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Investigation on origins of residual stresses in Ni-NiO system by X-ray diffraction at high temperature

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Abstract. — To characterize the respective role of oxidation stresses, thermal stresses and relaxation phenomena in the oxide scales, two high temperature chambers for X-ray diffraction have been designed allowing to determine residual stresses *in situ*, during oxidation of Ni, with the $\sin^2\psi$ technique. At room temperature, the scales are subjected to compressive stresses and compressive stresses are also analyzed in the substrate. During heating-cooling sequences, a reversible variation of the stresses is observed, without relaxation. The stresses determined at room temperature are thermal stresses and theoretical calculation fits well with experimental determination. *In situ* stress determinations at 900 °C show that slight tensile stresses are then generated in the scale. All these results show that the stresses found at room temperature are mainly generated during cooling, and that the role of Pilling and Bedworth ratio, often considered as the main factor for stress generation in Ni-NiO system, has little effect.

1. Introduction.

Many review articles [1-7] have provided information on the origins and the development of the residual stresses in the metal/oxide systems. But, the respective role of growth stresses, (developed during isothermal oxidation), thermal stresses, (created during cooling), and stress relaxation is not clearly determined.

Attempts have been made in the recent years to develop stress investigation techniques. But, as this date, most of the studies on stress determination in oxide-metal systems have been performed at room temperature and the results, mainly concerning Cu₂O [8], NiO [9-12], Cr₂O₃ [13] and alumina [14, 15] scales, are somewhat limited.

In order to clarify the situation, two high temperature chambers for X-ray diffraction were designed [16, 17]. Using the $\sin^2\psi$ method, the stress level can be determined in *both* the scale and the substrate at all steps of an oxidation process.

The Ni-NiO system was chosen due to the facts that only one oxide grows on nickel, the oxidation behaviour is well known, and residual stresses have already been determined mainly at room temperature [9-12]. Besides, this system has already been chosen for theoretical modelling [18-21].

Our results will be discussed on the basis of the possible origins of stresses in such a system and by comparison with the literature experimental or modelling data.

2. Experimental procedure.

2.1 OXIDATION TESTS. — The oxidation kinetic study was performed in a Cahn electronic thermobalance of high sensitivity ($1\text{ }\mu\text{g}$) mainly at $900\text{ }^{\circ}\text{C}$, in pure oxygen, room air and vacuum. Preoxidation treatments were conducted at $700 < T < 1130\text{ }^{\circ}\text{C}$, in dry, wet oxygen and room air. In most cases, the samples were cooled in the furnace.

2.2 X-RAY DIFFRACTION METHOD AND PROCESS. — For X-ray diffraction stress analyses, the $\sin^2\psi$ technique was used. The high temperature X-ray diffraction equipment used in this study [16, 17] is composed of two high temperature chambers, and of an improved computer-controlled Ω -setting goniometer equipped with a PSD (Position Sensitive Detector). $\text{CrK}\alpha$ and $\text{CoK}\alpha$ radiations were used for stress analyses in the oxide scale and the $\text{CuK}\alpha$ radiation for the diffraction from the metallic substrate. Residual stresses were deduced with mechanical X-ray elastic constants calculated from mechanical Young's modulus E [21] and Poisson's coefficient ν [17]. In order to visualize a possible stress evolution on short times, experiments were also carried out by continuously measuring the Bragg angle variation in a single direction (ϕ, ψ) of $\{222\}$ and $\{311\}$ planes of NiO and $\{220\}$ plane of nickel [16, 17].

3. Experimental results.

3.1 OXIDATION. — The weight gain curves vs. oxidation time (Figs. 1 and 2) indicate that differences between oxidation in O_2 and in room air are not significative. The variations of the substrate thickness do not have influence on the oxidation rate, (see the behaviour of nickel A, Fig. 2). So, it can be said that the oxidation rate of nickel B is greater than that of nickel A, (Fig. 2). This difference can be due to:

- (i) The difference in the initial substrate defects: nickel B was cold rolled.
- (ii) The surface roughness: the real surface of samples B is greater than its geometrical surface, and kinetic is hence overestimated.
- (iii) The impurity difference.

Fig. 1. — Kinetics of oxidation of nickel A.

Fig. 2. — Comparison of the oxidation kinetics of nickel A and B for various substrate thicknesses (t).

The nickel oxidation in primary vacuum is very low, (Fig. 1). So, the oxidation during stress determinations conducted in vacuum can be considered as negligible. The scale grows according to a parabolic law. The oxidation parabolic constant values collected in table I indicate that the observed differences are in the range of values reported for k_p in literature [22] and can be due to the three parameters mentioned above.

