Effect of electroplastic rolling on deformability and oxidation of NiTiNb shape memory alloy

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\begin{abstract}
Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} strips were successfully processed by electroplastic rolling at relatively low temperature compared to the traditional hot rolling. The result shows the deformability of Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} is improved by electropulse, with the maximum thickness reduction of 24% in a single pass. X-ray spectrum and TEM analysis indicates the main structure of Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} after electroplastic rolling is polycrystalline and Vickers hardness test shows electropulse can reduce the work hardening. In addition, electroplastic rolling can improve the surface quality of Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} owing to the short heat treatment time and low heat treatment temperature.
\end{abstract}

1. Introduction

In all the shape memory alloys, Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} (numbers indicate at.%), which is famous for its excellent property, is used for deformation at room temperature. Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} alloy is not the exception and often rolled at about 850 \degree C. The strips with the width of 5 mm, the thickness of 1.89 mm and the length of 1500 mm for EPR processing, produced by an induction vacuum melting furnace, and then was hot-forged and hot-rolled to the plates with the thickness of 1.89 mm at 850 \degree C. The strips with the width of 5 mm, the thickness of 1.89 mm and the length of 1500 mm for EPR processing, were made by spark cutting. The surface of samples was polished by the abrasive papers in order to get good electrical contact between electrode and strip. The schematic view of EPR is shown in Fig. 1.

The effect of electropulse on the flow stress during processing is called electroplasticity (EP). EP is observed in many alloys, such as Fe, Zn and W alloys. Conrad (2000) explained that the interaction of high velocity electron drift and dislocation could activate more dislocations for movement, thereby resulting in the improvement of plasticity. By employing EP, metals can have good plasticity even though the temperature of metals is low.

The rolling with the high energy density electropulse conducted to the deformation zone in the process is called electroplastic rolling (EPR). It is a novel method to manufacture thin strips. EPR has been successfully used to roll AZ31 strip at temperature of 200 \degree C with the thickness reduction of 23% done by Xu et al. (2007). The dynamic recrystallization phenomenon occurred in Mg alloy during EPR leads to the sharp drop of the rolling separation force compared to the rolling without electropulse. In this research, EPR is used in processing of Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} to improve its plasticity and reduce the oxidation in processing.

2. Experiments

The Ni\textsubscript{47}Ti\textsubscript{44}Nb\textsubscript{9} (hereafter annotated as NiTiNb) alloy, which has a composition of 47 at.% Ni, 44 at.% Ti and 9 at.% Nb, was produced by an induction vacuum melting furnace, and then was hot-forged and hot-rolled to the plates with the thickness of 1.89 mm at 850 \degree C. The strips with the width of 5 mm, the thickness of 1.89 mm and the length of 1500 mm for EPR processing, were made by spark cutting. The surface of samples was polished by the abrasive papers in order to get good electrical contact between electrode and strip. The schematic view of EPR is shown in Fig. 1.
Table 1

<table>
<thead>
<tr>
<th>Rolling no.</th>
<th>Thickness reduction (%)</th>
<th>Temperature before rolling (°C)</th>
<th>Frequency (Hz)</th>
<th>Duration (μs)</th>
<th>$J_m$ (A/mm²)</th>
<th>$J_e$ (A/mm²)</th>
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<tr>
<td>1</td>
<td>9</td>
<td>760</td>
<td>450</td>
<td>72</td>
<td>173</td>
<td>14.9</td>
</tr>
<tr>
<td>2</td>
<td>24.4</td>
<td>700</td>
<td>350</td>
<td>72</td>
<td>143</td>
<td>14.5</td>
</tr>
<tr>
<td>3</td>
<td>23.1</td>
<td>700</td>
<td>300</td>
<td>72</td>
<td>207</td>
<td>15.8</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>600</td>
<td>200</td>
<td>72</td>
<td>235</td>
<td>17.7</td>
</tr>
<tr>
<td>5</td>
<td>16.7</td>
<td>600</td>
<td>160</td>
<td>72</td>
<td>300</td>
<td>17.3</td>
</tr>
<tr>
<td>6</td>
<td>15.7</td>
<td>600</td>
<td>140</td>
<td>72</td>
<td>339</td>
<td>15.8</td>
</tr>
<tr>
<td>7</td>
<td>16.9</td>
<td>600</td>
<td>120</td>
<td>72</td>
<td>260</td>
<td>16.7</td>
</tr>
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</table>

Note: $J_e$ represents the root-mean-square value of the current density in EPR case according to the joule thermal effect produced and $J_m$ is the amplitude of current density.

