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The effect of cobalt element addition on the characteristics of equiatomic NiTi shape memory alloy

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Abstract The influence of cobalt addition on the transformation temperatures, microstructure, and micro-hardness of equiatomic NiTi shape memory alloy was studied. The alloys composition was (50 % at. Ni, 50% at. Ti) and (43.45 % at. Ni, 54.728 % at. Ti and Co 1.815 % at.). Vacuum induction melting method is used to produce the shape memory alloys. The investigation of the characteristics of the samples was carried out using, scanning electron microscope conducted with energy dispersive X- ray spectrometer, differential scanning calorimeter, x-ray diffraction measurement and vickers micro-hardness testing. The results show the microstructure of two alloys contain Ti2Ni precipitate phase, the martensite phase layers increase with cobalt addition. The micro-hardness increased, the austenite starts temperature and austenite finish temperature decreases, and thermal hysteresis becomes narrower, after adding a small amount of cobalt.

Keywords. equiatomic NiTi alloy, NiTiCo alloy, shape memory alloys, Ti2Ni phase, DSC.

1. Introduction

Equiatomic NiTi shape memory alloys (SMAs), they have gained a wide industry, aerospace industry, biomedical and engineering, applications in sensor and actuator forms. Besides, they are suitable for using in orthodontic wires due to their good biocompatibility and mechanical properties [1, 2, 3, 4]. Multi-step transformation or stepped transformation can be shown in NiTi SMAs [5, 6]. This means that during the cooling process they can transform from the "austenite phase" B2 to the "R-phase" and "martensite phase". In general, the "R-phase" is a prior phase composed before the martensite phase B19'. Furthermore, some minor phases such as Ti2Ni, Ni4Ti3, can be seen for a various proportion of NiTi alloys. It has been characterized that the transformation temperatures of NiTi based alloys depend on the alloy composition. "The transformation temperatures" and mechanical properties of the NiTi based alloys can be affected by a small change in Ni to Ti proportion or additing of a third alloying element [7, 8, 9, 10, 11].

Various elements do not have the same influence on the characteristics of NiTi SMAs, such as, the martensite transformation temperatures, thermal hysteresis, and thermomechanical properties. The transformation temperature of NiTi alloy increases with adding Hf, Pd, Zr, and Pt, whereas, Al, Fe, Mo, Nb could decrease the transformation temperatures [1, 4]. Andreasen was evaluated NiTiCo shape memory alloy wires to improve NiTi-based shape memory alloys for biomedical application [12]. Cobalt evidence to be a preferable option that can increase yield strength although it reduces the transformation temperatures of the NiTi SMAs in comparison with the other ternary alloying elements, [13, 14]. Due to increasing the yield strength when it's compared with the binary NiTi alloys, NiTiCo SMAs are obtaining higher significance in a different applications. The present work deals with the synthesis of titanium-rich NiTiCo shape memory alloy by vacuum induction melting. The changes in the

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microstructure, transformation temperatures, occurring phases and micro-hardness of the NiTiCo alloy were investigated and compared with characteristics of equiatomic NiTi shape memory alloy.

2. Experimental work

Titanium wire with purity 98.66 wt. %, Nickel plate with 99.9 wt. % purity and Cobalt (99.9 wt. %) were immersed in acetone and alcohol in an ultrasonic bath, and then they were washed with distilled water and dried before melting. NiTiCo alloy composition contains (43.45 % at. Ni, 54.728 % at. Ti and Co 1.815 % at.) Compared with equiatomic NiTi alloy contain (50 % at. Ni, 50% at. Ti). The ingredient elements of these two alloys are melted frequently three times in high-frequency induction vacuum, furnace using graphite crucible under argon atmosphere.

The selected two samples were heat treated at $865 \,^{\circ}$ C for 15 min, in a furnace under normal atmosphere and quenched in icy water. Optical microscope with a magnification of (4X) was used to investigate the microstructure of samples. The samples were grinded and polished, followed by etching using (30 ml H2O, 20 ml HNO3, 10 ml HF) solution for 10 sec to show the grain boundaries and the microstructure of alloys. For microstructure and chemical compositions, analysis of samples by "scanning electron microscope SEM" conducted with the "energy dispersive x-ray" analysis unit EDX model (VEGA3LM) was accomplished. X-ray diffraction test was carried out using a Shimadzu device, to analysis the different phases of the heat treated samples. Differential scanning calorimetry (DSC) produced by SETARAM, type 131 EVO. A different temperature range from (-100 °C – 300 oC) with heating/cooling rate 10° C/min in nitrogen atmosphere was used to determine the transformation temperatures of selected samples. For micro-hardness measurements, the test was done at room temperature using micro-hardness Vickers tester type (Laryee model VHS-1000), under 300 gf. load for holding time of 10 sec.