It was observed for all furnace cooled samples that internal oxidation occurs along the substrate grain boundaries.

Table I. — *Parabolic constants of nickel at 900 °C.*

sample	oxidation conditions	parabolic constant K_p ($\text{mg}^2\text{cm}^{-4}\text{h}^{-1}$)
Ni A	900°C pure oxygen	$8.22 \cdot 10^{-2}$
Ni A	900°C, air	$8.57 \cdot 10^{-2}$
Ni A	900°C primary vacuum	
Ni-B	900°C, pure oxygen	$17.5 \cdot 10^{-2}$
A. Aubry [9]	900°C, air,	$2.4 \cdot 10^{-3} \cdot 10^{-1}$
C. Courty [10]	900°C, air	$1.7 \cdot 5.2 \cdot 10^{-1}$

3.2 STRESSES AT ROOM TEMPERATURE.

(i) *In NiO scales:* the higher the oxidation temperature, the greater the absolute values of the stresses in the scale (Fig. 3). In all cases, compressive stresses are detected.

The stress variations in NiO scale, for different substrate thicknesses and for nickel A or B, vs. the oxidation time (Fig. 4) show that for short oxidation times, the stress absolute

Fig. 3. — Residual stresses at room temperature in NiO scale as a function of the oxidation temperature.

Fig. 4. — Residual stresses at room temperature in NiO scale as a function of the oxidation time.

value increases, then the stress becomes stable and for longer oxidation times the stress slowly decreases. This was already observed by Aubry [9]. The stress level for nickel B is much lower than for nickel A.

Concerning the effect of the substrate thickness, (Fig. 5), up to about 0.5 mm thickness a stress evolution in the NiO scale is observed: the smaller the substrate thickness, the smaller the stress absolute value, and this whatever the oxide scale thickness. For higher substrate thickness, the stress becomes stable. It was verified that the water vapor does not have a significative influence on the residual stresses in the NiO scales [23]. Results of the study of the stress gradient in the oxide scale (using two different X-ray tubes) are given in table II: the residual stress distribution in the NiO scale depth is uniform. This result agrees with theoretical modelling on this system [19-21].

(ii) *In Ni substrate*: compressive stresses (about -12 MPa) [23] are always detected regardless the oxidation conditions.

Fig. 5. — Residual stresses at room temperature in NiO scale as a function of the substrate thickness (t).

Table II. — Residual stresses in NiO scale using different X-ray tubes.

	Sample	Nickel A	Nickel A
	Oxidation conditions	900°C, room air, 77h, furnace cooling	900°C, room air, 336h, furnace cooling
	substrate thickness (mm)	1.6	1.6
	scale thickness (μm)	20	40
Using $\text{CrK}\alpha$ radiation $\tau = 5\mu\text{m}$	residual stresses in NiO scale (MPa)	-385 ± 22	-268 ± 23
Using $\text{CoK}\alpha$ radiation $\tau = 9\mu\text{m}$	residual stresses in NiO scale (MPa)	-351 ± 12	-280 ± 23

3.3 HIGH TEMPERATURE DETERMINATIONS.

(i) *During scale growth*: at 900 °C, (Fig. 6), the growing oxide scale is subjected to slight but always tensile stresses, whatever the substrate nature or thickness. Same results were obtained at 700, 1000 and 1100 °C [23] and are confirmed by the fact that no significative evolution of 2θ , (in a single (ϕ , ψ) direction), was observed (Fig. 7).

(ii) *During cooling and re-heating*: during cooling down to room temperature and re-heating to the oxidation temperature, (Fig. 8), a reversibility of the stress-temperature curve is observed. When re-heating to the oxidation temperature, stresses in the oxide scale become negligible. A similar effect is observed during cooling of a sample oxidized at 700 °C [23].

4. Discussion.

4.1 ORIGIN OF GROWTH STRESSES. — It is generally considered that the oxide scales are subjected to compressive stresses when the Pilling and Bedworth ratio (PBR) is greater than 1, especially if the scale growth is controlled by anionic diffusion. In case of Ni/NiO, though

Fig. 6. — Residual stresses in NiO scale during growth.

