Phase Transformation Kinetics of High Nb-TiAl Alloy during Continuous Heating

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Abstract—In this work, the phase transformation behavior of Ti−45Al−8.5Nb−(W, B, Y) alloy during continuous heating was investigated using dilatometer and optical microscopy. Results indicated that the phase transformation process of high Nb-TiAl alloy during continuous heating included two stages: ordered $\alpha_2 \rightarrow$ disorder $\alpha$ and tetragonal $\gamma \rightarrow$ hexagonal $\alpha$. According to the microstructure analysis, the initial $\alpha_2/\gamma$ lamellar structure transformed into the massive $\gamma$ phase and $\alpha$ phase (retained as $\alpha_2$) during the heating process. The activation energy of $\alpha_2 \rightarrow \alpha$ and $\gamma \rightarrow \alpha$ was 989.65 kJ/mol and 995.30 kJ/mol, respectively. Moreover, the lower the heating rate was, the faster the phase transformation reached the equilibrium state.

1. Introduction
As a substitute for heavy nickel-based superalloys, light-weight high Nb-TiAl alloy is one of the potential structural materials used in aerospace and automotive engineering, resulting from its excellent oxidation resistance, tensile resistance and creep properties at high temperature (>700 °C) [1-5]. Nevertheless, the poverty room temperature ductility and fracture toughness restrict their wide range of engineering applications. Therefore, the improvement of its mechanical properties is extremely important in industrial applications. All the properties of high Nb-TiAl alloy are closely related to the microstructure and phase compositions. The microstructure of alloy essentially relies on its thermo-mechanical process [6-9]. Understanding the phase transformation behavior and kinetics of high Nb-TiAl alloy is essential for making an optimum heat treatment process and improving its mechanical properties [10,11]. For the TiAl-based alloys, many researchers paid their attention to phase transformation and microstructural evolution after heating treatments (at high cooling rate), however, the influence of heating process is hardly considered.

In this work, the phase transformation behavior of high Nb-TiAl alloy during continuous heating was investigated by means of optical micrograph (OM) and dilatometer (DIL), from which the activation energy of phase transformation and transformation fraction were calculated.

2. Materials and Methods
The cast ingot alloy with a nominal chemical composition of Ti−45Al−8.5Nb−0.2W−0.2B−0.02Y
(at.%) (named as high Nb-TiAl alloy) was prepared using plasma cold hearth melting furnace. The detailed process of the experiment can be found in our previous published article[3]. In order to obtain homogeneous composition, the alloy was firstly heated from room temperature to 1340 °C (single-α phase) at the heating rate of 5 °C/min and kept at 1340 °C for 12 h. After that, it was cooled to 900 °C at the cooling rate of 5 °C/min, and then naturally cooled to room temperature in the furnace.

The cylindrical samples with 6 mm in diameter and 12 mm in length were cut using an electro-discharge machine, which were ground and polished using standard metallographic technique and then cleaned ultrasonically in ethyl alcohol for 20 min.

The thermal expansion of this alloy was measured using a computer-controlled horizontal pushrod dilatometer (Netzsch® DIL 402C) with a high-resolution displacement transducer. During the heating process, high purity Ar gas (≥99.999 %) was used to prevent from oxidizing, and the heating rates were 3 °C/min, 5 °C/min, 10 °C/min, 20 °C/min and 40 °C/min, respectively.

In order to obtain the microstructure of high Nb-TiAl alloy after heating treatment, the metallographic samples were heated in a furnace (Carbolite® CWF13/13) with the rate of 5 °C/min, and then water quenched at different temperature. After that, the samples were etched using the solution of 5 ml HF, 10 ml HNO3 and 85 ml H2O and the microstructure was observed using optical microscopy (Axio Observer.A1m, ZEISS).

