Grain Size Effects on Wear Resistance of Nanocrystalline NiTi Shape Memory Alloy

Hao Yin, Pan Liu and Qingping Sun

Abstract Depending on the property of superelastic behavior, NiTi shape memory alloy shows its good potential as a wear resistance material. The nanocrystalline NiTi shape memory alloy shows different mechanical properties, such as higher hardness, higher transformation stress and higher yield strength, compared to the coarse grain NiTi polycrystal. The wear resistance of nanocrystalline NiTi with the grain sizes of 10, 42 and 80 nm has been studied by using the method of nanowear test. Results show that the phase transformation is suppressed while the grain size decreases, the hardness will replace it to become the major factor in wear resistance, which brings some improvement in the material's wear resistance ability. However, the NiTi with 80 nm grain size still has the strongest resistance to wear so far.

Keywords Grain size • Wear • Nanocrystalline • Shape memory alloy

1 Introduction

Known as a type of smart materials, NiTi shape memory alloy (SMA) has the properties of shape memory effect and superelasticity (SE) (Miyazaki et al. 1983, 1981). Due to its superior recoverable deformation and wear resistance, SE NiTi shape memory alloy is widely used in many fields, such as microelectromechanical systems (MEMS), medical devices etc. (Kahn et al. 1998; Lagoudas 2004). The superelasticity of NiTi SMAs comes from the mechanism of reversible phase

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transition between the austenite phase and martensite phase. Even applied with large external load, SE NiTi SMA can recover from large deformation when the load is removed, accompanied by the stress induced phase transition. Compared with conventional metallic materials, SE NiTi SMA shows excellent wear resistance in many tribological test (Li 1998; Li and Liu 1999; Liang et al. 1996; Lin et al. 1997). Combined with traditional wear resistance materials, SE NiTi get its good place being as the matrix of composite, or the interlayer of thin film (Callisti et al. 2015; Li 2003). Many researches focus on the mechanism of NiTi's outstanding performance during the wear process, and point out that the martensitic phase transformation plays an important role in its wear behavior (Qian et al. 2004; 2005a, b; 2006).

Recently, research shown that when the grain size of NiTi polycrystalline decrease to nanoscale, the mechanical properties will change a lot (Meyers et al. 2006). Over the past decades, changing the grain size of metallic materials to nanoscale is recognized as the significant way to improve the mechanical properties of the raw materials (Li 2011). We manufactured the nanocrystalline NiTi via severe cold-rolling method and certain heat treatment (Nakayama et al. 2001; Tsuchiya et al. 2006). When the austenite finish temperature is lower than the ambient temperature, the NiTi SMA will perform superelastic property. In the wear process, stress induced phase transition plays a significant role and it has a close relationship with the environmental temperature. Phase transition stress increase with increasing temperature (Qian et al. 2004; Sun et al. 2012), and it also relate to the grain size. In the early research, the phase transition will be suppressed when the grain size decreases below 60 nm (Waitz et al. 2004, 2009). Recent research shows that nanocryalline NiTi has smaller latent heat and smaller hysteresis loop, exhibits weaker dependency of strain rate, compared to the coarse grain SE NiTi (Ahadi and Sun 2013, 2014, 2015; Sun et al. 2014). This kind of SE NiTi has potential application in the environment with large temperature variation. Moreover, changing the grain size of SE NiTi will also change its toughness and crack-growth resistance (Ahadi and Sun 2016).

Noticed that the nanocrystalline SE NiTi may have the novel properties compared with conventional one, and the grain size effects on the wear resistance of nanocrystalline NiTi SMA is still unknown. We have manufactured nanocrystalline NiTi with the grain sizes of 10, 42, 80 nm from raw NiTi plates. We check the hardness of nanocrystalline NiTi SMA with different grain size by nanoindentation test. Then we investigate the wear resistance of different grain sizes sample by nanowear method, to find out the grain size effects on their wear resistance behaviors.

