Spherical Indentation of NiTi-based Shape Memory Alloys

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Abstract

In this study, spherical indentation responses of room temperature superelastic (homogenized Ni_{50.8}Ti_{49.2} and 400°C 3h aged Ni_{45.3}Ti_{29.7}Hf₂₀Pd₅) and nonsuperelastic (Ni_{49.9}Ti_{50.1} and 600°C 3h aged Ni_{45.3}Ti_{29.7}Hf₂₀Pd₅) are revealed as functions of maximum loading level in nano and macro scales. Experimental results showed that for all alloys, the depth and work recovery ratio decrease and then saturate with $h_{\max}/R$. In contrast, indentation hardness increases and then saturates with indentation depth. Both NiTi and NiTiHfPd alloys have higher hardness in austenite than in martensite. NiTiHfPd alloys have a higher indentation hardness than NiTi alloys which was attributed to the higher strength of NiTiHfPd alloys.

Keywords: Spherical indentation; shape memory alloys; Hardness; NiTi, NiTiHfPd alloys; Phase transformation.

1. Introduction:

Shape memory alloys are well known for their unique properties such as shape memory effect (SME) and superelasticity (SE), where they can recover large deformations through reversible phase transformations. The most well-known shape memory alloys is NiTi since it has good ductility and large transformation strain (8%) that makes them suitable for many commercial applications such as actuators, sensors, dampers, sealing elements, couplers, biomedical devices and electrical components [1, 2]. However, low transformation temperatures (<100° C) and strength (<700MPa) of near-equiatomic NiTi alloys limit a wider use of their

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applications in high temperatures or strength environments [3]. Ni-rich NiTi shape memory alloys have better superelasticity and shape memory properties than near equiatomic NiTi shape memory alloys [4]. Aging and composition alteration can be employed to increase the strength and control their transformation temperatures to result in superelasticity at room temperature [4-9]. Recently, quaternary alloy $\text{Ni}_{45.3}\text{-Ti}_{29.7}\text{-Hf}_{20}\text{-Pd}_5$ (at.%) was developed where full strain recovery in superelasticity and shape memory effect without significant plastic deformation was observed at high stress levels (> 1 GPa). Moreover, they have high damping capacity (30-34J) , and their shape memory properties can be controlled by aging and orientation selection [9-13].

The design of SMA-based micro-electro-mechanical systems (MEMS) and elaborate medical devices require the characterization of material performance on small-scale system instead of bulk materials. Consequently, tools that can quickly and accurately interpret the mechanical properties on small-scale materials are required to be assembled [14]. One method to extract small-scale mechanical properties of metals is the instrumented indentation techniques. Indentation testing is usually carried out using an indenter whose material properties (e.g. elastic modulus and hardness) are known [15]. The most popular indenters used for nanoindentation are spherical or pyramidal (e.g. Berkovich) indenters. Spherical indenters are popular since they can produce a smooth transition from elastic to elastic-plastic contact and also produce compatible and repeatable indents at a single location. In recent years, spherical indentation techniques have been considered as a standard method of measuring the hardness of materials [15-17]. A popular method of measuring contact areas, hardness, and elastic modulus by instrumented indentation techniques was introduced in 1992 by Oliver and Pharr, and it has been widely used to characterize small-scale mechanical properties [18]. A numerical derivation was also observed to

explain the relationship between these mechanical properties [19]. Since then, numerous refinements and reinventions were brought out to understand the mechanics of elastic-plastic contact as well as the loading and unloading curves [20].

It has been shown that superelastic NiTi alloys have large recoverable depths [21], where the depth recovery ratio of a superelastic NiTi was about 45% for Berkovich (~200mN) and 95% for spherical (~2.75N) indenters [22]. Thus, it can be concluded that extensive plastic deformation can be omitted and superelasticity can be detected much easier by using a spherical indenter [22]. There are several studies on the indentation-induced shape memory and superelastic effects in NiTi thin films [23-25]. The shallow spherical indents in austenitic NiTi can fully recover upon unloading, while indents in martensite can partially recover after unloading and fully recover occurs upon heating to austenite phase, which is also known as 'self-healing' effect [26]. In this study, the spherical indentation responses of high strength NiTiHfPd and conventional NiTi alloys in austenite and martensite are systematically determined and then compared with their bulk behavior. This is a first indentation study on high strength NiTiHfPd alloys.

