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Interfacial toughness of the nickel–nickel oxide system

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Stress effects in high temperature oxidation of metals and alloys have been reviewed extensively by Evans [1]. Oxide growth stresses and/or thermal stresses due to temperature change during cyclic oxidation, or return to room temperature after exposure, may provoke the decohesion and the detachment of the protective thermally grown oxide (TGO) scales resulting in a drastic weakening of the oxidation resistance of the materials. These spallation mechanisms can either result from adhesive failures between the base metal and the TGO or cohesive failures within the oxide scale itself. The preferential route for spallation mainly depends on the relative strengths of the metal/oxide interface and the oxide according to the well-known buckling mode when the interface is weaker than the oxide or wedging mode when it is stronger. The degree of adhesion between the substrate and the oxide scale is an important factor that should be carefully investigated to understand the performances of materials at high temperature. Various experimental techniques to measure the interface strength—including tensile pulling, microindentation, scratch testing, residual stress induced delamination, laser induced or shock wave induced spallation, double cantilever beam bending, four points bending approaches—were critically reviewed in [2]. However to date, no universal and easy test providing reproducible and reliable results exists. Concomitantly, significant developments were made to evaluate the adhesion of physically, chemically or thermally deposited coatings to their substrate. The approach was particularly interesting because coatings are generally thicker than TGO and experimental constraints are less [3]. Recently, an original experimental method, based on an interfacial indentation technique, has been developed to measure the fracture toughness of the interface between various substrates and thermally sprayed coatings [4, 5].

In a recent paper addressing the oxide spallation mechanisms for heat resistant cast steels [6], it was suggested that the interfacial strength between the oxide and the substrate may decrease with exposure time at high temperature. In this letter, an attempt is made to use the interfacial indentation technique to address quantitatively the actual decrease of the interface strength with high temperature exposure time in the case of the nickel/nickel oxide system. Several 99.998% pure nickel coupons were oxidized at 1200 °C for various exposure times in order to grow nickel oxide scales with various thicknesses. The oxidation kinetics of specimens, whose outer surface after long term exposure at temperature is shown in the scanning electron microscope (SEM) images in Fig. 1 are close to parabolic and thus in good agreement with well documented literature on pure nickel oxidation, e.g. [7] that reports a value of the parabolic rate constant $k_p = 3.4 \times 10^{-3}$ mg^2/cm^4/s. Table I gives a few experimental mechanical and morphological parameters for both the nickel substrate and the nickel oxide, necessary to the calculation of the interface fracture toughness. Note that the thickness of the oxide is, in all cases, much greater than that of the substrate.

