Oxidation behavior of TiNi shape memory alloy at 450–750 °C

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Abstract

The isothermal oxidation behavior of a commercial TiNi shape memory alloy (SMA) in pure oxygen over the temperature range of 450–750 °C was studied. The oxidation products were identified by X-ray diffraction (XRD). Characterization of the specimens after oxidation was conducted using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The oxidation kinetics at different temperature was studied, according to parabolic and logarithmic laws. The mechanism and activation energy of oxidation were discussed based on the oxidation kinetics. The spallation of the multi-layer scale formed during oxidation was analyzed by growth induced thermal stresses.

Keywords: TiNi; Oxidation; Scale spallation; Activation energy; Diffusion coefficient

1. Introduction

TiNi alloy is one of the most popular shape memory alloys (SMAs) because of a shape memory effect up to 8% strain [1]. In recent year, it has been used in industrial applications as well as many biomedical applications [2,3] because of its unique properties such as thermal shape memory, particular toxicity, good biocompatibility and corrosion resistance. Phase transformation between austenite (B2) and martensite (B19') in TiNi alloy occurs at the temperature range of ~50 to 110 °C, depending on the composition of alloys and stresses [4]. Hot work can be applied on TiNi alloys at high temperature (B2 phase). Cold work can also be applied on TiNi alloys at low temperature (B19' phase). The alloys develop work hardening extremely rapid during cold-deformation, therefore, annealing is needed. Heat treatment to impart the desired memory shape is often done at 500–800 °C [4]. These treatments at high temperature in atmosphere containing oxygen will result in the oxidation of the alloys. The properties of oxide layers formed during oxidation may play important role against the corrosion. However, few research attention was paid to this area. A study on the oxidation of an equiatomic TiNi alloy at 23 and 400 °C in an oxygen pressure of 10^-4 Torr or in air revealed the formation of different oxides under different oxidation environments [5]. The oxidation of an equiatomic TiNi alloy in air from 700 to 1000 °C was studied [6], while scale spallation was not reported in this case. An early investigation on Ti suggested that the oxidation kinetics of Ti metal follow a logarithmic law below 400 °C, cubic law (transient log-parabolic law) between 400 and 600 °C, and parabolic law over 600 °C [7]. The oxidation behavior of a TiNi SMA in pure oxygen gas at a temperature range between 450 and 750 °C is investigated in this paper.

2. Experimental

The material used in the experiment is a commercial hot rolled TiNi plate with a nominal composition of 50.8 Ti and 49.2 Ni. Specimens were cut from the plate, to a size of 10 × 2 × 1 mm³, then ground on emery papers up to 1000 grit, washed in acetone and dried before oxidation test. Oxidation experiments were performed in a SETARAM LABSYS™ Thermo-gravimetric Analyzer. First, the specimen was heated in protective gas Ar to the oxidation temperature at a heating rate of 50 °C min⁻¹. Isothermal oxidation was conducted at the temperature range of 450–750 °C in 1 atm of oxygen for 4 h. The mass gain of the specimen was measured as a function of time by an electronic balance with an accuracy of 0.1 mg by the thermo-gravimetric an-
alyzer. Finally, the oxidized specimen was cooled to room temperature.

After oxidation, the specimens were examined directly using a Philips PW3710 X-ray Diffraction (XRD) machine to identify the crystal structures. Cu Kα X-ray was used at 30 kV, 40 mA, and scanning range of 20–80°. The characterization of the oxidized specimens were conducted using a scanning electron microscope (STEREOSCAN 440) equipped with an energy dispersive spectroscope.

3. Experimental results

3.1. Isothermal oxidation kinetics

The oxidation kinetics curves of TiNi alloy are plotted in Fig. 1, showing the mass gains versus time at 450, 550, 650 and 750 °C. The oxidation rate increased rapidly with temperature. Determination of the rate constant was attempted by following methods.

3.1.1. Determination of parabolic rate constant ($k_p$)

The parabolic rate constant ($k_p$) is determined by the mass gain per unit surface area of a specimen ($\Delta W/A$) and exposure time ($t$),

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t$$

($k_p$ can be obtained from the slope of a linear regression line on ($\Delta W/A)^2$ versus $t$ plot. It is clear from Fig. 2 that, although experimental data (thick line) deviated slightly from the regression lines (thin line), the deviation was not significant. The parabolic rate constants and the related correlation coefficients ($R$) obtained from the linear regressions for oxidation at 450, 550, 650 and 750 °C are listed in Table 1. High correlation coefficients ($R = 0.977–0.998$) indicate that the oxidation of TiNi alloy at 550–750 °C for 4 h obeys the parabolic law. There was a worse correlation coefficient ($R = 0.76$) for oxidation data obtained at 450 °C, suggesting that the oxidation of TiNi alloy at 450 °C does not obey parabolic law.

