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About the Role of Chromium and Oxygen Ion Diffusion on the Growth Mechanism of Oxidation Films of the AISI 304 Austenitic Stainless Steel

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Abstract To study the role of ion diffusion on the oxidation process of the AISI 304 austenitic stainless steel, chromium diffusion coefficients were determined in oxide films grown on this steel at 750, 800 and 850 °C, in air. The isotope ^{54}Cr was used as a chromium tracer and the diffusion profiles were established by SIMS. The bulk diffusion coefficients are five orders of magnitude smaller than the grain boundary diffusion coefficients. It was found that the values of the chromium diffusivities are lower than the corresponding oxygen diffusivities obtained in previous work. Parabolic oxidation constants calculated as a function of the chrome and oxygen diffusivities, using Wagner's theory, are close to those determined experimentally, which shows that the growth rate of chromia is controlled by ion diffusion, but inward oxygen diffusion plays the main role on the growth kinetics of chromia formed by the oxidation of the AISI 304 steel.

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Introduction

The AISI 304 austenitic stainless steel is traditionally used for high temperatures applications and its resistance against high temperature oxidation is ensured by the formation of protective chromia films [1, 2].

Recent studies show that the oxidation kinetics of the AISI 304 stainless steel follows a parabolic law, in the temperature range of 850–950 °C, in synthetic air [2]. This oxidation kinetics of the AISI 304 steel is confirmed in the present work at 750 and 800 °C. This indicates that the growth rate of the protective oxide film formed on the surface of the steel is controlled by inward oxygen ion diffusion from atmosphere or by outward cation diffusion from the metallic substrate or by both cation diffusion and oxygen ion diffusion [3]. Therefore, it is interesting to know the chrome and oxygen ion diffusion in chromia to understand the role of the ion diffusion on the oxidation process of the AISI 304 steel.

There is in the literature a number of data about chrome diffusion and oxygen diffusion determined in synthetic chromia (single crystals and sintered polycrystals) and also in some chromia-former alloys, but the microstructural or chemical characteristics of the materials used in these previous studies are not the same of the oxide films grown on the AISI 304 steel. These available data have been reviewed elsewhere [4–6].

Therefore, in order to investigate the role of ion diffusion on the oxidation process of the AISI 304 stainless steel, in conditions as similar as possible of those found in practice, chrome ion diffusion and oxygen ion diffusion should be determined in thermally grown oxide films on that steel.

Very recently, Sabioni et al. [7] studied the oxygen ion diffusion in oxide films grown on the AISI 304 stainless steel, and in this paper chrome ion diffusion coefficients measured, for the first time, in chromia films grown by the high temperature oxidation of that steel are presented. Effective, bulk and grain boundary diffusion coefficients were determined at 750, 800 and 850 °C, in air atmosphere, by using the stable isotope ^{54}Cr as chrome tracer and depth profiling by secondary ion mass spectrometry (SIMS) [8].

The role of the chrome ion diffusion and oxygen ion diffusion on the oxidation of the AISI 304 steel is investigated by comparing experimental parabolic oxidation constants to theoretical ones calculated as a function of the chrome and oxygen ion diffusivities according to Wagner′s theory [3].

Experimental Procedures

Sample Preparation

The samples of AISI 304 austenitic stainless steel were supplied by ArcelorMittal Inox of Brazil. Besides iron, the chemical analysis of this steel shows the following elements: (wt%): C (0.0466), Mn (1.37), Si (0.46), P (0.028), S (0.0006), Cr (18.07), Ni (8.11) and N (322 ppm).

The steel samples used as diffusion specimens were cut with the dimensions of 5 mm × 5 mm × 0.6 mm. One of the largest surfaces was abraded with 1,000 and 2,000 SiC papers, and polished with diamond suspensions of 3 and 1 μm. Then, the samples were oxidized in a tubular furnace at 750, 800 and 850 °C, in air, for durations of 120, 96 and 42 h, respectively, in order to grow an oxide film on the surface of the steel.

