



In situ measurement of oxidation evolution at elevated temperature by nanoindentation

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Received 25 February 2015; revised 13 March 2015; accepted 13 March 2015
Available online 25 March 2015

Nanoindentation is adopted to study the oxidation evolution of niobium-based alloy at nano-scale at elevated temperatures. An indentation pit at room temperature was created as a “marker” before the temperature was raised to 800 °C. A non-uniform oxide scale on the surface was observed real time by *in situ* scanning probe microscope. Elastic modulus and hardness obtained at different temperatures exhibit clearly the oxidation effect, which is also demonstrated by creep tests for 600s by using dynamic mechanical analysis of nanoindentation.
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Keywords: Oxidation; Nanoindentation; *In situ* scanning probe microscope; Creep

Nanoindentation has been used to determine the mechanical properties of materials at a microscopic scale [1–4]. With its relatively simple requirements for the preparation of specimen and faster acquisition of experimental data [2], it has been drawing more and more attention from a wide range of subjects, such as metals and alloys, soft matters and biomaterials [5]. The application of nanoindentation includes as well the study of plastic deformation and dislocation [3,6–10]. Moreover, due to its unique testing properties at micro/nano scale, nanoindentation has also been adopted for high temperature tests. For instance, nanoindentation tests have been conducted for high-temperature shape memory alloys and polymers to study their mechanical properties [11,12]. However, due to the technical difficulties, the temperature for nanoindentation has been limited to no higher than 600 °C [13]. Continuous efforts are being made to develop new methods to raise the temperature for oxidation study by using nanoindentation [14].

There are several traditional methods to study the oxidation of materials for instance, mass gain method, gas consumption method, accelerated life test, etc. [15]. However, these methods are labeled as “post-oxidation” characterization since none of these methods has the ability to characterize the real-time growth of the oxide film and its morphology evolution. These post-oxidation characterization methods on the one hand miss important

information during the oxidation process. On the other hand, in most cases, it is of great difficulty to characterize the oxide quantitatively and separately (e.g. for multi-layer oxidation), since the oxide product (composition and structure) at the end of the oxidation could be too complicated. There has been some pioneering and profound work concerning the oxidation at the earliest stage and atomic structure evolution at an atomic scale [16–18], which revealed the oxidation at the early stage with a thickness at magnitude of nanometer. However still, these researches are limited to the earliest stages of oxidation and they are unable to show the oxidation evolution once after the oxide film (which exceeds the atomic scale) is piled up on the substrate for a longer oxidizing time. Neither are these methods available to show how the oxidized layer would evolve during oxidation process. Thus it is of great importance to study the oxidation mechanism at a micro/nano scale bridging the atomic scale and meso/macro scale to quantitatively obtain and characterize the process of oxidation. In this work, we designed a nanoindentation test by using a scanning probe microscope (SPM) to *in situ* and real-time analyze the surface evolution of the sample at nano scale when oxidation occurs from room temperature up to 800 °C. The continuous increase of the thickness of the oxide film at each temperature point is recorded and calculated. The modulus and hardness are obtained from the indentation tests and a series of creep tests from room temperature up to 750 °C by using nanoindentation are also carried out for the validation of the oxidation evolution process.

Niobium-based (Nb-based) alloy (with 5.0 W, 2.0 Mo, 1.0 Zr, weight percentage) was used in the experiment.

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The specimens were processed by powder metallurgy and extruded. An automatic grinding machine was first used for the surface polishing with 200 to 1200-grit silicon carbide papers. Then polishing was performed with diamond paste with particle size of 0.5 μm to ensure the finish quality of the surface to meet the requirement of indentation test.

Nanoindentation tests were conducted by employing a specified indenter in heating chamber based on TI 950 (Hysitron Inc., USA) with displacement resolution 0.02 nm and load resolution 1 nN, respectively. Specimens were indented by using three-sided Berkovich indenter [19]. The Berkovich diamond indenter used in this test is specially designed for high temperature test and is brazed to a macor shaft with a low thermal expansion coefficient to reduce the thermal conduction from the surface of the specimen to the transducer. This design also prevents the standard probe holder from oxidizing or melting due to the high temperature effect. This indenter is later used as SPM tip to *in situ* and real-time scan the topographies of the indentations.