3.1.2. Determination of the logarithmic rate constant ($k_{log}$)

The oxidation data at 450 °C was fitted by cubic law, and a bad correlation coefficient was obtained. Then, logarithmic law was used to fit the oxidation data. The logarithmic rate constant ($k_{log}$) can be determined by

$$\left(\frac{\Delta W}{A}\right) = k_{log} \log(t) + A$$

where $A$ is constant. A value of $8 \times 10^{-5}$ for $k_{log}$ and a correlation coefficient of 0.93 were obtained, suggesting that the oxidation of TiNi alloy at 450 °C for 4 h approximately obeys logarithmic law.

3.2. Identification of phases on the surface of the oxidized specimens

After isothermal oxidation, the crystal structures on the surface of the specimens were examined by XRD, and results are listed in Table 2. No oxide was identified on the surface of specimens after oxidation at 450 °C. However, small amount of TiNi was found. The oxide layer is too thin to be identified by scanning electron microscopy (SEM). Rutile TiO$_2$ is main oxidation product for the oxidation of TiNi alloy at 550–750 °C. TiNi, B$_19$ and B$_2$ phases were also detected in these specimens. The phase of TiNi was formed at the area beneath oxide layer (Fig. 6(d)). The existence of martensite (B$_{19}$) demonstrates that the change in chemical composition due to oxidation may induce internal stress, which in turn may cause phase transformation on the TiNi substrate close to TiNi$_3$ layer.

3.3. Morphologies and micro-composition of oxide scales

The morphology of the oxide scale formed on the surface of the specimens varied considerably with oxidation tem-
Table 1
Oxidation rate constants of TiNi oxidation at 450–750 °C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>450</th>
<th>550</th>
<th>650</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_p$ (mg m$^{-2}$ sec$^{-1}$)</td>
<td>$8.12 \times 10^{-12}$</td>
<td>$1.34 \times 10^{-10}$</td>
<td>$1.16 \times 10^{-9}$</td>
<td>$6 \times 10^{-9}$</td>
</tr>
<tr>
<td>R, correlation coefficients</td>
<td>0.76</td>
<td>0.977</td>
<td>0.995</td>
<td>0.998</td>
</tr>
<tr>
<td>$k_x$ (mm$^2$ sec$^{-1}$)</td>
<td>–</td>
<td>$4.4 \times 10^{-11}$</td>
<td>3.8 $\times 10^{-10}$</td>
<td>$1.97 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Table 2
The identified phases on the surface of oxidized specimens

<table>
<thead>
<tr>
<th>Oxide</th>
<th>450</th>
<th>550</th>
<th>650</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>TiNi (B$_2$), TiNi</td>
<td>TiNi (B$<em>2$), TiNi (B’$</em>{19}$), TiNi</td>
<td>TiNi (B$<em>2$), TiNi (B’$</em>{19}$), TiNi</td>
<td>TiNi (B$<em>2$), TiNi (B’$</em>{19}$), TiNi</td>
</tr>
</tbody>
</table>

After oxidation at 450 °C, the scratch marks on the surface of specimens formed during the polishing process before oxidation can be seen in Fig. 3, suggesting that the oxide layer is very thin. The grain size of the oxide is too small to be measured. The morphologies of the oxide scales formed at 550 and 650 °C are very similar. However, the oxide grain size formed at 550 °C is much smaller (Fig. 4) than that formed at 650 °C (Fig. 5). The surface morphology of the specimen oxidized 750 °C is shown in Fig. 6. The oxide scale partially spalled, as shown in Fig. 6(a). The outside scale (dark areas at the top and bottom of Fig. 6(a)) is a solid oxide layer under high magnification (Fig. 6(b)), which is similar to the oxide in Figs. 4 and 5, except that the grain size is much larger. Bright area at the middle of Fig. 6(a) was observed under high magnification and some pores can be seen on an inside oxide scale in Fig. 6(c).

The cross section of the specimen after oxidation at 750 °C is observed by back scattering mode of SEM, as shown in Fig. 6(d). Combining with energy dispersive spectroscopy (EDS) analysis on the micro-composition, we can identify TiO$_2$ outer layer, TiNi$_3$ layer and TiNi substrate. A mixture layer between outside layer and TiNi$_3$ can be seen in Fig. 6(d). The dark particles in the mixture layer are TiO$_2$ and white area contains TiO$_2$ and small amount of Ni from EDS analysis. However, no Ni phase was detected by XRD.
Fig. 6. Scale morphology of TiNi after oxidized at 750°C, showing (a) the partial spallation of the scale, (b) the outside layer of the scale with grain size about 1.2 μm, (c) the inside layer of scale with loose structure, and (d) the multi-layer structure from cross section of the oxidized specimen.