The stable isotope ^{54}Cr was used as chrome tracer. The natural chrome has the following isotopic composition (atom%): ^{50}Cr (4.31), ^{52}Cr (83.76), ^{53}Cr (9.55) and ^{54}Cr (2.38). The source of the tracer used in this work was chrome powder enriched to 99.8 %, with the isotope ^{54}Cr, and also containing ^{50}Cr (<0.01), ^{52}Cr (<0.05) and ^{53}Cr (0.20). This ^{54}Cr enriched chrome was supplied by Eurisotop, Saint-Aubin, France.

A film of ^{54}Cr was deposited on the oxidized surface of the steel by electron-beam evaporation under ultrahigh vacuum and molecular beam epitaxy conditions, in a system (Vacuum Generator) with a base pressure of 2.0×10^{-10} mbar. The pressure during ^{54}Cr deposition, using an Oxford Applied Research EGCO4 mini evaporator installed directly ($\sim$20 cm) below the sample manipulator, was always better than 2.0×10^{-9} mbar. The typical deposition rate was 2.0 A min^{-1} and the thickness of the ^{54}Cr film was 10 nm, as determined by means of a quartz oscillator.

Oxidation Experiments

Oxidation constants of the AISI 304 steel were determined at 750 and 800 °C, in air, in order to enlarge available data on oxidation kinetics of this steel previously determined from 850 to 950 °C by one of the authors [1]. For these experiments, samples with the dimensions 10 mm × 10 mm × 0.6 mm were drilled near the center of an edge in order to hang them in the thermogravimetric analysis (TGA) system by means of a platinum wire. Both surfaces of the samples were polished using the same procedure previously described for the diffusion specimens. The oxidation treatments were performed in a TGA SETARAM TGDTA 92 system with sensitivity of ±5 μg. The oxidation kinetics was established by measuring the mass gain per unit area (ΔM/S) as a function of the oxidation time (t).

Diffusion Experiments

The ^{54}Cr diffusion annealings were performed from 750 to 850 °C, in synthetic air atmosphere, using a tubular furnace with the sample placed inside a silica tube. The ^{54}Cr diffusion profiles were established by SIMS using an Apparatus CAMECA IMS3/4F (magnetic sector dynamic SIMS) with a 10 keV Cs^{+} primary ion source. The current intensity of the primary ion beam was of 20 nA, and the incidence angle was of 27° with respect to the normal to the surface of the sample. The scanned area during the SIMS analyses was 200 μm × 200 μm, and the negative ionic signals of the isotopes ^{50}Cr^{-}, ^{52}Cr^{-}, ^{53}Cr^{-} and ^{54}Cr^{-} were collected from a zone of 62 μm in diameter centered on the scanned area. The chrome diffusion profiles were determined from the intensities of the signals of the negative ions ^{50}Cr^{-}, ^{52}Cr^{-}, ^{53}Cr^{-} and ^{54}Cr^{-} using procedure described elsewhere [9].

Results and Discussion

Oxidation Kinetics of AISI 304 Stainless Steel

The oxidation kinetics of the AISI 304 steel has been previously studied in the temperature range of 850–950 °C [1]. According to this study, the growth kinetics of the oxide film grown on the AISI 304 steel follows a parabolic law given by

$$(\Delta M/S)^2 = k_{op} + k_p t, \tag{1}$$

where k_p is the parabolic oxidation constant, and k_{op} is a constant. The parabolic oxidation constants (k_p), expressed in $g^2 \, cm^{-4} \, s^{-1}$, are equal to 2.1×10^{-13}, 6.9×10^{-13} and 1.4×10^{-12} at 850, 900 and 950 °C, respectively, in air atmosphere, for oxide films mainly containing chromia [1].

