COMPARISON AND CHARACTERIZATION OF NITI AND NITICU SHAPE MEMORY ALLOYS

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ABSTRACT

In this study, two different compositions of Nickel-Titanium (NiTi) shape memory alloy (SMA) are characterized. The composition of the alloys were Ti-49.9 at.% Ni and Ti-48.64 at.% Ni. After the small amount of Copper addition, (2.21% at. and 3.94% at.), shape memory characteristics of NiTiCu alloys are investigated. Vacuum Arc Remelting (VAR) technique is utilized to produce these alloys. Following the production of the samples, the characterization of SMA samples was carried out using Energy Dispersive Spectrometer (EDS) analysis, Hardness Vickers Testing, and Scanning Electron Microscope (SEM). After Copper addition, hardness is increased in NiTiCu SMA. However, Austenite start (A_s) and Austenite finish (A_f) temperatures are dramatically decreased under stress-free thermal cycling condition between 0ºC and 200ºC.

1. INTRODUCTION

NiTi based shape memory alloys show remarkable shape memory effect (SME) and superelastic (SE) behavior in comparison with the other SMA counterparts [1]. For this reason, they are used in a variety of applications in engineering, aerospace, and biomedical fields. A large number of NiTi SMA based functional products were commercially produced over the last two decades, such as stent and orthodontic arch-wire.

However, the production (i.e. vacuum arc/induction melting) and processing (hot/cold working) of the NiTi based SMAs is still expensive, complicated and time consumable. Moreover, the heat treatment (i.e. aging) and thermo-mechanical cycling can easily change their solid-to-solid phase transformation behavior, mechanical response and functional properties [2]. Therefore, many innovative efforts have been made to acquire the appropriate processing-microstructure-mechanical property combination [3] and to minimize undesirable characteristics (i.e. dimensional instability) of the NiTi based SMAs [4].

The addition of the ternary element is one of the most developing techniques to overcome one such disadvantage of the NiTi SMAs. NiTiX (X=Zr or Hf) alloys by substitution of Zr or Hf for Ti and NiTiY (Y=Pd or Pt) alloys by substitution of Pd or Pt for Ni were utilized to obtain potential high temperature SMA's [5]. On the other hand, the addition of copper as a ternary element shows a significant effect on the transformation temperature hysteresis that provided a narrow hysteresis loop different than the characteristics of other NiTi based counterparts. This specific characteristic used for the development of different commercial NiTiCu SMA actuators, such as one-way and two-way NiTiCu SMA springs.

The main focus of this study is to compare binary NiTi and NiTiCu alloys based on the effects of copper addition under stress-free thermal cycling condition.

2. EXPERIMENTAL PROCEDURE

NiTi and NiTiCu SMA as-cast ingots were successfully produced by using vacuum arc-remelting (VAR) method utilizing vacuum arc furnace with two different groups. In the first group of SMA preparation, 99.9% pure nickel and 99.7% pure titanium were repeatedly melted three times in an argon atmosphere [6]. After the addition of 99.9% pure copper, same process is repeated for the second batch of SMA preparation.

The produced ingots dimensions were 4mm.x4mm.x65mm. These ingots were cut into samples of 1mm.x1mm.x65mm in dimension using wire erosion machine with a minimum tolerance of accuracy. For the characterizations of the NiTi and NiTiCu ingots, four different samples were selected from four different as-cast ingots (NiTi-1, NiTi-2, NiTiCu-1, and NiTiCu-2).

The selected four samples were initially solutionized at 850° C for 1 hour in the furnace and water quenched. After solution treatment, a set of aging processes were carried out in order to modify the microstructure, transformation temperatures and mechanical properties of the samples.

For chemical composition analysis of the samples, energy-dispersive spectrometry (EDS) analysis was conducted by utilizing FESEM JEOL JSM 7000F.

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Phase transformation temperatures of the samples were determined by using Perkin Elmer Pyres-1 Differential Scanning Calorimeter (DSC) with 10°C/min heating and cooling rate in the temperature range from 0°C to +200°C. The same characterization procedure was carried out for each sample.

3. RESULTS AND DISCUSSION

The chemical composition analysis of the produced SMA (NiTi and NiTiCu) samples were determined by EDS analysis (minor elements were ignored). The chemical compositions of the samples are given in Table 1.