One possible reason is that the amount of Ni phase in this layer is too small to be detected. It was reported that Ni phase was detected after oxidation of TiNi alloy over 850°C [6].

4. Discussions

The oxidation kinetics of TiNi alloy and the morphologies of oxide scales are different at different oxidation temperatures. Oxidation behavior of TiNi alloy is discussed according to the two temperature ranges: 450 and 550–750°C.

4.1. Oxidation behavior of TiNi alloy at 450°C

TiNi alloy oxidation at 450°C approximately obeys a logarithmic rate law. The thickness of the oxide layer on the surface of the specimen for 4 h oxidation is very thin and difficult to be identified by SEM. The thickness of scale can be calculated from the mass-gain (3.1412 × 10^{-4} mg mm^{-2}) and the density of TiO_2 (4.25 mg mm^{-3}) [8], by assuming only TiO_2 formed during the oxidation, the result is about 185 nm.

A number of theories to explain the logarithmic law were summarized [9]. The mechanisms of oxidation are based on the transport of electrons or ions. The electric field set up by chemisorption of oxygen, aided by quantum-mechanical tunneling of electrons (thickness <10 nm) from metal through the oxide to the adsorbed oxygen. Since the potential difference between the metal and adsorbed oxygen species is constant, the thinner the oxide scale, the stronger the electric field and the faster the ionic transportation. As the oxide scale thickens, the field strength is reduced and reaction rate falls. In fact, low temperature oxidation kinetics is difficult to analyze. Thermo-gravimetric method is not sensitive enough to determine the mass change. Trace oxygen may cause the oxidation of the alloy during heating stage, which was not included in the calculation of oxidation kinetics.

4.2. Oxidation behavior of TiNi at 550–750°C

4.2.1. Oxidation kinetics

According to the rate constant analyses, the oxidation kinetics for TiNi alloy at 550–750°C obeys approximately the
parabolic rate law, indicating that the diffusion process was
the rate controlling mechanism. The effective diffusion co-
efficients can be estimated from the parabolic rate constants
using Smialek’s method [10]. The scale may be envisaged
as a moving boundary of fixed composition, and thus fol-
lowing a parabolic law:

\[ x^2 = D_{eff} t \approx k \rho \]

where \( x \) is the scale thickness, \( D_{eff} \) is an effective diffusion
coefficient, and \( k \) the parabolic growth constant in terms
of the scale thickness, which is obtained from its relation to \( k_p \)
by the equation

\[ k_p = \left( \frac{p_{TiO_2}}{W_{TiO_2}} \right)^2 k \rho \]

where \( p \) is the density of TiO\(_2\) (4.25 g cm\(^{-3}\)) [8], \( W_{TiO_2} \) is the
molar weight of oxygen in TiO\(_2\), \( W_{TiO_2} \) is the molar weight
of TiO\(_2\), \( k \) values for TiNi oxidation at 550–750 °C were
calculated by equation (4), which are also listed in Table 1.
The calculated \( D_{eff} \) values from present work and from TiNi
alloy oxidation in air [6] are drawn in Fig. 7. The diffusion
coefficients of O in TiO\(_2\) at 1 atm oxygen [11], O in TiO\(_2\) at
5 × 10\(^{-5}\)–8.4 × 10\(^{-3}\) atm oxygen [12], and Ti in TiO\(_2\) [12]
are also shown in Fig. 7. The data for the diffusion of O in
TiO\(_2\) cannot be compared directly to the data from this
work because they were obtained from different temperature
range. The effective diffusion coefficient \( D_{eff} \) lies between
the diffusion coefficients of O and Ti in TiO\(_2\) if the diffu-
sion coefficient of O in TiO\(_2\) is extrapolated to the lower
temperature region. This implies that the diffusion of O in
TiO\(_2\) is not the main mechanism for oxide growth. On the
other hand, Ti activity beneath oxide scale was reduced dur-
ing oxidation due to the formation of TiNi\(_3\) and Ni phases,
which in turn reduced the rate of Ti diffusion in oxide scale.

The effective diffusion coefficient for TiNi oxidation in
titanium (present work) is less than that of TiNi oxidized in
air [6]. Metal oxidation in air may form nitride or nitro-
gen as impurity may change defect concentration in oxide.
For example, AlN was found in the inner layer of the ox-
ide scale when Fe–37Al is oxidized in ambient atmosphere
[13]. The activation energy of a diffusion process with the
vacancy mechanism is the sum of the energy required to
form a vacancy and the energy required to move a vacancy
from equilibrium position to another [14]. The defects in
rutile TiO\(_2\) are oxygen anion and interstitial titanium ions,
which can be expressed as Ti\(_{1+x}\)O\(_2-x\) [7]. Nitrogen may ex-
ist in TiO\(_2\) scale as impurity. According to the defect equi-
librium theory, 2N\(^{2-}\) ions, as an impurity, occupy 2O\(^{2-}\) po-
sitions in TiO\(_2\). To satisfy electron equilibrium, one oxygen
vacancy is produced to balance the two negative electron
charges. In this way, nitrogen ions may increase the num-
ber of O vacancies, resulting in an increase in the oxidation
rate.