2 Experimental Setup

The SE NiTi SMA plates we used were purchased from Nitinol Devices Corporation (NDC, USA) with chemical composition of 50.9 wt% Ti and bal wt% Ni. The raw plates were 1.7 mm in thickness. After annealed in a furnace in the environment of

800 °C, the plates were quenched in cold water and repeatedly cold rolled to reduce the thickness to 1 mm. The samples would be annealed in a furnace at different temperatures and quenched in cold water to produce 10, 42, and 80 nm grain size sample (Ahadi and Sun 2014). The average grain sizes of the samples were measured by the transmission electron microscopy (HRTWM-JEOL 2010F). All types of plates were wire cut into 1 cm × 1 cm small pieces. To get appropriate surface for the nanoindentation and nanowear test, series 800, 1200, 2400 silicon carbide sandpaper were used to polish the samples. After rough polishing, all the samples were fine polished by using diamond suspensions with particle sizes 3, 1, 0.5 and 0.05 μm alumina oxide suspension. Every process took 25 min to ensure effective polishing, to satisfy the requirement of nanoindentation and nanowear test.

The nanoindentation test and nanowear test were conducted by using the triboindenter Ti-950 from Hysitron Inc., USA. Experiments were carried out at room temperature (23 °C). Two Berkovich diamond probes were used in the experiment. One with tip radius 70 nm; the other one with tip radius500 nm. We used the sharp probe in nanoindentation to test the hardness of sample, and used the blunt one in the nanowear test. 3 × 3 array and each point spacing 15 μm indentation were performed on every sample in order to eliminate the random error. The wear zones were set to 5 μm × 5 μm region, in which the probe would scratch along a straight line at the speed of 5 μm/s. A single wear pass contained 256 lines in total. Based on the feedback of tiny normal force (which is set to 2 μm) contacting the surface of samples, the topography of samples surface in 10 μm × 10 μm region would be obtained by the in situ SPM method from Hysitron Ti-950 triboindenter.

3 Results and Discussion

3.1 Mechanical Properties of the Nanocrystalline NiTi Shape Memory Alloy

The sharp Berkovich probe was penetrated the surface of 10, 42 and 80 nm at the speed of 1000 uN/s up to 8000 uN. The tip was hold on by peak force with 10 s in order to eliminate the influence of creep. Then the probe was withdrawn from the samples at the same speed of the loading rate. Corresponding to each grain size samples, we got the relationship between the load and depth in the Fig. 1. From the figure, we could see that the nanocrystalline became harder with the decrease of the grain size. Based on the Oliver and Pharr method (Oliver and Pharr 1992), the hardness could be calculated from the Eq. 1 as followed:

$$H = \frac{P_{\max}}{A_c} \tag{1}$$

where the P_{max} is the maximum loading force, and A_c is the projected area of the contact region (a quantities related to the tip shape geometry and the contact depth).

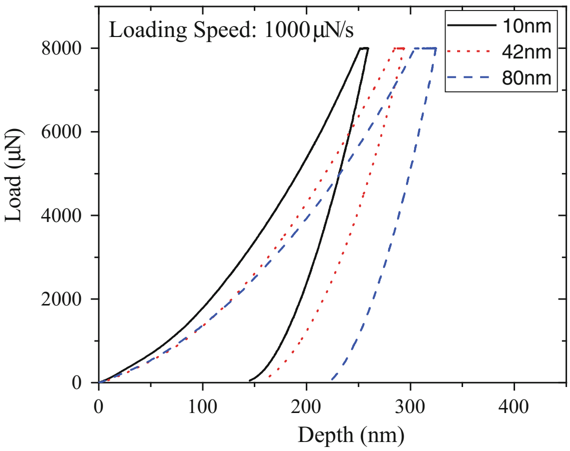

Fig. 1 The loading-unloading curve of the three different grain size samples under nanoindentation tests

