# The Effect of Annealing and Cold-drawing on the Super-elasticity of the Ni-Ti Shape Memory Alloy Wire

Lei Xu & Rui Wang (Corresponding author)

School of Textiles, Tianjin Polytechnic University

63 Chenglin Road, Tianjin 300160, China

Tel: 86-20-2452-8294 E-mail: wangrui@tjpu.edu.cn

**Abstract**

Annealing combined with cold-drawing are the necessary method in the processing of Ni-Ti shape memory alloy thin wires. In this paper, the annealing temperature scan of 450~800℃, time scan of 20min~3h and the cold-drawing amount of 6.9%~39% were chosen, and their effects on the thermo and mechanical performance of the Ni-50.5a.t.%Ti alloy wires have been studied. The DSC and tensile-recovery tests were adopted to obtain the phase transformation temperatures and mechanical hysteresis of the Ni-Ti SMA wires with different treatment conditions. The results show that the phase transition temperature of Ni-Ti wire can be changed by varying the annealing temperature and time; cold-drawing deformation and subsequent annealing have a great influence on the super-elasticity. Meanwhile, the surface oxide film and the flake cracks were obtained by SEM scanning. To obtain the best super-elasticity with the maximum cold working amount of 39%, the process with 39% cold drawing amount, 600 ℃ and 20 min annealing is shown to be effective.

**Keywords:** Annealing, Cold-drawing, Super-elasticity, Shape memory alloy, Ni-Ti alloy, Wire

## 1. Introduction

Ni-Ti alloys have been widely used due to their superior shape memory properties, mechanical properties and biocompatibility. Recently, there is a growing interest in the smart structures with embedded Ni-Ti actuators or dampers, thus the wire applications of Ni-Ti alloy become hot spots. The Ni-50~52 a.t.%-Ti alloys usually have super-elasticity at room temperatures. They exhibit unusual good super-elasticities and high damping capacities even they had been processed into ultra-thin wires. These wires can improve the damping of the structures that requiring the passive control the vibration, such as wings and fuselages, has been reported.(Pappada et al., 2009; Li et al., 2010; Ni et al., 2004; Xu et al., 2010).

Ni-Ti alloy exhibits good machinability to stretch, compression, scalability and ductility, but weak tolerance to drawing at high temperatures (above 450℃). On the contrary, it has exactly the opposite performance at low temperatures (below 100℃). So the processing of Ni-Ti alloy thin wire includes the initial thermal processing and the cold-drawing processing. The former is executed in high temperature -- it contains the melting, annealing, rolling and forging. In high temperature process, Ni-Ti alloys can be rolled into about Φ2-3.5mm wires. After the forging treatment, Ni-Ti alloy only gain a semi-super-elasticity due to the low yield strength of their austenite. The later process is the cold work; the wire is further refined and drawn. It is well known that Ni-Ti alloys can be tensile deformed in a ductile manner to more than 50% strain prior to fracture (Liu et al., 2003), but severe strain hardening accompanied by cold-working and wire-drawing hinders their workability. Therefore, annealing treatment is necessary to soften the cold-drawn wire, so that to withstand the tensile in the next mass of drawing.

The cold work of a Ni-Ti super-elastic wire with required fineness always includes multiple drawing–annealing cycles. Drawn-annealing is an effective way to improve the strength of the Ni-Ti austenite and obtained a required super-elasticity.

Most of the research works have focused on the strength and austenite temperature ranges of the Ni-Ti wire (Demersa et al., 2009; Wu et al., 2000, 2004; Zhang et al., 2006 ). Demersa et al. have developed equipment for cold work of the Φ1mm Ni-Ti wire, and optimized the pulling tensions and thickness reduction in a cold rolling. Wu et al. had also done lot work on the transformation temperatures, strength and the surface conditions of the drawn wires.

