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# Investigation of average growth stresses in $Cr_2O_3$ scales measured by a novel deflection method①

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**[Abstract]** The stress in the oxide film plays an important role to keep it intact so it is necessary to determine the stress in the oxide scale. Average growth stresses in $Cr_2O_3$ scales formed on Ni-base alloy (Ni80Cr20) at 1 000 ℃ in air were investigated by a novel deflection technique. It is found that the growth stress in the oxide scale is basically compressive and its average order is 100 MPa. The stress values are high for the thin scales and become low for thick scales after oxidized for 10 h. The planar stress distribution in metals is complex. It is both compressive and tensile at the beginning of oxidation procedure, and then become only tensile during further oxidation.

**[Key words]** growth stress; deflection test; creep analysis; $Cr_2O_3$ scale
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## 1 INTRODUCTION

During high temperature oxidation, the stresses are developed generally in oxide scales. The stresses mainly result from the isothermal growth of oxides and the thermal misfit due to the difference of the thermal expansion coefficients between the oxide and substrate. They can act as driving force for buckling, cracking and spalling, which usually lead to the loss of protective properties and accelerate the degradation of materials. Much work has been undertaken to understand and to measure such stresses. Especially, the measurement of the stress in oxide scale is fundamental. Many techniques were developed for in-situ measurement of the stresses during the isothermal treatment or the cooling process, such as deflection[1], high temperature X-ray diffraction[2], and spectroscopies[3, 4]. The deflection method may determine continuously, and equipment used in this method is quite simple. However, the preparation of the sample is very difficult, because it is necessary to apply protective coating on one side of the sample, the coating should protect the substrate from oxidizing and does not affect the deflection behavior of the sample. It was indicated that $SiO_2$ of 0.6~ 4.0 μm thickness can be applied as best coating[1, 5]. However, it was still limited to apply at low temperature or at high temperature for short time. There has been increasing trend for using high temperature X-ray diffraction, but the resolution of the technique seems insufficient to monitor rapidly changing levels of stress in the early stages of oxidation or low stresses in later stages of oxidation. Especially, neither deflection test nor X-ray diffraction can be easily used to measure the growth stress in thin $Al_2O_3$ scale and the stress distribution. The new application of Raman spectroscopy and fluorescence may make up their weakness. However, the kinds of measurable oxides were very limited[3, 4].

As mentioned above, the deflection method has many advantages, so this method is most generally used for stress measurement. The limitation and the precision of this method principally result from the protective coating. If the protective coating does not be required in the deflection test, the application of this method may be expanded. In fact, one method was developed for measuring the change of the growth stress in oxide scale due to ion implantation of rare earth(RE) element[6]. With this method, thin strip alloy was implanted with RE just on one side. Then the alloy was oxidized. Because of the difference of the stress between two oxide layers formed on the surfaces of RE-free and RE implanted, the sample would bend. Therefore, the effect of RE on the oxide stress could be studied quantitatively. But the extract growth stress could not be determined by this method.

In present paper, the average growth stresses in $Cr_2O_3$ scales formed on Ni80Cr20 alloy were studied by the deflection method.

## 2 EXPERIMENTAL

### 2.1 Fundamental of novel method

Thin strip alloy was oxidized directly for time $t_o$. Then oxide scale on one side of the alloy was removed by mechanical grinding. The alloy was then oxidized again at the same temperature. Therefore

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the thickness of the scales on two surfaces of the alloy was different. If the alloy happened bending, the level of the growth stresses in the oxide scale could be gotten basing on the formula as follows[6]

$$\sigma_2 \zeta_2 - \sigma_1 \zeta_1 = EH^2 D / [3(1-\upsilon) L^2] \qquad (1)$$

where $\sigma$ —average stress in oxide scale, $\zeta$ —oxide thickness, $E$ —elastic modulus of substrate, $\upsilon$—poisson's ratio of substrate, $D$ —deflection of specimen, $H$, $L$ —thickness and length of specimen, respectively.

In detail, the stress in the oxide scale formed during the oxidation for $t_o$ was obtained easily from the deflection of the sample after removing the oxide scale on one side of the alloy at room temperature and from that in the heating process. In the period of oxidation, $D$ value was measured at time $t$ ($t = t_o$, $2t_o$, $3t_o$, …). Depending on Eqn. (1), if $\sigma_1(\zeta_1, t_o)$ was known, $\sigma_2(\zeta_2, 2t_o)$ also could be gotten by calculation. All the same, $\sigma_3(\zeta_3, 3t_o)$ could be deduced from the relations with $\sigma_2(\zeta_2, 2t_o)$, then $\sigma_4$, $\sigma_5$, …. The value of $t_o$ determined the interval between two data points in the curves of the oxide stress vs time or the oxide thickness.

