Influence of Co Addition on Mechanical Behavior of TiNi for Orthodontic Applications

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Abstract

The purpose of this study was to investigate the mechanical behaviors of TiNi and TiNiCo shape memory alloys in order to obtain optimum fabricating conditions for using in orthodontic application. TiNi binary alloys with Ni-content 50.6 at%, TiNiCo alloys with Co-content ranges from 1 to 3 at%. The alloys were melted by electrical arc-melting method, and then the ingots obtained were homogenized at 800°C for 3600 s. Next, they were sliced into thin plates (1.5 mm) by EDM wire cutting machine in order to evaluate mechanical properties. The sliced specimens were cold-rolled with 10, 20 and 30% reduction, and then underwent heat treatment at 400°C for 3600 s, respectively. A Differential Scanning Calorimeter was used to detect transformation temperatures. Mechanical properties were evaluated by micro hardness and three-point bending tests. The results show that Co addition can increase the stress plateau, increase critical stress in superelastic curve and develop austenitic transformation temperature near the oral temperature. Transformation temperatures markedly decrease with increasing percentage of cold work. Superelastic behavior can be found in specimens having high dislocation or those having undergone cold rolling operation at a high percentage of cold work (30%) followed by heat treatment at 400°C. The data obtained can be used to determine optimum fabrication conditions of the materials used for orthodontic application.

Keyword: Shape memory alloys, TiNiCo, Mechanical behavior, Orthodontics

1. Introduction

The development of nickel-titanium wires were initially used for orthodontic applications in the United States in 1971 [1]. These nickel-titanium wires are widely used in clinical orthodontic treatment as optimal wires during certain stages of treatment, since their superelasticity property gives a low elastic modulus, and continuous and light forces transmitted to the dentition over a long activation period resulting in a desirable biological response [2-5]. The relative alloy composition of martensite and austenite is a function of mechanical stress and ambient temperature [6-8]. Small chemical composition variations can produce significant modifications of such behavior, which can be analyzed considering variation of the start of martensitic transformation (Ms) temperature [9-10]. The study that Co addition can increase the yield strength, decrease the ductility and yield good corrosion resistance of TiNi alloys has been reported [11].

The purpose of this study was to evaluate the mechanical properties and phase transformation behavior of the TiNiCo alloy with various Co-contents compared with TiNi alloy. The influence of degrees of cold-working and heat treatment temperatures was investigated to further develop TiNi alloys to be used in orthodontic purposes.

2. Experimental procedure

The raw materials used in this research were metals with high purity: nickel, 99.9%, titanium, 99.8% and cobalt, 99.95%. Firstly, nickel, titanium and cobalt were cleaned in acid ($HF:HNO_3:H_2O$, 1:4:5) and then rinsed by acetone to remove surface grease and oxide before melting. The alloys were prepared by arc-melting method under Ar atmosphere. Nominal compositions of each alloy are shown in Table 1. The ingot was turned over and remelted five times to ensure chemical homogeneity.

Table 1 Composition of the ingots used in this study.

Alloy		**Chemical composition (at%, (wt%))**		
		Ti	**Ni**	**Co**
TiNi	**1**	**49.4** (44.3)	**50.6** (55.7)	**-**
TiNiCo	**1**	**50.0** (44.9)	**49.0** (54.0)	**1.0** (1.1)
	2	**50.0** (44.9)	**48.0** (52.9)	**2.0** (2.2)
	3	**50.0** (44.9)	**47.0** (51.8)	**3.0** (3.3)

All melted ingots were then homogenized at 800°C for 3600 s. Subsequently, the as-melted ingots were sliced into plate-shape specimens with a thickness of 1.5 mm using an EDM wire cutting machine and then cold-rolled at reduction ratio 10, 20 and 30%. The lubricant used for the rolling was ISO cut 570A in combination with sodium strearate soap. To improve mechanical properties, the specimens were heat-treated again at 400°C for 3600 s after cold-rolling and then cut into specimen by a CNC wire cutting machine.

Three-point bending tests were carried out using an Instron Universal Testing Machine (load cell capacity 100N).

The span length was 10 mm. Specimens were loaded to a maximum deflection of 1.5 mm with a deflection rate of 5 mm/min (Fig.1).