The big roller processing material is cathode and the small one is anode.

Continuous electropulse was produced by a self-made electropulse generator with the maximum electrical current amplitude of 5000 A. The strips moved at the speed of 1000 mm/min through the distance of 160 mm between the two electrodes. It took about 9.6 s for the strip move from anode to cathode. The electropulse with different frequencies and the constant duration of 72 μs was applied in the strips. A proper pressure was put on the anode to keep a good electrical contact. The electropulse parameters, including frequency, root mean square current, amplitude and duration were detected by Hall effect sensor and oscilloscope. In addition, the temperature of strips ahead of cathode was measured by thermocouple, as shown in Fig. 1. The NiTiNb strips were rolled to the thickness of 0.5 mm through 7 passes and the detailed processing conditions are listed in Table 1. In EPR process, the temperature was controlled by adjusting the frequency of electropulse, while the charge voltage, the distance from cathode to anode, and the rolling velocity were kept constant. Due to the cross section area reduction for the strips, the frequency of electropulse was lowered with the increase of the processing pass in order to keep the proper temperature. In addition, the traditional heat treatment technology, which is annealed at 850 °C for 30 min in quartz capsules evacuated to 0.4 Pa and then furnace cooled, to process the tensile test samples done by Zheng et al. (2000), was employed for the electroplastic rolled (EPRed) NiTiNb alloy. Meanwhile, in order to illustrate the oxidation in the traditional processing, the mixed acid hydrofluoric acid, nitric acid and deionized water (1:4:20) was used to clean oxide on the surface, and then NiTiNb strip was treated at 850 °C for 30 min in air and was cooled in air, which is the same as the heat treatment in the traditional processing of NiTiNb alloy.

X-ray diffraction (XRD) was conducted to characterize the crystal structure of the NiTiNb strips by a Rigaku X-ray diffractometer with the scanning velocity of 2°/min. The hardness was measured by the Vickers hardness instrument with 5 kg for 30 s. TEM observations were carried by FEI Tecnai G2 F20 TEM operated at 200 kV. EBSD analysis was performed in a Hitachi S-4800 FEG SEM equipped with an HKL-EBSD system at 20 kV and 20 μA. The tensile tests of NiTiNb alloys annealed at 850 °C for 30 min were carried out.
Fig. 3. TEM bright field picture of NiTiNb strips before EPR (a), and NiTiNb strips after EPR (b)–(d), and TEM bright field picture (e) and EBSD map (f) with the restructured grain boundary and all the Euler of NiTiNb annealed at 850 °C for 30 min. The white circles denote the Nb phase. Euler space is an orientation space defined by the three Euler angles, which are the grains orientation with the specimen. All Euler means the three Euler angles (φ₁, Φ, φ₂).

out with the strain rate of 3.33 × 10⁻⁴/s in an environmental cabinet with a SUNS tensile test machine at −65 °C. The specimen was deformed up to the total strain of 16%, and then heated to 240 °C after unloading in order to observe the recovery.

3. Results

The samples before and after EPR processing are presented in Fig. 2(a) and (b), respectively. Fig. 2 (c) shows the cracked strips after cold rolling with the total thickness reduction of 47% for three passes rolling, which is the same as the first three passes of EPR. TiNi alloy is an intermediate alloy, which is very brittle and hard to deform at low temperature.

In the cold rolling, the dislocation sliding is difficult for NiTiNb alloy, therefore, the inner stress is produced and cracks appear. As a result, the hot rolling is often used for production of the thin NiTiNb strips in industries. As shown in Fig. 2(b), the NiTiNb strips are successfully processed to the strips with the thickness of 0.5 mm and the width of 10.8 mm. As shown in Table 1, the heating treatment temperature for EPR is 100 °C lower than that used in hot rolling. In addition, in the case of EPR processing time is a few seconds, while in the case of established hot rolling the sample is several hours on temperature. Therefore, the formation of surface oxide can be significantly reduced.