The results obtained in the present work, at 750 and 800 °C, for the oxidation kinetics of the AISI 304 steel are shown in Fig. 1a, b. The very good linearity observed in the plots of Fig. 1b demonstrates that the oxidation kinetics follows a parabolic law. This means that the growth rate of chromia is controlled by inward oxygen ion diffusion from atmosphere or by cation outward diffusion from metallic substrate or by both cation diffusion and oxygen ion diffusion [3]. The k_p values were determined from the plots of $(\Delta M)^2$ versus t, using the Eq. 1, as shown in Fig. 1b. The parabolic oxidation constants (k_p) are equal to 3.1×10^{-14} and $1.3 \times 10^{-13} \, g^2 \, cm^{-4} \, s^{-1}$, at 750 and 800 °C, respectively.

The variation of the parabolic oxidation constant as k_c, expressed in $cm^2 \, s^{-1}$, instead of k_p, in the temperature range of 750–950 °C is shown in Arrhenius' plot of Fig. 1c. The unit of k_c is more adequate for later discussions taking into account Wagner's theory. The conversion of k_p into k_c was performed by using the following expression [1]:

$$k_c(cm^2 s^{-1}) = (M_{ox}/3\rho_{ox}M_o)^2 k_p(g^2 cm^{-4} s^{-1}). \tag{2}$$

Chrome Ion Diffusion

For the experimental conditions used in the oxidation of the AISI 304 steel, the thermally grown oxides were adequate for diffusion studies, i.e., dense, continuous and adherent to the metallic substrate, and mainly made up of chromia (Cr_2O_3) [1]. Figure 2 shows the surface morphology of the oxide film grown on the steel oxidized at 800 °C. At all temperatures, there is a preferential oxidation at the grain boundaries of the AISI 304 steel as shown in Fig. 2a.

Figure 3 shows a typical depth profile for the ^{54}Cr diffusion in the oxide film, after diffusion for 4 h, at 850 °C, in air. For the determination of the oxygen diffusion coefficients, it was considered only the part of the diffusion profiles inside the chromia rich region of the oxide film as that delimited by the dot line shown in Fig. 4a, for the experiment at 850 °C, where the ionic signals of the isotopes $^{18}O^-$, $^{52}Cr^-$, $^{28}Si^-$, $^{56}Fe^-$ and $^{58}Ni^-$ are represented. Figure 4b shows the ionic signals of the chrome isotopes in that delimited zone: $^{50}Cr^-$, $^{52}Cr^-$, $^{53}Cr^-$ and $^{54}Cr^-$.
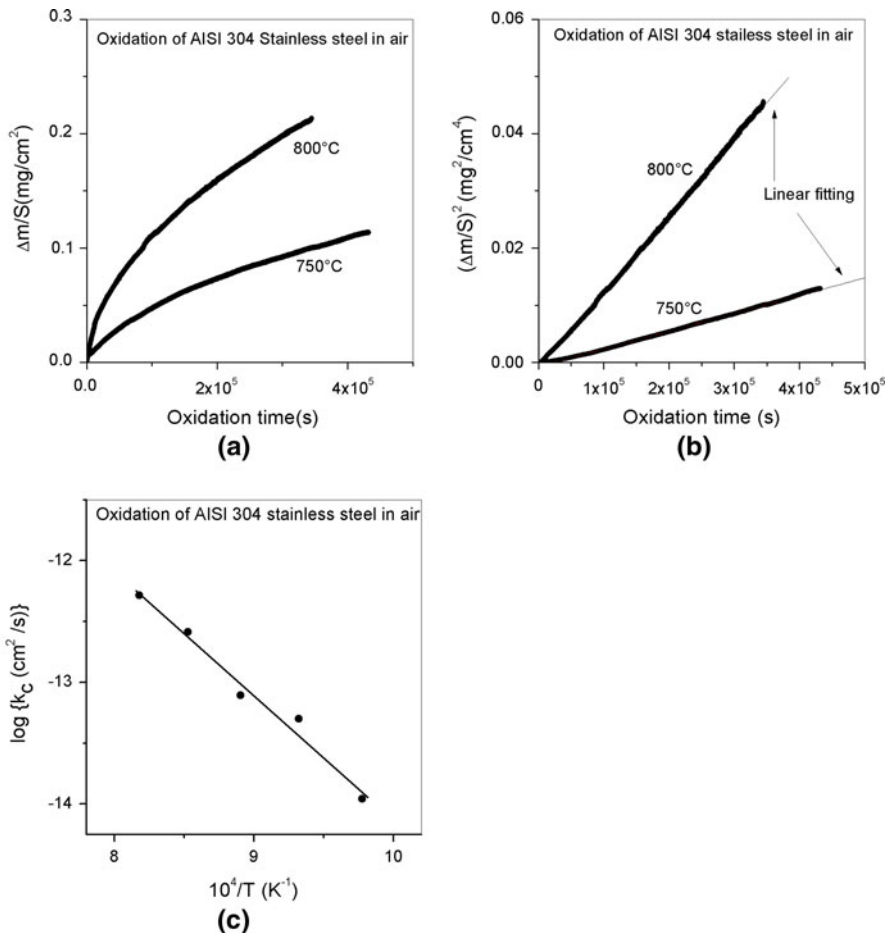
Fig. 1 Oxidation of AISI 304 stainless steel. **a** TGA analysis at 750 and 800 °C, **b** determination of the parabolic oxidation constants (k_p), and **c** Arrhenius' plot for k_c

