

Fundamentals of High Temperature Corrosion

Marker Technique

GOAL

The goal of the exercise is to become familiar with the marker method used to determine the scale formation mechanism on metals during high-temperature oxidation and as the way to interpret the obtained results.

INTRODUCTION

The oxidation mechanism and kinetics of metallic materials are decided first and foremost by the physicochemical properties of the scales formed on their surfaces. Identifying the mechanism of metal and alloy corrosion thus requires, aside from knowledge of point defect mobility in the oxides constituting the scale, full information on the defect structure and concentration.

In the case of compounds that exhibit deviation from stoichiometry, the first step in explaining the defect structure inside them is to determine which sublattice (anion or cation) the predominant disorder is present in. This information can be obtained by means of four basic methods: 1) determining in direct measurements of the self-diffusion coefficients of the metal (D_M) and oxidant (D_X) in the studied compound using stable or radioactive isotopes, 2) the two-stage oxidation method, 3) the scratch test method or 4) the so-called marker method. If the metal self-diffusion coefficient, determined using the direct method, is much greater than the oxidant self-diffusion coefficient ($D_M \gg D_X$), then the predominant disorder is present in the cation sublattice. On the other hand, a much lower metal self-diffusion coefficient compared to the oxidant self-diffusion coefficient ($D_M \ll D_X$) indicates that defects exist mainly in the anion sublattice.

Another method that allows for determining the mechanism of scale formation on metals is two-stage oxidation. This method consists of initial oxidation of the studied metal in an atmosphere not containing a radioactive isotope and then, without interrupting the reaction, entering a radioactive isotope of the oxidant. The oxidation process is still carried out in the

sample temperature and oxidant pressure until a scale of desired thickness is obtained. After that the oxidation process is stopped and the sample removed from the apparatus is cut in the direction perpendicular to the scale surface. A metallographic cross-section is then made from the sample prepared in this manner, on which the location of the radioactive isotope within the scale is studied. If the oxidation process took place only due to outward metal diffusion, then the radioactive oxidant isotope will be located mostly in the outer part of the scale grown in the second reaction stage. In the inner part of the scale, however, its presence will not be registered. In the case of inward mass transport inside the scale, the presence of the radioactive oxidant isotope will be registered in the inner part of the scale. If the scale grows due to simultaneous and oppositely directed lattice diffusion of both reagents, then the radioactive isotope will be found throughout the entire scale and its concentration will be lowest in the middle part of the sample.

Determining the oxidation mechanism using the so-called “scratch method” consists of intentionally leaving a scratch on the surface of the studied material before starting the oxidation process. After oxidation, it must be determined if the scratch is still visible on the surface of the grown scale. The presence of the scratch on the sample surface suggests that inward oxidant diffusion plays the dominant role in the scale formation process. On the other hand, if the scratch is not there, then it can be concluded that outward metal diffusion is the dominant mechanism. The “scratch method” is rarely used mostly due to the problems with interpreting results when mixed diffusion of individual reagents contributes to the general transport process of material through a scale.

Since the radioactive isotope method of determining the predominant disorder in MX-type compounds are very time-consuming and subsequently rarely used, the marker method is commonly used due to its simplicity. The essence of the marker method is to place on the surface of a pure metal or alloy a substance called a marker, which does not react with either the oxidant, the substrate material, or the reaction product, and finding its location after oxidation in the formed scale. Location of the marker at the metal/scale interface (in the case of a one-phase scale that is compact and well-adherent to the metallic core) means that the predominant disorder is present in the cation sublattice. If the marker is located at the scale/oxidant interface, on the other hand, it can be stated that defects can be found practically only in the anion sublattice. However, if the marker is found inside the scale, then the result suggests that both sublattices exhibit disorder to a comparable degree.

In order to obtain reliable results concerning the relative contribution of reagents in a scale formation process, studies on an oxidation mechanism are carried out sometimes by means of not one, but several of the methods described above.

PERFORMING THE EXERCISE

In order to practice depositing several types of markers, prepare three steel plates.

1. On the surface of the first plate deposit a marker in the form of Al_2O_3 powder. The powder should be placed on the surface so that individual grains are evenly distributed on the entire plate surface (surface coverage: around 1 grain/ mm^2).
2. On the surface of the second plate deposit markers in the form of short wires with around 1 – 10 μm diameters. Cut the wires into sections with around 2mm length, then place them on the plate surface parallel to one another, but perpendicular to the longer edge of the steel plate.
3. Wrap a wire around the third plate so that the wire coils tightly and evenly cover the steel plate for its entire length (the winding direction should be perpendicular to the longer side of the sample). Maintain equal spaces of around 0,5 – 1 mm between the coils.

With the help of a stereoscopic microscope carry out observations on the prepared samples and point out eventual mistakes made during marker deposition by means of the above-described methods.

Perform microscopic observations on the previously prepared metallographic cross-sections. Pay attention to scale thickness, marker diameter in comparison with layer thickness, marker location relative to metal/scale and scale/oxidant interfaces, and all scale characteristics (fractures, porosity, layer detachment). Take pictures of the observations, describe them and interpret the mass transport mechanism in the reactive system.

LITERATURE

1. S. Mrowec, Metal Oxidation Kinetics and Mechanism, Katowice 1982.
2. S. Mrowec, Solid State Diffusion Theory, PWN, Warszawa, 1989.