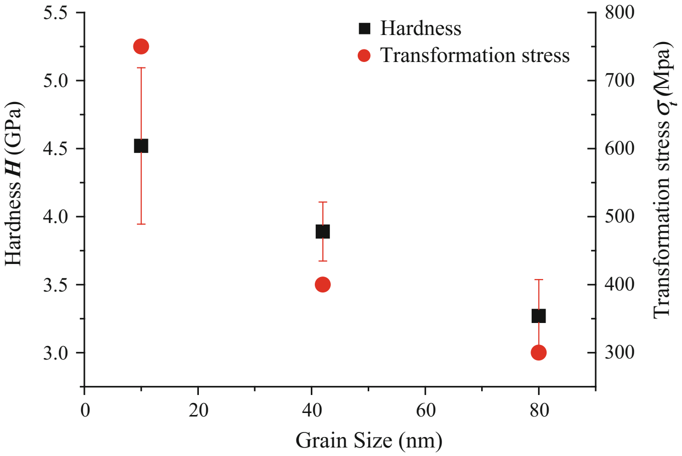

Fig. 2 The hardness and the transformation stress versus the grain size of the materials

The mean value and the standard deviation of the hardness (*H*) were plotted in Fig. 2. Due to the nature of cold rolling, the *H* of 10 nm grain size sample deviated significantly, but still in a reasonable level. We could see that *H* increased monotonically with the decreasing grain size. Since the results came from the experiments conducted at nanoscale, they reflected the properties of samples' microstructure to some extent.

As the earlier studies shows (Li 1998; Schuh et al. 2002), the change in the microstructure of the NiTi alloy will influence its wear resistance behavior. For most of the conventional materials, the wear resistance of the material is mainly related to the hardness. The higher hardness the material has, the stronger ability it will have to resist abrasion. For NiTi, on one hand, the grain refinement to nanoscale can improve the hardness of the material, so the wear resistance of the material should be strengthened; but on the other hand, phase transition plays a significant role in SE NiTi on its wear resistance behavior. When the grain size of the material is so small that the phase transition will be suppressed at the same time, which will adversely affect the wear resistance ability (Qian et al. 2006). As shown in Fig. 2, the transformation stress increased monotonically with the increasing grain size. Thus, we can suppose that the grain size effect will change the ability of wear resistance via changing the hardness and the phase transition behavior of nanocrystalline SE NiTi. However, the changes of these two properties gives opposite effects, so the material's wear resistance behavior depends on the competition between both.

3.2 Wear Resistance of Nanocrystalline NiTi Shape Memory Alloy

The blunt Berkovich, whose tip radius is nearly 500 nm, was used to conduct nanowear test on all the sample surfaces. The nominal force was set to 300 mN. According to Fig. 1, the penetrating depth would be far lower than 500 nm. In this case, only tip portion of the indentation probe kept in contact with the sample, and the geometric asymmetry from the pyramid shape Berkovich probe could be neglected, so the blunt pyramid Berkovich probe could be regarded as a spherical one. In accordance with the settings of the last section, one selected area experiences wear of 1 pass, 3 passes, and 10 passes. The typical topographies of samples' surfaces were obtained from the SPM method and displayed in Fig. 3.

From the Fig. 3, graphs displayed in each column were the initial surface before wear, the surface morphology after wear 1 pass, wear 3 passes and wear 10 passes, respectively. After wear one pass, some shallow volume of the nanocrystalline SE NiTi with 10 nm grain size was ploughed to the edge of the region, or worn from the bulk material (the dark brown area in Fig. 3b). In contrast, the samples with the 42 and 80 nm grain size did not show any different from the initial status, in spite of a shallow mark "⊥", which might be caused by the probe tip scratching when it moved to the initial position across the surface. It hardly made influence on the overall wear resistance behavior of the samples since most area still stayed flat. At the same setting of nominal force, we could say the wear resistance of 42 and 80 nm grain sizes NiTi were better than the 10 nm grain size NiTi after the first pass, this is because the change of surface depth of wear region can reflect the degree of wear. As the wear process went by, the depth increased with the increase in the number of wear passes. Different from the sample with 10 nm grain size, the depth of 42 and 80 nm grain sizes NiTi samples wear region did not change at the first pass; but they were all going to change after three passes, and of course after

