Influence of copper addition on the properties of equiatomic NiTi shape memory alloy prepared by vacuum induction melting method

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Abstract In this study the effect of Cu addition on the phase transformation behavior, microstructure, and micro hardness of equiatomic Ni-Ti shape memory alloy was investigated. NiTiCu SMA prepared with the composition (52.119 % at. Ni, 41.731% at. Ti and Cu 6.15 % at.) and compared with the properties of the equiatomic NiTi SMA with composition (50% at. Ni, 50% at. Ti). Vacuum induction melting method used in the preparation of Both SMAs. The Differential Scanning Calorimetry, Scanning Electron Microscope, X-ray Diffraction Analysis, optical microscope and vicker's microhardness test was used to investigate the characteristics of the equiatomic NiTi and NiTiCu SMAs. The results revealed that when Cu element was added the phase transformation temperatures decreased below body temperature. NiTi matrix phase and Ti2Ni secondary phase exist in both SMA samples, also Cu-rich phase appeared in NiTiCu SMA and this is one of the reasons that lead to increasing the microhardness of alloy when Cu element was added. The value of equiatomic NiTi increases from 238.74 to 329 when Cu element was added (for NiTiCu alloy) after heat treatment.

Keywords: shape memory materials, NiTi shape memory alloys, DSC, XRD, phase transformation

1. Introduction

Shape Memory Alloys (SMAs) are metallic alloys that exhibit reversible martensitic phase transformations when a thermomechanical loads are applied and have the ability to recover the permanent strains when subjected to heating above a specific transformation temperature [1]. NiTi (nickel-titanium) SMAs are the most common alloys and widely utilized due to their excellent mechanical properties and excellent material characteristics, like shape memory effect, biocompatibility, good wear resistance, good cyclic performance and excellent corrosion resistance, these properties allow them to be utilized in the biomedical applications [2]. NiTi SMAs have two crystal phases, the parent phase austenite (the hot phase) which is stable at the high temperatures, and the product phase martensite (the cold phase) which is stable at the low temperatures [3]. Adding a third alloying element to binary NiTi shape memory alloy, which has desirable properties, such as; mechanical properties, phase transformation temperatures, etc. by adding Cu as a ternary element, mechanical properties of the NiTi SMA and phase transformation temperatures can be changed [4,5]. Also with the addition of Cu element the thermal hysteresis change from 10°C to less than 4.5°C [5]. Vacuum induction melting (VIM) method using graphite crucible to melt the gradient elements and that made it attractive method because of low
cost and produce excellent chemical homogenization because of electrodynamic forces that produce a good mixing of the melt [6, 7]. In the present work the effect of adding Cu element to equiatomic NiTi SMA was studied, both alloys equiatomic NiTi and NiTiCu SMAs were synthesized using the vacuum induction melting method. The Microstructure, Microhardness, Transformation Temperatures, and phases of equiatomic NiTi and NiTiCu were investigated.

2. Experimental work

Titanium wire with 98.66 wt. % purity, Nickel plate with purity 99.9 wt. % and Copper with purity (99.9 wt. %) were immersed in an ultrasonic bath in acetone and alcohol, and using distilled water to wash them and then dried before melting. (52.119 % at. Ni, 41.731 % at. Ti and Cu 6.15 % at.) The composition of NiTiCu SMA and (50 % at. Ni, 50% at. Ti) the composition of equiatomic NiTi SMA. The elements of both alloys were melted in graphite crucible using high-frequency induction vacuum furnace under argon atmosphere, the melting process was repeated three times to ensure the homogeneity. The solution heat treatment process were carried out to the yield samples at 865°C for 15 mints in normal atmosphere, followed by quenching process in icy water. The grinding and polishing processes were carried out to the yield samples before the investigation, followed by etching process using etching solution (10 ml HF, 20 ml HNO₃,30 ml H₂O) for 10 sec to investigate the microstructure and the demonstrate the grain boundary of the produced alloys. The microstructure of the induced samples was investigated using the Optical Microscope with a magnification of (4X). Scanning Electron Microscope SEM was used to show the microstructure and chemical composition of the phases in the produced alloys conducted with energy dispersive x-ray EDX, model (VEGA3LM). By using shimadzu x-ray diffraction device, the solution heat-treated NiTi and NiTiCu samples different phases were analyzed. The phase transformation temperatures of the solution heat-treated samples were determined by the Differential scanning calorimetry (DSC) at temperatures range from -100°C to 300°C with 10°C/min as a rate of cooling/ heating in nitrogen atmosphere using device produced by SETARAM type (131 EVO). At room temperature the microhardness test was carried out by using Layree model VHS-1000 Vickers tester, under 300 gf for holding time 10 sec.