The shape of the chrome ion diffusion profiles is typical of the B-type diffusion regime [10]. In the first part of the profile, near the surface, there is fast decrease of the tracer concentration, and, far from the surface, the concentration slowly decreases. In the diffusion profile (Fig. 3), the first part of the profile should correspond to the bulk diffusion, and the second part of the profile should correspond to the grain boundary diffusion. However, due to the small grain size of the microstructure of the thermally grown oxides, between 0.65 μm, at 750 °C, and 1.0 μm, at 850 °C, it is assumed that the first part of the diffusion profile corresponds to an effective diffusion resulting of the bulk diffusion more grain boundary diffusion as explained elsewhere [5, 6]. The relationship between the grain boundary diffusion coefficient (D_{gb}), bulk diffusion coefficient (D_b) and effective diffusion coefficient (D_{eff}) is given by Hart's relationship as follows [11]:
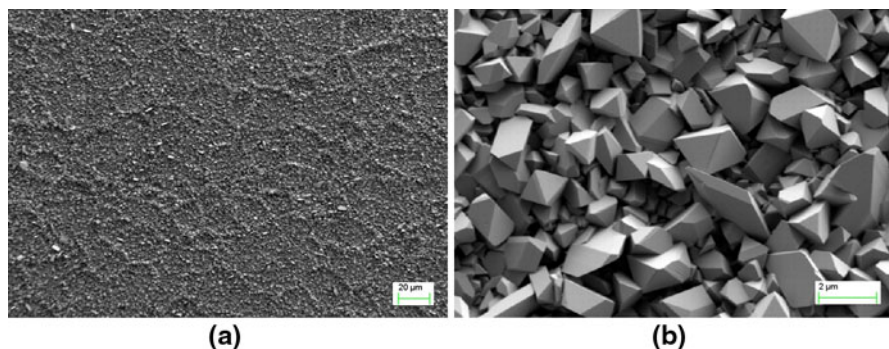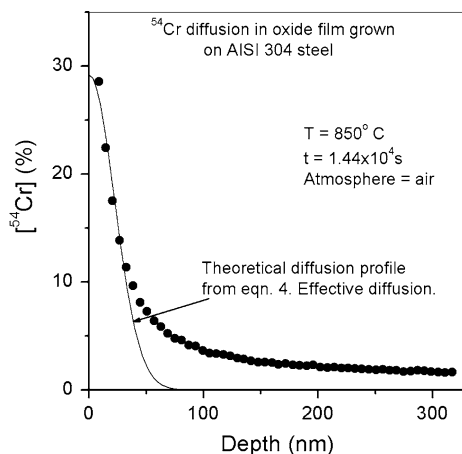
Fig. 2 Microstructure of the oxide film grown on AISI 304 after 96 h oxidation at 800 °C. **a** Global view of oxidation surface morphology, **b** detail view of surface Cr_2O_3 crystals