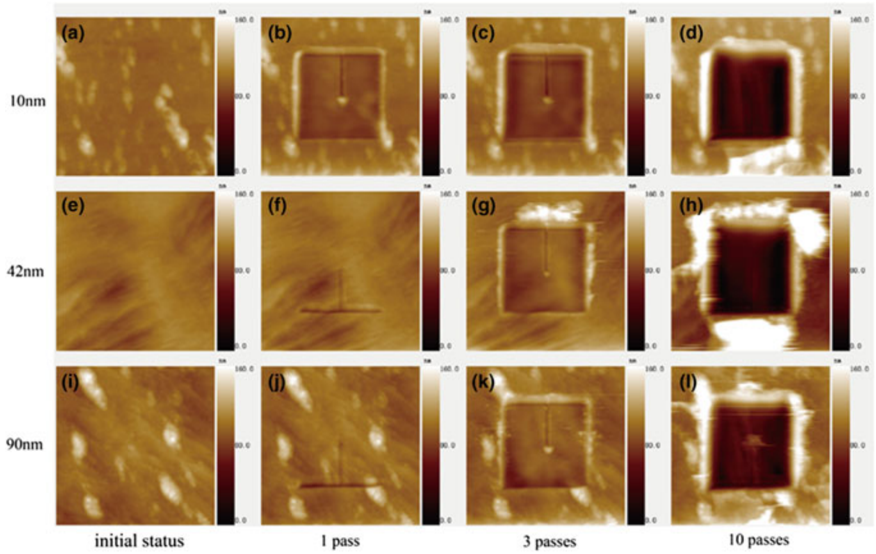

Fig. 3 The initial surfaces and the morphology after 1, 3 and 10 passes of the samples

the tenth pass, which can be seen in Fig. 4a–c. To make the quantitative analysis of the nanowear test, we measured and calculated contours of the same cross-sectional wear area in Fig. 4a–c and showed the average depth of the whole wear region in Fig. 4d. The schematic diagram was shown in Fig. 4e. The data used for the contours of the cross-sectional wear area was selected form the place where the black dash line is.

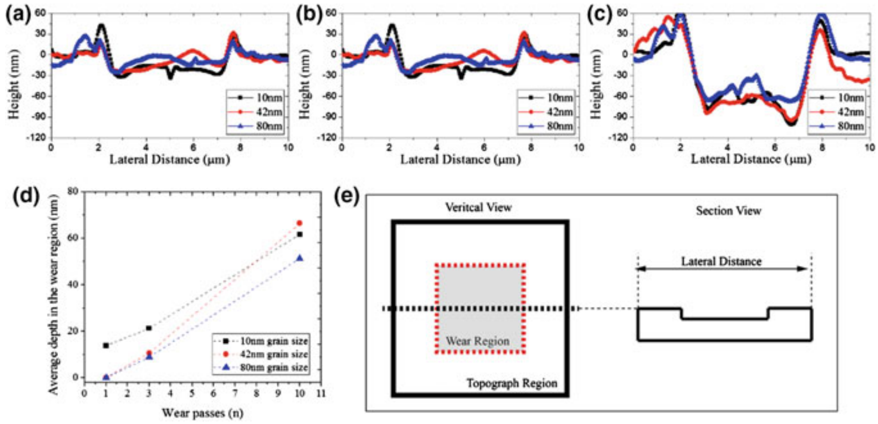

Fig. 4 The surface depth after 1, 3 and 10 passes of the three different grain size samples

From the Fig. 4a, after the first pass wear, the depth of 10 nm grain size NiTi was lower than the other two grain size samples, which meant more abrasion happened on its surface. The contour of other two samples was close to each other, and the contours of the wear region were on the same plane that the region without abrasion. In the Fig. 4b, the contours showed that all the samples have significant wear phenomenon. The degree of wear of 10 nm ample was the highest among all types of grain sizes. After three passes wear, the degree of 42 nm grain size SE NiTi sample was close to the sample with 10 nm grain size, while the samples with the grain size of 80 nm still has the shallowest contour. The wear process was continued until 10 entire passes had been finished. The contours of three grain sizes sample were displayed in the Fig. 4c. The contour of the 42 nm grain size sample's cross-sectional wear region was closed to the outline of the wear region of the 10 nm grain size sample. The sample with 80 nm average grain size had the highest wear resistance ability among the three types of grain sizes. To make a further understanding of the wear depth in the nanowear test, we made a statistic of each grain sizes average depth in every step of passes we set. The depth data in the red dash square were obtained by the SPM method. That is to say, the depth change of the wear region were averaged to a mean value. The final results were show in Fig. 4d. After the first pass of wear, the average depth of 10 nm grain size sample was the largest one among all the samples, while the other ones were closed to zero. When number of passes reached three, all the samples were going to be worn. The wear resistance of all grain sizes NiTi were arrange in the order of 80 nm > 42 nm > 10 nm. When number of passes was up to ten, the trends of depth change showed significant difference, the 42 nm grain size sample had the poorest wear resistance behavior among all the grain sizes samples, but the 80 nm grain size sample still kept the smallest depth among all the samples, the ability of three grain sizes samples were rearranged in the order of 80 nm > 10 nm > 42 nm.