Eqn. (1) is gotten by the elastic deformation analysis. However, it was much more likely that deformation will occur by thermally-activated creep processes under high temperature condition[5, 7]. If so, in the two-side oxidation induced deflection test, basing on the condition of equilibrium of forces and moments, we has got the average stress in oxide scale according to the relations of the stresses with neutral planar axis[8].

Before the new method is applied, two problems must be solved above all. The first one is, if there is difference between the oxide scales formed after the oxidation directly for $2t_o$ and firstly for $t_o$ then for another $t_o$ with an interval between cooling-heating sequence. Under the same oxidation condition, if the single phase oxide scales do not occur to crack during isothermal exposure and cooling, the cooling-heating sequence does not change the properties of the scale obviously, then these process has little influence on the stress in the scale. The second one is how to determine $\sigma_1$ value corresponding with time $t_o$. In the next part, the step for determining $\sigma_1$ value will be explained in detail.

## 2.2 Deflection test procedure

The tests were undertaken on $Cr_2O_3$ scale formed on the surface of Ni80Cr20 alloy. A specimen of 50 mm × 10 mm × 0.24 mm was prepared by hot-rolling, careful grinding with 600 grit SiC and then cleaning in acetone ultrasonically, then pre-oxidized at 1 000 ℃ for 1 h in Muffle furnace. After oxidation, the oxide scale on one surface of the specimen was removed by grinding (600 grit SiC paper). The grinding was also carried out to remove certain depth surface in which Cr may be depleted.

After removing of the oxide scale on one surface, the specimen deflected to the side of the oxide scale being remained. Theorically, the stress in $Cr_2O_3$ scale formed on Ni80Cr20 alloy is compressive. Therefore, comparing with the stress in $Cr_2O_3$ scale, the bigger residual compressive stress in the surface layer of the alloy was considered to be generated due to grinding.

Afterwards, the deflection test was carried out in special equipment[8]. The upper side of the specimen was fixed by In738 clamps. A quartz fibre with a hook at one end was hung from the hole in the lowest end of the specimen.

At first, the system was evacuated to $6.66 \times 10^{-3}$ Pa, then the specimen began to be heated. When the temperature was up to 1 000 ℃, the specimen was kept further in vacuum for 0.5 h for annealing. Then air was introduced into the chamber. The deflection of the specimen due to oxidation was recorded through the quartz fibre by a traveling telescope.

# 3 RESULTS

## 3.1 Measurement for average stress in oxide scales

It was found that, during heating, the specimen deflected to the negative direction. During annealing, specimen happened to deflect, and this deflection was small comparing with that during heating. The deflections of the specimens in the different conditions were measured, and listed in Table 1.

**Table 1** Deflection of Ni80Cr20 specimens in different steps during test (mm)

| Deflection symbol | Deflection value | Measurement conditions |
|---|---|---|
| $D$ | 0.910 | After removing oxide scale on one side |
| $\Delta D$ | −0.854 | During heating to 1 000 ℃ in vacuum (500 ℃/h) |
| $\Delta D$ | −0.080 | During annealing at 1 000 ℃ in vacuum (0.5 h) |
| $D_0$ | −0.024 | Position at beginning of oxidation |

Fig. 1 shows the deflection of the specimen during the oxidation at 1 000 ℃ in air. It can be seen that the specimen always bend to the negative direction. The changes of the deflections are not very big. The oxidation kinetics of Ni80Cr20 alloy at 1 000 ℃ in air is presented in Fig. 2.

Under the high temperature condition, the creep of Ni80Cr20 alloy will occur. Therefore, the stress analysis of the deflection test under creep conditions proposed by Evans[7] is used here. According to the condition of the curvature of specimens and the equations for stress calculations[8], the stresses in oxide scales are calculated by using a computer program. In the calculation, the different parameters

