

Influence of Cerium Additives on High-Temperature Corrosion of Chromium

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ABSTRACT. The results of studying the kinetics of oxidation of unalloyed chromium at $T=1100^{\circ}\text{C}$ in oxygen are presented. It is shown that small additives of Ce ($\geq 0.5\%$) have fundamental influence on the formation mechanism of Cr_2O_3 -scale, redirecting the diffusion mass transfer from the dominant external diffusion of chromium to the internal diffusion of oxygen. In this case formation of Cr_2O_3 -scale occurs on the interface metal/scale and this may lead to improvement of protective properties of coating (adhesion, durability, etc.). © 2010 Bull. Georg. Natl. Acad. Sci.

Key words: chromium, oxidation, scale.

Oxidation of unalloyed chromium in oxygen at high temperatures leads to the formation of scale from Cr_2O_3 with protective properties. The overall reaction process can be described by the chemical equation: $\text{Cr} + 3/2\text{O}_2 = \text{Cr}_2\text{O}_3$. However, this simple equation hides a complex character of the whole process [1]. Thus, depending on the microstructure and grain size of the metal, pretreatment of the sample surface, the oxygen pressures and experimental techniques used to study the oxidation process, or the means of its initiation, the rate of oxidation of chromium may vary by two orders of magnitude.

This difference in rates of oxidation may be described by significant structural pressures in the scale. For its part, it leads to the development of extensive deformations (bulging, warping, swelling of the surface, cracking of the samples). As a rule, the tendency of scale deformation intensifies with decreasing of the partial pressure of oxygen [2].

Such a nature of growth of Cr_2O_3 -scale is usually interpreted [1, 3] as being based on the following considerations: the growth of oxide phase in the scale occurs by means of counter grain boundary diffusion of

chromium and oxygen. Meantime, it is believed that the outward diffusion of chromium is the dominant process and the formation of oxide occurs at the grain boundaries within the scale near the surface of the gas/scale. The oxide grains are formed in smaller parts, growing not only perpendicularly to the metal surface, but also transversally along the surface. As a result, an extensive strain of growth develops, which is facilitated by means of elastic damage (bulging, swelling of the surface, cracking of samples) or plastic deformation (high-temperature creep).

Alloying of chromium with REE significantly affects the diffusion character of Cr_2O_3 -scale growth, redirecting the diffusion mass transfer from the dominant external diffusion of chromium to the internal diffusion of oxygen. In this case formation of Cr_2O_3 -scale occurs on the surface of the metal/scale and this may lead to good adhesion of the latter. In addition, the presence of REE reduces the rate of oxide growth and improves the oxidation resistance. This effect is presumably caused due to the segregated oxides of rare-earth metals at the grain boundaries of Cr_2O_3 -scale, which is facilitated by

an internal diffusion of oxygen [1,3].

Researches on the influence of the rare-earth metals on the oxidation resistance of the matrix are mostly carried out with alloys of chromium [1-6]. Therefore, it is of interest to perform similar studies with unalloyed chromium with additions of cerium, which was often used in alloys.

Materials and Methods.

Samples of 10mm diameter and of 1mm thickness ($d=10\text{mm}$; $h=1\text{mm}$) from fused and extruded rods of unalloyed Cr and from alloy Cr+0.5%Ce were prepared. The samples were subjected to special machining (grinding, polishing with diamond paste) and degreased (washed in acetone). The prepared samples were placed in a high-temperature furnace and in high vacuum ($P_{O_2}=10^{-9}\text{atm}$), where their thermal etching was carried out ($T\sim 800^\circ\text{C}$, $\tau\sim 10\text{ min}$).

Study of the formation of scale (process of the oxidation of the surface of the sample) was conducted in an atmosphere of oxygen $P_{O_2}=0.01$ and 1.0 atm at temperatures 1000 and 1100°C. The specific weight gains of the samples was determined by the method of continuous weighing.

The microstructure of scale was investigated by means of optical metallography and scanning electronic microscopy.

The presence and character of distribution of cerium was investigated by means of X-ray spectral local analysis on the microanalyzer "Cameca".