Fig. 3 ^{54}Cr diffusion profile in the oxide film grown on the AISI 304 steel at 850 °C

$$D_{eff} = fD_{gb} + (1 - f)D_b \qquad (3)$$

where f is the volume fraction of the grain boundaries, which may be given by the expression $f = 3\delta/\Phi$, where Φ is the grain size and δ is the grain boundary width. The value of δ is usually assumed to be equal to 1 nm [12]. From the first part of the diffusion profile, an effective diffusion coefficient was determined using an appropriate solution of the Fick's diffusion equation. In our experimental conditions, the ^{54}Cr film is not sufficient thin in comparison with the depth of the first part of the diffusion profile. So, the effective diffusion coefficient (D_{eff}) was determined using the solution of Fick's given by [13]:

$$C(x, \ t) = \frac{C_o}{2} \left[erf \frac{a + x}{2\sqrt{D_{eff}t}} + erf \frac{a - x}{2\sqrt{D_{eff}t}} \right] \qquad (4)$$

where C_o is the concentration of the tracer in the chrome film deposited on the oxidized surface, a is the thickness of the film and D_{eff} is the effective diffusion coefficient. The D_{eff} values were determined by nonlinear fitting of Eq. 3 to the ^{54}Cr
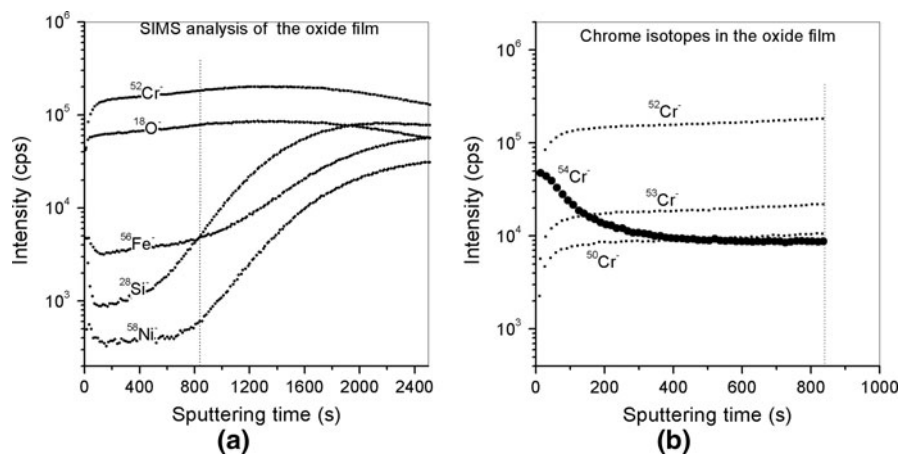
Fig. 4 **a** SIMS analysis of the oxide film grown on the AISI 304 stainless steel after ^{54}Cr diffusion, at 850 °C, showing the chromia rich region delimited by the *dot line*, and **b** the ionic signals of the chrome isotopes in that region

depth profiles as shown in Fig. 3. For B-type intergranular diffusion, the product δD_{gb} may be determined by means of Le Claire's relationship given by [14]:

$$\delta D_{gb} = 1,32 \left(\frac{D_b}{t}\right)^{1/2} \left(-\frac{d \ln C}{dx^{6/5}}\right)^{-5/3} \quad (5)$$

where $C = [^{54}Cr]$, and the gradient $d\ln C/dx^{6/5}$ is determined from the tail of the diffusion profile in a plot of $\ln C$ versus $x^{6/5}$ as shown in Fig. 5.

Taking into account that the values of D_{eff} and $d\ln C/dx^{6/5}$ can be determined from Figs. 3 and 5, respectively, the values of D_b and D_{gb} can be calculated by the resolution of the system formed by the Eqs. 3 and 5.