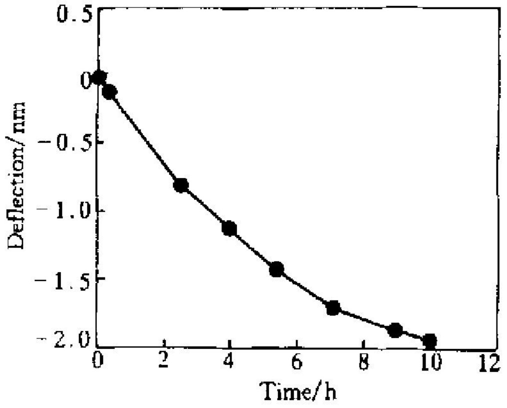


**Fig. 1** Curves of deflection vs time obtained after oxidizing at 1 000 ℃ in air

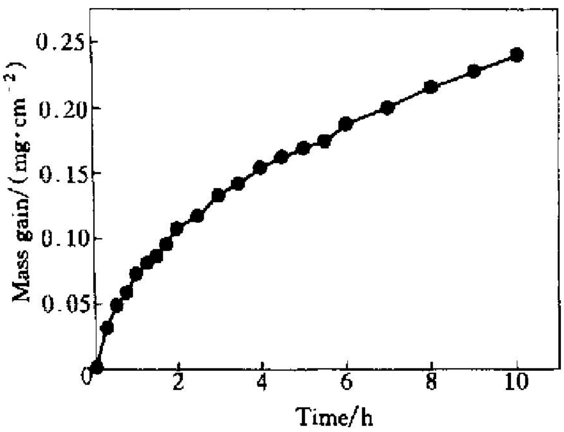


**Fig. 2** Oxidation kinetics of Ni80Cr20 alloy at 1 000 ℃ in air

are needed, such as oxide thickness, creep rate and change of radius of curvature with time. Firstly, because the oxide scales do not happen to crack, the mass change of the alloy can be converted to the thickness of $Cr_2O_3$ scale by using the factor of 1 mg/cm$^2$ mass change corresponding to 6.08 μm change of scale thickness. The change of thickness of the oxide scale on Ni80Cr20 alloy with time in 1 000 ℃ air is then obtained, as shown in Fig. 3, according to the correspond relation on the basis of oxidation kinetics curve in Fig. 2. About the creep rate of Ni80Cr20 at 1 000 ℃, it is expressed as[9] $\dot{\varepsilon} = 6.114\times10^{-42}\times\sigma^{5.29}$, $s^{-1}$. Secondly, the expression of the deflection $D$ with time $t$ can also be obtained by fitting the curves of $D$ vs $t$, presented in Fig. 1, and the fitting result is: $D = -0.0204 - 0.339t + 0.0147t^2$. Finally, the variations of average stresses in exposure period are given in Fig. 4. In the calculation, more than one of solutions may be found. However, because of monotonous characters of the deflection curves, the sign of the stress should maintain the same, its value decreases with oxidation time, and the absolute value of $x_0$ (the neutral axial of base alloy) should be much smaller than that of $r$ (the curvature radius of the neutral axial)[8].

It can be seen from Fig. 4(a) that, the stresses in all thickness scales are compressive, and decrease with increasing oxide thickness. The order of the stress value in the scale on Ni80Cr20 is − 0.1 GPa during the oxidation period of 10 h.