3. Results and discussion

The microstructure of equiatomic NiTi SMA and NiTiCu SMA before and after solution heat treatment at 865°C, which investigated using the optical microscope illustrate in Figure 1 and Figure 2. Grains with Equiaxed shape rather than dendrites appear in the microstructure of the equiatomic NiTi SMA after solution heat treatment. The microstructure of NiTiCu consist of dendritic structure that confirms the inhomogeneity in the microstructure. This result assured the contrast with the result related to equiatomic binary NiTi alloys, which do not show the dendritic structure. The macroscopic investigation also revealed the presence of Ti₂Ni as a second phase, which can be seen clearly in NiTiCu alloy after solution heat treatment. In Figures 1 & 2 solid pointer refers to the secondary phase Ti₂Ni. The dashed pointer represent the NiTi matrix phase.

Figure 1. The optical microstructure of equiatomic binary NiTi SMAs; a) before heat treatment, b) after solution heat treatment at 865°C for 15 min.
Figure 2. The optical microstructure of NiTiCu, SMAs; a) before heat treatment, b) after solution heat treatment at 865°C for 15 min.

The solution heat treated equiatomic NiTi alloy and NiTiCu SMAs microstructure using scanning electron microscope (SEM) illustrate in Figure 3a and Figure 3b. The results show that both SMAs have the matrix phase (NiTi) represented by solid pointer and the secondary phase (Ti2Ni) represented by the dashed pointer. The chemical composition of the phases that existed in the microstructure of the equiatomic NiTi and NiTiCu SMAs analyzed by EDX test explained in Table1. SEM/EDX inspection also revealed a Cu-rich NiTiCu phase presented by the black pointer in figure 3b. The decrement in Cu and Ni content in the matrix can be attributed to the formation of the Cu-rich NiTiCu phase with high content of Ni.

Figure 3. SEM microstructure of specimen after solution heat treated at 865°C for 15 min a) equiatomic NiTi SMA, and b) NiTiCu SMA.

Table1. The solution heat treated NiTi and NiTiCu SMAs chemical composition in (at. %).

| Phase                | Ti   | Ni   | Cu   |
|----------------------|------|------|------|
| NiTi (matrix phase)  | 50.2 | 49.8 | 0    |
| NiTiCu (matrix phase)| 48.4 | 46.61| 4.99 |
| Ti2Ni (0 % at. Cu)  | 68.28| 31.72| 0    |
| Ti2Ni (6.15 % at. Cu)| 61.75| 35.03| 3.17 |
| Cu-rich NiTiCu       | 35.332| 41.314| 23.354|
The x-ray diffraction patterns of solution heat treated equiatomic NiTi and NiTiCu SMAs illustrate in figure 4. The test was carried out at room temperature in the range of diffraction angle (2θ) between (30° to 80°) to determine the crystalline phases.

A very strong peak (112) for the R- phase is appear in equiatomic NiTi SMA. The martensite phase corresponding to the diffraction from (002), (1-11), (020), (021), (012) and (112) planes. The diffracted peak (443) refer to the secondary phase Ti$_2$Ni.

In NiTiCu SMA, very clear reflections of the austenite phase corresponding to the diffraction from (110) and (200). Martensitic B19' phase diffraction peaks are corresponding to the planes (103), (110) and (204). The coexist of austenite and martensite peaks means that the complete transformation from martensite to austenite will not occur at room temperature. The diffracted peak from (422) refer to secondary phase Ti$_2$Ni. The NiTiCu patterns are sharper and narrower than the patterns of the equiatomic NiTi SMA that mean the NiTiCu SMA has larger grain structure. The Scherrer formula [8] used to calculate the grain size and measuring the Bragg width of peak at half the maximum intensity. Equation (1) refer to scherrer formula:

$$D = \frac{0.9 \lambda}{B \cos \theta}$$  \hspace{1cm} (1)

where $\lambda$ is wavelength, $D$ is a grain size, $\theta$ is for the Bragg angle, $B$ is (FWHM) the peak width at half the maximum intensity, and. The average grain size of NiTiCu and equiatomic NiTi SMAs is 21.18 nm and 14.52 nm, respectively.

![Figure 4](image)

**Figure 4.** XRD patterns of a) the NiTi SMA and, b) NiTiCu SMA after solution heat treatment at 865°C for 15 min.
Figure 4, shows the heat flow curves of the equiatomic NiTi and NiTiCu SMAs. The austenite start temperature ($A_s$), austenite peak temperature ($A_p$), austenite finish temperature, martensite start temperature ($M_s$), Martensite peak temperature ($M_p$), martensite finish temperature ($M_f$), R start temperature ($R_s$), R peak temperature ($R_p$), R finish temperature ($R_f$) values Thermal Hysteresis (TH) of NiTiCu and equiatomic NiTi SMAs after solution heat treatment at 865 °C for 15 min are illustrate in Table 2. The enthalpy of transformation (J/g) of equiatomic NiTi, NiTiCu SMAs after solution heat treatment at 865 °C for 15 min, are presented in Table 3. From the table it can be seen that the equiatomic NiTi SMA has a highest average enthalpy $\Delta H$ of transformation value. The average enthalpy $\Delta H$ of the transformation in equiatomic binary NiTi shape memory alloys decreased when Cu alloying elements were added to the stoichiometric NiTi. This decrease in $\Delta H$ average directly results in a decrease of MS. this result agrees with J. frenzel et al. [9].