2. Experimental procedure:

Three alloys with the nominal compositions of $\text{Ni}_{49.9}\text{Ti}_{50.1}$, $\text{Ni}_{50.8}\text{Ti}_{49.2}$, and $\text{Ni}_{45.3}\text{Ti}_{29.7}\text{Hf}_{20}\text{Pd}_5$ were used in this study. The alloys were electrical-discharge machined to a standard compression sample (4mm*4mm in cross section and 8mm in length). Mechanical testing was conducted in an MTS Landmark servo hydraulic test platform with a 100kN load cell. Transformation temperatures were determined by using a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC). The surface roughness of samples were reduced to 0.05 μm in five

steps by using Buehler EcoMet 250 Grinder-Polisher with an AutoMet 250 Power head. Vickers hardness values were determined by using Sun-Tec model FM-7 microhardness test equipment, and they were performed with a 100 gf force and 15 seconds dwell time. Spherical indentation tests were conducted by using a conical diamond indenter with a spherical tip of 5 μm in radius, and the maximum testing load was 500 mN. Indentation experiments were done by using the Nano Test Vantage indentation instrument from Micro Material Ltd. Hardness was calculated by dividing the force to the contact area and elastic modulus was calculated from the initial stage of the unloading curve by using the Nano Vantage Software.

Figure 1 shows a representative loading and unloading curve where the important indentation parameters are shown. The recoverable work energy, W_e , can be obtained by integrating the unloading curve, where L is the applied load, D is the penetration depth, D_{max} is the maximum depth, and D_r is the recovery depth. Total deformation energy, W_t , is the area under the loading curve. The area between the loading and unloading curve shows the irrecoverable work, W_{irr} , also known as dissipation energy. The ratio of the recoverable energy to the total energy is defined as η_w , which can be expressed as:

$$\eta_w = \frac{W_e}{W_t} = \frac{\int_{D_r}^{D_{\text{max}}} F dD}{\int_0^{D_{\text{max}}} F dD} \quad (1)$$

Figure 1. Indentation loading and unloading curve with important indentation parameters.

3. Results

With a cone angle of 60 degree, according to Cheng and Cheng's analysis on tip geometry [27], the spherical tip results in a maximum spherical contact depth of $h=2.5\mu\text{m}$ for the spherical tip of $5\mu\text{m}$ in radius. Thus, indentation depths deeper than $2.5\mu\text{m}$ (or $h_{\text{max}}/R>0.5$) will not result in perfect spherical contact. Table 1 lists h_{max}/R of NiTi and NiTiHfPd alloys at selected load levels from 10mN to 500mN. The results with $h_{\text{max}}/R>0.5$ are indicated in red in table 1 and will not be taken into consideration for the recovery ratio analysis in this paper. However, they will be used in the hardness section for discussions.

Table 1. Calculated h_{max}/R of NiTi and NiTiHfPd alloys at selected load level of 10mN, 25mN, 50mN, 100mN, 250mN, and 500mN.

Load (mN)\ h_{max}/R	NiTi-M	NiTi-A	NiTiHfPd-M	NiTiHfPd-A
10 mN	0.042	0.032	0.025	0.021
25 mN	0.091	0.066	0.049	0.040
50 mN	0.147	0.113	0.085	0.070
100 mN	0.258	0.211	0.153	0.126
250 mN	0.652	0.534	0.353	0.300
500 mN	1.311	1.035	0.720	0.626

