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Determination of diffusion coefficients using thermogravimetric measurements during high temperature oxidation

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Abstract. Thermogravimetry measurements associated to concentration profiles allow determining a diffusion coefficient at high temperature of the most oxidable one among the metallic elements belonging to the chemical composition of an alloy. In this work the employed method is described and applied to chromia-forming alloys essentially based on nickel but also to selected cobalt-based and iron-based alloys. More precisely D_{Cr} values were estimated for chromium diffusing through the carbide-free zones developed during high temperature oxidation. The effects of the base element, of the chromium carbides density and of the dendritic orientations on the chromium diffusion were evidenced.

Introduction

When an alloy is subjected to oxidation at high temperature, the easiest to oxidize among the elements present in the alloy's chemical composition, generally diffuses toward the oxidation front to be selectively oxidized, if it is present with an amount high enough [1]. This is for example the case of chromium or of aluminum, the oxidation of which leads to the formation of a continuous external layer of protective oxide of chromia or alumina respectively. This diffusion leads to a sub-surface zone depleted in chromium which grows inwards, and across which is established a profile of Cr or Al decreasing from the bulk content down to a lower value at the {alloy – external oxide} interface. In parallel the oxidation progress can be followed by recording continuously the sample mass using a thermo-balance in order to quantify the increasing mass of oxygen involved in the growing oxide scale, which allows elsewhere quantifying the increasing mass of oxidized metallic element (Cr or Al).

The sample mass variation measured by thermogravimetry allows knowing the final rate of outside arrival of oxygen in the oxide, then the rate of inside arrival of the metallic element if the formed oxide is of a single nature. The concentration profile of the metallic element can be known by microprobe measurements on the metallographic sample prepared from the oxidized alloy, which allows the determination of the corresponding gradient in the neighborhood of the oxidation front. The exploitation of the two types of results allows estimating the diffusion coefficient, at the studied temperature, of the selectively oxidized element through the external part of the alloy [2].

In this work it was attempted to assess diffusion coefficients of chromium by preparing specific alloys and submitting them to oxidation at several high temperatures, by following the mass gain rate and characterizing the sub-surface depletion by microprobe profiles.

Experimental details

Several alloys were elaborated from pure elements, using a high frequency induction furnace (CELES), under an inert atmosphere (pure argon, 300mbars). 30wt.% is the chromium content which was chosen for all the alloys of this study, to favor a chromia-forming behaviour for all of them, and no other easily oxidable element than chromium was added to the chemical compositions. Thus only binary M-30Cr and ternary M-30Cr-xC alloys were elaborated, with M=Ni, Co and Fe to study the effect of the base element on Cr diffusion, and x=0.2, 0.4 and 0.8wt.%C to study the effect of the carbide density. The solidified ingots were cut in order to obtain parallelepipeds of about 10 mm × 10 mm × 3 mm, with special cutting orientations for the samples destined to the study of the effect of the dendritic orientation.

The thermogravimetry tests were performed at 1000, 1100 or 1200°C in dry synthetic air, during 50 hours. After cooling (at about -10K min⁻¹), the oxidized samples were covered by cathodic pulverization of gold (to make their external oxide superficially electrically conductive), by electrolytic nickel deposition in a Watts bath, cut, embedded in cold resin mixture (Escil) and polished with first SiC papers from 120-grit to 1200-grit, and second 1µm-abrasive particles. They were observed by Scanning Electron Microscopy (SEM Philips XL30) in Back Scattered Electrons mode with an acceleration voltage of 20kV to visualize both the external oxides and the carbide-free zone. Concentration profiles were performed by Wavelength Dispersion Spectrometry across the external oxide and the whole carbide-free zone to specify the natures of the oxides present in the external scales, and the chromium gradients through the carbide-free zone, using Cameca SX50 and SX100 microprobes.

The mass gain results were plotted in a $m = f(t)$ scheme (m: mass gain per surface unit area) and the slope of the tangent straight line at the end of the parabolic curve was determined to estimate the final mass gain rate $(dm/dt)_{end}$ (Fig. 1, left). The Cr-concentration profiles were also plotted, versus the distance from the {scale/alloy} interface, with also the estimation of the chromium gradient close to the oxidation front by measuring the slope of a tangent straight line (Fig. 1, right).

