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Room temperature plasticity in thermally grown sub-micron oxide scales revealed by micro-cantilever bending

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ABSTRACT

We propose a new geometry for focused ion beam milled micro-cantilevers, which allows production of residual stress-free, isolated thin film specimens from film-substrate systems. This geometry was used to demonstrate the presence of permanent deformation in about 200 nm thick thermally grown oxide scales on a Ni-base superalloy, after applying large bending displacements in-situ in a scanning electron microscope. Stiffness measurements performed before and after the bending tests confirmed the absence of micro-cracks, leading to the conclusion that plastic deformation occurred in the oxide scale. The proposed method is extendable to other film-substrate systems and testing conditions, like non-ambient temperatures.

The properties of protective oxide scales on engineering alloys play a crucial role in determining their service life in many applications. One example of this is the ability of oxide and underlying substrate to relax both growth stresses and thermal stresses to avoid scale cracking and spallation [1]. Other typical situations involve the reduced life during out-of-phase thermo-mechanical fatigue, where the oxides formed during the hot part of the cycle under compressive load undergo ductile-to-brittle transition and fracture during tension at low temperatures [2], and the repeated formation and fracture of oxide intrusions at crack tips during dwell-fatigue crack growth of superalloys [3,4]. In order to mitigate such problems, it is imperative to understand the mechanical properties of these scales under service conditions.

The mechanical properties of protective oxide scales have previously mostly been measured on macro-scale film-substrate systems using indirect techniques, such as acoustic microscopy and vibration technique [5,6], or by post-test inspection of the surfaces [7]. Even in the case of direct testing through nano-indentation, certain assumptions have to be made since the unloading curve is non-linear [6]. A critical point in such film-substrate testing is that the residual stresses and strains in the oxide scale are usually not well known, and the interpretation of measured fracture stresses and strains are therefore ambiguous.

Oxide scales are generally considered to be brittle, and also typically contain inherent defects and residual stresses which lead to crack initiation and fracture [1,7]. Whereas plasticity has been observed in e.g. α-Al_2O_3 [8] and Cr_2O_3 [9] at high temperatures, it is not expected to occur at room temperature, as below a transition temperature, the stress required for fracture is less than the flow stress [10]. Conventional indirect measurements of oxide scale behavior have traditionally been limited to thicker oxide scales, often in the range 5–50 μm, in which the probability of defect occurrence is high. More recently, test methods using bi-layer beams extracted from macroscopic specimens have been used to measure in-plane elastic properties [11] and delamination toughness [12] of thermal barrier coatings. With the advancement of technologies such as focused ion beam (FIB) milling and micro-mechanical testing methods, the use of direct tests at the micro- to nano-scale, such as micropillar compression, has become possible [13–15]. Through such testing methods, a size-dependent transition from brittle to ductile behavior [16] has been shown for several material systems, such as metallic glasses [17], quasicrystals [18], sapphire [14] and silicon [13], which are brittle in bulk form. However, with few exceptions [17,18], testing has been performed in compression, which delays crack initiation and therefore promotes plastic deformation which would potentially be absent in other loading modes.

Here we present a novel method for measuring properties of thin films using micro-cantilever bending experiments applicable on sub-μm scale, and use this method to demonstrate the occurrence of room temperature plasticity during tensile loading of thermally grown oxide scales with thicknesses in the order of 200 nm. In particular, the properties measured by the proposed method are not subject to influence from residual stresses, which can influence the results [7,11,19] and represent the isolated properties of the oxide scale, free of interactions with the substrate. Importantly, the method is applicable to different film-substrate systems, and is easily extendable to non-ambient temperatures, which is crucial for assessing the behavior during most service-like conditions. Nevertheless, the room temperature behavior of

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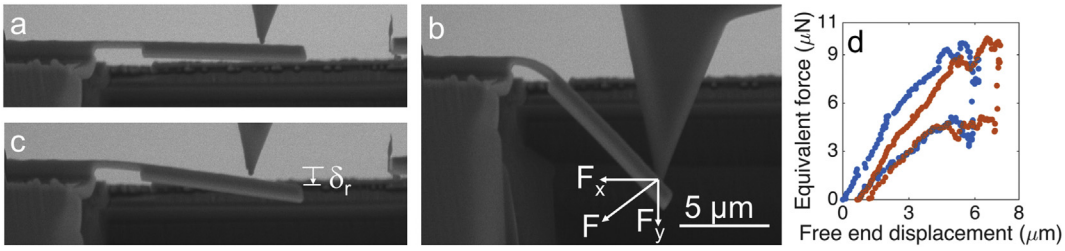

Fig. 1. (a) TEM high-angle annular dark field (HAADF) image of oxide scale. (b) Results from TEM linescan showing the concentration of different elements in the scale. The vertical yellow line in (a) shows the position of linescan. The horizontal dotted line shows the position of the bottom of the cantilever after final specimen preparation (see text for more details). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

thermally grown oxide scales treated in this investigation is also of great interest in its own right, referring to e.g. out-of-phase thermo-mechanical fatigue, as mentioned above.

