rely on the establishment and maintenance of Al_2O_3 scales for protection against oxidation. This oxide is thermodynamically very stable with respect to the metal while transport of reactive species (metal ions or oxygen) through the scales is slow. As the concentration of aluminium needed to establish such scales on binary alloys can result in unacceptable mechanical properties, it is usual for chromium to be added since this reduces the amount of aluminium needed to establish the Al_2O_3 scale, to acceptable levels [1].

However, although Al_2O_3 scales are good barriers to transport of metal cations and oxygen, they are prone to mechanical failure, due to stresses generated during scale growth and arising from differential thermal contraction between the alloy and the scale on cooling [2]. Such failure is particularly prevalent during thermal cycling since the stresses are rapidly induced and cannot be relieved by time-dependent creep processes [3]. There has been much research into the factors that influence the adhesion between an alloy and a growing oxide scale in contact with the surfaces. For instance, it has been demonstrated that the scale/alloy interface is intrinsically strong on an atomic scale [4]. However, segregation of sulphur impurities from the alloy to the interface are believed to weaken the normally strong interfacial bond of Al_2O_3 scales to nickel- or iron-base alloys [5], facilitating spallation of the scale on thermal cycling (the sulphur effect). In addition, small amounts of so-called reactive elements, such as yttrium, in the alloy can be very beneficial in improving considerably the adhesion and mechanical integrity of alumina scales during isothermal and thermal-cycling exposures. In view of its importance, there has been much research into the effect and various hypotheses have been proposed to account for it [6]. One well-supported view is that the reactive element or its oxide somehow prevents segregation of sulphur impurities to the scale/alloy interface, thereby enhancing adhesion of the scale to the alloy substrate.

The aim of the present research is to develop a better understanding of the mechanisms of oxidation of alumina-forming iron-chromium-aluminium alloys for use as resistors in electrical furnaces at 1000° to 1300°C, as a basis for optimization of composition for effective, long-term exposure under isothermal

Table 1
Analysis of the Alloys

	C (ppm)	S (ppm)	O (ppm)	N (ppm)	Ce (wt%)	La (wt%)	Y (wt%)
Fe-26.6Cr-6.2Al	12-17	<10	17-18	36-40	-	-	-
Fe-26.6Cr-6.2Al-0.1Y	12-21	<10	8	5	-	-	0.10
Fe-26.6Cr-6.2Al-0.1Ce	14-35	<10	20-21	28-30	0.12	-	-
Fe-26.6Cr-6.2Al-0.1La	11-33	<10	24-25	12-15	-	0.11	-
Fe-26.6Cr-6.2Al-0.1M	14.39	<10	20	4	0.048	0.023	-
Fe-26.6Cr-6.2Al-0.5M	24-29	<10	20	4	0.22	0.11	-
Fe-27Cr-4Al	90	70	550	40	-	-	-

and thermal-cycling conditions. Emphasis is being placed on high-purity alloys, containing low sulphur concentrations, with and without reactive elements, to investigate both the sulphur-effect and the reactive-element effect. The main programme involves tests under thermal-cycling conditions at 1300°C. This paper presents some preliminary results from the programme.

2. EXPERIMENTAL METHODS

2.1 Materials

The main materials are alumina-forming alloys, based on Fe-26.6%Cr-6.2%Al. In view of the effects of sulphur impurities on scale integrity, they were specified as very low sulphur content (< 10 ppm) and were produced by Ecole National Supérieure Des Mines, Saint-Etienne. The alloys contained 0.1%Y, 0.1%Ce, 0.1%La, 0.1% mischmetal (M), 0.5% mischmetal (M) or no reactive elements (Table 1). Mischmetal contains cerium and lanthanum. A standard alumina-forming alloy, Fe-27%Cr-4%Al, containing 70 ppm sulphur, was included for comparison. The specimens (20 x 10 x 1 mm) were abraded to 600 grit SiC paper, degreased and dried, before being annealed under vacuum for 2 h at 1050°C. They were finally lightly abraded on 600 grit SiC paper, degreased and weighed.