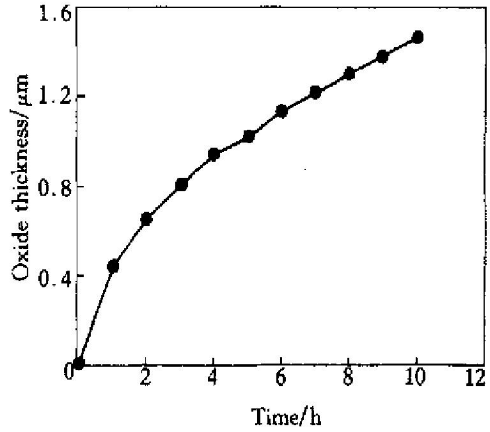


**Fig. 3** Corresponding oxide thickness of Ni80Cr20 alloy at 1 000 ℃ in air

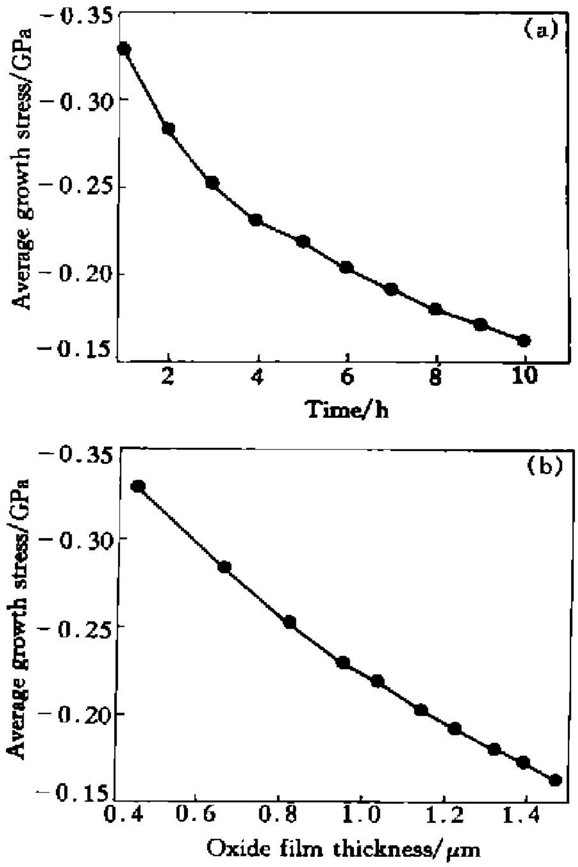


**Fig. 4** Variation of average stresses with time (a) and oxide thickness (b)

$x_0$ is very important factor for understanding the bending states of specimen. The values of this factor and radius of curvature, $r$, are listed in Table 2. It can be seen that the neutral plane for the metal is always within the metal.

### 3.2 Stress distribution in metals

As mentioned above, the neutral plane of the metal changes its location since the oxidation time for about 10h. As a consequence, the planar stress in metals keeps the state of both compressive and tensile stresses coexisted at the beginning oxidation procedure, then becomes only tensile during the rest of oxidation procedure.

**Table 2** Values of $x_0$ and $r$ used in analyses for different oxidation times

| Time/h | $x_0$/mm | $r$/m | Time/h | $x_0$/mm | $r$/m |
|---|---|---|---|---|---|
| 1 | 0.14470 | -55.7435 | 6 | 0.54433 | -0.8436 |
| 2 | 0.19910 | -3.2990 | 7 | 0.68160 | -0.7456 |
| 3 | 0.24988 | -1.7780 | 8 | 0.86240 | -0.6797 |
| 4 | 0.3340 | -1.2564 | 9 | 1.12220 | -0.6347 |
| 5 | 0.43030 | -0.9965 | 10 | 1.55500 | 0.6047 |

## 4 DISCUSSION

When the two-side oxidation induced bending technique is used, the oxide scale formed during the pre-treatment on one main face of specimen should be removed firstly by grinding. This operation may induce residual stress in the surface layer of the substrate. According to the corresponding deflection, the residual stress is compressive, and the value is bigger than that in the remainder oxide scale remained. At present time, the stresses existing in the oxide-metal system at room temperature are explained as follows,

main face 1 (surface layer of metal): $\sigma_r$

main face 2 (oxide scale): $\sigma_g + \sigma_t$

where $\sigma_r$ —residual stress, $\sigma_g$ —growth stress and $\sigma_t$ —thermal stress.

During heating, $|\sigma_r|$ and $|\sigma_t|$ decrease, but $|\sigma_r|$ decreases in a higher rate, so the specimen bends to the negative direction (main face 1). When the temperature is 1000 ℃, $|\sigma_t|$ equals zero. Because the heating rate is low (1000 ℃/2h), and the value of curvature of specimen is big during heating, the residual stress resulting from grinding should be relaxed enough. During the annealing procedure, the specimen continues to bend towards the negative direction. It can be seen from equation in Ref.[8], the stresses do not depend on the value of $D_0$ (the deflection of specimen at the beginning of the oxidation at 1000 ℃). Therefore, the grinding, the heating and annealing processes do not affect stress measurement. In fact, the method for oxide stress measurement has been applied basing curvature of strip specimen due to removing a thin layer scale by mechanical grinding or chemical solution[10].

The stress calculation indicates that the substrate alloy and the oxide scale happen to creep, this process can decrease the value of the stress due to relaxing effect. It can also be seen from Fig. 3, the value of the average growth stress in $Cr_2O_3$ scale decreases with increasing the oxide thickness, but the decreasing degree is little. The growth stress kept in the order of $-0.1$ GPa.

To the bending specimen, one main face is concave, and the other face is convex. The geometry may have effect on the stress[11]. However, When $R$ (the curvature radius of specimen) $\gg L$, this effect is unimportant. When the deflection is small, the relation $R \gg L$ can be satisfied. When the deflection is big, the value of $R$ becomes small, the error may be produced due to neglecting the geometry effect and using the equation $R = L^2/2D$. In the calculation, it also supposed that $R \gg H$ and $R \gg x_0$. It can be seen from Table 2, these two suppositions can be satisfied under almost all conditions, besides in the early stage and the later stage of the oxidation for Ni80Cr20 specimen.

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