The martensite and austenite start and finish temperatures (M_s , M_f , A_s and A_f , respectively) of NiTi and NiTiHfPd alloys are determined from DSC responses and summarized in Table 2. It has been found that Ni_{49.9}Ti_{50.1} and 600°C-3h aged NiTiHfPd alloys are martensite while Ni_{50.8}Ti_{49.2} and 400°C -3h aged NiTiHfPd alloys are austenite at room temperature. For simplicity, Ni_{49.9}Ti_{50.1} and 600°C -3h aged NiTiHfPd will be named as (NiTi-M) and (NiTiHfPd-M), respectively, while 1000°C -2h aged Ni_{50.8}Ti_{49.2} and 400°C -3h aged NiTiHfPd are named as (NiTi-A) and (NiTiHfPd-A), respectively, throughout the text. It should be noted that A_f of both NiTi-A and NiTiHfPd-A are below room temperature indicating that these alloys show superelasticity at room temperature. Table 2 also shows the conventional Vickers hardness results of the alloys tested. The original unit of Vickers hardness (HV) were converted to GPa. NiTiHfPd alloys show higher Vickers hardness than NiTi alloys, and NiTiHfPd-A has the highest hardness of 4.54 GPa. It was found that NiTi-A and NiTiHfPd-A have higher Vickers hardness than NiTi-M and NiTiHfPd-M, respectively.

Table 2. Transformation temperatures observed from DSC and Vicker's hardness at room temperature for NiTi and NiTiHfPd alloys:

	Ms (°C)	Mf (°C)	As (°C)	Af (°C)	Phase at room temperature	Vickers hardness (GPa)
NiTi-M	78	45	85	122	Martensite	2.37
NiTi-A	-15	-34	-4	10	Austenite	2.19
NiTiHfPd-A	-90	-114	-23	-9	Austenite	4.54
NiTiHfPd-M	95	63	110	160	Martensite	4.14

Figure 2 shows the compressive responses of all four selected alloys at room temperature.

NiTiHfPd-A and NiTi-A show their superelasticity. It should be noted that NiTiHfPd-A has full strain recovery without any plastic deformation after being loaded to an extreme high stress level of 1.4 GPa. This unique polycrystalline alloys also present a very high damping capacity (30-34 J-cm⁻³), high work output (30-35 J-cm⁻³) and high mechanical hysteresis (900 MPa). NiTi-M and NiTiHfPd-M show martensite reorientation upon loading which does not fully recover back upon unloading.

Figure 2. Superelastic experiment results of NiTi and NiTiHfPd alloys on bulk material.

Figure 3(a) shows the selected load-displacement (L-D) curves for the spherical indentation of NiTi-A and NiTi-M alloys where samples were loaded till the selected load levels of 10, 25 and 50mN, and then unloaded at room temperature. Significant differences in the indentation response of the two NiTi alloys are the work recoverable ratio and hardness. The work recoverable ratio of NiTi-M and NiTi-A are calculated to be 32.4% and 50.3%, respectively, under 50mN loading. It clearly shows that NiTi-A with superelasticity (SE) behavior has a higher work recoverable ratio than that of NiTi-M. In superelasticity, austenite transforms to martensite during loading and martensite transforms back to austenite during unloading, while martensite reorientation occurs during loading and it does not recover back after unloading for the martensitic SMAs tested at temperatures below A_s . Thus, superelastic NiTi-A performs a higher recoverable ratio than NiTi-M. Figure 3(b) presents L-D curves of NiTiHfPd alloys at selected loads of 10, 25 and 50mN. The indentation curve demonstrates superelasticity with a hysteresis loop at load level of 10mN, which means that the material transformed to martensite in the loading process can transform completely back to the original austenite state. Similar behavior was observed previously in NiTi alloys with superelasticity [22, 28-30]. The work recoverable ratios of NiTiHfPd-M and NiTiHfPd-A were calculated as 65.4%, and 97% at the load level of 10mN. At higher load level (100, 250 and 500mN), load-displacement curves were plotted as Figure 3 (c) and (d) for the NiTi and NiTiHfPd alloys, respectively. It can be observed that work recovery ratios at high loads are much smaller than ones at low loads. Figure (c) shows deeper indentation depth than Figure (d) which indicates that NiTiHfPd alloys are harder than NiTi alloys.