3. Results and discussion

Figure1 and figure 2 show the microstructure of equiatomic NiTi alloy and NiTiCo alloy before and after heat treatment at 865 °C, which determined by the optical microscope. Equiaxed grains rather than dendrites dominate the microstructure of the equiatomic NiTi SMA after heat treatment. The grain size seems to be smaller after heat treatment. With adding Co element, the microstructure reveals the presence of elongated grains morphology and dendritic structure. Finer dendritic structure *can* be noticed after heat treatment, this caused by rapid cooling after solution treatment. Ti2Ni phase precipitates in the interior of the grains and within the grain boundaries of both alloys. Solid pointer in figures 1, 2 refer to the Ti2Ni phase. The matrix NiTi phase represented by the dashed pointer.

Figure 3a and figure 3b show the microstructure of the equiatomic NiTi alloy and NiTiCo alloy by SEM analysis after heat treatment at 865°C. This reveals the two alloys consist of NiTi phase (matrix) presented by dashed pointer and precipitates of Ti2Ni phase presented by the solid pointer. Table1 shows the chemical composition analysis of various phases existed in the microstructure of the investigated alloys using EDX. NiTiCo alloy microanalysis shows that the alloy consists of NiTiCo matrix phase (matrensite), and Ti2Ni phase precipitates. From figure 3b can be seen the martensitic layers (matrix phase), with the addition of Co element the martensite phase increases in the matrix as reported by Nawal D. Alqarni, et al. [15]. Ti2Ni phase precipitated in agglomerated nongeometric shapes as well as small orbicular shapes. Well distributed Ti2Ni phase can be seen in NiTiCo SMA with smaller size in comparison with that in NiTi alloy illustrated in figure 3b.fish farm study

The samples were collected from the common carp farms north of Basrah city. A total of 30 live infected fishes was collected, during the autumn season of the year 2019, samples were placed in ice box and transferred to the laboratory of department marine vertebrate marine science center and to Al Noor vet. lab. Within 3hrs. Fish weights and lengths from 150 -350 gm, and 15-35cm respectively.

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Figure 1. Optical micrograph of equiatomic NiTi alloy a) before, b) after heat treatment at 865°C for 15 min.



Figure 2. Optical micrograph of NiTiCo alloy a) before, b) after heat treatment at 865°C for 15 min.



Figure 3. SEM micrograph of a) equiatomic NiTi alloy, and b) NiTiCo alloy, after heat-treatment at 865°C for 15 min.

 Table 1. The chemical composition in (at. %) of heat-treated NiTi and NiTiCo alloys at 865°C.

phase	Ti	Ni	Со
NiTi (matrix)	50.2	49.8	0
NiTiCo (matrix)	49.6	47.6	2.8
Ti ₂ Ni (0 % at. Co)	68.28	31.72	0

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Ti ₂ Ni (1.815 % at Co)	68.2	31.1	0.7	

Figure 4. Illustrate the patterns of X-ray diffraction XRD measurement of the heat-treated equiatomic NiTi SMA and NiTiCo alloy, the investigations of x-ray diffraction were accomplished at room temperature in the diffraction angle range from 30° to $80^{\circ}(2\Theta)$ for two samples to identify the crystalline phases. In equiatomic NiTi alloy, a very strong peak (112) of the "R- phase" is apparent. The diffraction reflections from (002), (1-11), (020), (021), (012) and (112) planes of martensitic phase appear, other diffracted peak from (422) refer to Ti2Ni precipitates phase.

The reflections corresponding to the planes (111), (020), (002), (1-11) and (112) of the martensitic phase and (112) of the R- phase and (422) of the Ti2Ni phase are found in NiTiCo alloy. Of these reflections, the line around 42.0°, corresponding to the R (112), is found to be most prominent. It can be seen that the peaks (111), (1-11) and (112) are sharper with higher intensity and more clear than in equiatomic NiTi alloy, these results which intimate that the martensite phase increase with adding cobalt to the alloy, as can be seen, the SEM micrograph in figure 3b. The patterns of NiTiCo are narrower and sharper than equiatomic alloys, which mean have larger grain structure. According to Scherrer formula [16], by measuring the Bragg width of peak at half the maximum intensity, the grain size can be calculated by using the Scherrer formula, equation

$$d = \frac{0.94\,\lambda}{B\cos\theta} \tag{1}$$

Where "d is for grain size", " λ stands for the wavelength", "B is (FWHM) the peak width at half the maximum intensity", and " θ is the Bragg angle". The average grain size of equiatomic NiTi alloy and NiTiCo calculated using Scherrer formula is 14.52 nm and 21.27 nm, respectively.



Figure 4. X-ray diffraction of NiTi alloy and NiTiCo alloy after heat treatment at 865°C for 15 min .