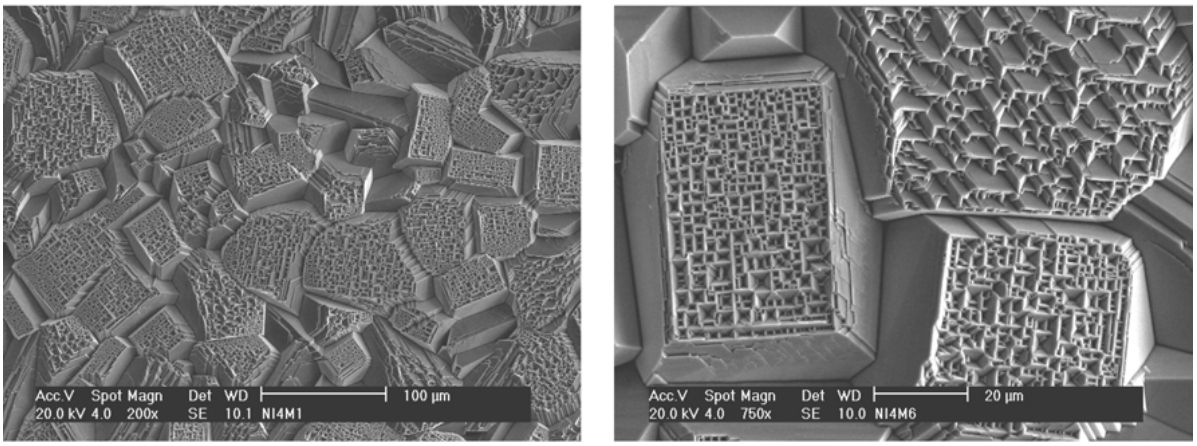
Fig. 2 shows SEM images of the interface between the nickel substrate and the nickel TGO. Seen in Fig. 2a, is the high roughness of the interface for a specimen exposed 288 h at 1200 °C though specimens are mirror polished prior to exposure at high temperature. Note also that void formation occurred along the interface. The density of voids increases with exposure time. Fig. 2b shows a typical Vickers indentation pattern at the metal/oxide interface including the definition of a and d, respectively the length of the interfacial crack produced by the application of the load P and the diagonal of the pyramidal indent imprint. Each indentation was performed carefully to ensure a perfect alignment of the loading system of the hardness machine and the specimen so that the indent diagonal accurately penetrates the Ni/NiO interface. For statistical purposes and to check for satisfactory reproducibility of experimental results, a minimum of three indentations was performed for each oxide scale thickness and each load. Interfacial indentation tests were carried out on all oxidized specimens using various loads from 20 N to 2500 N (2 Kgf to 250 Kgf). The overall variation of the diagonal of the indent imprint, which was independent of the oxide thickness, versus the applied load including all tests is plotted in Fig. 3.

The linear relationship between Lnd and LnP showing a slope close to 0.5 is in good agreement with the general standard formula relating the constant Vickers hardness (HV) of bulk materials to the ratio between

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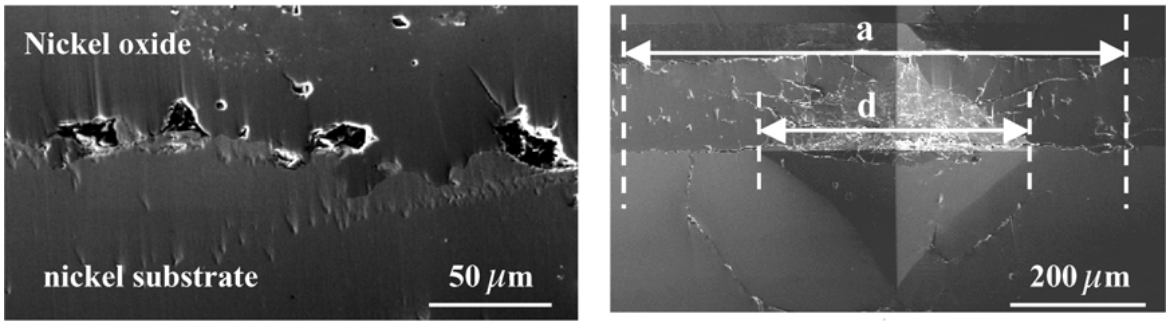
TABLE I Ni and NiO mechanical and morphological parameters used in the calculation of the fracture toughness

			Thickness (μm) versus exposure time (h)					
	E (GPa)	H (GPa)	96 h	144 h	192 h	240 h	288 h	336 h
Thermally grown oxide NiO	189	6.04	122 μm	135 μm	145 μm	162 μm	288 μm	336 μm
Substrate Ni	199.5	0.9	5000 μm					



(a) (b)

Figure 1 Morphology of the nickel oxide after isothermal oxidation at 1200 °C for 408 h, low magnification SEM image (a) and detail of individual oxide grains (b).



(a) (b)

Figure 2 Morphology of the interface Ni/NiO after oxidation at 1200 °C for 288 h (a) and typical crack pattern after interface indentation of a specimen oxidized 192 h at 1200 °C (a is the length of the indentation induced crack and d is the diagonal of the indentation imprint) (b).