![Diagram of heat flow curves](image)

**Figure 5.** The DSC curves of a) equiatomic NiTi and b) NiTiCu SMAs after solution heat treatment at 865 °C for 15 min.

The equiatomic binary NiTi alloy undergo two steps transformation during heating and cooling processes. During cooling process, two exothermic peaks appear which refer to the transformation from B2 (austenite phase) to R-phase and from R-phase to B19' (martensite phase) respectively. During heating process two endothermic peaks are appear which indicate to the transformation from the B19' (martensite phase) to R-phase and from R-phase to B2 (austenite phase) respectively.

In NiTiCu, when Cu substitutes Ti. The alloy undergo two-step phase transformation during cooling process, and single-step phase transformation during heating process, as shown in figure 4.
An endothermic peak is obtained during heating process which refers to transformation from martensite to austenite, whereas two exothermal peaks are obtained during cooling process which refers to a transformation from austenite to R-phase and from R-phase to martensite. Because of the internal stress field around the precipitates, R-phase probably appears [1, 10]. It can also be seen that there is a noticeable reduction in transformation temperatures of this alloy, where the A_s below the body temperature as mentioned in Table (2). Furthermore, although M_s is insensitive to the substitution of Ni by Cu, M_p decreases as Cu substitutes Ti. The M_s Temperature becomes less sensitive to the variation in the ratio of NiTi when the Cu element is present [11]. DSC measurements indicate that NiTiCu alloy has substantially narrower hysteresis than the binary alloy. It can be seen that this thermal hysteresis is reduced from around 129.6°C for the equiatomic binary NiTi alloy to 38.27°C for alloy with copper. SMAs with small thermal hysteresis, such as NiTiCu SMAs are good candidates for applications where fast activation of SME is required. So, NiTiCu SMAs are very interesting for applications of thermo-mechanical actuators and sensors [12].

**Table 2.** The transformation temperatures (°C) of equi-atomic binary NiTi and NiTiCu SMAs after heat treatment.

| Sample | R_s | R_f | A_s | A_f | M_s | M_f | A_p | M_p | R_p | TH(A_f–M_s) |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------------|
| Heating | NiTi | 14.4 | 89.5 | 100.1 | 137.2 | - | - | 108.46 | - | 43.98 | 129.6 |
|        | NiTiCu | - | - | -26.2 | 6.27 | - | - | -7.19 | - | - | 38.27 |
| Cooling | NiTi | 39.7 | 12.7 | - | - | 7.6 | -42.6 | - | 1.35 | 19.16 |
|        | NiTiCu | -1.43 | -29.3 | - | - | -32 | -77.6 | - | -13.65 | -49.56 |

**Table 3.** The enthalpy of transformation (J/g) of NiTi and NiTiCu SMAs after solution heat treatment at 865 oC for 15 min.

| SMAs sample | ΔH_Heating | ΔH_Cooling | ΔH_average = (ΔH_Heating + ΔH_Cooling) / 2 |
|-------------|------------|------------|--------------------------------------------|
| NiTi        | -5.24      | 16.19      | 5.475                                      |
| NiTiCu      | -11.15     | 9.67       | -0.74                                      |

Table 4. Shows the effect of the Cu addition on the microhardness values of equiatomic NiTi SMA before and after heat treatment. The micro hardness values were determined by taking the average of the seven measurements on each sample. In equiatomic NiTi SMA, it is obviously manifested that there is an appreciable increase in microhardness after solution heat treatment [13]. It is observed that the hardness of the alloy is increased with the addition of Cu element to NiTiCu SMA before and after heat treatment. The reason related to this behavior can be attributed to the formation of Cu-rich phase (as presented in SEM micrograph analysis) and also due to the solid solution hardening of Cu in alloy matrix [14]. Another reason associated to the hardness improvement represented by the formation of intermetallic Ti₃Ni hard phase which reduces the movement of dislocations within the metallic structure and consequently enhance the hardness.
Table 4. Microhardness of equiatomic NiTi and NiTiCu SMAs before and after heat treatment.

| SMAs sample | Before heat treatment | After heat treatment |
|-------------|-----------------------|----------------------|
| NiTi        | 186.06                | 238.74               |
| NiTiCu      | 323                   | 329                  |

4. Conclusion

Both SMAs equiatomic Ni-Ti and NiTiCu prepared using vacuum induction melting method and solution heat treated at 865 °C and quenched in icy water; the characteristics of two alloys were studied and the effect of Cu addition were investigated; the results are summarized as follow:

1. Phase transformation temperatures decrease with adding Cu element to equiatomic NiTi SMA which is under body temperature.
2. Microhardness enhanced with adding Cu element before and after solution heat treatment because the formation of Cu-rich phase and the solid solution hardening of Cu in the matrix phase of alloy.
3. SEM investigation revealed the formation of Cu-rich phase in addition to the intermetallic phase Ti2Ni phase and that lead to enhance the hardness.
4. Thermal hysteresis decreased with the addition of Cu element.

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