Preparation and characterization of equiatomic NiTi shape memory alloy

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Abstract. The present study investigated the vacuum induction melting of equiatomic NiTi (Ni 50 at. %, Ti 50at. %) shape memory alloy using graphite crucible. The cast alloy heat-treated at 865 °C for 15 mints, followed by quenching the sample in icy water. The microstructure and micro hardness of alloy were investigated before and after heat treatment by using an optical microscope and Vickers micro hardness tester. Transformation temperatures upon heating/cooling were investigated by using differential scanning calorimeter (DSC). Scanning electron microscope (SEM) supported with energy dispersive X-ray (EDX) and X-ray diffraction analysis (XRD) were carried out to investigate the chemical composition and the phases present in the alloy after heat treatment. The results show that the vacuum induction melting process in a graphite crucible provides binary NiTi shape memory alloys with good chemical homogeneity. The microstructure becomes more homogenous and the Vickers's micro hardness increases from 186.06 to 238.74 after heat treatment with highly controlling on the composition of the alloy. The DSC curve shows that the R-phase exists upon the heating and cooling process. In addition the precipitate phase Ti₂Ni was also exist.

Keywords: equiatomic NiTi alloy, NiTi shape memory alloys, DSC, XRD.

1. Introduction

Shape memory alloy is a type of smart material that has two distinct properties such as superelasticity (SE) and superior thermal shape memory effect (SME). SMAs are the materials that can achieve high deformation and regain the original shape upon unloading or after heating above a certain temperature. Shape memory effect refers to the phenomena where the SMA will automatically come to its original position after heating and super elasticity effect is where SMAs may undergo non-linear deformation and comes back to its original shape upon unloading. Due to these amazing properties, SMA’s have found various applications in the biomedical field as well as in industrial sectors such as for making fasteners, coupling, actuators, etc., [1-3]. Shape memory behavior detected in 1965 by Buehler and Wiley of the U.S. Naval Ordnance Laboratory (NOL), received a United States patent for a group of NiTi alloys, which is called 55-Nitinol. These compounds have chemical compositions in the range of (53-57) wt. %, corresponding to a (48-52) at. %, which implies they are near equiatomic alloys. NiTi shape memory alloys known as (Nitinol) alloys according to their chemical element symbols and the Naval Ordnance Laboratory acronym [4]. NiTi Shape memory alloys contain two phases, first is the martensite phase which is stable at low temperatures formed by rapid cooling is defined according to the German physicist Adolf Martens, and it has an eccentric and highly crystalline phase, the second phase is the...
Austenite phase which is stable at high temperatures, which is named according to the English physicist Charles Austen; it has a face-centered cubic structure geometry [4]. In near equiatomic Nitinol alloys, the thermo elastic martensitic transformation between B2 austenite phase and B19′ martensite phase gives an increase to the shape memory effect (SME) and super elasticity (SE). Furthermore, high mechanical strength and ductility are noticed in Nitinol alloys [5, 6]. Vacuum induction melting (VIM) is a common method used for producing NiTi alloys, because of the electrodynamics' forces that give excellent stirring of the melt and produce a greater chemical and microstructural homogeneity in the alloy [7-9]. This experimental work deals with, preparation of equiatomic NiTi (Ni50Ti50) shape memory alloy using vacuum induction melting method, and investigates the phase transformation temperature, micro hardness, and microstructure of binary NiTi shape memory alloy.

2. Experimental work

2.1 Materials

Nickel plate with high purity 99.9 wt. % and titanium wire 98.66 wt. % were used to produce NiTi alloys. The constituent elements of the alloy, titanium wire and nickel plate were dipped in acetone and alcohol in an ultrasonic bath, then they were rinsed with distilled water and dried by pressurized air before melting.