Table 1.Chemical composition of the samples

Alloy	Ni %wt.	Ti % wt.	Cu% wt.
NiTi-1	54.97	45.03	-
NiTi-2	53.72	46.28	-
NiTiCu-1	59.66	37.75	2.59
NiTiCu-2	51.70	43.64	4.66

After detailed examination of the EDS results, the copper peaks were also easily detected in the NiTiCu-1 and NiTiCu-2 samples in addition to the nickel and titanium peaks. The details of the EDS results were shown in Fig. 1, 2, 3, and 4.

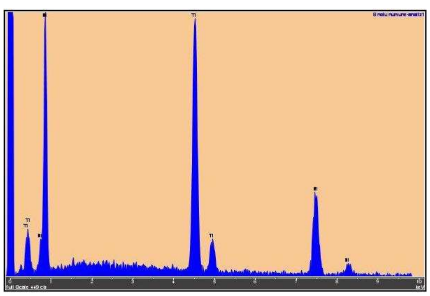

Figure 1. EDS result for NiTi-1.

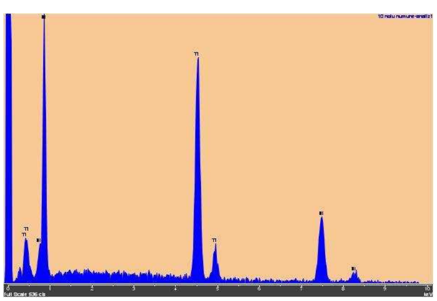

Figure 2. EDS result for NiTi-2.

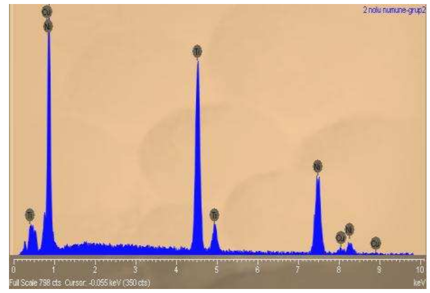

Figure 3. EDS result for NiTiCu-1.

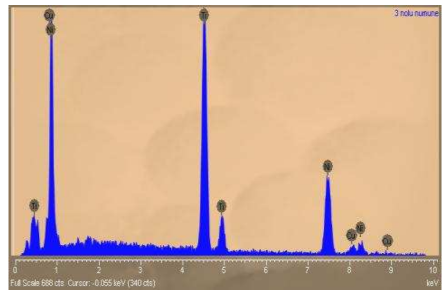

Figure 4. EDS result for NiTiCu-2.

After the heat treatment of the samples, microstructure investigation has also been carried out. Nikon Light Optical Microscope (OM) was used for microstructure observations. The samples were initially etched in the solution of HF, HNO_3 and CH_3CO_2H. After etching process, optical micrographs were collected at the magnifications of x200 and x400 as shown in Fig. 5.

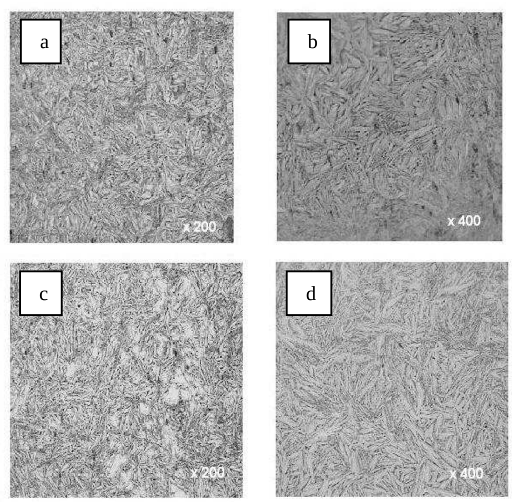

Figure 5. Micrographs of NiTi-1 (a, b), and NiTi-2 (c, d) after heat treatment.

With regards to the microscopic results, a complete martensitic microstructure was detected on NiTi samples (Fig. 5 a, b, c, and d). In contrast to the NiTi samples, a partial austenitic microstructure was observed on NiTiCu samples as seen in Fig. 5 e, f, g, and h. Furthermore, a spherical $NiTi_2$ precipitates were observed in the matrix of the

NiTi-1 and NiTi-2 samples microstructure different than the NiTiCu-1 and NiTiCu-2 samples as shown in Figure 5.