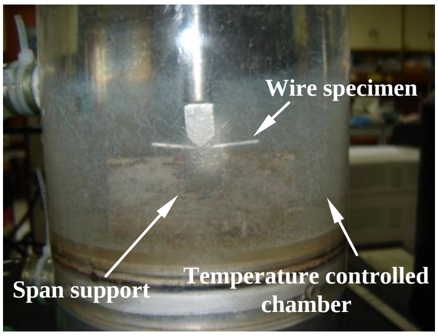

Fig. 1 Three-point bending test method.

The hardness of the specimens was determined by a Vickers Microhardness tester with a Vickers diamond tip at room temperature under a maximum load of 500 g_f. Phase-transformation temperatures were detected by Differential Scanning Calorimeter (DSC) under cooling and heating rates of 10°C/min.

3. Results and Discussion

3.1 Three-point bending test

Three-point bending tests were conducted at oral temperature or at 37°C. We observed two types of Stress-Strain curves as shown in the Fig. 2. One with superelastic behavior application of the stress lead to linear increase in strain up to point where martensitic transformation started to occur during loading. This plateau-phase was due to formation of stress-induced martensitic transformation (SIM). In unloading, a relationship exists between stress and strain down to point where austenitic transformation starts to occur. Thereafter, the unloading plateau increases where restoration of austenitic structure is complete. This is known as superelasticity.

Fig. 2(a) shows stress-strain curves of $Ti_{49.4}Ni_{50.6}$ at% alloys with 10, 20 and 30 percentage of cold work. Shape recovery was observed by unloading, i.e., superelasticity was enhanced with increasing percentage of cold work. The unloading curves of 30 percentage of cold work specimens showed shape recovery more than that of 10 and 20 percentage of cold work specimens. The stress plateau, determined by the slope of the loading path after the critical stress, tended to increase with increasing percentage of cold work.

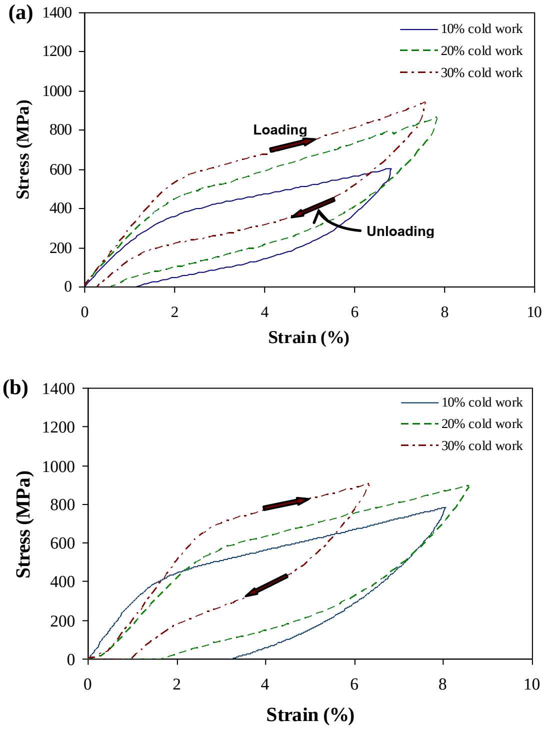

Fig. 2 Stress-strain curves as functions of loading and unloading of (a) $Ti_{49.4}Ni_{50.6}$ and (b) $Ti_{50}Ni_{47}Co_3$ alloys cold-rolled at 10, 20 and 30 percentage of cold work followed by heat-treatment at 400°C for 3600 s (tested at 37°C)

From Fig. 2(b) for $Ti_{50}Ni_{47}Co_3$ at% alloy, the complete reverse transformation could not be obtained from any condition. Interestingly, when the percentage of cold work increased to 30, the shape recovery could be clearly noticed on the unloading curve, while partial superelasticity could be confirmed in specimens with a percentage of cold work of 10 and 20.