The heat flow curves of equiatomic NiTi and NiTiCo alloys are given in figure 5 the "R start temperature (Rs)", "R peak temperature (Rp)", "R finish temperature (Rf)", "Austenite start temperature (As)", "Austenite peak temperature (Ap)", "Austenite finish temperature (Af)", "Martensite start temperature (Ms)", "Martensite peak temperature (Mp)", "Martensite finish temperature (Mf)" values and thermal hysteresis of equiatomic NiTi and NiTiCo alloys are illustrate in Table 2. In figure 5. The DSC profile of equiatomic NiTi alloy and NiTiCo alloy undergo a two-step phase transformation during heating and cooling. Upon cooling two exothermal peaks appear which indicate to the transformation from "austenite phase (B2)" to "R- phase" and from "R- phase" to "martensite phase (B19')", respectively. In addition, two endothermal peaks are revealed upon heating which indicates to the transformation from martensite phase (B19') to R- phase and from R- phase to austenite phase (B2), respectively. This behavior is contrary to most of the results characterized in literatures, where two-step transformation occurs only during cooling process [17].

Forming of coherent Ti2Ni precipitates causes this behavior because it produces local stress fields [18, 19]. In addition, fine precipitates have a high resistance to phase transformation with large strain

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such as B2–B19', but has much less resistance to phase transformation with small strain such as B2–R. adding a small amount of cobalt (1.815 at. % Co), made a change in the transformation temperatures, where austenite transformation temperatures (As and Af) decreased but martensite transformation temperatures (Ms and Mf) increased, also, the thermal hysteresis NiTiCo alloy is narrower than in equiatomic NiTi alloy as presented in table 1. The increasing in martensitic transformation temperatures can be attributed to decreasing Ni content with adding Cobalt element, where, Cobalt added to "NiTi SMA" as a substitute of Ni, this means that the Ni atomic percentage decreases, with increasing the Cobalt amount in that alloy, As reported by He and Miyazaki [20], with increment the Ni amount in NiTi alloy the martensitic transformation temperature decreases. This result agrees with that achieved by Lekston et al. [21], that Ms of NiTi SMA has increased from -20 to +5 °C with the addition of Co, and El-Bagoury [22], where, he reported that Ms increases from 15 to 31°C by adding Co element. Also, these results agree with that reported by Jing et al. [23], where he reported that the austenitic transformation temperatures decrease with adding cobalt element.

 Table 2. The transformation temperatures of equiatomic NiTi and NiTiCo SMAs after heat treatment at 865°C.

a	ılloy	Rs (°C)	R₁ (⁰C)	As (°C)	A _f (°C)	Ms (°C)	M _f (°C)	A _p (°C)	M _p (°C)	R _p (°C)	Thermal hysteres is (A _f –M _s)
ati g	NiTi	14.4	89.5	100.1	137.2	-	-	108.46	-	43.98	129.6
Не	NiTiCo	30.1	55.1	55.1	87.17	-	-	74.2	-	49.7	68.21
ng	NiTi	39.7	12.7	-	-	7.6	-42.6	-	1.35	19.16	
Cooli	NiTiCo	47.3 5	18.96	-	-	18.96	-11.8	-	20.76	34.4	



Figure 5. The DSC profile of equiatomic NiTi alloy and NiTiCo alloy after heat-treatment at 865°C for 15 min.

Table 3 illustrates the co addition effect on the micro hardness values of equiatomic NiTi SMA before and after heat treatment. The values of micro harness detreminded by taking the average of the seven measurements on each sample. The micro-hardness values of equiatomic NiTi SMA improved by adding Cobalt element before and after heat treatment. This result can be attributed to the increasing of the martensite phase or to the matrix phase solution hardening by addition of cobalt element. Moreover, increasing the amount of the hard Ti2Ni precipitate phase in the alloy supports the microhardness improvements [22]. After heat treatment, the microhardness of NiTiCo alloy slightly increased. **Table 3.** Micro-hardness of equiatomic NiTi and NiTiCo SMAs before and after heat-treatment

alloy	before heat-treatment	after heat-treatment		
NiTi	186.06	238.74		
NiTiCo	279	291		

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4. Conclusions

In this study, the change in the characteristics of equiatomic NiTi shape memory alloy studied after adding cobalt as a ternary alloying element. The results are summarized as follow:

- 1. The martensite phase increases with adding cobalt element.
- 2. SEM analysis show that, with the cobalt addition to the NiTi SMAs, the Ti2Ni phase is well distributed at the grain boundaries and grain size of this phase is smaller than that in equiatomic NiTi alloy.
- 3. The austenitic transformation temperatures decreased in alloy with cobalt addition, while the martensitic transformation temperatures increased.
- 4. Thermal hysteresis decreases with adding cobalt.
- 5. In NiTiCo, the micro-hardness increases remarkably, which can be attributed to the matrix phase solution hardening with Co addition and an increasing amount of Ti2Ni phase.

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