The oxide scales used in the present study were thermally grown on a solution treated and aged Allvac 718Plus superalloy (nominal composition in wt% Ni-18Cr-9.1Co-9.5Fe-5.4Nb-2.7Mo-1.45Al-1W) in dry oxygen environment at 700 °C for 100 h, which resulted in an oxide layer about 200 nm in thickness (see supplementary material). The structure of the oxide was investigated using transmission electron microscopy (TEM) in a Titan 80-300 microscope operated at 300 kV. The oxide consisted of an outer spinel layer with a thickness of about 50 nm, typically constituted by a single layer of spinel grains, followed by a chromia layer of about 150 nm thickness (Fig. 1a). Below the surface scale, isolated internal alumina could be found. The EDS (energy dispersive X-ray spectroscopy) line scan in Fig. 1b shows the different elements present in the oxide layer, indicating a mixed $(Ni,Co)(Fe,Cr)_2O_4$ spinel. While the cubic structure of the outermost part of the scale was verified by transmission Kikuchi diffraction, the details of the oxide scale has not been further studied at this stage.

Micro-cantilevers were prepared from the oxidized specimens using FIB milling in FEI Versa3D (see supplementary material for details). The geometry of the cantilevers (Fig. 2) was designed in such way that the oxide layer was isolated towards the fixed end for about 2.5 μm in length. This ensures that the residual stresses are relieved in this region, and that there is no metal underneath supporting the oxide layer. Attempts to produce longer oxide cantilevers without metal substrate failed due to the excessive bending from residual stress relaxation. Therefore, the metal was left below the remaining part of the cantilever, as it provided stable conditions for load applications, and the extended length acted as an amplifier for more accurate displacement measurements (see below). The dotted line in Fig. 1a shows the typical location of the final bottom edge of the finished cantilevers. As material was only removed from the bottom of the cantilever, minimal ion implantation was obtained at the top surface, which is the region subjected to tensile stresses in the tests.

The bending experiments were conducted in FEI Quanta 200 FEG ESEM scanning electron microscope (SEM) in high vacuum using a Kleindiek micromanipulator setup. The force was measured using a Kleindiek force measurement sensor (FMS), which provides a voltage signal from a bending piezo-electric beam used to apply a displacement to the cantilever. The FMS was calibrated against a copper spring with known spring constant (uncertainty of about 10%), and the accuracy of the calibration procedure itself was determined to be in the order of ±5%. Displacements were measured through post-processing of images taken in the SEM at a frequency of 1 Hz during testing. A schematic of the experimental setup is shown in Fig. 2a.

Initially, three tests were performed on micro-cantilevers with similar size (denoted A, B and C in Table 1, where all relevant dimensions are included). For each cantilever, a number of consecutive bending cycles were applied, with progressively increasing maximum displacement. The displacement of a point at the fixed end was measured to give an estimate of the drift during testing, which was negligible in all tests reported herein.

As the FMS tip is made of silicon, it does not indent the surface of the cantilever. Instead the tip slides along the oxide surface with increasing displacements (as seen from Fig. 3a and b), changing the effective span length, η. In order to allow representation of the bending tests in terms of force and displacements, we chose to use an equivalent force, $F_{eq} = F_p \cdot (\eta/L)$, which represents a force applied to the free end of the cantilever resulting in the same bending moment as the actual force applied (F_p), and the free end displacement. Fig. 3d shows a representative example of such force–displacement curves for two consecutive loading cycles. While the initial response is linear, as expected, a non-linear behavior is observed at loads above approximately 4 μN. This behavior is observed in all cantilevers, but the force and displacement levels where the transition occurs varies. A non-linear response at large displacements during micro-cantilever bending is not necessarily an indication of plastic deformation. There are several other factors leading to deviations from linearity, in particular a horizontal force component (F_x in Fig. 3b), which develops as the angle, θ, between the cantilever and the horizontal plane increases during bending [20]. This can be corrected for analytically by a factor $(\tan\theta/\theta)^{1/2}$ [20], but the correction amounts to around 13% at an angle of 45°, which is not enough to obtain a fully linear response at higher loads in the present case, indicating that there are other contributing factors.

Another prominent feature of the force–displacement curves in Fig. 3d is the force oscillations in the non-linear region, which are thought to be related to the slipping of the FMS tip over the rough oxide surface.

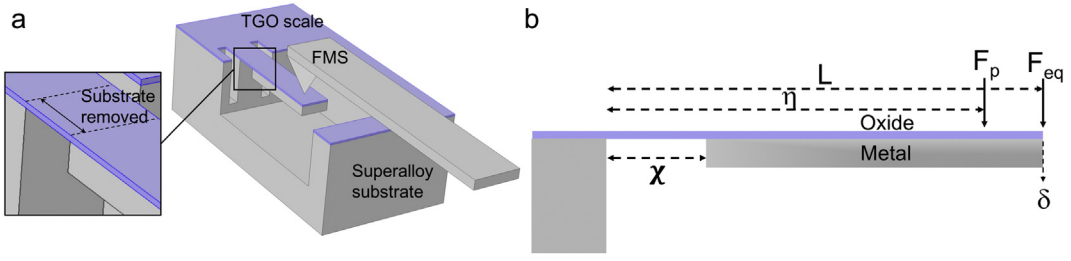

Fig. 2. (a) Experimental setup for micro-cantilever bending tests. The oxide layer is shown in purple and the metal in grey. The oxide layer is isolated from the metal towards the fixed end. (b) Schematic of cantilever geometry with relevant notation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)