However, the super-elasticity of the Ni-Ti wire, including the hysteresis loop area, the maximum hysteresis strain and the critical stress of the martensite transformation, plays the most important role for the application use. The use of appropriate thermal - mechanical treatment process may improve the energy dissipation of the super-elastic Ni-Ti wire. The strength and others are not decisive factors but still need taken into consideration. In this paper, a systematic research of the cold-work was made. The effect of cold drawing amount, the annealing temperature and time on the processing of Ni -50.5a.t.%-Ti wire was discussed. The thermo processed Φ2 mm wires were drawn in a die-less drawing machine. The DSC, mechanical hysteresis and surface conditions of the Ni-Ti wire were obtained. The relevant conclusions were made and the optimized annealing for the maximum drawing was proposed.

## 2. Experimental works

### *2.1 Materials and the initial thermal processing*

Spongy titanium (purity, 99.87%) and nickel rods (purity, 99.98%) were blended with the atomic ratio of 49.5: 50.5. The mixture were melted and re-melted by a vacuum induction furnace (ZG-25A) with the protection by an argon atmosphere.

The Ni-Ti ingot was first homogenized at 800℃ for 15 h and then hot rolled into plate with a 15mm thickness, and then by further hot-rolling machine, a plate of 2.5mm thickness was obtained. Finally, the specimens 2.5mm×2.5mm×1000mm were obtained by cutting using wire-cut machine and forged into the Φ2mm wires. The naturally cooled wire was the commercial super-elastic wire and also the raw material for cold-work.

### *2.2 The cold-drawing and annealing*

A die-less drawing was used in this study. The drawing process can be conducted under the controlled speed of 5-10 m/min. The drawing amount of 6.9%, 22%, 31% and 39% were carried. Cold-drawing created a dislocation in the alloy micro structures, thus hardened the wire. To remove the residual stress and obtain a complete super-elasticity, annealing is essential. Different annealing conditions were adopted, the temperature ranges from 450℃ to 800℃, the annealing time varies from 20min to 1h, 2h and 3h, and the atmosphere was air. In the multi-pass cold drawing- annealing process, the annealing temperature and time were kept same for each pass.

### *2.3 Test of phase transformation*

The annealed Ni-Ti super-elastic wire was immersed in the mixture solutions of hydrofluoric acid (HF 30 w.t.%), concentrated nitric acid ($HNO_3$ 65 w.t.%), distilled water (volume ratio of 1:7 : 20) for 20 minutes to remove the surface graphite layer. The transformation behavior of the Ni-Ti wire was tested by using differential scanning calorimeter measurement (PERKIN ELEMER DSC-7, Denmark).Test temperature ranged from -50 to 100℃ with a cooling/heating rate of 6℃/min.

### *2.4 The tensile-recovery test*

The annealed wires were rinsed and processed into tensile specimens. The tensile-recovery test was executed in constant 20℃ by Shimadzu AG-X, Japan. The speed of the free end is 4mm/min, the gauge of the specimen was 30mm and the maximum elongation 1.5mm.

### *2.5 The surface morphology observation*

Despite the protection of graphite glue, Ni-Ti wires still get oxidized by the annealing treatment. The chemical composition of surface material is proved to be $TiO_2$. The thin oxidize layer will not bring any damage to the wire, and it can be removed directly through pickling. When the wires get over-oxidation in annealing, the strength loss will be significant.

After the two-pass of drawing-annealing, the wire samples were polished to get the desired roughness. The samples were etched using the mixture solutions of hydrofluoric acid (HF 30 w.t.%), concentrated nitric acid ($HNO_3$ 65 w.t.%), acetate(HAc 30 w.t.%) (volume ratio of 1:7:20) as an etchant. The microstructures were observed using scanning electron (SEM) microscopes (KYKY-2800, from CAS, China).

## 3. Result and Discussion

### *3.1 The effect of Annealing on the phase transition temperature*

#### 3.1.1 Annealing temperature

Figure 1 shows the effect of the annealing temperature on the phase transformation temperatures of the Ni-50.5 a.t.%-Ti alloy wires. The peak of the curves represent for the phase transformation happened by temperature change. The peaks R, M and A represent the R-phase (rhombohedra crystalline structure), martensite B19 (monoclinic crystalline structure) and the parent phase B2 (the CsC1-typed crystalline structure) phase transition, respectively.