The nanocrystalline NiTi with the 10 nm grain size has the highest hardness than any other grain sizes samples, but it didn't show the best wear resistance ability, especially in the first pass of nanowear process. It seems that the higher hardness does not show any advantage over other larger grain size sample. This is because the harder sample, the more difficult to induce phase transition. In contrast to conventional material, for NiTi SMA, the hardness does not occupy the leading position in the wear resistance, which is used to be the major property that conventional material can resist worn-out from abrasion. What's more, the softest sample with the 80 nm grain size shows ascendant wear resistance than the harder ones. When the grain size is 42 nm, both of hardness and phase transition of the material is suppressed. Though in the first pass, or the early stage or wear process, the 42 nm grain size NiTi may perform better than the 10 nm grained NiTi alloy since it is easier to make phase transition. After long use of material, the 42 nm grain size specimen performs the worst in wear resistance since its phase transition is suppressed and its hardness is not enough to resist the wear. Furthermore, when the wear process goes by, the wear resistance of the 42 nm grain size specimen decreases, also for the 80 nm grain size specimen, evidenced by the gap between it and the 10 nm GS specimen becomes smaller in Fig. 4d. In our point of view, as the wear number increases, the wear section of the specimen experienced ratcheting, which might lead plasticity and residual martensite, and makes the wear resistance property weaker. So, the phase transition becomes much harder than the as received specimen. Meanwhile, for the 10 nm GS specimen, as there is rarely phase transition during wear, its wear resistance property is much more stable, and the hardness is always dominant. When the wear process further continues, phase transition mechanism in 42 and 80 nm GS specimen becomes trivial. Here, we can make a summary that the decrease in grain size will make the nanocrystalline NiTi harder to transform its phase, so the hardness will replace the phase transition, and becoming the control factor of wear resistance.

4 Conclusions

From the results and the discussion above, we can say the grain refinement of nanocrystalline NiTi may not bring significant improvement in the wear resistance, but it can make the wear resistance stable, which is very applicable for long term usage. The grain size affects the wear resistance of nanocrystalline NiTi shape memory alloy via affecting its hardness and phase transition, i.e. the smaller grain will increase the materials' hardness but suppress the phase transition. So, we have the following conclusions:

(1) Both hardness and phase transition will take effect in the process of wear resistance. When the grain size becomes smaller enough, the hardness will replace the phase transition to be the dominant factor of wear resistance.
(2) Results show that the phase transition provides with more positive impact on the wear resistance in the competition with the decrease in hardness.

References

Ahadi A, Sun Q (2013) Stress hysteresis and temperature dependence of phase transition stress in nanostructured NiTi—effects of grain size. App Phys Lett 103(2):021902

Ahadi A, Sun Q (2014) Effects of grain size on the rate-dependent thermomechanical responses of nanostructured superelastic NiTi. Acta Mater 76:186–197

Ahadi A, Sun Q (2015) Stress-induced nanoscale phase transition in supere lastic NiTi by in situ X-ray diffraction. Acta Mater 90:272–281

Ahadi A, Sun Q (2016) Grain size dependence of fracture toughness and crack-growth resistance of superelastic NiTi. Scr Mater 113:171–175

Callisti M, Danek M, Yasuda K, Evaristo M, Tichelaar FD, Cavaleiro A, Polcar T (2015) Ni–Ti(–Cu) shape memory alloy interlayers supporting low friction functional coatings. Tribol Int 88:135–142