2.2 Experimental Rig

The rig consists of a horizontally-mounted recrystallized alumina reaction tube, connected to the gas supply. In the experiments, air was flowed through a molecular sieve, via a flow meter, into the reaction tube and over the specimens in the hot zone. The tube was heated by a horizontally-mounted furnace, manufactured by Severn Furnaces Ltd, and capable of being maintained at a temperature up to 1600°C. The furnace was supported on wheels and connected to a motor, enabling it to be moved over, or away from, the specimen location, to heat the specimens or allow them to cool, as required.

2.3 Experimental Procedures

Several specimens were placed in a vertical position in the reaction tube; the system was sealed and purged with dry air, at a flow rate of 50 ml per min. The furnace was moved over the specimen location and switched on; once the reaction temperature (1300° ± 5°C) had been attained (about 90 min), the test was commenced. After the required period, the furnace was moved away from the specimens which cooled rapidly, attaining 300°C within 5 min and less than 100°C within 25 min. For thermal-cycling experiments, the specimens were cooled for a total of 30 min; the heated furnace was then moved over

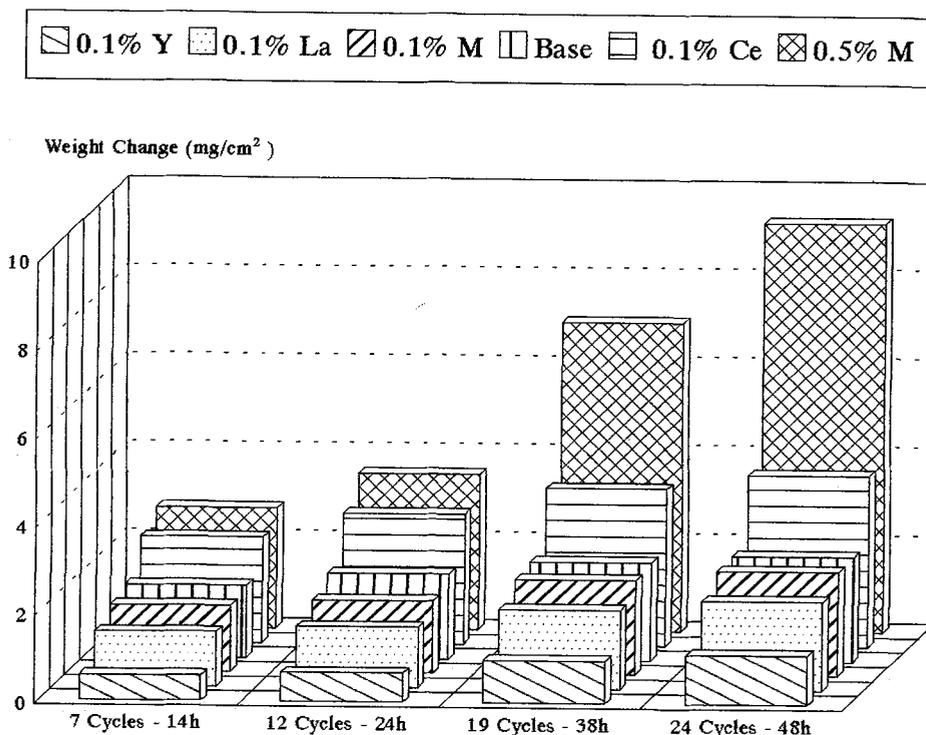


Figure 1: Plots of weight gain after 7, 12, 19 and 24 cycles of 2 h at 1300°C for the Fe-26.6Cr-6.2Al alloys containing Y, La, mischmetal (M), Ce and no reactive element.

the specimens again which re-attained 1300°C within about 20 min. After the required period at temperature, the cycle was repeated. In the present paper, the thermal-cycle programme consisted on 24 cycles of 2 h at temperature, with cooling periods between each cycle.

Following the tests, specimens were examined in plan and cross section, after mounting and polishing, in an analytical scanning electron microscope and an electron probe microanalyzer.