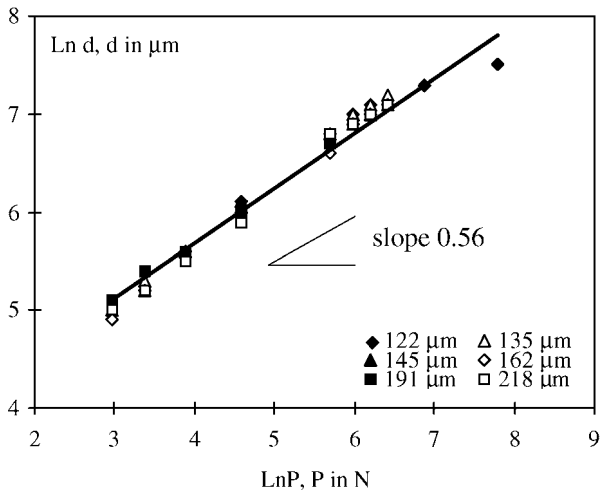


Figure 3 Diagonal of the indentation imprint d versus applied load P for various nickel oxide thicknesses ranging from 122 μm to 218 μm.

the applied load P and the square of the diagonal length d^2. Depending on both the oxide thickness and the applied load, the interface may crack upon indentation.

For a given oxide thickness, the variation of the length a of the indentation-induced crack versus the applied load P also fits a single regression line on a Log-Log scale which can serve to evaluate the critical load P_c necessary to initiate interfacial detachment. The principle for the determination of this critical load is given in Fig. 4 where both the Lnd–LnP (taken from Fig. 3) and the Lna–LnP lines are shown for the case—as an example—of a 162 μm thick oxide scale corresponding to 240 h exposure. The intercept between the two lines discriminates the two domains where the applied load is respectively, (i) too low to initiate interfacial cracking, (ii) high enough to provoke the initiation and the propagation of an

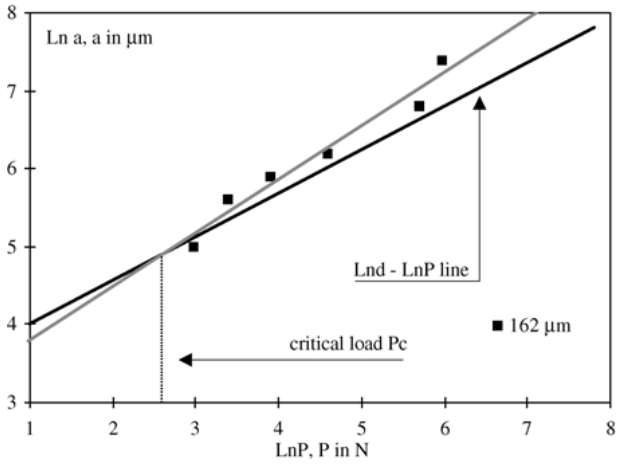


Figure 4 Principle for the determination of the critical load to initiate interface cracking by Vickers indentation illustrated for 162 μm thick NiO (see text for detail).

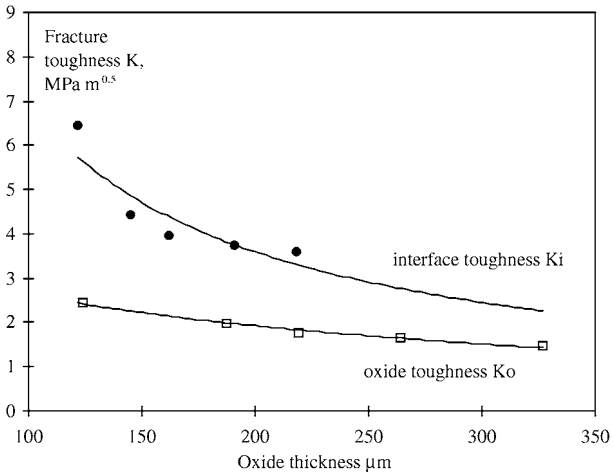


Figure 6 Comparative evolution of the interface and oxide fracture toughness versus oxide thickness.

interfacial crack. For the case shown in Fig. 4, the critical load is 12.8 N (1.30 Kgf). This procedure can be repeated as often as necessary to determine graphically the critical load for each oxide thickness. As expected, the critical load to indent the interface between the nickel substrate and the TGO and produce a measurable interfacial crack, decreases with the TGO thickness as indicated in Fig. 5 according to an exponential relationship.

