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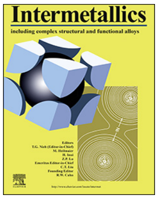

Surface oxidation of NiTi and its effects on thermal and mechanical properties

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ABSTRACT

This study investigated the surface oxidation process of near equiatomic NiTi at elevated temperatures in air. The surface oxidation is found to involve the formation of several distinctive product layers in a particular sequence. The oxidation initiates by selective leaching of Ti from the alloy matrix to form an outer TiO_2 layer, resulting in Ti depletion within the matrix and the formation of an inner $TiNi_3$ layer. Further oxidation leads to the formation of a composite layer consisting of TiO_2 and Ni(Ti) in between the outer TiO_2 and the inner $TiNi_3$ layers when the $TiNi_3$ layer reaches a critical thickness. This marks the onset of a steady state oxidation with the continuous expansion of the composite layer and inward movement of the inner $TiNi_3$ layer. The chemical reactions for the formation of various layers are identified and a diffusion-based physical model is proposed to explain the oxidation process. Surface oxidation resulted in the significant decrease of the latent heat and increase of the critical stress for inducing the martensitic transformation of the oxidised samples, due to the formation of oxidation-related layers and a significant Ti-depleted zone underneath.

1. Introduction

Near-equiatomic NiTi shape memory alloys exhibit unique properties including the shape memory effect and the pseudoelasticity, and the ability to produce a mechanical work in these processes when resisted [1]. These properties have rendered the alloys being used in a wide range of applications, such as sensors [2,3], actuators [4,5] and medical devices [6].

The shape memory effect and the pseudoelastic effect of NiTi shape memory alloys originate from the thermoelastic martensitic transformations of these alloys, namely the B2↔B19′, B2↔R and R↔B19′ transformations [7]. These transformations are, at the microscopic level, mechanical lattice distortion processes as well as crystal structural transformations. As a result, the shape memory and the pseudoelastic properties of near-equiatomic NiTi alloys are sensitive to the metallurgical conditions of the matrix, e.g., composition, precipitates and dislocations, as well as external conditions, such as stress and temperature. For this reason, thermomechanical processing, including mechanical working and heat treatment, have been used as means for property control of NiTi alloys, in industrial production, laboratory research and in practical application of these alloys [8,9].

Whereas some laboratory heat treatment may be conducted in vacuum or inert gas environments to avoid oxidation, most heat treatments in industrial production and practical application are performed in air. For example, shape setting treatment of delicate medical NiTi implants or orthodontic arch wires is commonly performed in air [10,11].

Heat treatment in air has also been purposely applied to NiTi biomedical implants to achieve a protective oxide layer on the surface to minimise nickel release, which is known to be toxic and allergic for Ni-sensitive patients [12–14]. The surface oxidation of NiTi has been extensively studied with a main focus on oxide product identification and free nickel formation in the surface region. An earlier study by Satow et al. identified the surface oxidation products of TiO_2, $TiNiO_3$, free Ni and $TiNi_3$ phases in sequence from the outer surface when heating NiTi to between 1023 K and 1223 K in air [15]. Chu et al. investigated the oxidation of an equiatomic NiTi alloy in air from 973 to 1273 K and identified a multilayered scale consisting of an outer rutile TiO_2 layer, an intermediate layer of mixture of TiO_2 and Ni(Ti) and a thin inner $TiNi_3$ layer [16]. Firstov et al. reported that after thermal exposure in air at 573–773 K for 30 min, TiO, pure hcp Ni and B2 NiTi were detected in the surface layers using the grazing incident X-ray diffraction

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method [17]. Following oxidation at 873 K, they observed different phases including TiO_2, Ni and Ni_3Ti in the outer surface layers and a mixture of austenite and martensite underneath the inner Ni_3Ti layer [17]. Plant et al. reported the presence of free Ni in the surface oxide layers after treatment at 573–773 K by means of X-ray photoelectron spectroscopy (XPS) analysis [18]. Shabalovskaya et al. studied the cross section of the oxide layers by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) and showed the presence of metallic Ni particles within the surface of TiO layer [19]. Tian et al. studied Ni stability in TiO_2 (rutile) and TiO by means of density functional theory simulation and found that Ni atoms can be dissolved in TiO but not in rutile TiO_2 [20]. They suggested that ultra-fast oxidation at sufficiently high temperatures is required to achieve a fully stabilized TiO_2 layer without formation of a TiO layer. The reaction kinetics of NiTi surface oxidation has also been extensively investigated in the literature by simply measuring the weight gain of the samples during isothermal heating at various temperatures, which all showed the oxidation to follow a parabolic rate law. By using the Arrhenius law, Smialek et al. calculated the activation energies for isothermal oxidation to be in the range of 210–260 kJ/mol [21,22], whereas other researchers reported lowers values of 130–150 kJ/mol [23,24], and the reason of the deviation is not clear. However, considering the multiple products formed and the complexity of the reactions and their sequences, the so-determined “activation energy” can only be a nominal average value corresponding to the specific condition and oxidation process of a particular experiment. This might be the reason of the large discrepancies in activation energy values reported in the literature. This also implies that there is no such an “activation energy” for oxidation of NiTi, but separate “activation energies” for each specific reaction.