It is convincing that the martensite and the R-phase transition occurs in the cooling stage, while the austenite transition occurs in the heating stage. R-phase is a prominent feature of the Ni-rich Ni-Ti alloys. When the anneal temperature is above 600℃, the cooling process in the R phase transition does not recur. This indicates that the complete annealing temperature of the Ni-50.5 a.t.%-Ti alloy is above 600℃. In these temperatures, the

Ni-Ti wire can obtain a relatively stable microstructure like been re-melted. As the R-phase is mechanical instable, for engineering applications, the annealing temperature of the Ni-50.5 a.t.%-Ti alloy is preferably above 600℃.

As the atom ratio of the alloy is fixed, the shape of the DSC peaks are stable, thus the peak values of the DSC curves indicate a certain phase transition temperatures rather than that of the start and end points of the peaks. Figure 1 also shows that when the annealing temperature ascended from 450℃ to 550℃, the A→R transition temperature slight decreased, the R→M temperature rise and the M→A temperature decreased. When R transition disappears in the temperature span of 600℃~800℃, with the increases of the annealing temperature, the A→M temperatures still increased, but the M→A temperature increased.

The height of the DSC peak indicates the intensity of the phase transition. It is convincing that the A→R and R→M transition will be more intense with the increase of the annealing temperature. The intensity of M→A transition is not affected by the annealing.

3.1.2 Annealing time

Figures 2 and 3 show the phase transitions of the samples annealed for different processing times at 450℃ and 550℃, respectively.

It is seen in figure 2 that the peak of the M→A transition is not clear. This indicates that the annealing temperature of 450℃ can not eliminate the internal stress of the samples. In the cold-drawing, dislocations were generated in the Ni-Ti micro-cells. When the annealing temperature is indeed low, a large many of residual dislocations will create inner stresses and disturb the M→A transition of the samples. The figure 3 shows that the M→A transition peak is clear with the annealing at 550℃. The intensity of the phase transition is greater with a longer annealing time. But when the annealing time exceeds 2h, this effect becomes not significant.

It is believed that the R→M and M→A transition temperature slightly increased with a longer annealing time. The A→R transition is stable with the increase of annealing time. However, compared to the atomic ratio and annealing temperature, the effect of annealing time on the phase transition temperature can be neglected.

*3.2 The effect of drawing amount and annealing on the mechanical hysteresis loop*

To obtain the wire with a finer diameter and reduce the mass of the drawing-annealing cycles, the drawing amount should be as large as possible. However, Ni-Ti alloy wire severely hardened when the drawing amount exceed 30%. On this account, the drawing process is hard to continue. Figure 4 shows the hysteresis loops of the samples after 450℃, 20min after annealing.

It is seen in figure 4 that each specimen have a mechanical hysteresis curve, the area of the hysteresis loop characterize the extent of the super-elasticity. It is believed that the initial phase transition stress is increased by the increasing of the drawing amount. But for 450℃, 20min annealing, the extensive drawing of 39%, the wire was hardened to cause the initial phase transition stress excessively high. The incomplete annealing process can't eliminate the hardening. In the stress recovery, the stress is still very high.

Figure 5 shows the hysteresis loops of the samples with different annealing temperature after 39% drawing. It is seen that the higher annealing temperature cause the lower initial phase transition stress. Because the cold drawn Ni-Ti alloy has massive dislocations, the wire will be softer after being exploded to a higher annealing temperature. The annealing temperature also has obvious influence on the shape of the hysteresis loop: The phase transition yield will become apparent with the increased annealing temperature. When the annealing temperature exceed 600℃ and high up to 800℃, the area of the hysteresis loop will expand. As the annealing temperature too high, the large austenite grains will emerge in the wire, to make the deformation of tensile not completely recovered.

