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Materials Science

Corrosion of Chromium in Ambient CO+CO_2 Mixtures

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ABSTRACT. The results of an investigation of high-temperature corrosion of unalloyed chromium and the binary alloy Cr+0.5%Ce in an ambient 75%CO+25%CO_2 gas mixture under a pressure of 0.01 atm are presented. It is shown that cerium additions have a beneficial effect on the oxidation resistance of chromium. *© 2012 Bull. Georg. Natl. Acad. Sci.*

Key words*: chromium, cerium, scale, gas mixture.*

Introduction

During the operation of aircraft engines and other installations used in various branches of industry (chemical, power) metallic materials come into contact with carbon- and oxygen containing gases and are subjected to their aggressive action. Researches aimed at creating corrosion-resistant protective outer zones able to protect the base metal against the chemical and mechanical action of corrosive environments are therefore essential.

The known method for preprocessing Cr_2O_3-forming alloys to improve their oxidation resistance at high temperatures in the ambient air [1] has been successfully used in the case of complex gas mixtures under low oxygen partial pressure.

In the presence of the CO+CO_2 gas mixture the reaction product resulting from its interaction with the metal can either be oxides or carbides. When chromium (Cr) or alloys based on chromium are subjected to such chemical action and oxygen activity (oxygen partial pressure P_{02}) in the system is below the range of stability (dissociation pressure) of Cr_2O_3 the occurrence of carbide phases [2] predominates. In contrast to chromium oxide (Cr_2O_3) the latter do not possess protective properties and they cannot serve as diffusion barriers.

Moreover, it is known that rare-earth metals, including cerium (Ce) intensify selective formation of Cr_2O_3 scale, slow down its growth and improve adherence [3]. Besides, the presence of these elements slows down the growth of grains in the scale and ultimately changes the diffusion direction of mass transfer from predominantly external diffusion of chromium (Cr) to internal diffusion of oxygen (O_2).

Furthermore, it is known that the grain boundaries of the material under investigation [3] play an essential role in the oxidizing process.

In this investigation the effect of graininess as well as cerium additions on the oxidizing rate of chromium in the $CO+CO_2$ environment has been studied, taking into consideration the foregoing.

Materials and methods

Sample processing procedures for the experiments are described in [3].

Thermally oxidized specimens were placed in the reaction zone of the installation after establishing the specified parameters for the experiment: temperature 1100^{0}C, the pressure of gaseous atmosphere (75%CO+25%CO_2) 0.01 atm. Recording specific weight gain of test specimens was initiated ~ 30 seconds on, the reaction products were then removed from the reaction zone and the ratio of the initial components (75%CO+25%CO_2) as well as the pressure of gaseous atmosphere (0.01 atm) were re-established. The experimental conditions continued to be stabilized during the whole process.

Electrodeposited chromium with the grain size ~ 0.01 μm was used as the initial material; A coarse-grained metal with the grain size 20-30 μm was obtained through annealing of the initial material at 1100-1200^{0}C.

Weight gains of the specimens (mg/cm^2) were determined by the continuous weighing method, while the microstructure of the scale was investigated with the help of the scanning electron microscope.

Experimental results and evaluation

1) Thermogravimetric investigation

Specimens of fine-grained and coarse-grained chromium as well as the binary alloy Cr+0.5%Ce were oxidized at 1100^{0}C in gaseous atmosphere comprising 75%CO+25%CO_2 under a pressure of 0.01 atm. Under these conditions (high temperature and low oxygen activity) no evaporation of chromium oxide was observed, as could be expected.

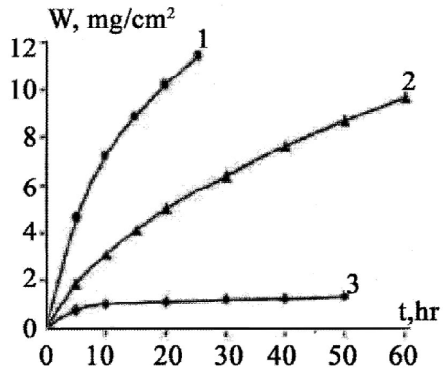

Fig. 1. The kinetics of oxidation of unalloyed chromium (Cr) and the binary alloy Cr+0.5%Ce ; 1 - fine-grained chromium; 2 - coarse-grained chromium; 3 - alloy Cr+0.5%Ce.

The results of the investigation are given in Figure 1.

Like the tests conducted in pure oxygen [3] the effect of cerium on the oxidizing rate was detectible in this particular case as well. Besides, it is demonstrated that fine-grained chromium oxidizes much faster than coarse-grained chromium.

The obtained results have corroborated the premise of previous investigations concerning the enhancement of the oxidation resistance of Cr_2O_3-forming alloys by virtue of rare-earth metal additions and are in agreement with the concept that a reduction in the dimensions of grain boundary surfaces or blocking them by diffusion barriers slows down mass transfer through the scale [4,5].