2.2 Melting and Homogenization

The alloy composition was equiatomic NiTi alloy 50 % at. Ni and 50 % at. Ti (which is equivalent to 55 % wt. Ni and 45 % wt. Ti). The ingredient elements nickel and titanium are charged in a graphite crucible and melted in high-frequency induction furnace type (EQ-SP-25TC-15AB) made in the U.S.A. the furnace evacuated to $10^{-3}$ mbar and after that purged with high purity argon. The melting process was carried out under argon atmosphere. After that, the melting process repeated three times to obtain a good homogenization of the chemical composition. The sample was heat-treated at 865 °C for 15 min, in a programmable furnace. Followed by quenching the samples in icy water. The sample were poured with dimensions (25mm×20mm), and then it is sectioned into same dimensions for different examinations. Differential scanning calorimetry (DSC) produced by SETARAM, type 131 EVO, made in French. A different temperature range from (-100°C – 300 °C) with heating/cooling rate 10°C/min in nitrogen atmosphere was used to investigate the thermal behavior of prepared alloy. Scanning electron microscope SEM supported with the energy dispersive x-ray analysis unit EDX model (VEGA3LM), is used to investigate the chemical compositions of samples. The analysis of the different phases of the heat-treated sample, x-ray diffraction test was carried out using Shimadzu device, made in japan. Microstructure study was carried out at various stages of processing. The sample was grinded and polished followed by etching using (10 ml HF, 20 ml HNO3, and 30 ml H2O) solution for 10 sec. Optical microscope with magnification of (4X) was used to investigate the microstructure of samples. For hardness measurements, the test was carried out at room temperature using micro hardness Vickers tester type (Laryee model HVS-1000) made in china, under 300 gf. load for holding time 10 sec.

3. Results and discussion

Figure 1 shows the DSC profile of binary Ni50Ti50. The transformation temperatures, austenite start temperature (As), austenite finish temperature (Af), martensite start temperature (Ms), martensite finish temperature (Mf), R- phase start temperature (Rs) and R- phase finish temperature (Rf) are given in (Table 1). The alloy was found to undergo a multi-stage martensitic transformation. There are four peaks in the DSC curve, two exothermal peaks appear during the cooling process which refers to the transformation from the austenite phase (B2) to the R- phase and from R- phase to martensite phase (B19′), respectively [10]. Also, two endothermic peaks are revealed during heating which indicates the transformation from the martensite phase (B19′) to the
R-phase and from the R-phase to the austenite phase (B2), respectively [10]. This phenomenon is different from most of the results that characterized in previous works of literature, where R-phase transformation occurs only during cooling [11]. This behavior may be predicated to the formation of coherent Ti$_2$Ni precipitates, which produces local stress fields [12, 13]. This transformation behavior is most alike to that presented by Niraj N. et al [10].

![Figure 1. DSC profile of heat treated Ni$_{50}$Ti$_{50}$ shape memory alloy.](image)

**Table 1.** The transformation temperatures of heat treated Ni$_{50}$Ti$_{50}$ shape memory alloy.

| Transformation temperatures °C | Martensite phase | R-phase | Austenite phase |
|-------------------------------|-----------------|---------|-----------------|
|                               | start | finish | Start | finish | start | Finish |
| Heating                       |   -   |  -     | 14.4  |  89.5  |  100.1 | 137.2  |
| Cooling                       |  7.6  | -42.6  |  39.7 |  12.7  |   -   |   -   |

Figure 2 show the microstructure of the Ni$_{50}$Ti$_{50}$ alloy by SEM analysis, the microstructure of the alloy consist of NiTi phase (matrix) presented by dashed pointer and precipitates of intermetallic compound of Ti$_2$Ni phase presented by solid pointer. Table 2 show the microanalysis, by energy dispersive X-ray spectrometry, of different phases found in the microstructure of the investigated alloy that presented in figure 2. It can be noticed that, the matrix has approximately the same content of Ni and Ti. The matrix phase has the composition of Ni 49.8% at. And Ti 50.2% at., (which is equivalent Ni 54.9 % wt. and Ti 45.1 % wt.), which is very close to the percentage of Nickel and Titanium elements that are mixed before melting, these results indicate to the successful mixing process during melting. Ti$_2$Ni phase has higher Ti percentage, almost double,
than Ni in its precipitates. Ti content in the latter phase reaches around, 68.28 % at while Ni content is about 31.72 % at (equivalent to Ti 63.71%wt and Ni 36.29%wt).