Figure 6 shows the effect of annealing time on the hysteresis of wires. Increase of the annealing time will not significantly enhance the super-elasticity. On the contrary, the excessively long time will generate the internal defects in the wire, which will seriously hinder the deformation from complete recovery.

*3.3 The effect of annealing on the surface oxide film*

Many researches had studied the effect of the oxide film ($TiO_2$) to the mechanical properties of the Ni-Ti wires. The tensile of $TiO_2$ is poor; the oxide film will turn into cracks in the next of drawing pass. So it is considered that a thin oxide film is sufficient for use as a lubricant during the drawing. In contrast, a thick oxide film will damage drawing properties.

Figure 7 shows the surface morphologies of the samples by different annealed. Figures (a) ~ (d) shows the growth of oxide films over time at 450℃, silk surface oxide layer gradually thicken and roughed. As the annealing temperature is low, there are no visible cracks on the surface of the wires. While at a higher temperature of 600℃, as shown in figures (e)~(h), some flake-shaped micro-cracks occurred on the surface of the samples. With the annealing time increasing, cracks gradually get spitted. When the temperature reaches 800℃, as shown in figures (i)~(l), the surfaces of the samples get badly roughed, with time growing, a large number of deep cracks occurred.

Another effect of annealing is the growing of austenite grains. The higher the annealing temperature makes grain size smaller and more uniform. But in a long annealing time, the austenite grains will convergent syntheses into large austenite grain size, which will increase the cracking of the oxide layer. 600℃ is considered appropriate for annealing and the time should not be too long.

## 4. Conclusions

The annealing temperature and time are decisive for the phase transition temperature of the Ni-50.5a.t.%-Ti alloy wire. The A→R transition can be removed by annealing above 600℃. The R→M or A→M transition temperature increases with the increasing of annealing temperature, M-A transition temperature first decreases and then increases with the increasing of annealing temperature.

Cold-drawn deformation and subsequent annealing have great influence on the hysteresis loop of the wire. When the annealing temperature is low (below 500℃), the cold-drawn amount will significantly affect the super-elastic hysteresis. With the annealing temperature increased to fully annealed, the area of the hysteresis loop increases, thus the wire has a better super-elasticity. The impact of annealing time is weak, but long annealing time will prevent the deformation of super-elastic wire from fully recovered.

The surface oxide layer was observed after the samples get annealed. Annealing temperature is considered mostly affects the cracks on the oxide layer, and annealing time has a significant affection on the thickness of the layer. According to the previous discussion results, for the largest drawing amount of 39%, a 600℃, 20 min annealing is appropriate for the cold work of Ni-50.5a.t.%-Ti alloy wire.

## Acknowledgement

The authors would like to thank the foundation of applied basic research programs in Tianjin metropolis, China (08JCYBJC11400). The corresponding author appreciates the assistance provided by the Shinshu University, Japan, during his visit to that institution.

## References

Pappada, S., Gren, P., & Tatar, K. (2009). Mechanical and vibration characteristics of laminated composite plates embedding shape memory alloy superelastic wires. *Journal of Materials Engineering and Performance,* 18, 531-537.

Li, S.R., Yu, W.S., & Batra, R.C. (2010). Free vibration of thermallypre/post-buckled circular thin plates embedded with shape memory alloy Fibers. *Journal of Thermal Stresses*, 33, 79-96.

Ni, Q.Q., Zhang, R.X., Natsuki, T., & Iwamoto, M. (2007). Stiffness and vibration characteristics of SMA/ER3 composites with shape memory alloy short fibers. *Composite Structures*, 79, 501-507.

Xu, L., Wang, R., Yang, Q.H., & Dong, L. (2009). Vibration characteristics of Ni-Ti pseudo-elastic wire inter-weaved fabric composites. *Proceedings of SPIE,* 749323, 1-12.