Fig. 1. Determination of the final mass gain rate (left) and of the chromium gradient in the alloy close to the external oxide scale (right), before estimating the Cr diffusion coefficient

These values of the final mass gain rate and of chromium gradient in sub-surface can be used to specify the terms present in Eq. 1. Indeed the first and the second members of Eq. 1 can be written as presented in Eq. 2 and in Eq. 3, respectively. The $(dm_O/dt)_{\text{end}}$ term can be corrected by adding a volatilization constant K_v for the thermogravimetry results obtained at 1100 and 1200°C by taking into account the mass loss by chromia volatilization. Knowing then the values of these two quantities the diffusion coefficient can be deduced according to Eq. 4.

$$\frac{dn_{\text{Cr}}}{dt} = D_{\text{Cr}} \cdot \left\| \overrightarrow{\text{grad}} [\text{Cr}] \right\| \quad (1)$$

$$\frac{2}{3 \cdot M_{\text{O}}} \cdot \frac{dm_{\text{O}}}{dt} \Big|_{\text{end}} \quad (2)$$

$$D_{\text{Cr}} \cdot \left\langle \left(\frac{\rho_{\text{all}}}{M_{\text{Cr}}} \right) \cdot \left(\frac{\Delta\%_{\text{w}} \text{Cr}}{\Delta x} \right) \right\rangle \quad (3)$$

$$D_{\text{Cr}} = \frac{2 \cdot M_{\text{Cr}}}{3 \cdot M_{\text{O}}} \cdot \frac{\frac{dm}{dt} \Big|_{\text{end}} + K_v}{\rho_{\text{all}} \cdot \frac{\Delta\%_{\text{w}} \text{Cr}}{\Delta x}} \quad (4)$$

Results and discussion

Cr diffusion coefficient versus the alloy's base element. Applying the technique described above to the oxidized nickel alloys was possible for all carbon contents and all temperatures. In contrast, despite the absence of any other very oxidable element (as tantalum for example) in the studied alloys, Cr_2O_3 was not always the single oxide to form. Indeed, CoO and CoCr_2O_4 also formed in most cases for the cobalt alloys and Fe was often mixed with chromium in the M_2O_3 external oxide covering the iron alloys, with varying Fe/Cr ratio along the scale of a same oxidized sample (Fig. 2, left). Thus, generally it was not attempted to value the diffusion coefficient of chromium by using the mass gain results and WDS chromium profiles. However, since it was observed that the oxide present on the 0.4C-containing cobalt-based and iron-based alloys oxidized at 1000°C was essentially pure chromia, the values of chromium diffusion coefficient were assessed for these two cases. The results for the three 0.4C-containing alloys oxidized at 1000°C are graphically presented in Fig. 2 (right).

Fig. 2. Left: examples of surface states of the oxidized samples: Cr_2O_3 for all Ni alloys, possible presence of additional CoO for many cobalt alloys and of Fe in the M_2O_3 oxide for the iron alloys; Right: the values obtained for the diffusion coefficient of chromium in the carbide-free zones of the M-30Cr-0.4C alloys oxidized at 1000°C (on which Cr_2O_3 is the exclusive or main oxide present)

The value obtained for the Ni-30Cr-0.4C alloy is the lowest one. However it is twice the one later obtained for a Ni-20Cr alloy at the same temperature [3]. The highest value is the one of the ferritic Fe-30Cr-0.4C alloy: this would show that Cr more easily diffuses in a centered cubic matrix than in an face centered cubic one, accordingly with older observations done about the differences of Cr diffusion at 850°C seen between a ferritic Fe-15Cr-0.5C-1Si and an austenitic Fe-15Cr-0.4C-1Si-1Ni [4] despite that the later was probably helped for Cr diffusion by chromium carbides.

The Cr diffusion is thus slower in the nickel alloy than in the cobalt one, although it is on the contrary generally considered that Cr diffuses faster in nickel alloys than in cobalt alloys. This may be explained by the fact that 1000°C is not a very high temperature and then Cr diffused more through the grain boundaries and interdendritic spaces (short circuit diffusion paths) than in volume.

Cr diffusion coefficient versus the carbides density. For the binary Ni-30Cr and the ternary Ni-30Cr-xC with x varying from 0.2 to 0.8wt.%C chromia was obviously the single oxide formed. The technique was then applied for these four alloys for the three temperatures, which led to the results graphically presented in Fig. 3. One can see first that the diffusion coefficient of chromium logically increases with temperature. But the most interesting observation concerns the dependence of this coefficient D_{Cr} on the alloy's carbon content or the carbide fraction in the alloy. Indeed, D_{Cr}

Fig. 3. Left: chromia scales and carbide-free zones of the Ni-30Cr-0.2C and -0.8C alloys oxidized at 1200°C; Right: the obtained chromium diffusion coefficients

increases with the C content. Between the binary Ni-30Cr and the carbon-poor Ni-30Cr-0.2C the ratio is $\times 2.7$ for 1000°C while there is no significant difference for D_{Cr} between the two alloys at 1100 and 1200°C. The ratio between Ni-30Cr and the C-richest Ni-30Cr-0.8C is higher but decreases when temperature increases ($\times 4$, $\times 3.6$ and $\times 2.8$ for respectively 1000, 1100 and 1200°C). This decrease of the difference for an increase in temperature probably results from an increasing part of the diffusion in volume which can be less influenced by the density of the carbides initially present. For the three alloys the diffusion coefficient of chromium obeys an Arrhenius plot, especially in the case of the Ni-30Cr-0.2C alloy (Fig. 4). The activation energies are all around 300,000 J / mol.