Fig. 5 Plot of $\ln [^{54}Cr (\%)]$ versus $x^{6/5}$ for ^{54}Cr diffusion in oxide film grown on the AISI 304 stainless steel at 850 °C
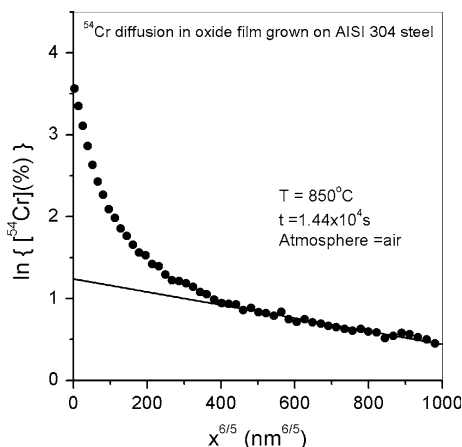
The experimental conditions and the values obtained for the bulk, grain boundary and effective chrome diffusion coefficients are listed in Table 1, where t_{ox} is the time of oxidation for growing the oxide film, and t_d is the time of the diffusion annealing. It is worth noting that the chrome diffusion takes place predominantly along the grain boundaries.

Relationship Between Ion Diffusion and Oxidation of AISI 304 Stainless Steel

As far as we know the only available data about chrome and oxygen ion diffusion in chromia grown on AISI 304 are those of the present work, for chrome ion diffusion, and those of Sabioni et al. [7] for oxygen ion diffusion in the temperature range of 750–900 °C. These chrome and oxygen diffusivities are compared in Arrhenius diagram of Fig. 6, which shows that the oxygen ion diffusion coefficients are greater than the chrome diffusion coefficients. It may be observed that the bulk diffusion coefficients are five orders of magnitude smaller than the grain boundary diffusion coefficients both for chrome diffusion and for oxygen diffusion. This means that the grain boundaries are the preferential paths for the ion diffusion in the oxide films grown on the AISI 304 steel.

In order to verify the relationship between the oxygen and chrome ion diffusion and growth mechanism of oxidation film grown on AISI 304 steel, theoretical oxidation parabolic constants were calculated by means of Wagner′s theory [3] and compared to the experimental constants shown in Fig. 1c. Assuming that the defect concentration in the chromia grown on the AISI 304 steel does not depend on the oxygen pressure, as suggested in previous work [1], the parabolic oxidation constants may be calculated by the following expression [1]:

$$k_c(cm^2/s) = (1,5D_{Cr}^{eff} + D_o^{eff}) \ln \frac{P_{O_2}(e)}{P_{O_2}(i)} \qquad (6)$$

where k_c is the parabolic oxidation constant, expressed in $cm^2 \ s^{-1}$, $P_{O_2}(e)$ is the oxygen pressure at the interface oxide/atmosphere (equal to 2.1×10^4 Pa), $P_{O_2}(i)$ is the oxygen pressure at the interface metal/oxide (10^{-24}–8×10^{-18} Pa in our case), D_{Cr}^{eff} is the chrome effective diffusion coefficient and D_O^{eff} is the oxygen effective diffusion coefficient.

Figure 7 shows the experimental values of the parabolic oxidation constant, k_c (exp), from 750 to 950 °C; and theoretical values of the parabolic oxidation constant determined by means of Wagner′s theory for the following cases: (a) taking into account only the contribution of the oxygen ion diffusion, k_c (^{18}O) (b) taking into account only the chrome ion diffusion, k_c (^{54}Cr), and taking into account both

Table 1 Chrome ion diffusion coefficients determined in oxide films grown on AISI 304 steel

T (°C)	t_{ox} (s)	t_d (s)	D_{eff} (cm^2 s^{-1})	D_b (cm^2 s^{-1})	D_{gb} (cm^2 s^{-1})	D_{gb}/D_b
750	4.32×10^5	3.36×10^4	6.6×10^{-17}	1.0×10^{-19}	1.4×10^{-14}	1.4×10^5
800	3.45×10^5	2.16×10^4	7.2×10^{-17}	1.0×10^{-19}	2.4×10^{-14}	2.4×10^5
850	1.51×10^5	1.44×10^4	1.6×10^{-16}	1.1×10^{-19}	5.3×10^{-14}	4.8×10^5