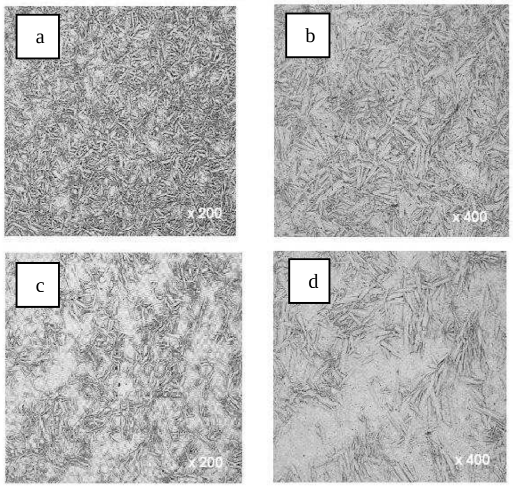

Figure 6. Micrographs of NiTiCu-1 (a, b), and NiTiCu-2 (c, d) after heat treatment.

In order to determine the transformation temperatures, DSC analyses were carried out with 4 thermal cycles at the heating/cooling rate of 10°C/min between 0˚C and 200˚C. The results of the DSC analysis of each sample were shown in the following Figures (Fig. 6, 7, 8, and 9). We note that intermediate rhombohedral R-phase does not occur in between martensite and austenite transformation temperatures in DSC results of the NiTi and NiTiCu samples. It is observed that a dramatic decrease was occurred on the NiTiCu-1 and NiTiCu-2 for the A_f and A_s temperatures. Moreover, NiTiCu DSC results show much smaller thermal hysteresis than the NiTi results. Since a negligible change occurred on the M_s and M_f temperatures of the NiTiCu samples, a narrow phase transformation temperature hysteresis was obtained after four thermal cycles under stress-free condition.

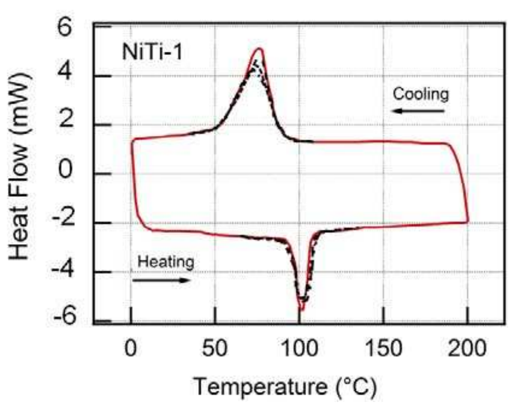

Figure 7. DSC result for NiTi-1.

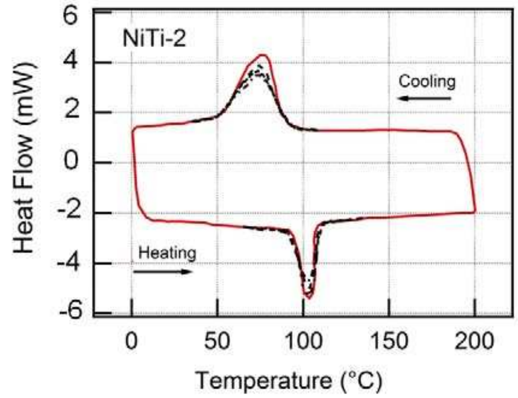

Figure 8. DSC result for NiTi-2.

Analyzing the DSC related Figures (Fig. 6, 7, 8, and 9); it can be observed that NiTi samples show more stable DSC results in comparison with the NiTiCu samples. Particularly, the thermal energy dissipation and storage peaks of the NiTi samples are higher than the NiTiCu counterparts. Moreover, martensite and austenite phase transformation temperatures of the NiTi dramatically decreased with the addition of Copper as seen Table 2.