Some earlier investigations have correlated the diffusion
coefficient \( D \) and temperature \( T \) through the Arrhenium
equation

\[ D = D_0 \exp \left( -\frac{Q}{RT} \right) \]

where \( R \) is the gas constant (8.31 J mol\(^{-1}\) K), \( T \) is the
absolute temperature, \( Q \) is the activation energy and \( D_0 \) is the
pre-exponential factor. Plots of \( D_{eff} \) versus 1/T for TiNi al-
loy from 550 to 750 °C in Fig. 7 showed a very good linear
relation (correlation coefficient = 0.999), with activation en-
ergy \( Q = 133 \text{ kJ mol}^{-1} \). The activation energies of O and Ti
in TiO\(_2\) oxide can be evaluated in same manner as 260 and
36 kJ mol\(^{-1}\), respectively.

### 4.2.2. Morphology of the oxide scale

The higher the temperature of oxidation, the larger the
grain size of the oxide will be. The average grain sizes of
the oxide on the surface of the specimens oxidized at 550, 650 and
750 °C for 4 h are about 0.25, 0.6, and 1.2 μm,
respectively.

A complex scale structure, TiO\(_2\), TiO\(_2\)+Ni, TiNi\(_2\) and
TiNi substairate, was formed during high temperature oxida-
tion. The free energy of formation \( \Delta G \) (750 °C) of NiO and
TiO\(_2\) is –147 and –759 kJ mol\(^{-1}\) [15], respectively. Oxi-
dation of Ti is easier than Ni, therefore, TiO\(_2\) outside scale
was formed. Less Ti concentration was found beneath oxide
scale due to Ti oxidation. Ni and TiNi\(_2\) phases developed
due to depletion of Ti. From the alloy phase diagram, Ti can
form a solid solution in Ni (over 10 at % Ti in solid solution
at 750 °C) [16]. When oxygen diffused into Ni(Ti) phase,
less noble component Ti (more negative \( \Delta G \)) was oxidized
to form TiO\(_2\) particles due to low oxygen pressure there,
resulting a mixture layer of Ni(Ti) and TiO\(_2\).

The oxide scale partially spalled from the surfaces of the
specimens oxidized at 750 °C in Fig. 6(a). However, the
curve of mass-gain versus time in Fig. 1 is smooth, suggest-
ing that scale spallation took place during cooling stage. It
is reported that scale spallation occurred during the isother-
mal oxidation of titanium metal at 750 °C if the thickness
of TiO\(_2\) scale was over 3 mg cm\(^{-2}\) for long time oxidation.

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**Fig. 7.** Comparison of the apparent parabolic growth constants for TiO\(_2\) with diffusion data.
In present study, oxide layer formed at 750 °C for 4 h is calculated to be about 1 mg cm⁻², based on mass gain data. The structure of the scale/substrate interface for Ti oxidation is much different from that for TiNi oxidation. A multi-layer scale with low concentration of Ti was formed on the surface of the TiNi specimens oxidized at 750 °C for 4 h in Fig. 6(d). High stress can be built up in the scale due to the volume difference between the oxide and metal. High stress may induce cracks in oxide scale during high temperature oxidation. When the oxidized specimen was cooled from high temperature to room temperature, the thermal stresses can develop at the interfaces of multi-layer structure, due to the differences in thermal expansion coefficients of the alloys and oxide. Usually, alloy shows larger ductility than oxide, therefore, the scale spalled between the mixture and outside oxide layer.

5. Conclusions

The oxidation kinetics of TiNi alloy at 450 °C for 4 h obeys logarithmic law. The thickness of the scale is about 185 nm.

The oxidation kinetics for TiNi alloy at 550–750 °C for 4 h obeys parabolic law. The activation energy of the diffusion to form oxide scale is 133 kJ mol⁻¹, based on the calculation of parabolic rate constants. Formation of the oxide scale was mainly controlled by the diffusion of Ti in alloy and in oxide scale.

The oxide formed on the surface of TiNi alloy at 550–750 °C in oxygen for 4 h is rutile TiO₂. A multi-layer structure, TiO₂ oxide, mixture of Ni(Ti)–TiO₂ and TiNi₃ layer, was formed on the surface of TiNi specimens. The outside TiO₂ scale spalled possibly due to high stresses developed at the interface.

Acknowledgements

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References