Fig. 6 Arrhenius diagram for chrome and oxygen diffusion in oxide films grown on the AISI 304 stainless steel, in air. Chrome diffusivities: *circle* D_{gb}, *square* D_{eff}, *inverted triangle* D_b
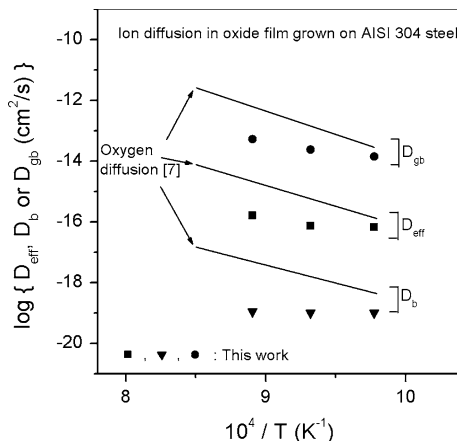
chrome and oxygen effective ion diffusion coefficients, k_c (theor) $= k_c$ (^{54}Cr) $+ k_c$ (^{18}O).

The analysis of Fig. 7 enables us to draw the following conclusions:

– The contribution of the chrome ion diffusion to the oxidation constant, k_c (^{54}Cr), is less important than the experimental oxidation constant, k_c (exp). So, only the chrome ion diffusion is not enough to assure the growth kinetics of the oxide film.
– Oxygen ion diffusion is found to be large enough to assure the growth rate of the oxide film above 800 °C, because k_c (^{18}O) is more important than k_c (exp). Below this temperature, k_c (exp) is somewhat greater than k_c (^{18}O), so that only the oxygen ion diffusion in not sufficiently high to ensure the growth rate of the oxide film under 800 °C.
– Between 750 and 850 °C, the total contribution to the oxidation constant of both ion diffusion k_c (theor) $= k_c$ (^{18}O) $+ k_c$ (^{54}Cr) is slightly greater than k_c (exp). In fact, Wagner's theory appears to be adequate to describe the oxidation

Fig. 7 Arrhenius diagram for the parabolic oxidation constant of AISI 304 stainless steel, where k_c (exp) is the experimental value of the oxidation constant from 750 to 950 °C; k_c (theor) is the oxidation constant calculated by means of Wagner's theory taking into account chrome and oxygen effective diffusion coefficients
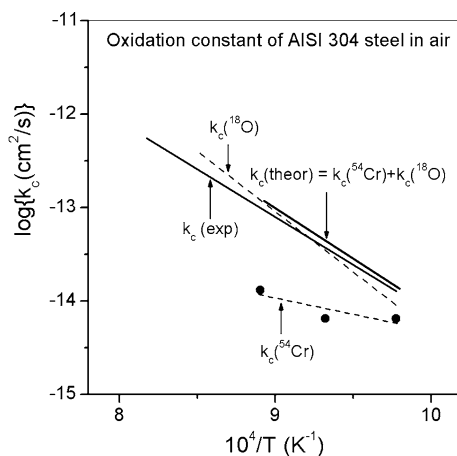
mechanism of AISI 304 steel, which shows that the growth rate of chromia films on AISI 304 steel is controlled by ion diffusion.

– It is clear that oxygen ion inward diffusion is the main atomic transport way for the growth mechanism of oxide films on AISI 304 stainless steel.

Conclusions

– For the first time the effective, bulk and grain boundary diffusion coefficients for chrome ion in chromia grown by oxidation of AISI 304 stainless steel were determined.
– The bulk diffusion coefficients are five orders of magnitude smaller than the grain boundary diffusion coefficients, which show that the grain boundaries are the preferential paths for the chrome diffusion in the oxide films grown on the AISI 304 steel.
– Oxygen ion diffusivities are greater than the chrome ion diffusivities in the chromia film grown on the AISI 304 steel.
– Parabolic oxidation constants calculated as a function of the chrome and oxygen diffusivities, by using Wagner's theory, are close to the experimental ones, which shows that the growth rate of chromia is controlled by ion diffusion, but inward oxygen diffusion plays the main role on the growth kinetics of chromia formed by the oxidation of the AISI 304 steel.

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