### 3. Results and Discussion

#### 3.1 Dilatometric analysis

Fig. 1 shows the dilatometric and displacement derivative curves of high Nb-TiAl alloy heated at the rate of 5 °C/min. During the heating, the increase in the length of sample was attributed to lattice expansion and phase transformation [3]. According to the dilatometric curve, with the temperature increasing, the expansion rate of high Nb-TiAl alloy was linear in the primary stage, exhibiting no phase transformation. However, when it came up to 1209 °C, a small peak appeared in the derivative curve, resulting from the phase transformation of α2 → α [12]. Moreover, a large peak ranging from 1228 °C to 1343 °C appeared, attributing to the phase transformation of tetragonal γ→ hexagonal α [12]. Overall, for the high Nb-TiAl alloy exposed to continuous heating, there were two phase transformation processes: ordered α2→ disorder α and tetragonal γ→ hexagonal α [12].

![Fig. 1 Dilatometric and displacement derivative curves of high Nb-TiAl alloy exposed to continuous heating][3].

#### 3.2 Microstructure analysis

Fig. 2 shows the microstructure of high Nb-TiAl alloy after homogenized treating. It can be seen that
the micro morphology of this alloy was uniformed fine-grained near-lamellar structure, including lamellar γ phase and α₂ phase. The colony size was about 130 μm and the inter-lamellar spacing was approximately 2.4 μm, which were determined by Image-Pro Plus software.

Fig. 2 Microstructure of high Nb-TiAl alloy after homogenized treating.

Fig. 3 shows the microstructure of high Nb-TiAl alloy after water quenching at different temperatures (1209 °C, 1228 °C, 1292 °C and 1343 °C). As shown in Fig.3a, the alloy exhibited uniformed near-lamellar structure after water quenching at 1209 °C, consisting of γ phase and α₂ phase with the colony size of about 118 μm, which was smaller than that before heating. However, the interlamellar spacing was approximately 6 μm, and it was slightly larger than the initial state. When the quenching temperature came up to 1228 °C, the colony size was about 35 μm and the interlamellar spacing was approximately 10 μm, as shown in Fig.3b. Similarly, quenched at 1292 °C, γ phase and α₂ phase coexisted (see Fig.3c), the colony size and the interlamellar spacing were 32 μm and 8.5 μm, respectively. The disordered α phase transformed into the ordered α₂ phase when the alloy was quenched at over 1135 °C with a high cooling rate [13]. When the high Nb-TiAl alloy was quenched at 1343 °C (only phase α at this temperature), it was composed of massive γ phase (dark field) and α phase (light field) [14-16], as shown in Fig.3d. From the above findings, it can be concluded that, for the quenching temperature ranging from 1209 °C to 1292 °C, the microstructure of high Nb-TiAl alloy was near lamellar (NL) structure, consisting of γ phase and α₂ phase. Besides, the colony size decreased with the quenching temperature increasing while the interlamellar spacing showed an increasing trend.
Fig. 3 Microstructure of high Nb-TiAl alloy after water quenching at different temperature.
(a) 1209 °C (b) 1228 °C (c) 1292 °C (d) 1343 °C.

3.3 Kinetics of phase transformation during continuous heating

The kinetics of phase transformation is usually investigated according to the dilatometric curve, and the activation energy can be determined from that, since the inflection point of thermal expansion curve is strongly related to the heating rate [17,18]. Kissinger equation is widely used in such a case for differential thermal analysis, as follows [19-22]:

\[
\ln \left( \frac{\beta}{T_{\text{max}}^2} \right) = \ln \left( \frac{AR}{E} - \frac{E}{RT_{\text{max}}} \right)
\]

where, \( \beta \) is the heating rate; \( T_{\text{max}} \) is the temperature where \( d(\Delta L/L_0)/dT \) is the highest; \( A \) is the pre-exponential factor; \( R \) is the universal gas constant; \( E \) is the activation energy, which can be determined from the slope of \( \ln \left( \beta / T_{\text{max}}^2 \right) \) versus \( 1/T_{\text{max}} \).

In accordance with the dilatometric curves, Daoudi et al. obtained the apparent activation energy of Al-Si-Mg alloy using the Kissinger equation, which agreed with the results obtained from DSC and other techniques [22]. However, two conditions should be considered for the use of Kissinger equation: 1) it can only be used for calculating the activation energy at the single point reaction peak; 2) the equation must be used for the heating process [23].