3. EXPERIMENTAL RESULTS

3.1 Kinetics of Oxidation

Weight change data are commonly used to provide information on oxidation kinetics since oxidation involves reaction between metal elements and oxygen. If the resulting oxide is solid and forms a scale layer that remains attached to the alloy surface, there is an increase in weight and the rate of such increase gives a measure of the kinetics of oxidation. However, if the scale layer spalls from the alloy surface, there is a decrease in weight. In the present case, the measured weight change data result from increases in weight due to scale growth and, in some cases at least, decreases in weight due to spallation of parts of the scale. Any spalled oxide scale was not included in the recorded specimen weights.

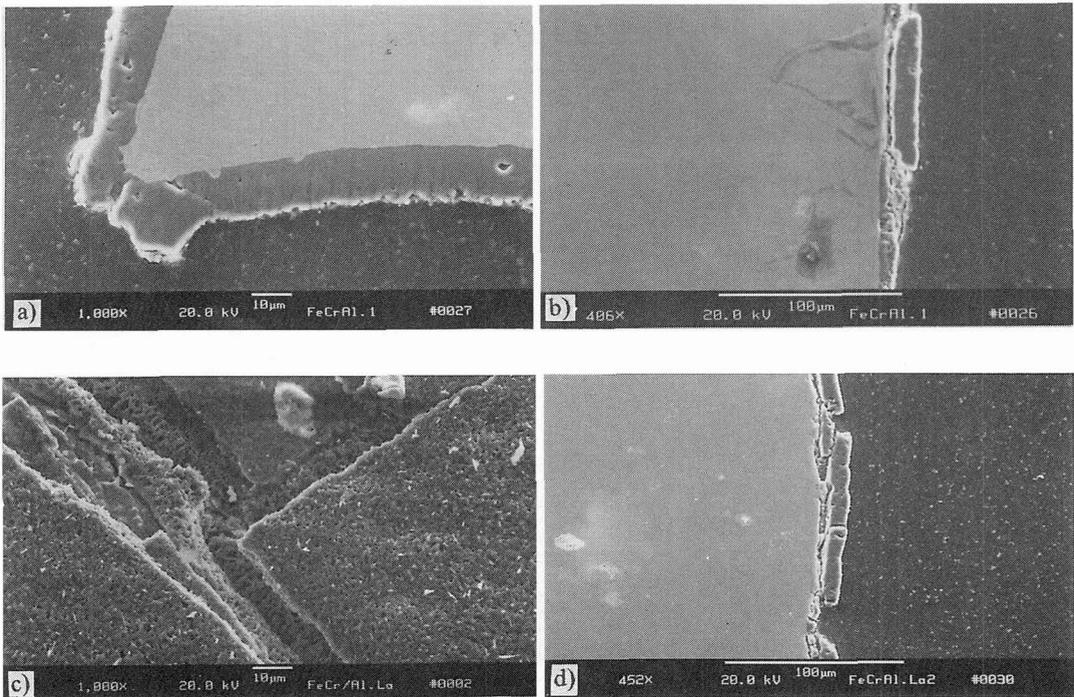


Figure 2: Scanning electron micrographs of specimens after 24 cycles of 2 h at 1300°C.

- | | | | |
|----|-------------------------------|----|---------------------------------|
| a) | Fe-26.6Cr-6.2Al (section) | b) | Fe-26.6Cr-6.2Al (section) |
| c) | Fe-26.6Cr-6.2Al-0.1 La (plan) | d) | Fe-26.6Cr-6.2Al-0.1La (section) |

Weight change data were recorded after 7, 12, 19 and 24 two-hour cycles. The data are presented in figure 1, with each datum point being the average of measurements made from two specimens. Usually, these weight changes were very reproducible, being within $\pm 0.1 \text{ mg cm}^{-2}$ for Fe-26.6Cr-6.2Al and the alloys containing 0.1%Y, 0.1%La and 0.1%M, increasing to $\pm 0.5 \text{ mg cm}^{-2}$ for the alloy containing 0.1%Ce. However, for the alloy containing 0.5% M, the weight gains after 48 h were 15 and 3 mg cm^{-2} (giving an average of 9 mg cm^{-2}). Similar tests on the Fe-27Cr-4Al alloy resulted in extensive scale spallation on every cooling cycle, giving large weight losses; hence, these data have not been included.