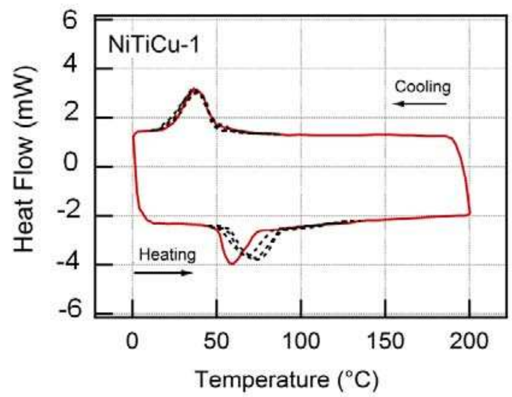

Figure 9. DSC result for NiTiCu-1.

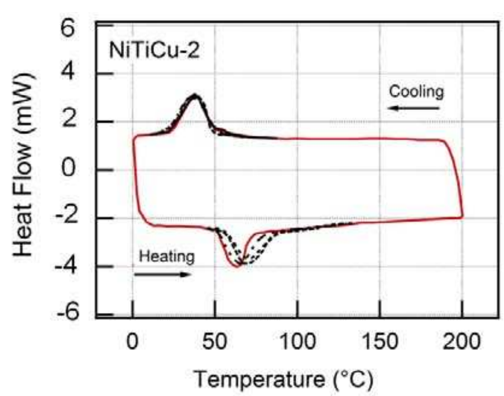

Figure 10. DSC result for NiTiCu-2.

Table 2. DSC analysis results for NiTi and NiTiCu samples after 4 cycles at the heating/cooling rate of 10°C/min between 0 and 200˚C.

Temp. (°C)	NiTİ-1	NiTi-2	NiTiCu-1	NiTiCu-2
M_s	72	71	48	47
M_p	67	64	38	41
M_f	54	48	24	21
A_s	91	95	51	49
A_p	105	101	62	58
A_f	114	110	67	71

M_s: Martensite Start, M_p: Martensite Peak
M_f: Martensite Finish, A_s: Austenite Start
A_p: Austenite Peak, A_f: Austenite Finish.

Following to the DSC analysis, scanning electron microscopy (SEM) analysis was conducted in order to observe the distribution of the precipitates in the matrix. The martensite plates were easily detected in the microstructure. A large amount of spherical shape Ti_2Ni precipitates were also clearly observed in the matrix of the NiTi samples as seen in Fig 11. The existence of the Ti_2Ni precipitates in the micrographs was also proved with the SEM result.

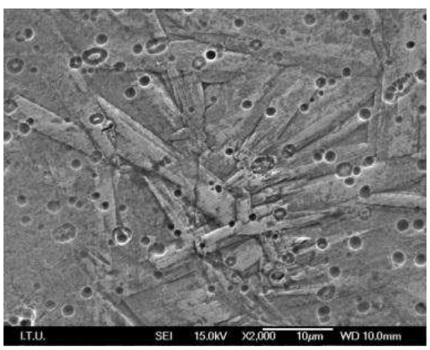

Figure 11. SEM micrographs of the NiTi-1 sample.

During Vickers hardness test, six hardness measurements were collected for each sample. The results of the Vickers hardness test are tabulated below in Table 3. It is observed that the hardness of the samples is increased with the addition of Copper. Among the four samples, NiTiCu-1 sample showed the highest hardness among the four samples. Added copper is most probably precipitated in α-Ti and SMA sample hardness increased.

Table 3. Hardness test results of the samples

Alloy	HV 0.1kg/mm^2
NiTi-1	204
NiTi-2	235
NiTiCu-1	319
NiTiCu-2	298

4. CONCLUSION

Vacuum arc remelting technique was successfully used for the production of the as-cast NiTi and NiTiCu specimens. A sufficient homogenous microstructure obtained in the ingots after three back-to-back melting. An effort was made to determine the effect of the stress-free thermal cycling on the NiTi and NiTiCu SMA samples. The following concluding remarks have been reached after the characterization of the as-cast NiTi and NiTiCu samples.

1) The addition of Cu into NiTi SMA as a ternary alloy dramatically decreased A_f and A_s temperatures after four thermal cycles under the stress-free condition between 0ºC-200ºC. However, a slight increase was observed on M_f temperature.

2) Hardness tests showed that the hardness of the NiTi samples is lower than the NiTiCu samples.

3) As-cast production technique can be easily improved to product low cost SMA materials for any future applications.

4) Further work is required to investigate the thermo-mechanical response and transformation characteristics under stress-loaded condition for NiTiCu SMAs.

5. REFERENCES

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