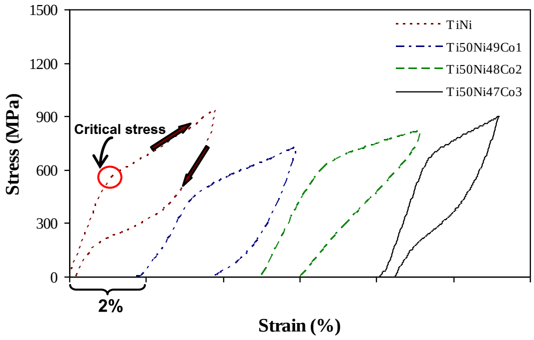

Fig. 3 Comparison of Stress-strain curves as functions of loading and unloading between TiNi and TiNiCo at% alloys cold-rolled at 30% followed by heat treatment at 400°C for 3600 s (tested at 37°C)

Fig. 3 shows the comparison of load-unloading curves between TiNi and TiNiCo alloys. It seems that the stress plateau and critical stress for induced Martensite phase slightly increased by adding Co. In present study, superelastic properties such as smooth stress-plateau and low recovery stress are expected to enhanced by adding Co as a third element. It can be seen that TiNiCo with Co-content of 3 at% exhibits the best superelastic curve and mechanical behavior. Consequently TiNiCo remains the most appropriate shape memory alloy for orthodontic or medical applications.

3.2 Vickers hardness test

The micro-indentation hardness was measured at the cross-sectional areas of each specimen. Fig. 4 shows the relationship of the hardness values with various cold-rolled reduction ratios. Consequently, our comparative study concerns the TiNi and TiNiCo alloys. From among these both, Co addition to 3 at% exhibited hardness properties nearly equal that of TiNi. The hardness increased with increasing percentage of cold work and consistent with the three-point bending test.

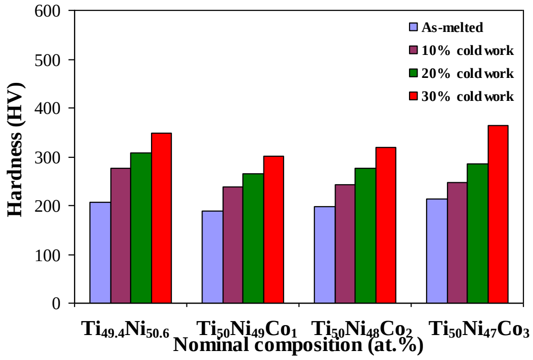

Fig. 4 Vickers hardness test of TiNi and TiNiCo alloys cold-rolled at 10, 20 and 30% followed by heat-treatment at 400°C for 3600 s

3.3 Transformation temperature behavior

The transformation temperatures of TiNi and TiNiCo. Austenetic finish (A_f) and Martensitic start (M_s) are critical factors of their transformation behavior. The results of A_f and M_s values are shown in Fig. 5 for DSC for $Ti_{50}Ni_{47}Co_3$ at% with 10, 20 and 30 percentage of cold work followed by 400°C heat treatment for 3600 s. Considering the shape of the peaks, the peaks broadened when percentage of cold work increased. It meant that the phase transformation would occur more difficultly and temperature hysteresis from peak to peak tended to decrease. This alloy could be classified as the active austenitic in oral temperature for the 30 percentage of cold work.

Fig. 6 shows the alloys have nominal compositions of $Ti_{49.6}Ni_{50.6}$, $Ti_{50}Ni_{49}Co_1$, $Ti_{50}Ni_{48}Co_2$ and $Ti_{50}Ni_{47}Co_3$ at% provided was melting. Austenite finished temperature (A_f) set as 32°C to 64°C. Actually, we intended to make a superelastic TiNi alloy having a transformation temperature lower than the oral temperature.

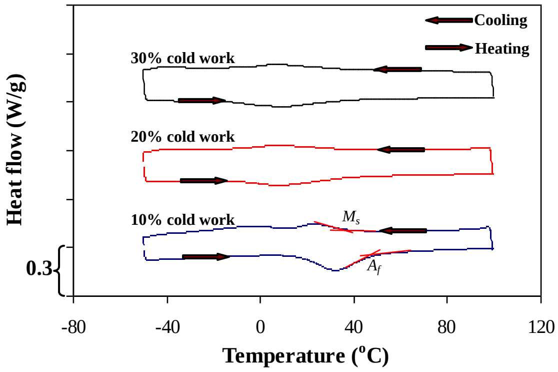

Fig. 5 Thermographs of $Ti_{50}Ni_{47}Co_3$ alloy cold-rolled at 10, 20 and 30% followed by heat treatment at 400°C for 3600 s