Figure 3. Nano-indentation results of typical load-displacement relationships. Load-displacement curve of (a) NiTi-M and NiTi-A at 10mN, 25mN, and 50mN (b) NiTiHfPd-M and NiTiHfPd-A at 10mN, 25mN, and 50mN (c) NiTi-M and NiTi-A at 100, 250 and 500mN (d) NiTiHfPd-M and NiTiHfPd-A at 100, 250 and 500mN.

4. Discussion:

4.1. Work/Depth recovery

Figure 4 summarizes the work recovery ratio of NiTi and NiTiHfPd alloys as a function of h_{max}/R . Data were calculated from the typical load-displacement curves show in figure 3. It shows that W_e/W_t decreases quickly and then saturates with the h_{max}/R for all the alloys. Moreover, at the same h_{max}/R , it is observed that alloys with SE behavior (NiTi-A and NiTiHfPd-A) have higher work recovery ratio than non-SE alloys (NiTi-M and NiTiHfPd-M). The work recovery ratio of NiTiHfPd-A is the highest. Work recovery ratios saturate to a plateau of 0.2 as h_{max}/R reaches to about 0.5. It should be noted that $h_{max}/R=0.5$ was calculated as a spherical contact limit. This can be attributed to the plastic deformation that impedes martensite to austenite back transformation. At low load levels, plastic deformation can be avoided which result in high recovery ratio. In the alloys with superelastic behavior, the recovery ratio is higher since in addition to classical elastic recovery they have the ability to demonstrate recovery due to back transformation during unloading. The plastic deformation increases with load levels and prevents the back transformation of stress induced martensite which results in lower work recovery ratio.

Figure 4. Work recoverable ratios as a function of h_{max}/R of NiTi and NiTiHfPd alloys. Data were calculated from six load levels of 10mN, 25mN, 50mN, 100mN, 250mN and 500mN.

Table 3 demonstrates the depth recovery ratios of spherical indentation in NiTi and NiTiHfPd alloys. It is clear that depth recovery ratio of NiTiHfPd-A and NiTi-A are higher than NiTiHfPd-M and NiTi-M, respectively. The depth recovery has the same behavior as work recovery where it decreases as a function of indentation depth. Such of decrease was also reported on SE NiTi spherical indents by using FEM modeling and experiments [28].

Table 3. Depth recovery ratio of spherical indents on NiTi and NiTiHfPd alloys at selected load levels.

Indentation load (mN)		10	25	50	100	250	500
Depth recovery ratio %	NiTi-M	0.466	0.431	0.396	0.374	0.377	0.349
	NiTi-A	0.773	0.719	0.647	0.501	0.318	0.187
	NiTiHfPd-M	0.748	0.62	0.549	0.417	0.3	0.189
	NiTiHfPd-A	0.952	0.865	0.742	0.583	0.437	0.279

Figure 5 shows the depth recovery ratio of current NiTi and NiTiHfPd alloys and the modeling results from Zhang *et al* [28] as a function of maximum indentation depth. Depth recovery ratios of those four alloys behave the same way as work recovery ratios where they initially decrease and then saturate beyond the maximum spherical indentation depth of 2.5 μm . The experimental results are in good agreement with the modeling results of superelastic NiTi alloy.

Figure 5. Depth recovery ratio as function of maximum indentation depth for NiTi and NiTiHfPd alloys.

Zhang's results from modeling of superelastic NiTi were added for comparison [28].