Fig. 4. D_{Cr} versus temperature in Arrhenius plot; the activation energies are 355 (Ni-30Cr), 283 (-0.2C) and 327 (-0.8C) kJ mol⁻¹

Cr diffusion coefficient versus the dendrite orientation. The diffusion kinetic probably depending on the orientation of grain boundaries and the more numerous interdendritic spaces, some samples for oxidation tests were cut following special procedures to favor a main surface either parallel to dendrites or perpendicular to dendrites (Fig. 5). Per alloy and per test temperature two samples were cut with two different orientations with regard to the external surface of the ingot, and subjected to the same high temperature oxidation test.

Fig. 5. Ni-30Cr-0.8C alloy oxidized at 1100°C for 50h; cutting methods and bulk microstructure orientation for a main surface parallel to dendrites (left) or perpendicular to dendrites (right)

Obtaining the two diffusion coefficients for the two types of orientation from mass gain rates which are global measurements needs to uncouple the contributions of the two types of surfaces. For the whole sample the global mass gain can be described by Eq. 5, which can be also formulated as Eq. 6. The two later equations allow writing Eq. 7. The principle consists in performing two thermogravimetry tests in the same conditions for two samples from a same alloy but prepared following the two cutting methods illustrated in Fig. 5. This allows obtaining two different values of the ratio {surface parallel to dendrites / total surface} and also two different values of the ratio {surface perpendicular to dendrites / total surface} and then the two equations written on the model of Eq. 7, for the two distinct samples, are not dependent to one another, permitting to solve the system by deducing an unique solution couple ($K_{p//}$; $K_{p\perp}$). Knowing the uncoupled local parabolic constants it is now possible to estimate the two local mass gain rates at the end of thermogravimetry experiment. Since the concentration gradients are also local measurements, applying Eq. 4 for each of the two orientations allows obtaining the Cr diffusion coefficient through the carbide-free zone developed from the surface parallel to dendrites and the one through the carbide-free zone developed from the surface perpendicular to dendrites.

$$\frac{\Delta m}{S}(t) = \sqrt{2.K_p} \cdot t^{\frac{1}{2}} - K_v.t \quad \left[S = S_{//} + S_{\perp} \right] \quad (5)$$

$$\frac{\Delta m}{S}(t) = \frac{1}{S} \cdot (S_{//} \cdot \frac{\Delta m_{//}}{S_{//}}(t) + S_{\perp} \cdot \frac{\Delta m_{\perp}}{S_{\perp}}(t)) = \frac{S_{//}}{S} \sqrt{2.K_{p//}} \cdot \sqrt{t} + \frac{S_{\perp}}{S} \sqrt{2.K_{p\perp}} \cdot \sqrt{t} - (\frac{S_{//}}{S} + \frac{S_{\perp}}{S}) K_v.t \quad (6)$$

$$\frac{S_{//}}{S} \sqrt{2.K_{p//}} + \frac{S_{\perp}}{S} \sqrt{2.K_{p\perp}} = \sqrt{2.K_p} \quad (7)$$

Unsurprisingly the two distinct diffusion coefficients of chromium are almost the same for the Ni-30Cr-0.2C alloy which contained initially few carbides in the carbide-free zone while the differences are considerably enhanced for the Ni-30Cr-0.8C alloy in which the highest carbide fraction let to more marked diffusion paths in the carbide-free zone, the orientation of which plays an enhanced role (diffusion easier when they are oriented in the same direction as the general Cr diffusion).

Fig. 6. Values obtained for the diffusion coefficients of chromium through a carbide-free zone in which the interdendritic carbides were aligned parallel to the external surface or aligned in the perpendicular direction

However the value obtained for the Ni-30Cr-0.8C alloy at 1200°C is maybe too high to be realist. It is true that solving the equation system may possibly lead to exaggerated differences between the two values of local parabolic constants, with thereafter detrimental consequences for the accuracy of the D_{Cr} determination. But one can reasonably consider that there is effectively a significantly easier diffusion of chromium for the perpendicular orientation that for the parallel one.

Conclusion

Values of coefficient diffusion of chromium given by more classical techniques (diffusion couples, ...) are surely more accurate in general. However the carbide-free zone is not a classical binary alloy since it contains two-dimensional zones which are the locations where existed the initial carbides before their oxidation-induced disappearance. Despite it is not very accurate, the technique used here probably allows better characterizing the diffusion rate of chromium, with consequently possible deeper interpretation of eventual differences of behavior in oxidation at high temperature, not really about the mass gain kinetic which was employed at the origin for this determination, but about some phenomena governing this behaviour.

Unfortunalety applying this method cannot be envisaged as soon as other oxides different from chromia also exist in not negligible quantities, except in the cases in which it is sure that these other oxides only appeared at the early beginning of oxidation. It can be also applied for alumina-forming alloys, but in other alloys free of any carbide.

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