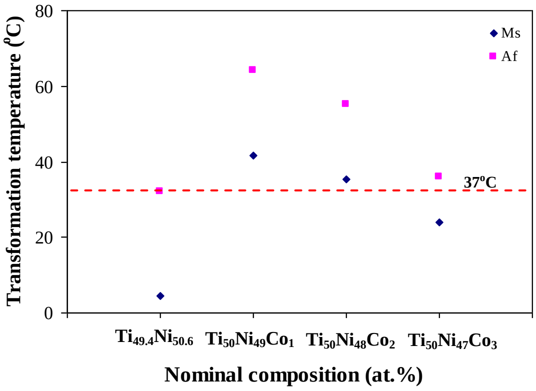

Fig. 6 Transformation temperatures of TiNi alloy and TiNiCo alloys provided was melting by DSC

The A_f and M_s of the alloys obtained from all conditions are shown in Table 2. We intended to make a superelastic TiNi alloy having transformation temperature (A_f) near oral temperature. Interestingly, it is clearly seen that A_f temperature becomes nearly oral temperature after applying 30 percentage of cold work. This can be implied that percentage age of cold work has an impact on phase transformation, and could be explained by phase transformation which was suppressed due to cold-working. In other words, the internal structure of the work-hardened material was composed of multiple dislocations that hindered the phase transformation.

Table 2 Transformation temperatures of the specimens heat-treated at 400°C for 3600 s with various percentage of cold work.

Nominal Composition (at%)	**Percent cold work**	**Transformation temperature (°C)**	
		A_f	R_s and M_s
$Ti_{49.4}Ni_{50.6}$	10	47	40
	20	40	39
	30	37	36
$Ti_{50}Ni_{49}Co_1$	10	67	53
	20	64	55
	30	60	54
$Ti_{50}Ni_{48}Co_2$	10	55	41
	20	53	50
	30	49	47
$Ti_{50}Ni_{47}Co_3$	10	51	39
	20	41	38
	30	39	37

4. Conclusions

The influence of Co addition on mechanical behavior of TiNi can be used to determine optimum alloy composition for orthodontic applications. The following conclusions can be obtained.

1. TiNiCo alloy with Co-content of 3 at% reveals nearly similar mechanical and transformation behavior to those of TiNi alloy. However, critical stress and hardness of TiNiCo alloys seems to be slightly increase.

2. transformation temperature can be moved close to oral temperature by adding 3 at% of Co, resulting in a superior superelastic property.

3. Mechanical and transformation behavior of TiNi and TiNiCo alloys can be enhanced by cold-rolling at 30% and heat-treatment at 400°C. Good superelasticity can be obtained at oral temperature which is suitable for orthodontic application.

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References

[1] Proffit W, Fields., Jr H. (2000). Mechanical principles in orthodontic force control. In: Contemporary orthodontics. 3rd ed. ed. St.Louis: Mosby.

[2] Ingram SB, Gripe DP, Smith RJ. (1986). Comparative range of orthodontic wires. Am J Orthod. pp. 296-307.

[3] Kusy RP. (1997). A review of contemporary archwires: their properties and characteristics. Angle Orthod . pp. 197-207.

[4] Gil FJ, Solano E, Pena J, Engel E, Mendoza A, Planell JA. (2004). Microstructural, mechanical and citotoxicity evaluation of different NiTi and NiTiCu shape memory alloys. J Mater Sci Mater Med. pp. 1181-1185.

[5] Ingram SB, Grip DP, Smith RJ. (1986). Comparative range of orthodontic wires. Am J Orthod. pp. 296-307.

[6] Meling TR, Odegaard J. (1998). The effect of temperature on the elastic responses to longitudinal torsion of rectangular nickel-titanium archwires. Angle Orthod. pp. 357-368.

[7] Meling TR, Odegaard J. (1998). The effect of short-term temperature changes on the mechanical properties of rectangular nickel-titanium archwires tested in torsion. Angle Orthod. pp. 369-376.

[8] Meling TR, Odegaard J. (1998). Short-term temperature changes influence the force exerted by superelastic nickel-titanium archwires activated in orthodontic bending. Am J Orthod Dentofac Orthop. pp. 503-509.

[9] Otsuka K, Wayman. Shape memory materials. United Kingdom: Cambridge University Press (1998).

[10] T.W. Duerig et al., Engineering aspect of shape memory alloys**.** London: Butterworth-Heinemann (1990).

[11] K. Venkata Ramaiah, C.N. Saikrishna and S.K. Bhaumik. (2005). Processing of the Ni-Ti Shape Memory Alloy Wires. Proceedings of ISSS 2005. pp.141-147.