4.2. Dimensionless analysis of L-D.

Figure 6 shows the non-dimensional load-displacement curves which correspond to load-displacement results shown in Figure 3. Dimensionless analysis provides a better understanding of unloading curves than the traditional load-displacement curves. Figure 6 (a), (b), and (c) are the non-dimensional L-D curves of NiTi alloys at selected load levels of 10, 25, and 50mN,

respectively. $F_{\max}$ is the maximum force applied during loading, $h_{\max}$ is the maximum depth the indenter reached during the indentation processing. F and h represent the applied load and depth, respectively. It clearly shows from figure 6 (a), (b) and (c) that NiTi-A has a larger back recovery during unloading than NiTi-M which results in higher work recoverable ratio. Figure (d), (e) and (f) present non-dimensional L-D curves of NiTiHfPd alloys at selected load levels of 10, 25, and 50mN. Similar to NiTi, NiTiHfPd-A has a larger work recovery ratio than NiTiHfPd-M. It should also be mentioned that almost perfect shape recovery observed in NiTiHfPd-A at load level of 10mN (Figure 6(d)), which proves the perfect SE behavior. Increasing load level results in reduced work recovery for NiTi and NiTiHfPd alloys.

Figure 6. The corresponding dimensionless load-displacement curves (a) NiTi alloys at 10mN, (b) NiTi alloys at 25mN, (c) NiTi alloys at 50mN, (d) NiTiHfPd alloys at 10mN, (e) NiTiHfPd alloys at 25mN, (f) NiTiHfPd alloys at 50mN.

4.3. Hardness

Figure 7 shows the spherical hardness as a function of maximum indentation depth. It shows the hardness values of NiTi and NiTiHfPd alloys as a function of indentation depth that is calculated from the load-displacement curves from Figure 3. It should be noted that the maximum depth is proportional to the applied maximum load. The spherical hardness significantly depends on the indentation depth and the average hardness value increases with increasing indentation depth, and saturates at higher loads. This depth dependent behavior of spherical hardness of NiTi SMAs is the opposite of the hardness values obtained by sharp indenter[31]. The increase in the spherical hardness can be explained by the increase in the transformed region and plastic deformation during loading. Equation (2) is the well-known Hertz's theory for a purely elastic contact on a material without any phase transition, where the spherical hardness H can be expressed as:

$$H =$$

(2)

where E is the elastic modulus, $\nu=0.3$ is the Poisson's ratio, and R is the spherical tip radius, h is the indentation depth. Evidently, Eq (2) indicates that spherical hardness increases with the square root of indentation depth ($h^{1/2}$) for a purely linear elastic material. Eq (2) cannot be directly applied to NiTi SMAs due to the phase transformation. However, a recent report revealed that the spherical hardness of NiTi is proportional to indentation depth (h) if the phase transformation involved during indentation loading[32].

The spherical hardness of NiTi and NiTiHfPd alloys show a good agreement with literature where hardness increases with indentation depth, but the increase is not proportional to h or $h^{1/2}$. Indentation at austenite phase can result in phase transformation to martensite, and hardness of both phases contributes to the overall hardness. In this study, both NiTi and NiTiHfPd alloys have higher hardness in austenite than martensite. NiTiHfPd-A has the highest hardness and NiTiHfPd alloys are harder than the NiTi alloys at the selected indentation depth. This observation is in good agreement with the mechanical results where the extreme high strength levels were observed in NiTiHfPd alloys as shown in figure 2. Vickers hardness results were also included in table 2. It also shows that NiTiHfPd alloys have higher Vickers hardness values than the NiTi alloys, and indeed, NiTiHfPd-A possess the highest Vickers hardness. These observations from Vickers hardness experiments are in good agreement with the nanoindentation hardness.

Figure 7. Hardness vs. maximum depth relationship of NiTi and NiTiHfPd alloys. Data were calculated at selected load of 10mN, 25mN, 50mN, 100mN, and 250mN.