Sample was mounted between the bottom plate and the top plate and was subsequently heated to the target temperature by the heaters integrated in both plates. The indenter was then put in contact with the sample using a small contact load (2 μN below 400 °C and 4 μN when the temperature is 500–800 °C) and this contact was maintained until the temperature of the sample became thermally stable from top to bottom before the indentation tests were operated. Nitrogen gas was used to provide protection during the whole test to reduce oxidation effect. By carefully controlling the flow of nitrogen gas, we were able to control the oxidation rate of the specimen at high temperatures at a relatively slow pace and avoid the catastrophic oxidation of the surface.

Two types of tests were carried out. Firstly, the surface of the specimen was indented with a load of 7250 μN at room temperature. An indent (indentation marker) was created with a final depth of 146.02 nm as shown in Figure 1 ($T = 20$ °C). The indentation was performed with a linearly increasing period of 5 s to the maximum load and a holding period of 5 s at the maximum load and then 5 s linearly unloading period. Then the temperature was raised from room temperature up to 800 °C with a temperature interval of 100 °C. The increasing rate of temperature was controlled by software, with an average increasing rate of 3 °C/s. When the expectant temperature was reached and the temperature remained steady with a fluctuation of ± 0.05 °C, the *in situ* SPM imaging was conducted to obtain the surface topography of the indentation marker and the results are shown in Figure 1. The thickness of the oxide film can be calculated from the different depths and geometry of the indentation obtained by SPM. Secondly, at each pre-set temperature under stable condition, the conventional loading–unloading indentation tests were also carried out on the surface of the specimen to measure the hardness and modulus of the material to reveal the oxidation effect on the mechanical properties. Similarly, the load function was adopted with a linearly increasing period of 5 s to the maximum load and a holding period of 5 s at the maximum load and then 5 s linearly unloading period. For each temperature, at least 6 indentations were performed. The drift rate was measured over the last 20 s of the testing period before loading. The load–displacement curves were analyzed using Oliver and Pharr method [1].

The SPM results in Figure 1 demonstrate clearly the variation of the indentation marker at different

temperatures. When the temperature is below 400 °C, the profile of the indentation is identifiable. However, when the temperature is above 400 °C, the surface morphology in each profile (4 $\mu\text{m} \times 4 \mu\text{m}$) in Figure 1 starts to change sharply. The surface roughness is evidently increased especially at temperatures higher than 400 °C compared to the smooth surface at the initial stage (room temperature) and lower temperature (below 400 °C). This observed growth pattern of oxide scale obviously is unsatisfactory for the classical Wagner's theory of oxidation in which the oxidation is assumed to be uniform in different directions [15]. But this phenomenon of non-uniform growth of oxides agrees with some earlier oxidation study carried out at nano-scale by Zhou et al. on Cu [16,17].

In order to illustrate the evolution of oxidation thickness in a simpler way, we choose the indentation pit (the marker) and consider it as a representative area for the average oxide thickness change. Since the size of the indentation is quite small ($\sim 2 \mu\text{m}$), we assume that the oxide film grown on the surface of the indentation is isotropic. The thickness change of the oxide film over the tested temperature range was used to represent the oxidation evolution. By using the integrated software of the equipment, the final indentation depth h after oxidation at each temperature can be directly obtained. By directly calculating the difference between the measured depths at each temperature point (here the thickness of the oxide film at room temperature is set to be 0 as reference), one can get the reduction in depth for each temperature interval and this depth change is regarded as the accumulated thickness of the oxide film. The second way is to first calculate the average side length a of the triangle impression of the indentation and then convert it into oxide film thickness via a geometrical relation. Due to the geometrical similarity, we then assume that there is a consistent correlation between the depth h and average side length a . Thus, using the average side length change Δa , the change of depth can be calculated. The thickness of the oxide film calculated using the aforementioned two methods shows a consistent correlation. In Figure 2 it shows the values of average side length a and the calculated oxide film thickness at different temperatures. As can be seen, the oxide thickness remains stable under temperature 400 °C, while it accumulates quickly when the temperature is increased above 400 °C.