The main features of the weight change data are as follows:

- The weight gains recorded for the base Fe-26.6Cr-6.2Al specimens and those containing 0.1%La and 0.1%M increased progressively with time under thermal-cycling conditions and the final weight increases were very similar in each case. The alloy containing 0.1%Y showed similar trends, although the weight gains were significantly less than for the other alloys.
- Fe-26.6Cr-6.2Al-0.1Ce also gave progressive increases in weight with time, although the weight increases after a given number of cycles were significantly larger than for the previous alloys.
- One of the two specimens containing 0.5%M gave slightly larger weight increases than the 0.1%Ce-containing alloy; however, the other gave much larger weight increases, particularly after 12, 19 and 24 cycles, when the recorded values were 5, 11 and 15 mg cm^{-2} respectively; this is consistent with growth of a less protective oxide, as confirmed later.

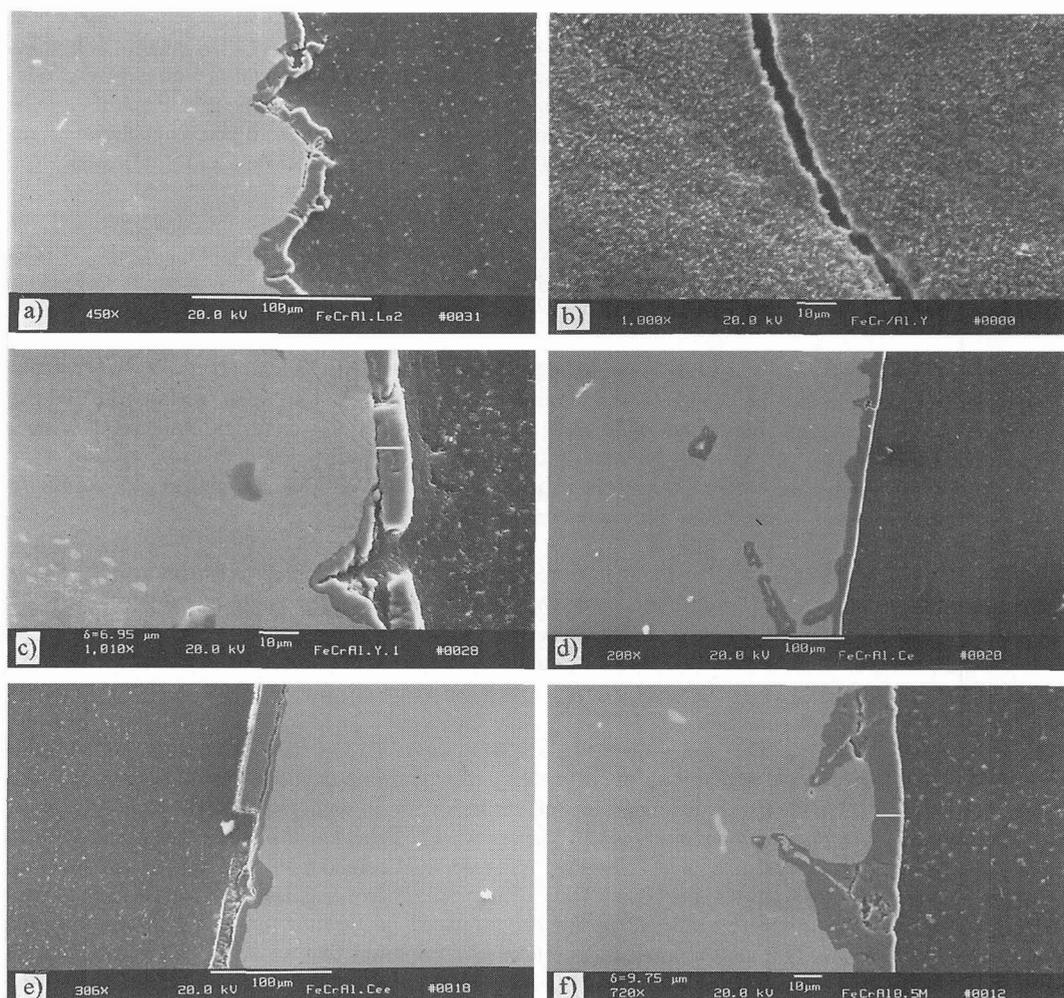


Figure 3: Scanning electron micrographs of specimens after 24 cycles of 2 h at 1300°C.