2) The characteristics of oxidized specimens

A scale formed during high temperature oxidation of unalloyed chromium bulges out heavily and deforms (Fig.2); it is characterized by poor adhesion and easily separates from the matrix. Fig. 3 shows the underside of the scale presented in Fig. 2. It is cracked and deformed. The oxide grain size in this section of the scale is small, which makes it qualitatively different from a similar scale formed under ambient oxygen [6].

Fig. 4 illustrates a scale formed on the surface of the alloy Cr+0.5%Ce specimen following its heating to 1100^{0}C in ambient gas mixture (75%CO+25%CO_2). It can be seen that a part of it has broken away.

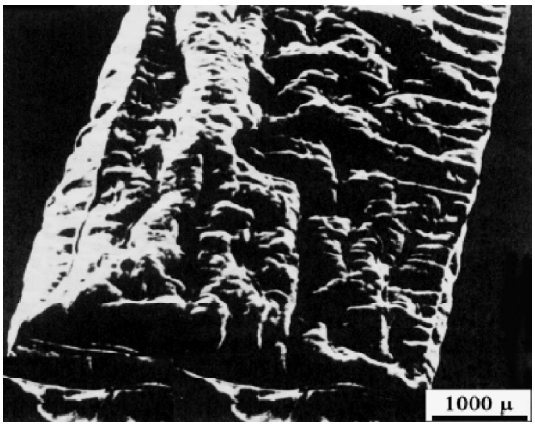

Fig. 2. SEM image of the oxidized unalloyed chromium surface.

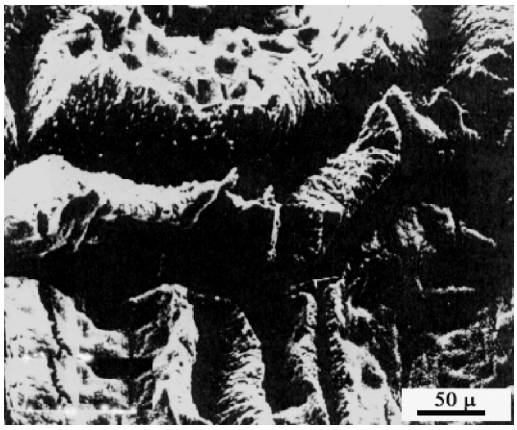

Fig. 3. SEM image of the underside of the scale shown in Fig. 2.

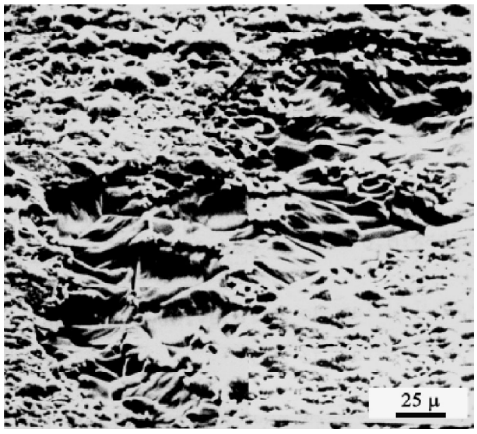

Fig. 4. SEM image of the oxidized Cr+0.5%Ce alloy surface

Moreover, during corrosion of unalloyed chromium and an alloy with cerium additions under the conditions described above no significant difference in the gross features of morphology of scales development are observed (Fig. 2 and Fig. 4). The difference is significant, however, in the case of using the medium of pure oxygen. However, the scale is significantly thinner on the alloy specimens (Fig. 1) pro rata with lower weight gains.

Conclusion

The results of the investigation are thus indicative of a positive effect of small additives of cerium on the oxidation resistance of chromium in the gas atmosphere (75%CO+25%CO_2) at high temperatures and under low oxygen activity. This is reflected in a significant slowdown of oxidation of unalloyed chromium and is accounted for by the formation of high density inner layer of the scale.

The impact of cerium on the morphology of the scale growth is less pronounced, although its thickness significantly decreases in the process.

მასალათმცოდნეობა

ქრომის კოროზია გარემომცველ $CO+CO_2$ ნარევებში

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(წარმოდგენილია აკადემოკოს ი. ჟორდანიას მიერ)

ნაშრომში განხილულია სუფთა ქრომისა და ცერიუმთან მისი შენადნობის (Cr+0,5%Ce) მაღალტემპერატურული კოროზიის კვლევის მეთოდიკა და შედეგები (75% CO + 25% CO_2) შედგენილობის აირად ატმოსფეროში 0,01 ატმ წნევის პირობებში. ნაჩვენებია, რომ ქრომის ცერიუმით ლეგირება დადებითად მოქმედებს მის კოროზიულ მდგრადობაზე. ახსნილია მიღებული შედეგის მექანიზმი.

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