Results of Experiments

a) Thermogravimetric investigations

The results of thermogravimetric investigations of samples of unalloyed chrome and Cr+0.5%Ce in an

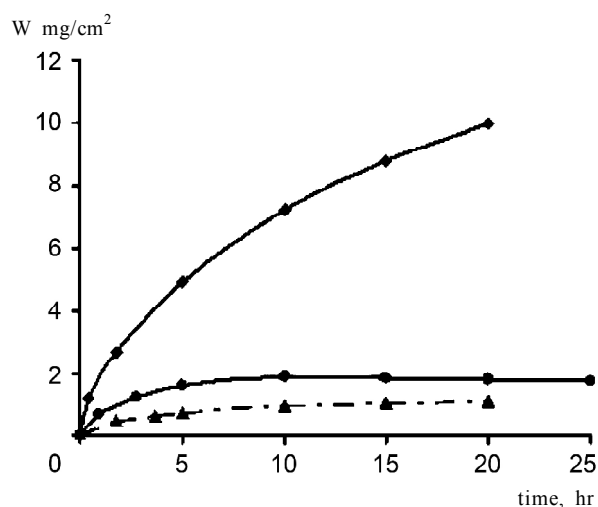


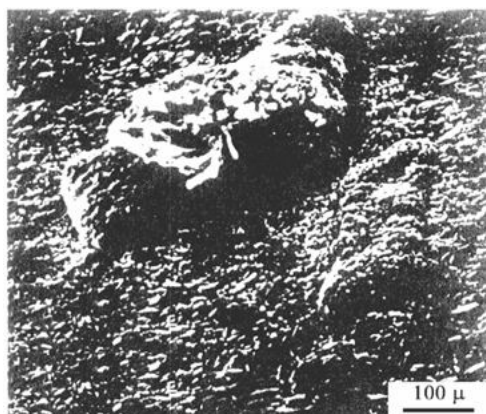
Fig. 1. Kinetics of oxidation of samples at 1100°C in oxygen
 ◆ - unalloyed chromium at 0.01atm
 • - Cr+0.5%Ce at 0.01 atm
 ▲ - Cr+0.5%Ce at 0.01 atm

atmosphere of oxygen at 1100°C (Fig.1) confirm the beneficial effect of small additives of cerium on the oxidizing stability of Cr_2O_3 - scales. One can see that after 10 hour oxidation the weight-gain rate approximates zero.

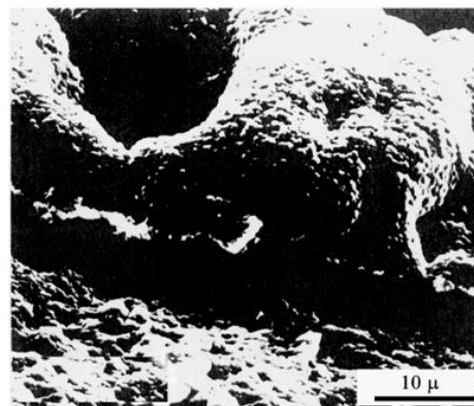
Most likely, at this temperature oxidative evaporation of chromium oxide takes place:

$1/2 \text{Cr}_2\text{O}_3 + 3/4 \text{O}_2 = \text{CrO}_3$ [1]. However, loss of weight in consequence of such evaporation is so small that its quantitative definition is made difficult.

As follows from Fig.1, at oxidation of Cr+0.5%Ce, an unusual dependence of the reaction rate on the pressure of oxygen is observed: thus, at lowered pressure of oxygen oxidation happens quicker than at $P_{O_2}=1\text{atm}$. This fact may presumably be linked to the distinction in the microstructure of the scales generated in these conditions.



a



b

Fig. 2. SEM images of the sample of an oxidized alloy Cr+0.5%Ce
 a - surface b - fragment of a damaged surface

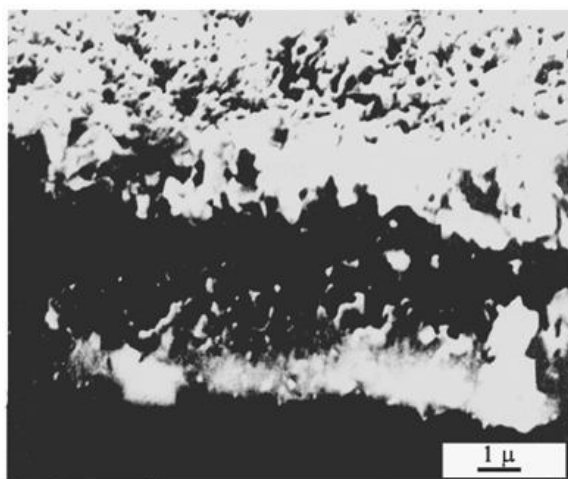
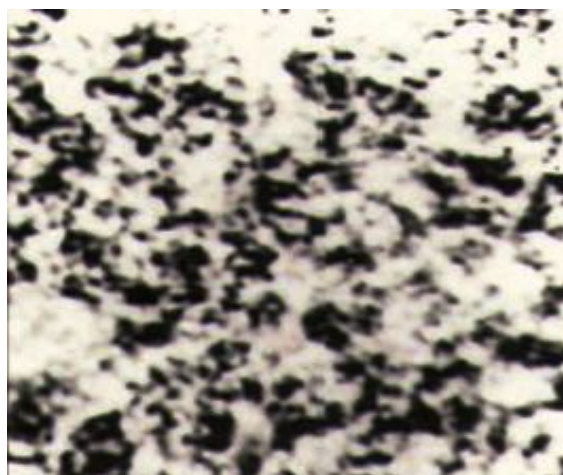