- | | | | |
|----|---------------------------------|----|---------------------------------|
| a) | Fe-26.6Cr-6.2Al-0.1La (section) | b) | Fe-26.6Cr-6.2Al-0.1Y (plan) |
| c) | Fe-26.6Cr-6.2Al-0.1Y (section) | d) | Fe-26.6Cr-6.2Al-0.1Ce (section) |
| e) | Fe-26.6Cr-6.2Al-0.1Ce (section) | f) | Fe-26.6Cr-6.2Al-0.5M (section) |

3.2 Examination of the Exposed Specimens

3.2.1 Fe-26.6Cr-6.2Al. After thermal cycling, the scale was very adherent to the alloy surface, with a very flat scale/alloy interface; there was very little, if any, scale spallation. Intimate contact between the scale and the substrate was generally maintained, even at the specimen corners where there was evidence for deformation of the alloy (Fig. 2(a)), although some areas of cracked and lifted scale were apparent (Fig 2(b)). The scale was 12 to 15 μm thick after 48 h exposure. Microanalysis in cross section confirmed that the scale was entirely Al₂O₃, with no iron or chromium being detected, even on the outer surface. There was no significant depletion of aluminium in the alloy at the alloy/scale interface.

3.2.2. *Fe-26.6Cr-6.2Al-0.1La*. Although there was no significant scale spallation from this alloy, the scale was sometimes thinner over emergent alloy grain boundaries than over the rest of the surface (Figs. 2(c) and Fig. 2(d)); these micrographs suggest that some scale had spalled from over the boundaries, while contact between the scale and alloy surface elsewhere was less intimate than for the Fe-26.6Cr-6.2Al specimens. In some regions, the scale/alloy interface was very undulating, with cracks in the overlying scale (Fig. 3(a)). The scale was again entirely Al_2O_3 , with no iron or chromium being detected.

3.2.3 *Fe-26.6Cr-6.2Al-0.1M*. The scale was Al_2O_3 containing no measurable basis metal elements. It was adherent, usually maintaining close contact with the alloy, but with some areas where contact had been lost. There was some inward penetration of scale along alloy grain boundaries, resulting in an irregular scale/alloy interface.

3.2.4 *Fe-26.6Cr-6.2Al-0.1Y*. This alloy developed a flat, adherent Al_2O_3 scale that was significantly thinner (typically 10 μm after 48 h) than the scale on the other alloys. Examination in plan revealed gaps in the scale, over alloy grain boundaries (Fig. 3(b)). In section, it is apparent that any initial scale in such locations had spalled off, allowing oxidation of the underlying alloy grain boundaries (Fig. 3(c)). Elsewhere, the alloy/scale and scale/gas interfaces were flat with good adhesion between the scale and alloy. No aluminium depletion in the alloy adjacent to the alloy/scale interface was detected.

3.2.5 *Fe-26.6Cr-6.2Al-0.1Ce*. Again, the Al_2O_3 scale showed close contact with the alloy. Inward penetration of scale along alloy grain boundaries was more severe than for Fe-26.6Cr-6.2Al-0.1M (Fig. 3(d)), while the scale was very irregular in thickness, ranging from 12 to 30 μm , which accounts for the larger weight gains for this alloy. In a few areas, cohesive failure of the scale was apparent, with cracks parallel to the surface. Figure 3(e) shows where a crack has resulted in loss of scale.