The fracture toughness of both the thermally grown oxide and the interface Ni/NiO can be estimated from the expression initially developed by Ansis *et al.* [8] for bulk materials, and applied to the case of the interface between a substrate and a coating by Chicot *et al.* [5] in the following form:

$$K_{o/i} = 0.016 \frac{P_c}{c^{3/2}} \left(\frac{E}{H}\right)_{o/i}^{1/2}$$

where subscripts o and i stand respectively for oxide and interface substrate/oxide, E is the Young modulus, H the hardness and P_c is the critical load to produce a crack of length $2c$. In the case where the indentation is performed at the interface between the substrate and the oxide, the hardness and the elastic modulus of both materials are included in the calculation of the ratio $(\frac{E}{H})_i$ as follows [5]:

$$\left(\frac{E}{H}\right)_i^{1/2} = \frac{\left(\frac{E}{H}\right)_s^{1/2}}{1 + \left(\frac{H_s}{H_o}\right)^{1/2}} + \frac{\left(\frac{E}{H}\right)_o^{1/2}}{1 + \left(\frac{H_o}{H_s}\right)^{1/2}}$$

where subscript s stands for substrate. The evolution of the fracture toughness of the oxide as well as the fracture toughness of the interface versus the oxide thickness is plotted in Fig. 6. Note that the fracture toughness of the oxide varies very little with the TGO thickness whereas the fracture toughness of the interface strongly depends on the oxide thickness. The thinner the oxide, the higher the interfacial fracture toughness. For the thinnest oxide scale studied, the toughness of the interface is about three times that of the oxide and remains much greater in the whole range of oxide thickness investigated. This indicates that the occurrence of nickel oxide fracture is likely to result from cohesive rupture within the oxide itself or at least should initiate by oxide cracking and subsequent oxide decohesion and detachment at the interface according to the so-called wedging mode for spallation. This is in good agreement with experimental results on nickel oxidation and nickel oxide spallation showing that, generally no interface damage occurs. This can be related to the very small difference in thermal expansion coefficient between Ni and NiO (respectively 17.6 and $17.1 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$).

For such alloy/TGO systems where the buckling route for spallation is favored, the fracture toughness will be lower than the toughness of the oxide indicating that the oxide is stronger than the interface and better resists the thermal stresses due to temperature changes. For systems where a change in spallation mode is observed depending on the oxide thickness, the expected intercept between plots of K_o and K_i versus oxide thickness defines the critical thickness for the change in the spallation mode. This change in preferential mode of spallation was recently observed in chromia former high alloy heat resistant cast steels and was attributed to the enhanced coalescence of voids at the interface, also reported in

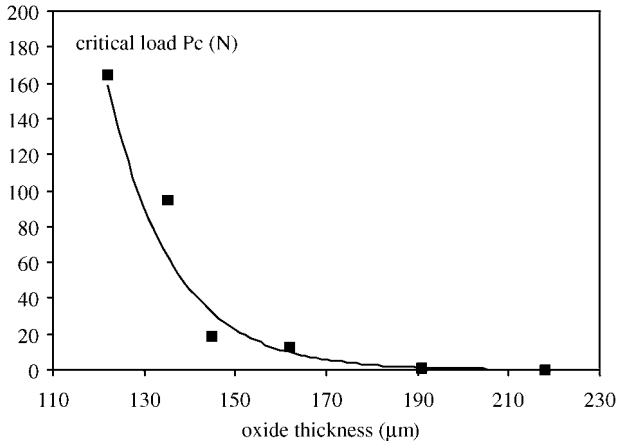


Figure 5 Variation of the critical load with oxide thickness.

this study, as the exposure time at high temperature increased [6].

Acknowledgments

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