Summarizing all the studies reported in the literature, it is apparent that oxidation of near-equiatomic NiTi is a complex process involving multiple products, including TiO_2, TiO, $TiNi_3$, free Ni and Ti depletion within the matrix. However, most of these previous studies have been focused on identifying the oxidation products [16,17], oxidation kinetics [21,22], corrosion resistance [25,26], and for medical application oriented studies on characterising Ni release [27–30]. In comparison, little discussion has been made of the oxidation mechanisms, forming sequences and the interactions among the various oxidation products. The formation of the heterogeneous structure of oxide-related phases is a complex diffusion process and the current understanding of the process is unsatisfactory. Clear understanding of this diffusion process is important for process design and quality control of NiTi alloys and for surface modification of their products.

In addition, the surface oxidation inevitably changes the alloy chemistry, thus is expected to alter the thermal and mechanical characteristics of the alloy. However, information on the effects of the surface layers on phase transformation behaviour and shape memory properties is scare in the literature. One reason for this could be due to the fact that the oxide layer formed is usually very thin (< 200 nm), especially when the alloy is heat treated at below 873 K [17]. However, with regard to NiTi thin film materials and miniaturisation of shape memory devices, even thin oxidation layers may be considered excessive and critical in affecting the properties of the alloys and the performances of the devices [31–33]. Excessive oxidation may impair the shape memory properties by two reasons. Firstly, the oxide, being a brittle ceramic compound, shows no martensitic transformation and no shape memory effect, thus functions as a mechanical resistance to shape memory deformation and recovery [34]. Secondly, due to the difference in affinity to oxygen, Ti oxidises more preferentially than Ni [35], causing Ti-depletion to the matrix composition, thus affecting the transformation behaviour of the alloy.

To address these uncertainties, we have conducted a detailed study on the oxidation behaviour of NiTi in flowing argon as the oxygen-deficient condition [36]. This paper reports a further study on the oxidation behaviour of a near-equiatomic NiTi alloy in air as the oxygen-sufficient condition at elevated temperatures. The influence of surface oxidation on the transformation behaviour and mechanical properties of the alloy were characterized.

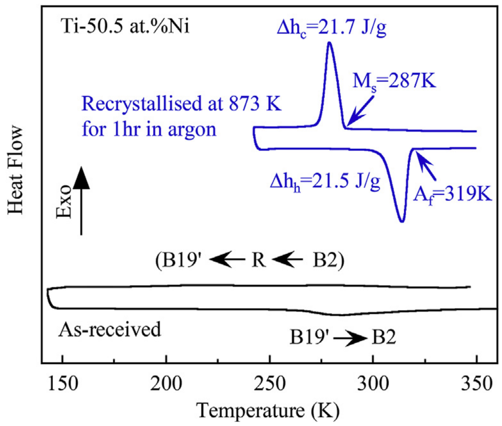

Fig. 1. Transformation behaviour of the Ti-50.5 at.%Ni wire in the as-received and recrystallisation annealed conditions. The enthalpy changes of the annealed sample for the forward (cooling) and the reverse (heating) transformations are determined to be $\Delta h_c = 21.7$ J/g and $\Delta h^c = 21.5$ J/g, respectively.

2. Experimental procedure

A commercial Ti-50.5 at.%Ni alloy wire of 1.50 mm in diameter was used in this study. The wire material was received in cold worked condition and a subsequent recrystallisation anneal was carried out in a protective argon atmosphere at 873 K for 1 h. The transformation behaviour of the as-received and recrystallised samples are shown in Fig. 1. The as-received sample exhibited very weak transformations. The recrystallised sample presented a typical single-step B2↔B19′ transformation, with a hysteresis of 32 K and enthalpy change of 22 J/g. Prior to the oxidation experiments, the surface of the recrystallised wires was polished using 800-grit sandpapers to remove pre-existing surface oxidation. The polished wires were placed in ceramic crucibles inside of a tube furnace with both ends open and heat treated at different temperatures up to 1223 K in static air to encourage surface oxidation. The samples were cooled to the ambient temperature in open air after the heat treatment. Transformation behaviour of the samples was analysed by means of differential scanning calorimetry (DSC) using a TA Q10 DSC in N_2 atmosphere with a cooling/heating rate of 10 K/min. The DSC samples were pre-cut into disks of $\phi 1.5 \times 1.5$ mm, with an average mass of 20 mg. All the DSC samples that sectioned from the heat treated samples contained the surface oxidation product. Microstructure of the cross section of the wire samples was examined by SEM using a Zeiss 1555 instrument equipped with an X-ray energy dispersive spectrometry (EDS) analyser for compositional analysis. The electron beam was set at 20 kV and the working distance was set at 16 mm, with this setting producing an electron beam spot size of approximately 10 nm. Monte Carlo simulation of trajectories of back-scattered electrons and X-rays in bulk Ti-50.5 at.%Ni under such condition was performed using CASINO software Version 2.4.8.1. The beam lateral spatial resolution was approximately 1 μm for the back-scattered electron signal and 1.5 μm for the X-ray signal. This resolution was practically good to avoid spot overlapping for reliable composition analysis. The crystal structures of the NiTi surface layers were studied by means of X-ray diffraction (XRD) using an Empyrean X-ray diffractometer (XRD) with Cu-Kα radiation.

3. Results

3.1. Surface oxidation

Fig. 2 shows the XRD spectra of the samples exposed at different