Liu, Y., Van H.J., Stalmans, R. & Delaey, L. (1997). Some aspects of the properties of NiTi shape memory alloy. *Journal of Alloys and Compounds,* 247, 115-121.

Demers, V., Brailovski, V., Prokoshkin, S.D. & Inaekyan, K.E. (2009). Optimization of the cold rolling processing for continuous manufacturing of nano-structured Ti-Ni shape memory alloys. *Journal of Materials Processing Technology,* 209, 3096-3105.

Wu, S.K., Lin, H.C., Yen, Y.C. & Chen, J.C. (2000). Wire drawing conducted in the r-phase of Ti-Ni shape memory alloys. *Materials Letters,* 46, 175-180.

Chang, S.H., & Wu, S.K. (2004). Textures in cold-rolled and annealed ti50ni50 shape memory alloy. *Scripta Materialia,* 50, 937-941.

Zhang, L., Xie, C., & Wu, J. (2006). Martensitic transformation and shape memory effect of Ti-49 a.t.%-Ni alloys. *Materials Science and Engineering: A,* 438-440, 905-910.

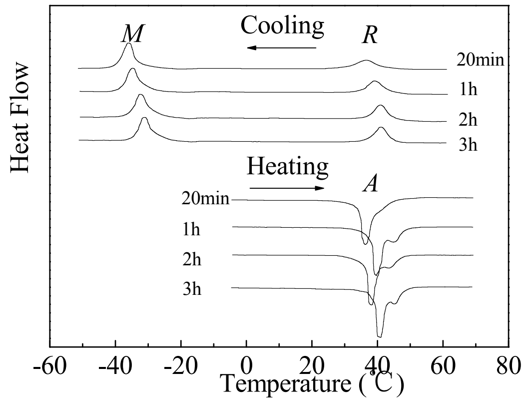



Figure 1. The DSC curves of the Ni-50.5a.t.%-Ti super-elastic wire annealed with different temperatures (annealing time: 20min, cold-drawing amount: 39%)

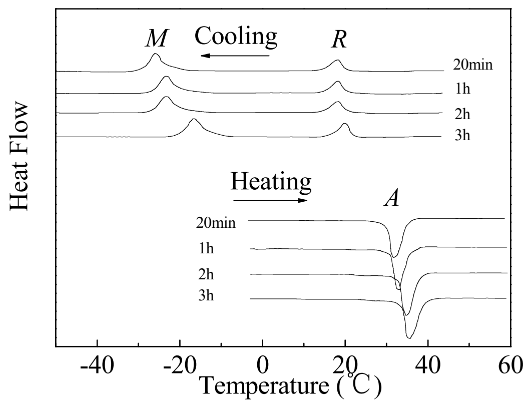



Figure 2. The DSC curves of the Ni-50.5a.t.%-Ti super-elastic wire annealed with different annealing times (annealing temperature: 450℃, cold-drawing amount: 39%)

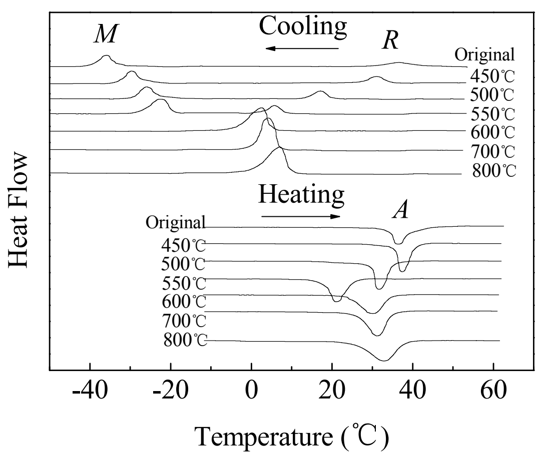
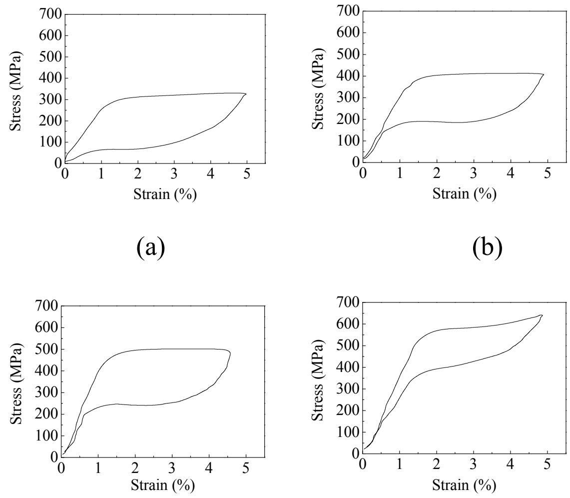