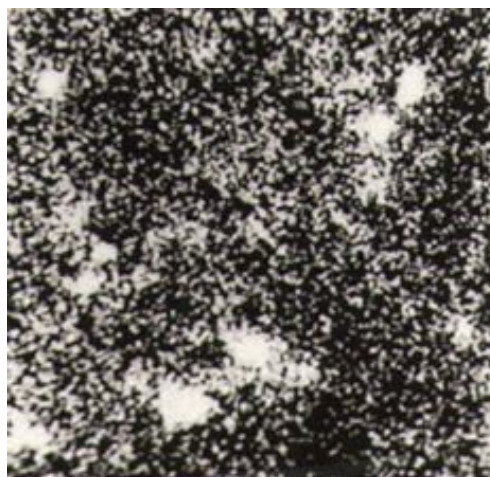
Fig. 3. Cross-section of Cr+0.5%Ce scale on alloy Cr+0.5%Ce

b) Characterization of the oxidized samples

In comparison with scales generated on unalloyed chromium, scales on Cr+0.5%Ce (Fig. 2, *a* and *b*), are



a



b

Fig. 4. Electronic micrograph of the oxidized surface of (T=1100°C the scanning area - 100x100 μm)

a - In absorbed electrons *b* - In x-ray Ce - L_{α} radiation

characterized by significant decrease of the tendency to distortion and deformation. These Figures show the outside surface of scale on a sample and a section where part of the scale is raised.

The cross-section of defective scale is illustrated in Fig. 3. An external layer of scale less dense than internal

and significant porosity is observed. Close to the interface scale/gas, scale is appreciably deformed. Therefore, it is reasonable to conclude that it is precisely the internal layer of scale that provides high oxidizing resistance.

X-ray analysis of the surface of Cr+0.5%Ce-scale showed the presence of Ce-enriched local sites (Fig. 4, *a* and *b*). On these sites Cr_2O_3 -scale has a fairly smooth level surface, whereas the sites grown poor by Ce are warped and deformed (Fig. 2, *a* and *b*).

Conclusion

Thus, the results of studies have shown that small additives of cerium (Ce) increase the resistance of chromium to oxidation, confirming the early assumptions about the improvement of oxidizing resistance of chromic alloys by the effect of REE [4-6].

The given effect is accounted for by the change of the mechanism of oxidation: oxides of the alloying elements segregate on the borders of grains of Cr_2O_3 -scale, changing the direction of mass transfer from the

dominant external diffusion of chromium to the internal diffusion of oxygen.

Besides, the segregated oxide phases can have a considerable effect on other properties of scale (for example: growth of grain, adhesive properties, high-temperature creep, deformation, etc.).

მასალათმცოდნეობა

ცერიუმის გავლენა ქრომის მაღალტემპერატურულ კოროზიაზე

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ნაშრომში წარმოდგენილია ქრომის მაღალტემპერატურული ჟანგვის მექანიზმისა და კინეტიკის კვლევის შედეგები. ნაჩვენებია, რომ ქრომის ცერიუმით ლეგირება ცვლის ლითონურ ფუძეზე დამცავი Cr_2O_3 -ფურჩის წარმოქმნის მექანიზმს: კონცენტრირდებიან რა ფურჩის მარცვლის საზღვრებზე ცერიუმის ჟანგეულები, ხელს უწყობენ კომპონენტების დიფუზიის მიმართულების შეცვლას – ქრომის მოჭარბებულ გარე დიფუზიას ანაცვლებს ჟანგბადის დიფუზია ლითონური ფუძის მიმართულებით. ასეთ შემთხვევაში Cr_2O_3 -ფურჩი ფორმირდება გამყოფ ზედაპირზე, ლითონური ფუძე - ფურჩი, რის შედეგადაც უმჯობესდება ამ უკანასკნელის რიგი თვისებები (აღპეზია, სიმტკიცე, მაღალტემპერატურული კრიპი და სხვა).

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Received June, 2010