Fig. 3(a)–(e) shows the TEM bright field picture of the NiTiNb alloy. Fig. 3(a) indicates the grain size of NiTiNb before EPR is more than 4 μm. After EPR, the grain size definitely becomes small, with the average size of about 2 μm. In the EPR sample, twin martensites with the thickness of 160 nm are found in Fig. 3(c), which was also observed by Tsuchiya et al. (2009) in the deformed NiTi shape memory alloys. In addition, the Nb phase was found in all the samples. Basically, the soft Nb phase has smooth boundaries. Fig. 3(e) and (f), respectively, shows the TEM bright field pictures and the EBSD map with the restructured grain boundary and all Euler of
NiTiNb annealed at 850 °C for 30 min. Obviously, the grains grew after annealing and the grain size is about 5–30 μm.

Fig. 4 presents the X-ray diffraction spectrum of NiTiNb after EPR processing. Peaks for B2 phase can be indexed before and after annealing. The result indicates the main structure of NiTiNb after EPR is polycrystalline, while Tsuchiya et al. (2009) observed that NiTi alloys easily appear amorphous during cold working. Furthermore, the grains have preferred orientation alignment. Compared to NiTiNb before annealing, the annealed sample appears the new peak of (2 2 0) and the existed peaks are narrowed. In addition, the peaks for Nb phase were apparent before and after annealing.

Fig. 5 shows the shape memory properties of NiTiNb after EPR and annealing. The specimen was deformed up to the total strain of 16%, and then developed recovery to 12.6% unloading to zero stress. The NiTiNb alloy was then heated to 240 °C, and the specimen recovered with the strain of 12% and the recovery rate of 95% was gained. The result was thus higher than the report that 60% of NiTiNb recovered with the strain of 12% and the recovery rate of 95%.

Table 2 gives the Vickers hardness of NiTiNb at different stages. Hardness increases with the deformation, but the maximum hardness is lower than that of the cold rolled sample. This indicates electropulse can promote the stress relief and recrystallization in the process, making the NiTiNb material to be easily deformed. The EPRed sample after annealing has the hardness of 2.42 GPa, close to the as-received sample. The hardness of the NiTiNb strip of cold rolling with total thickness reduction of 47% for three passes reaches the maximum value of 4.86 GPa. Therefore, the high stiffness lays an obstacle for the further deformation and consequently the crack was produced at cold rolling, as shown in Fig. 1(c).

4. Discussion

4.1. Effect of electropulse on the oxidation reduction of NiTiNb alloy in EPR process

Electropulse has a famous application in powders sintering, which uses electropulse to heat powder during pressing. Due to the short heat time, it is beneficial to gaining fine crystalline material, improving efficiency and saving energy, which was reported by Biswas et al. (2007). In EPR processing of NiTiNb strips, electropulses directly contact the rolled metals, so the metals only needs 5.6 s to be heated to the destined temperature. Moreover, the temperature between two electrodes is gradient and increases from room temperature to the maximum temperature when material moves from anode to cathode. Jiang et al. (2009) proved by experiment measurement and simulation that the relationship of the strip temperature and the distance from anode to cathode is almost linear. As a result, the time to reach the temperature higher than 500 °C and the length of strip of 25–53 mm respectively is about 1.5–3.2 s and, which can largely reduce the surface oxide of NiTiNb and the good surface is thus gained after EPR. According to oxidation kinetics of metals, Tao et al. (2005) proposed that oxidation can be expressed by the following equation:

$$\left( \frac{\Delta W}{A} \right)^n = k_n t + c \quad (1)$$

where $\Delta W$ is the mass difference before and after oxidation; $A$ is the area; $n$ is the index number of oxidation rate; $k_n$ is the coefficient of oxidation velocity; $t$ is the time and $c$ is the constant. The equation implies that the metals at high temperature for longer time will have more oxidation, thus the time for metals at high temperature should be reduced. EPR can definitely decrease the heat treatment time of the NiTiNb strips in processing. But in the traditional production of NiTiNb strips, the total time for heat treatment is several hours when NiTiNb plates are rolled from the thickness of 1.89 mm strips to the one of 0.5 mm.

Fig. 6(a) and (b) shows the cross section microstructures of the electroplastic rolling NiTiNb strips and the NiTiNb strips treated at 850 °C for 30 min in air. The surface of NiTiNb strip treated in air is severely oxidized and the oxygen is accumulated on the surfaces of NiTiNb strips. The surface is obviously separated into three layers. The composition of the innermost layer is still NiTiNb, which is checked by EDS. In the outmost layer with the thickness of about 12 μm, Ti and O are assembled and there are many voids distributed in this layer. The middle layer with the thickness of 4 μm had more Ni element than matrix. The total thickness of oxidized layer and element-changed layer is 16 μm and they would be cleaned before NiTiNb strips were made into the final products. So there is a huge material waste and the low successful rate of the finished products.