5. Conclusion:

This paper explores the spherical indentation responses of room temperature superelastic (homogenized $\text{Ni}_{50.8}\text{Ti}_{49.2}$ and 400°C 3h aged $\text{Ni}_{45.3}\text{Ti}_{29.7}\text{Hf}_{20}\text{Pd}_5$) and nonsuperelastic ($\text{Ni}_{49.9}\text{Ti}_{50.1}$ and 600°C 3h aged $\text{Ni}_{45.3}\text{Ti}_{29.7}\text{Hf}_{20}\text{Pd}_5$) alloys. Major findings can be summarized as follows:

1. At low load level of 10mN, almost perfect work recovery (97%) and depth recovery (95.2%) obtained in NiTiHfPd-A, and NiTiHfPd-M shows 65.4% of work recovery and 74.8% of depth recovery. In addition, NiTi-M has the lowest work recovery (50%) and depth recovery (46.6%) while NiTi-A shows 71% of work recovery and 77.3% depth recovery.
2. Alloys with SE behavior (NiTi-A and NiTiHfPd-A) have higher hardness and work recoverable ratio than non-SE alloys (NiTi-M and NiTiHfPd-M) at the same indentation

depth.

3. The highest spherical indentation hardness was observed in NiTiHfPd-A which has extreme high strength of 2GPa.
4. The work recoverable ratio decreases with increasing h_{max}/R due to the fact that at shallow indentation depths (corresponds to low loads) mainly elastic deformation (and reversible phase transformation) takes place which results in high recovery ratio. For deep indentations, plastic deformation impedes the back phase transformation and results in partial work recovery.

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References:

- [1] D.C. Lagoudas, Shape memory alloys, Science and Business Media, LLC, (2008).
- [2] T. Duerig, R. Zadno, An engineer's perspective of pseudoelasticity, Butterworth-Heinemann, Engineering Aspects of Shape Memory Alloys(UK), 1990, (1990) 369-393.
- [3] K. Otsuka, X. Ren, Physical metallurgy of Ti–Ni-based shape memory alloys, Progress in materials science, 50 (2005) 511-678.
- [4] H. Karaca, I. Kaya, H. Tobe, B. Basaran, M. Nagasako, R. Kainuma, Y. Chumlyakov, Shape memory behavior of high strength Ni₅₄ Ti₄₆ alloys, Materials Science and Engineering: A, 580 (2013) 66-70.
- [5] J. Ma, I. Karaman, R.D. Noebe, High temperature shape memory alloys, International Materials Reviews, 55 (2010) 257-315.
- [6] P. Potapov, A. Shelyakov, A. Gulyaev, E. Svistunov, N. Matveeva, D. Hodgson, Effect of Hf on the structure of Ni-Ti martensitic alloys, Materials Letters, 32 (1997) 247-250.
- [7] H.E. Karaca, S.M. Saghaian, G. Ded, H. Tobe, B. Basaran, H.J. Maier, R.D. Noebe, Y.I.

Chumlyakov, Effects of nanoprecipitation on the shape memory and material properties of an Ni-rich NiTiHf high temperature shape memory alloy, *Acta Materialia*, 61 (2013) 7422-7431.

[8] H.Y. Kim, T. Jinguu, T.-h. Nam, S. Miyazaki, Cold workability and shape memory properties of novel Ti–Ni–Hf–Nb high-temperature shape memory alloys, *Scripta Materialia*, 65 (2011) 846-849.

[9] H.E. Karaca, E. Acar, H. Tobe, S.M. Saghaian, NiTiHf-based shape memory alloys, *Materials Science and Technology (United Kingdom)*, 30 (2014) 1530-1544.

[10] H.E. Karaca, E. Acar, G.S. Ded, B. Basaran, H. Tobe, R.D. Noebe, G. Bigelow, Y.I. Chumlyakov, Shape memory behavior of high strength NiTiHfPd polycrystalline alloys, *Acta Materialia*, 61 (2013) 5036-5049.

[11] E. Acar, H. Tobe, I. Kaya, H.E. Karaca, Y.I. Chumlyakov, Compressive response of Ni_{45.3}Ti_{34.7}Hf₁₅Pd₅ and Ni_{45.3}Ti_{29.7}Hf₂₀Pd₅ shape-memory alloys, *Journal of Materials Science*, 50 (2015) 1924-1934.

[12] E. Acar, H.E. Karaca, B. Basaran, F. Yang, M.J. Mills, R.D. Noebe, Y.I. Chumlyakov, Role of aging time on the microstructure and shape memory properties of NiTiHfPd single crystals, *Materials Science and Engineering: A*, 573 (2013) 161-165.