Fig. 7. — Simultaneous measurements of Bragg angle of NiO scale and Ni substrate during oxidation.

cationic diffusion is predominant at 900 °C [22], stresses would be expected to be compressive during NiO growth due to the PBR value ($= 1.65$). It was shown here that the NiO growth does not induce compressive stresses in the scales, nor stress evolution during scale growth (Fig. 6). Stresses observed during oxidation are negligible compared to the stresses found at room temperature and the Bragg angles of NiO and Ni do not vary with oxidation time (Fig. 7). Though small, the stresses determined during oxidation at 900 °C are always tensile. This result agrees with those obtained by Homma *et al.* [11]: at 1027 °C, their NiO scale grows under tensile stresses. Using high temperature values of mechanical X-ray elastic constant [21], we recalculated the stress values of Homma *et al.* and found σ values of the same order of magnitude than ours. Our results obtained from *in situ* measurement agrees neither with the theoretical prediction of Bernstein [18], nor with the model proposed by Touati [21], nor with the experimental observation by Stout *et al.* [19]. Bernstein [18], then Touati [21] calculated the stresses during high temperature oxidation of Ni on the basis of the Pilling and

Fig. 8. — Stress evolution during cooling and reheating to oxidation temperature (nickel A).

Bedworth ratio model, (although the NiO scale growth at 900-1000 °C is essentially controlled by cationic diffusion). In their calculations of the stresses created by the volume difference between the consumed substrate and the grown oxide, a correction factor is introduced to keep stresses due to volume differences reasonable. This factor has no physical meaning. The results of Stout *et al.* [19] show changes of lattice parameter during oxidation. The substrate is under tensile stresses during oxidation, and stress accumulation and relaxation are successively observed. But, with their experimental conditions, the sensitivity on the Bragg angle shifts is low and the variations of the Bragg angle are small.

Three suggestions can explain the slight tensile stresses in the NiO scale observed in our case during oxidation:

(i) Though cationic diffusion is predominant, anionic diffusion is not negligible [22] and can introduce compressive stresses in the newly formed oxide layer near the oxide/substrate interface. This induces tensile stresses in the outside oxide layers which are subjected to the X-ray diffraction analysis.

(ii) Inner oxidation of the substrate introduces compressive stresses in the substrate and hence tensile stresses in the oxide layer. Compressive stresses can be estimated according to $\varepsilon = [(PBR)^{1/3} - 1] / R$ [24], R being the ratio of the distance between two inner oxide particles to the width of the inner oxide. With a grain size of $\sim 100 \mu\text{m}$ and an inner oxide width of $\sim 0.1 \mu\text{m}$, the induced deformation is found to be equal to 2×10^{-4} , and the corresponding stresses in the substrate to $\sim -50 \text{ MPa}$ which is of the same order of magnitude than stresses observed at room temperature [9, 10].

(iii) A temperature gradient could exist through the scale: in case of samples tested in the direct heating chamber [16, 17], the temperature is higher at the metal/oxide interface than at the outside surface. Stresses induced by a temperature difference of 10°C can easily be as high as 20 MPa according to $\sigma_{\text{ox}} = \frac{E_{\text{ox}}}{1-\nu_{\text{ox}}} \alpha_{\text{ox}} \Delta T$.

Recently, Bennett [13] found tensile stresses in Cr_2O_3 scales. The growth of this scale is considered as controlled by cationic diffusion [22], as for NiO scales and the $\text{PBR}=2.07$. So, it appears that a greater PBR does not induce compressive stresses in oxide scales. This suggests that tensile stresses appear during scale growth controlled by predominant cationic diffusion, and perhaps compressive stresses could appear during scale growth controlled by

anionic diffusion. This has to be verified.

4.2 THERMAL STRESSES. — The various observations suggest that stresses found at room temperature in the NiO scales are thermal stresses developed during cooling due to the differences between the expansion coefficients α of the scale and of the nickel substrate. Thermal stresses can be calculated according to:

$$\sigma_{\text{ox}} = - \int_{T_i}^{T_f} \frac{\frac{E_{\text{ox}}(T)}{1 - \nu_{\text{ox}}} (\alpha_{\text{ox}}(T) - \alpha_{\text{m}}(T))}{1 + \frac{t_{\text{ox}}}{t_{\text{m}}} \frac{E_{\text{ox}}(T)}{E_{\text{m}}(T)} \frac{1 - \nu_{\text{m}}}{1 - \nu_{\text{ox}}}} dT$$

As literature values of thermal expansion coefficients α_{Ni} , α_{NiO} are scattered, we measured the thermal expansion coefficients of nickel and nickel oxide by both X-ray diffraction and dilatometry [23]. The average values of α , between 20 and 900 °C, for Ni and NiO are equal to $17.6 \times$ and $14.5 \times 10^{-6} \text{ K}^{-1}$ respectively. Then, thermal stresses induced by cooling were calculated and compared with stress values determined by X-ray diffraction at room temperature (Fig. 9). Thermal stresses accumulated from 900 °C down to room temperature are equal to -540 MPa . Same calculations for the substrate, indicate that the thermal stresses are very low [23].