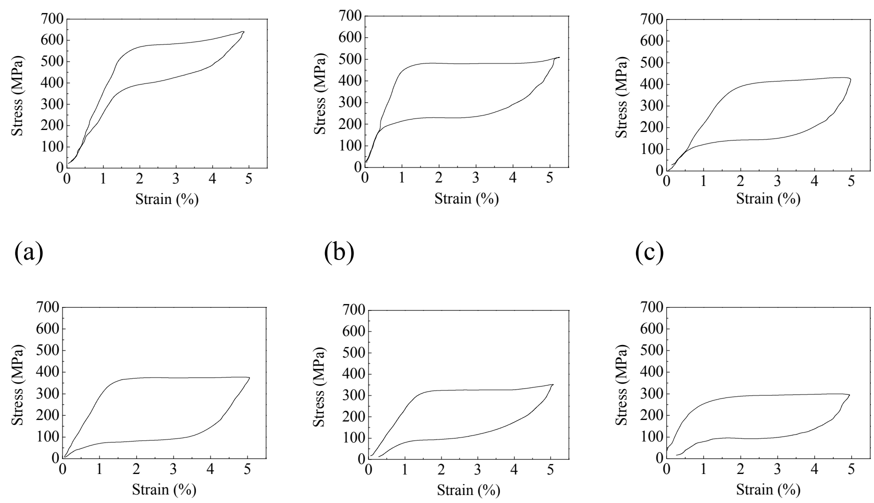

Figure 3. The DSC curves of the Ni-50.5a.t.%-Ti super-elastic wire annealed with different annealing times (annealing temperature: 550℃, cold-drawing amount: 39%)




(a) (b)

(c) (d)

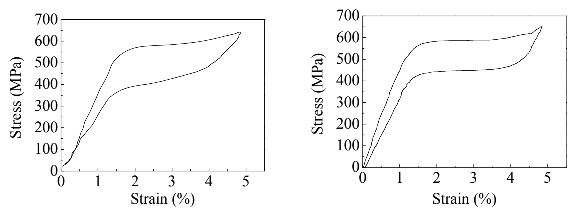
Figure 4. The hysteresis loop of the samples with the cold drawing amount of (a) 6.9%, (b) 22%, (c) 31%, and (d) 39% (annealing at 450 ℃, for 20min)



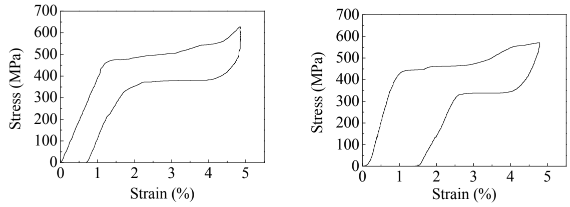

(a) (b) (c)

(d) (e) (f)

Figure 5. The hysteresis loop of the samples with the annealing temperature of (a) 450, (b) 500, (c) 550, (d) 600, (e) 700, and (f) 800 (39% cold drawing, annealing for 20min)