<table>
<thead>
<tr>
<th>Table 2 Vickers hardness of NiTiNb strip in rolling.</th>
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<tr>
<td>Before EPR</td>
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<tr>
<td>Vickers hardness (GPa)</td>
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</table>

![Fig. 4. XRD of EPR NiTiNb strips: (a) before annealing and (b) after annealing at 850 °C for 30 min.](image_url)

![Fig. 5. Tensile behavior of NiTiNb after EPR and annealing at ~65 °C.](image_url)
Fig. 6. SEM morphologies and linear element analysis of cross sections of NiTiNb strips: (a) and (b) EPR NiTiNb strip, (c) and (d) NiTiNb strip treated at 850°C for 30 min in air.

Fig. 7. TEM bright filed image and SAED of NiTiNb strips after 20% thickness reduction: (a) and (b) cold rolling, (c) and (d) electroplastic rolling.
NiTiNb processing. Table 3 shows the element content of strips in the central part after removing the oxidation. Obviously, the NiTiNb after treating at 850 °C for 30 min in air, which is often used in traditional hot rolling, has the highest oxygen content. So if the traditional hot rolling process is used in the whole processing, the oxygen content will be higher.

4.2. Effect of electropulse on the deformability of NiTiNb strips

Fierce debate on the mechanism of electroplastic has lasted for long time. Okazaki et al. (1980) believes that the thermal effect of electropulses play an important role in the reduction of deformation resistance and the improvement of plasticity. Okazaki et al. (1980) gave the equation that a single electropulse can produce adiabatic temperature rise,

$$\Delta T = \frac{I^2 R_{te} \rho}{C_p D}$$

where $I$ is the effective current density, also called the root-mean-square value of the current density, $\rho$ is the resistivity, $t_{e}$ is the electropulse duration, $C_p$ is the specific heat, and $D$ is the density. In the EPR of NiTiNb, temperature definitely affects plasticity. Table 1 shows the temperature of material increase to 600 °C or above when electropulse goes through the strips. Xu et al. (2007) proposed the heat can give rise to dynamic recrystallization in EPR, which can also be observed by the reduction of hardness shown in Table 2. Fig. 7 gives the TEM bright field image and 500 nm aperture SAED of NiTiNb strips after the rolling with the thickness reduction of 20% without and with electropulse. The microstructures of the cold-rolled sample present a lot of plate martensities, which are easily produced for some cold deformation of NiTi alloy. However, due to the thermal and athermal effects of electropulse, the strips underwent dynamic recovery and recrystallization and thus coarse grains were found in the EPR samples. The recrystallization released the inner stress and decreased the work hardening.

Meanwhile, Zhu et al. (2009) concluded that electropulse could accelerate the movement of dislocation and reduce the deformation resistance of the alloys. Sprecher et al. (1986) proposed the collision of high-rate electrons with atomic nuclei produces electron wind, which is beneficial for mobility of dislocations. In this paper, electropulse with a small duration of 72 μs is used to reduce the heat effect and enhance the effect of current on deformability. Commonly, NiTiNb is rolled at 850 °C or rolled after the intermediate annealing at 850 °C reported by Yan et al. (2010). However, by electroplastic rolling, NiTiNb strip can be successfully rolled at a low temperature compared to hot rolling, and the maximum thickness reduction can reach 24% in single pass, as shown in Table 1.

5. Conclusions

NiTiNb strip was successfully rolled from 1.89 to 0.5 mm by EPR at a relatively low temperature compared to the traditional hot rolling. The cold rolling with the total thickness reduction of 47% for three passes makes NiTiNb strip cracked, while in EPR the deformability rate can reach 74%. Meanwhile, it only takes 9.6 s to heat the sample to the required temperature and only a small segment of strips have the temperature be more than 500 °C for 2–3 s. Consequently, good surface can be obtained by the new method as less oxide is produced in the process. The EPR technique thus seems to be promising for manufacturing high quality strip of NiTiNb. Electropulse contributes to the dynamic recrystallization and reduced work hardening, and thus the improvement of plasticity makes it possible for the samples to be rolled at low temperature.

Acknowledgement

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References