Kahn H, Huff MA, Heuer AH (1998) The TiNi shape-memory alloy and its applications for MEMS. J Micromech Microeng 8(3):213–221

Lagoudas DC (2004) Shape memory alloys: modeling and engineering applications, 1st edn. Springer, NewYork

Li DY (1998) A new type of wear-resistant material: pseudo-elastic TiNi alloy. Wear 221(2):116–123

Li DY (2003) Development of novel tribo composites with TiNi shape memory alloy matrix. Wear 255(1–6):617–628

Li DY, Liu R (1999) The mechanism responsible for high wear resistance of pseudo-elastic TiNi alloy—a novel tribo-material. Wear 225:777–783

Li JCM (ed) (2011) Mechanical properties of nanocrystalline materials. Pan Stanford Publishing, Singapore

Liang YN, Li SZ, Jin YB, Jin W, Li S (1996) Wear behavior of a TiNi alloy. Wear 198(1–2):236–241

Lin HC, Liao HM, He JL, Chen KC, Lin KM (1997) Wear charac teristics of TiNi shape memory alloys. Metall Mater Trans A Phys Metall Mater Sci 28(9):1871–1877

Meyers MA, Mishra A, Benson DJ (2006) Mechanical properties of nano crystalline materials. Prog Mater Sci 51(4):427–556

Miyazaki S, Kimura S, Takei F, Miura T, Otsuka K, Suzuki Y (1983) Shape memory effect and pseudoelasticity in a Ti-Ni single crystal. Scr Metall 17(9):1057–1062

Miyazaki S, Otsuka K, Suzuki Y (1981) Transformation pseudoelasticity and deformation behavior in a Ti-50.6 at%Ni alloy. Scr Metall 15(3):287–292

Nakayama H, Tsuchiya K, Umemoto M (2001) Crystal refinement and amor phisation by cold rolling in TiNi shape memory alloys. Scripta Mater 44(8):1781–1785

Oliver WC, Pharr GMJ, WC Oliver (1992) An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation. J Mater Res 7:1564. J Mater Res, 7(6):1564–1583

Qian L, Sun Q, Xiao X (2006) Role of phase transition in the unusual micro wear behavior of superelastic NiTi shape memory alloy. Wear 260(4–5):509–522

Qian L, Xiao X, Sun Q, Yu T (2004) Anomalous relationship between hard ness and wear properties of a superelastic nickel–titanium alloy. Appl Phys Lett 84(7):1076

Qian L, Zhou Z, Sun Q (2005a) The role of phase transition in the fretting behavior of NiTi shape memory alloy. Wear 259(1–6):309–318

Qian LM, Sun QP, Zhou ZR (2005b) Fretting wear behavior of superelastic nickel titanium shape memory alloy. Tribol Lett 18(4):463–475

Schuh CA, Nieh TG, Yamasaki T (2002) Hall-Petch breakdown mani fested in abrasive wear resistance of nanocrystalline nickel. Scripta Mater 46(10):735–740

Sun Q, Aslan A, Li M, Chen M (2014) Effects of grain size on phase tran sition behavior of nanocrystalline shape memory alloys. Sci China Technol Sci 57(4):671–679

Sun QP, Zhao H, Zhou R, Saletti D, Yin H (2012) Recent advances in spatiotemporal evolution of thermomechanical fields during the solid–solid phase transition. C R Mec 340(4–5):349–358

Tsuchiya K, Inuzuka M, Tomus D, Hosokawa A, Nakayama H, Morii K, Umemoto M (2006) Martensitic transformation in nanostructured TiNi shape memory alloy formed via severe plastic deformation. Mater Sci Eng A 438–440:643–648

Waitz T, Kazykhanov V, Karnthaler HP (2004) Martensitic phase transformations in nanocrystalline NiTi studied by TEM. Acta Mater 52(1):137–147

Waitz T, Tsuchiya K, Antretter T, Fischer FD (2009) Phase transformations of nanocrystalline martensitic materials. MRS Bull 34(11):814–821