The comparison, for several systems, of the experimental and calculated thermal stresses, (Tab. III), shows that the residual stresses found at room temperature are mainly thermal stresses, whatever the scale growth mechanism. Indeed, the results on the MCrAl/Al₂O₃ system concern a scale whose growth is controlled by predominant anionic diffusion [23], while for the others, cationic diffusion predominates.

Fig. 9. — Generation of thermal stresses: experimental observation and theoretical calculation.

4.3 STRESSES AT ROOM TEMPERATURE. — It was already found that residual stresses in the scale vary with oxidation time [9, 10], (U-shape curve as in Fig. 4). It can be suggested that, for thin oxide scales, relaxation occurs and that, for thick oxide scales, only the outer part of

Table III. — Comparison between theoretical calculations of thermal stresses and experimental determinations of stresses at room temperature for several oxide scales. a) This study, from 900° C, b) this study, from 1000 °C, c) from 700 and 800 °C, d) from 760 to 927 °C, e) from 950 °C, f) from 875 °C, g) from 1100 °C, h) from 1150 °C.

	Ni / NiO	NiCr / Cr ₂ O ₃	Cr / Cr ₂ O ₃	MCrAl / Al ₂ O ₃
Theoretical calculations (MPa)	-540 ^a -640 ^b	-4000 ^a [23] -4500 ^{b+} [20]	-820 ^a [23] -1100 ^{b+} [20]	-5200 ^g [14]
Experimental measurement (MPa)	-550 ^a -450 to -650 [9,10] -20 to -70 ^c [12] -170 to -240 ^d [25]	-2000 ^a [24] -3300 ^e [26]	-400 ^f [13]	-5700 ^g [14] <300 ^h [15]

the scale is analyzed by X-ray, and the result does not take into account the layers near the substrate, subjected to the highest stresses (see Fig. 10).

At room temperature the stress in the oxide scale depends on the substrate thickness (Fig. 5). The thinner the substrate, the weaker the stresses in the oxide scale on account of stress relaxation during cooling. But, for a thickness > 0.4 mm, the stress level in the oxide scale does not vary any more with the substrate thickness.

We observed [23] that H₂O in the atmosphere does not change the stress level at room temperature, while it modifies the morphology of the scale, the oxidation rate and the infrared spectrum of NiO. So, this parameter has an influence on isothermal growth but no effect on the scale stresses. In the same order of idea, the impurities of the substrate, though having an effect on the oxidation rate, do not influence the stress level in the scale. These observations can be generalized by saying that *factors playing a role during isothermal growth do not act much on the stress level in the scale at room temperature, because residual stresses in the scale are mainly generated during cooling.*

4.4 STRESSES IN THE METALLIC SUBSTRATE. — At room temperature, the nickel substrate is subjected to slight compressive stresses regardless the oxidation conditions. This is due to inner oxidation of the nickel substrate. Stresses introduced by inner oxidation were calculated and are equal to ~ -50 MPa, which is higher than the calculated thermal stresses [23] and of the same order of magnitude than experimental results.

4.5 STRESS DISTRIBUTION.. — According to our results, a scheme of the stress distribution at room temperature can be proposed (Fig. 10). The compressive stresses in the scale are due to the thermal stresses. In the substrate, a first zone, (depth equal to the internal oxidation penetration), is characterized by compressive stresses in both Ni and NiO particles. After this zone, tensile stresses must be present in the substrate. This zone is not analyzed by X-ray diffraction due to the limited X-ray penetration (Tab. II).

Fig. 10. — Scheme of the stress distribution in Ni/NiO system, at room temperature.

5. Conclusions.

The *in situ* stress determinations in Ni-NiO system allow to conclude the following:

(i) The thermal stresses, resulting from the difference of expansion coefficients between the substrate and the scale, are responsible of the stresses observed at room temperature. The stress level in the scale at room temperature depends on the difference between the expansion coefficients, the oxidation temperature, the mechanical properties of materials. Experimental results are in good agreement with theoretical modelling.

(ii) Slight tensile stresses are found to generate in the scale during its growth. Several factors, as internal oxidation of the substrate, anionic diffusion or temperature gradient are considered as being possibly at the origin of the growth stresses. Anyway, growth stresses are very low compared to thermal stresses. A model based on the Pilling and Bedworth ratio cannot explain the experimental observations.

(iii) In the substrate, compressive stresses are also observed at room temperature due to internal oxidation whose effect on the stresses is higher than thermal stresses.

(iv) Parameters, such as the initial thickness of the substrate, the oxidation time and temperature can modify the stress level at room temperature due to stress relaxation. Other parameters, such as impurities in the substrate or in the atmosphere, which modify the growth rate and the scale morphology, do not seem to have much influence on the stress level as stresses are mainly generated during temperature changes.

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