Fig. 4 shows the dilatometric curves of high Nb-TiAl alloy treated at different heating rates. From that, the relationship between \( \ln \left( \beta / T_{\text{max}}^2 \right) \) and \( 1/T_{\text{max}} \) are plotted and shown in Fig. 5. Based on the Kissinger equation, the apparent activation energy of \( \alpha_2 \rightarrow \alpha \) and \( \gamma \rightarrow \alpha \) was 989.65 kJ/mol and 995.30 kJ/mol, respectively. They were closed to the results obtained by Sha, 1060 ± 84 kJ/mol for \( \alpha_2 \rightarrow \alpha \) in Ti-25Al-11Nb alloy [24].

As an iso-conversional method, the Kissinger equation is usually used for performing the kinetics analysis of solid-state transformation [23, 25]. The fraction of \( \alpha \) phase at a given temperature was calculated using the following equation [21]:

\[
f_\alpha = \frac{\Delta L_{T} / L_0}{\Delta L_{T_{\text{max}}} / L_0}
\]

Where \( \Delta L_{T}/L_0 \) and \( \Delta L_{T_{\text{max}}}/L_0 \) are the relative length change corresponding to full precipitation of \( \alpha \) phase [22]. Fig. 6 shows the transformation fraction of \( \alpha \) phase as a function of temperature for the high Nb-TiAl alloy treated at different heating rates, by using Eq. (2). It can be seen that the phase transformation fraction curves are typical S-shaped, including nucleation and growth of \( \alpha \) phase. For the heating rate of 3 °C/min, the volume fraction of \( \alpha \) phase was 37.8% at 1280 °C and it reached to 97.8% at 1320 °C. However, when the heating rate came up to 40 °C/min, the volume fraction of \( \alpha \) phase at 1280 °C and 1320 °C was 1.57% and 28.2%, respectively. It can be concluded that the less
the heating rate is, the more complete the phase transformation is. This is because a low heating rate gave enough time for the nucleation and growth of α phase\cite{17}.

![Fig. 4 Dilatometric curves of high Nb-TiAl alloy treated at different heating rates.](image)

\[ \text{Fig. 4 Dilatometric curves of high Nb-TiAl alloy treated at different heating rates.} \]

![Fig. 5 ln(β/\(T_{\text{max}}^2\)) versus \(1/T_{\text{max}}\) plots for phase transformation. (a) α₂→α, (b) γ→α.](image)

\[ \text{Fig. 5 ln}(\beta/\(T_{\text{max}}^2\)) \text{ versus } \frac{1}{T_{\text{max}}} \text{ plots for phase transformation. (a) } \alpha_2 \rightarrow \alpha, \text{ (b) } \gamma \rightarrow \alpha. \]

![Fig. 6 Transformation fraction of α phase as a function of temperature for the high Nb-TiAl alloy treated at different heating rates. (a) α₂ → α, (b) γ → α.](image)

\[ \text{Fig. 6 Transformation fraction of } \alpha \text{ phase as a function of temperature for the high Nb-TiAl alloy treated at different heating rates. (a) } \alpha_2 \rightarrow \alpha, \text{ (b) } \gamma \rightarrow \alpha. \]

### 4. Conclusions

The phase transformation of high Nb-TiAl alloy during continuous heating was investigated using dilatometer and optical microscopy. The research result can further optimize the heat treatment process,
and it provides a new thinking and a new method for research, development and performance analysis of TiAl alloys. Several important conclusions obtained from this work are as follow:

1. During continuous heating, the transformation process of $\alpha_2 + \gamma \rightarrow \alpha$ included two stages, $\alpha_2 \rightarrow \alpha$ and $\gamma \rightarrow \alpha$.

2. When the alloy was quenched into water at different temperatures, the initial $\alpha_2/\gamma$ lamellar structure transformed into the massive $\gamma$ phase and $\alpha$ phase (retained as $\alpha_2$).

3. The activation energy of $\alpha_2 \rightarrow \alpha$ and $\gamma \rightarrow \alpha$ was 989.65 kJ/mol and 995.30 kJ/mol, respectively. The heating rate had a significant effect on the process of phase transformation. The lower the heating rate was, the faster the phase transformation reached the equilibrium state.

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