3.2.6 *Fe-26.6Cr-6.2Al-0.5M*. The scales on this alloy were again Al_2O_3 ; these generally retained good contact with the alloy. Inward penetration of scale along alloy grain boundaries was more extensive than for other alloys (Fig. 3(f)). The light phases in the centre of the inward growths are residual second-phase precipitates. Such growth accounts for the larger weight gains for this alloy compared with the others. In addition, there was extensive failure of the scale, at the specimen corners, for the specimen that showed the very large weight increase. Here, much faster growing iron-rich oxide had formed, resulting in very thick scales. Presumably, the deep inward penetration of Al_2O_3 along the grain boundaries at the corners had caused such a depletion of aluminium that an Al_2O_3 scale could not be maintained and less protective oxides were eventually able to develop, following failure of the scale.

4. DISCUSSION

Despite being ongoing, this research has already generated some interesting results:

- (i) Although not containing reactive elements, the low sulphur Fe-26.6 Cr-6.2Al developed an Al_2O_3 scale that maintained good adhesion to the alloy throughout, while the Al_2O_3 scale on the higher sulphur Fe-27Cr-4Al spalled very extensively on thermal cycling; these are consistent with the hypothesis that sulphur segregation to the alloy/scale interface leads to poor scale adhesion.
- (ii) There was evidence for flow of the alloy during oxidation of Fe-26.6Cr-6.2Al, leading to development of protrusions at the specimen corners (Fig. 2(a)). Such effects have been observed previously for alloys containing very small amounts of yttrium and were accounted for in terms of flow of the alloy providing relief of scale-growth stresses [1, 7]. Nonetheless, the scale was able to maintain contact with the alloy surface, presumably either by a creep-type process or by a pseudoplastic process involving continuous cracking and rehealing of the scale. The convoluted alloy/scale interface for the La-containing alloy (Fig. 3(a)) can be accounted for similarly.

(iii) Although scale adhesion was generally good for the low sulphur alloys, some spallation or, at least, partial cracking of the scale, particularly over alloy grain boundaries, resulted from relief of the compressive stresses developed during cooling, due to differential contraction between the scale and alloy. Previous work [7] has reported extensive convoluted scales over such boundaries on higher sulphur-containing alloys, which spalled easily on thermal cycling. It was proposed that such features result from scale growth. In an analysis of scale failure under compression, Evans and Lobb [8] proposed that failure can occur by one of two routes. If the interface is more resistant to rupture than the scale, decohesion proceeds by compressive shear cracks, termed Route 1 (wedging). If the reverse is true, decohesion occurs without through-thickness cracking of the scale; scale buckling and stress relaxation take place by propagation of tensile cracks at points of maximum curvature of the scale, termed Route 2. Here, there is evidence for both modes of failure, with loss of convoluted scales over grain boundaries proceeding via Route 2 while the partially detached scale (Fig. 2(b)) has almost the exact appearance of the spalled scale presented by Evans and Lobb for failure by Route 1 [8]. Similar features are shown in Figs 2(d) and 3(e).

(iv) The alloys containing the reactive elements, cerium and mischmetal, but not yttrium or lanthium, exhibited deep inward penetration of the Al_2O_3 scale, mainly along alloy grain boundaries, probably incorporating second phase cerium- and/or lanthium-rich precipitates in the boundaries. Similar features have been observed previously [7] and may involve preferential inward transport of oxygen through the precipitates or along the precipitate/alloy interfaces. Further investigations of the mechanisms of development of these features are in progress.

5. CONCLUSIONS

Although this programme is still at an early stage, some initial conclusions can be drawn.

1. The adhesion of Al_2O_3 scales to the substrate was considerably better for low sulphur- than for high sulphur-containing iron-chromium-base alloys.
2. The additions of reactive elements to such low sulphur-containing alloys resulted in little improvement in performance during thermal cycling from 1300°C.
3. Stresses developed during growth of the Al_2O_3 scales were sometimes relieved by flow of the alloy, resulting in an irregular scale/alloy interface or protrusions of alloy at specimen corners. The growing scales were able to maintain close contact with the alloy surface.
4. Although not extensive, all the low-sulphur-containing alloys exhibited some scale spallation, due to compressive stresses developed during cooling.
5. In some cases, second-phase precipitates in alloy grain boundaries facilitated inward growth of the Al_2O_3 , to incorporate such precipitates, resulting in a very irregular scale thickness.

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