Furthermore, in Figure 3a and b the elastic modulus and hardness from room temperature up to 800 °C are presented. The elastic modulus and hardness remain relatively stable when the temperature is not higher than 400 °C. However noticeably, both the elastic modulus and hardness started to increase as the temperature was higher than 400 °C, i.e., the higher the temperature is, the more unstable the elastic modulus and hardness are. This is caused by the oxidation and formation of oxide layer on the surface, which changes the surface properties of the specimen evidently at temperatures higher than 400 °C. This change in the mechanical properties is also consistent with the SPM morphologies shown in Figure 1 and the oxide thickness in Figure 2. As for Nb-based alloy, the content of Nb dominates. Thus here we mainly take into consideration of the oxidation of Nb. The oxidation kinetics shows that the oxidation of Nb is characterized by inward diffusion of oxygen through the oxide scale [15]. A uniform and flat protective oxide layer is initially formed on the surface. Afterward however, the temperature increases and the oxidation process accelerates. Due to the extremely high Pilling–

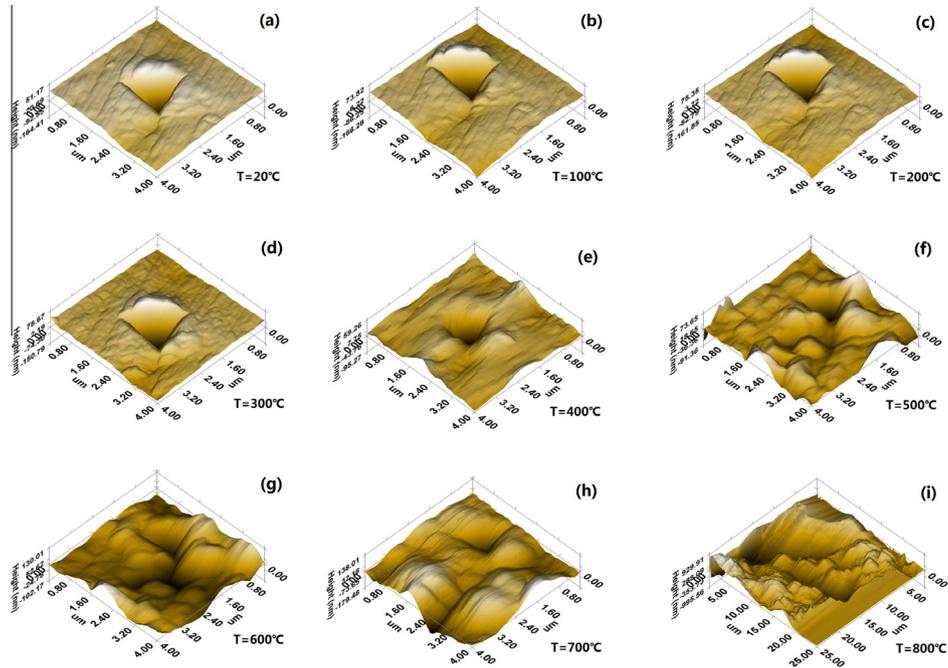


Figure 1. *In situ* SPM images for the surface topography at different temperatures.

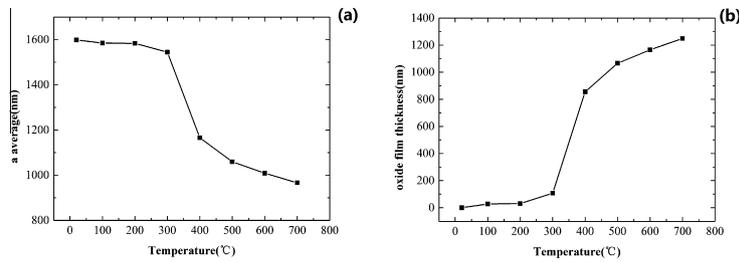


Figure 2. (a) Average side length of the indentation at different temperatures; (b) oxide film thickness at different temperatures calculated using average side lengths of the indentation.