Figure 2. SEM micrograph showing the microstructure of heat treated Ni$_{50}$Ti$_{50}$ Shape memory alloy.

Table 2. Chemical composition of different phases in heat treated binary Ni$_{50}$Ti$_{50}$
Shape memory alloy

| Phases       | Ti % at. | Ni % at. |
|--------------|----------|----------|
| Matrix (NiTi)| 50.2     | 49.8     |
| Ti$_2$Ni     | 68.28    | 31.72    |

The crystalline phases of the heat-treated Ni$_{50}$Ti$_{50}$ alloy were investigated by X-ray diffraction (XRD) at room temperature, Figure 3 shows that the Ni$_{50}$Ti$_{50}$ alloy contains both R- phase (rhombohedral) and martensite (B19') phase (monoclinic). In addition to diffraction peaks of Ti$_2$Ni phase are observed in the alloy. Coexist of R- phase and martensite phase because the martensite finish temperature (Mf) of the Ni$_{50}$Ti$_{50}$ SMA is lower than the room temperature, which leads to incomplete transformation of Ni$_{50}$Ti$_{50}$ SMA from martensite (monoclinic) to R- phase (rhombohedral) at room temperature.
Figure 3. X-ray diffraction (XRD) of heat treated Ni$_{50}$Ti$_{50}$ shape memory alloy.

The microstructures of Ni$_{50}$Ti$_{50}$ SMA before and after heat treatment determined by the Optical Microscope are presented in Figure 4. From the images found that the microstructures of the equiatomic NiTi SMA after heat treatment at 865 °C is more homogenous because of solution treatment dominated by equiaxed grains rather than dendrites. From figure 4 the grain size after heat treatment seems to be smaller than the grain size before the heat treatment (grain refinement) Also, there are precipitates Ti$_2$Ni in the grain interior as well as at the grain boundary, represented by a solid pointer in figure 4b. The matrix NiTi phase represented by dashed pointer in figure 4b.

The results of micro hardness test for Ni$_{50}$Ti$_{50}$ are shown in Table 3. The optioned values was determined by taking the average of the seven measurements on the specimen. By comparing the micro hardness values of the specimen, before and after the heat treatment at 865 °C in normal atmosphere, it is obviously, an appreciable increase in micro hardness after heat treatment because the structure becomes more homogenous, and also due to the refinement of the grain size, with grain refinement, that's mean there are more and more grains that are nearby are turned to have a different orientation. This makes it difficult for a dislocation to cross between grains, also, introduces more and more grains boundaries which effect the movement of dislocations and that's make the material harder and stronger.
Figure 4. Optical Micrograph showing the microstructure of Ni50Ti50 shape memory alloy: a) before heat treatment, b) after heat treatment at 865 °C for 15 min.

Table 3. Micro hardness of Ni50Ti50 sample before and after heat treatment.

| Sample    | Before heat treatment | After heat treatment |
|-----------|-----------------------|----------------------|
| Ni50Ti50  | 186.06                | 238.74               |

4. Conclusions
It was proved by EDX that the composition of the alloy could be controlled by using a vacuum induction melting process for preparation NiTi shape memory alloy. Binary NiTi shape memory alloy with two-steps martensitic transformation during cooling and heating can be produced. XRD patterns revealed that the strongest peak belongs to the R-phase (rhombohedral) which is a form of martensitic phase. The optical micrographs show homogenous structure of NiTi alloy after heat treatment. There is a noticeably increasing in hardness value after heat treatment at 865°C.

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