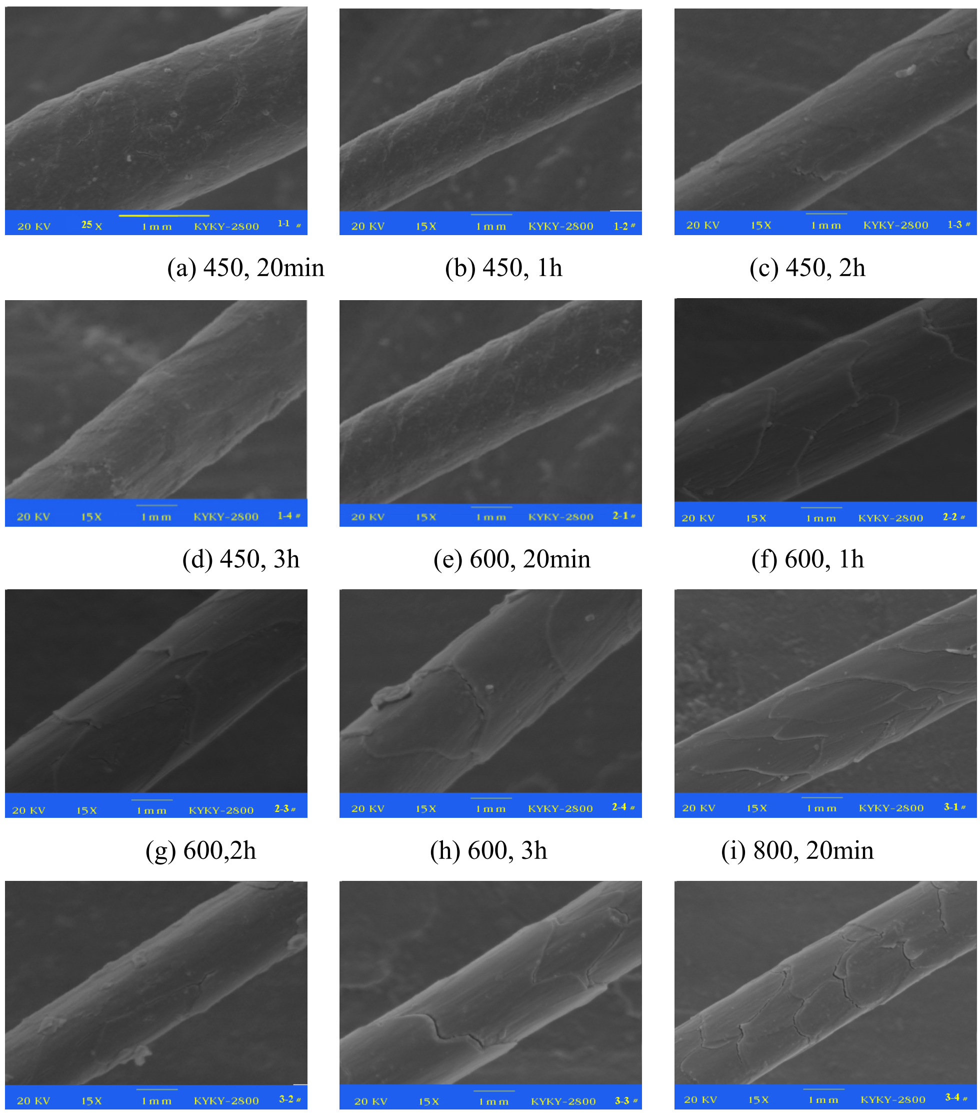



(a) (b)




(c) (d)

Figure 6. The hysteresis loop of the samples with the annealing time of (a) 20min, (b) 1h, (c) 2h, and (d) 3h (39% cold drawing, annealing at 450 ℃)



(a) 450, 20min (b) 450, 1h (c) 450, 2h

(d) 450, 3h (e) 600, 20min (f) 600, 1h

(g) 600,2h (h) 600, 3h (i) 800, 20min

(j) 800, 1h (k) 800, 2h (l) 800, 3h

Figure 7. The surface morphology of Ni-Ti alloy wire after the second mass of annealing (39% cold drawing)