[13] H.E. Karaca, E. Acar, B. Basaran, R.D. Noebe, Y.I. Chumlyakov, Superelastic response and damping capacity of ultrahigh-strength [111]-oriented NiTiHfPd single crystals, *Scripta Materialia*, 67 (2012) 447-450.

[14] K. Gall, K. Juntunen, H.J. Maier, H. Sehitoglu, Y.I. Chumlyakov, Instrumented micro-indentation of NiTi shape-memory alloys, *Acta Materialia*, 49 (2001) 3205-3217.

[15] A.C. Fischer-Cripps, *Nanoindentation*, Springer, 2011.

[16] D. Tabor, *The hardness of metals*, ClarendonP, 1951.

[17] B.W. Mott, *Micro-indentation hardness testing*, Butterworths Scientific Publications, 1956.

[18] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *Journal of materials research*, 7 (1992) 1564-1583.

[19] C.-M. Cheng, Y.-T. Cheng, On the initial unloading slope in indentation of elastic-plastic solids by an indenter with an axisymmetric smooth profile, *Applied physics letters*, 71 (1997) 2623-2625.

[20] W.C. Oliver, G.M. Pharr, Measurement of hardness and elastic modulus by instrumented

indentation: Advances in understanding and refinements to methodology, *Journal of materials research*, 19 (2004) 3-20.

[21] R. Liu, D. Li, Y. Xie, R. Llewellyn, H. Hawthorne, Indentation behavior of pseudoelastic TiNi alloy, *Scripta Materialia*, 41 (1999) 691-696.

[22] W. Ni, Y.-T. Cheng, D.S. Grummon, Microscopic superelastic behavior of a nickel-titanium alloy under complex loading conditions, *Applied Physics Letters*, 82 (2003) 2811.

[23] W. Ni, Y.-T. Cheng, D.S. Grummon, Microscopic shape memory and superelastic effects under complex loading conditions, *Surface and Coatings Technology*, 177-178 (2004) 512-517.

[24] X.-G. Ma, K. Komvopoulos, Nanoscale pseudoelastic behavior of indented titanium–nickel films, *Applied physics letters*, 83 (2003) 3773-3775.

[25] Y.J. Zhang, Y.T. Cheng, D.S. Grummon, Indentation stress dependence of the temperature range of microscopic superelastic behavior of nickel-titanium thin films, *Journal of Applied Physics*, 98 (2005).

[26] W. Ni, Y.-T. Cheng, D.S. Grummon, Recovery of microindents in a nickel–titanium shape-memory alloy: a “self-healing” effect, *Applied physics letters*, 80 (2002) 3310-3312.

[27] Y.-T. Cheng, C.-M. Cheng, Further analysis of indentation loading curves: Effects of tip rounding on mechanical property measurements, *Journal of Materials research*, 13 (1998) 1059-1064.

[28] Y. Zhang, Y.-T. Cheng, D.S. Grummon, Finite element modeling of indentation-induced superelastic effect using a three-dimensional constitutive model for shape memory materials with plasticity, *Journal of Applied Physics*, 101 (2007) 053507.

[29] W. Yan, Q. Sun, X.-Q. Feng, L. Qian, Analysis of spherical indentation of superelastic shape memory alloys, *International journal of solids and structures*, 44 (2007) 1-17.

[30] Z. Farhat, G. Jarjoura, M. Shahirnia, Dent Resistance and Effect of Indentation Loading Rate on Superelastic TiNi Alloy, *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, 44A (2013) 3544-3551.

[31] A. Sinha, P. Chattopadhyay, Nanomechanical response of martensite in Ti-(~ 49at.%) Ni alloy, *Materials Science and Engineering: A*, 552 (2012) 540-546.

[32] A. Amini, C. Cheng, Nature of hardness evolution in nanocrystalline NiTi shape memory alloys during solid-state phase transition, *Scientific reports*, 3 (2013).