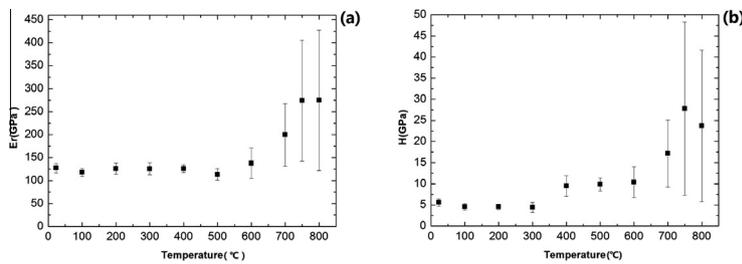


Figure 3. (a) Elastic modulus at different temperatures; (b) hardness at different temperatures.

Bedworth ratio (*PBR*) [20] for the oxide from Nb, which is 2.68 [15,21], this huge expansion of the oxide scale would result in high compressive stress in the oxide scale. This high compressive stress would cause the oxide scale to rupture and further lead to a higher rate of oxidation and a serrate rough surface. An illustration of the rupture morphology can be found in Ref. [21]. Here *PBR* is a parameter which characterizes the volume expansion of the oxide scale (V_{ox}) in comparison to the original volume of the substrate metal (V_m), i.e., $PBR = V_{ox}/V_m$.

Furthermore, once the oxide becomes rough, the surface topography and its local curvature would affect the local diffusion, except the surface is smooth enough. Then the oxidation evolves along the non-uniform surface, which can further aggravate the surface roughness as indicated in Figure 1e–i. The present result indicates that when the oxide surface becomes initially rough, it inclines to increase the roughness afterward.

We also conducted creep tests on the sample from room temperature up to 750 °C, where the experimental

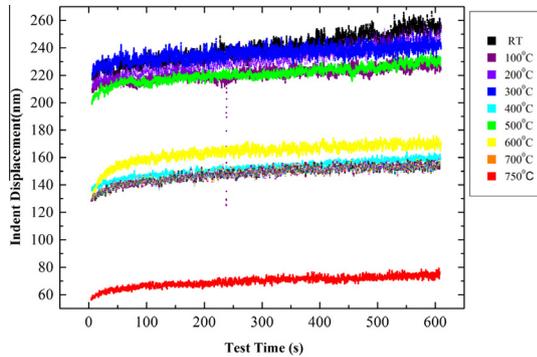


Figure 4. Creep test at different temperatures.

condition is load control to keep the load constant during the whole creep test. The load is kept constant as $4750 \mu\text{N}$ for 600 s during the whole experimental process. As illustrated in Figure 4, the higher the temperature, the smaller the indent displacement. The explanation is that the higher the temperature, the thicker the oxide scale and also the bigger the hardness as depicted in Figures 1–3. This increase in the hardness on the surface results in a smaller indent displacement. More obviously, the creep results demonstrate a distinction between the curves at temperatures higher than 400°C and lower than 400°C , respectively. This indicates that there might be a transition for oxidation mechanism on the surface of the specimen around 400°C .

In conclusion, we recorded real-time the oxidation evolution of the indentation pit on Nb-based alloy at nano-scale from room temperature to 800°C . The thickening effect as well as the roughening effect of the oxide scale were observed and carefully calculated through two geometrical methods focusing on the deliberately pre-indented indentation marker. Surface morphology, mechanical properties such as modulus and hardness, as well as creep test all indicate that the oxidation behavior of Nb-based alloy has a transition temperature at 400°C . *In situ* scanning probe microscope (SPM) image combining with nanoindentation technique can be properly used to study the oxidation at elevated temperatures. The experimental technique and method can serve as a state-of-art method to study oxidation bridging the atomic scale and meso/macro scale. The results may serve as a solid experimental foundation for

potential simulation and theoretical model development, where the conventional Wagner's theory no longer holds under some circumstances for materials science.

We gratefully acknowledge the support from the National Basic Research Program of China (Grant No. 2015CB351904), National Natural Science Foundation of China (Grant Nos. 11222220, 11320101001, 11227801) and Tsinghua University Initiative Scientific Research Program.

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