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EFFECT OF AGING ON MICROSTRUCTURE AND MARTENSITIC TRANSFORMATION AND MAGNETIC PROPERTIES OF NI GA FE TI SHAPE MEMORY ALLOY

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ABSTRACT

The effect of ageing on the microstructure, martensitic transformation and magnetic and mechanical properties of Ni51Fe18Ga27Ti4 shape memory alloy was investigated. There are five specimens of this alloy aged at 573 up to 973K for 3 h per each. This range of ageing temperature greatly affects the microstructure of investigated alloys. As the ageing temperature increases from 573K up to 973 K, the microstructure of Ni51Fe18Ga27Ti4 alloy gradually changed from entirely martensitic matrix at 573K to fully austenitic microstructure at 973K. The volume fraction of precipitated Ni3Ti particles increased with increasing ageing temperature from 573K up to 773K. Further increasing in ageing temperature up to 973K decreased the percentage of Ni3Ti in the microstructure. Martensitic transformation temperature was decreased steadily by increasing ageing temperature. The magnetization saturation, remnant magnetization and coercivity increased with ageing temperature up to 773K. Further increase in ageing temperature decreases these magnetic properties. Moreover, hardness measurements was gradually increased at first by increasing ageing temperature up to 773K then dramatically decreased to the lowest value at 973K.

KEYWORDS: Magnetic Shape Memory Alloys, Ageing, Microstructure, Martensitic Transformation, Magnetic and Mechanical Properties

INTRODUCTION

The practical applications of Ni–Mn–Ga alloys have been limited to some extent due to their extreme brittleness and low strength although they exhibit low twinning stress and high magnetic anisotropy. In order to improve the mechanical properties without sacrificing its magnetic and thermoplastic properties, the modification of Ni–Mn–Ga FSMAs by adding the fourth element is becoming a new research field. For this purpose, several rare earth elements have been added into ternary Ni–Mn–Ga alloys, such as Tb, Sm, Dy and Nd, and their effects on the phase transformation behavior, magnetic and mechanical properties have been studied [1–4].

Heusler alloys have attracted much attention for their unique potential as actuators in microelectromechanical systems [5, 6], especially Ni-Mn-Ga, in which a magnetic-field-induced strain up to 6% has been reported [7]. Subsequently, some new Heusler alloys, such as Co-Ni-Al, Co-Ni-Ga and Ni-Fe-Ga were explored [8, 9]. Recently, Oikawa et al. have found Ni-Ga-Fe alloys to be promising FSMA candidates [10, 11].

Lately, it was found that by adding Ti in a polycrystalline Ni53Mn23.5Ga23.5 alloy, a significant improvement in the mechanical properties is achieved by the proper aging treatments [12 - 15]. Therefore, the effect of Ti addition to the ternary Ni-Fe-Ga alloys and its effects on microstructure, martensitic transformation magnetic and mechanical properties have been studied [15].

On the other hand, a significant improvement in the shape memory effect of Fe13.5Mn4.86Si3.82Ni0.16C alloy was achieved by deformation ageing [16]. However, the influence of aging treatment on the system of Ni-Fe-Ga-Ti alloy has not been yet reported.

In this work, the effect of aging conditions on the martensitic transformation, microstructure and magnetic and mechanical properties of polycrystalline Ni51Fe18Ga27Ti4 alloy will be investigated to get the appropriate aging process.

EXPERIMENTAL PROCEDURES

Polycrystalline Ni51Fe18Ga27Ti¬4 magnetic shape memory alloy was manufactured using arc-melting under argon atmosphere (purity of elements is higher than 99.99%). The alloy was melted four times to ensure homogeneity and cast into a cylindrical copper mold set at the bottom of the furnace to prepare a rod with diameter of 10 mm and height of 70 mm. The master rod was sealed in a quartz tube under a vacuum, then annealed at 1273K for 24 h followed by iced-water quenching for homogeneity. Subsequently, the solution treated samples were aged for 3 h within a temperature range of 573–973 K, respectively, and consequently quenched into iced water.

Microstructure of the investigated alloys was examined by Meiji optical microscope fitted with a digital camera. The specimens for microstructure examination were prepared by standard metallographic procedures according to Standard ASTM E3-11 then etched in a solution of HNO3, HF and H2O in a ratio of 4:1:5, respectively. The phase transformations of the aged alloys were measured by Netzsch CC 200 F1 differential scanning calorimetry (DSC) with a cooling/heating rate of 10 K/min in the temperature range from 243 to 423 K. Moreover, X-ray diffraction (XRD) was carried out to identify the existing different phases in the structure by using Cu Kα radiation with a step-scanning in 2θ range of 30–90°. Magnetic properties were evaluated as well using VSM lakeshore 7400 USA. Additionally, hardness measurements were carried out according to standard ASTM E348-11e1 using LECO Vickers Hardness Tester LV800AT, as indicator to the mechanical properties for these investigated alloys.

RESULTS AND DISCUSSIONS

Crystal Structure of Aged Ni51Fe18Ga27Ti4 Alloys

The effect of aged temperature on the crystal structure of the Ni51Fe18Ga27Ti4 alloy was thoroughly studied. Fig. 1 shows the XRD patterns for the samples aged at different temperature (573-973K) for 3h measured at room temperature. The 573K aged sample shows patterns that indexed for the tetragonal martensite structure. The main diffraction peaks corresponding to (202), (004), and (224) planes related to tetragonal martensite were observed. As the aging temperature increases, most of the martensite patterns disappeared except of (202) plan that is visible in all aged samples except the one aged at 973K. The broadening of (202) plane and the disappearance of the remaining plans can be referred to the transformation from tetragonal martensite structure to the cubic austenite structure [8] since the main pattern of austenite (220) are too close to the main pattern of martensite (202). This also means that the martensite may not completely transform into austenite. With aging temperature at 773K and more, new patterns of plan (400) and plan (422) appeared that can be indexed into cubic austenite phase. The austenite patterns are dominant at this ageing temperature (773K) showing a strong patterns at (220), (400) and (422). With a further increase in aging temperature up to 873K, the intensity of the main peak of austenite (220) became sharper than in case of 773K; however the intensity of the other two peaks (400) and (422) are remarkably decreased. Additionally the main peak of martensite phase still exist at plan (202). At 973K aging temperature, martensite peaks disappeared completely and only the existing peaks are related to the austenite phase, as shown in Fig. 1.

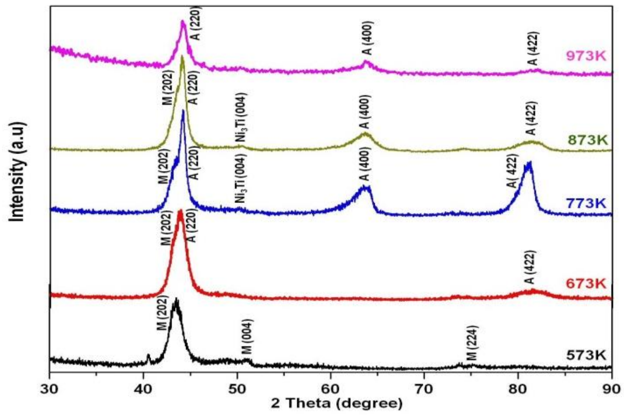

Figure 1: XRD Patterns at Room Temperature of Ni51Fe18Ga27Ti4 Alloy Aged at 573-973 K for 3 h

In addition, some minor peaks can be observed with increasing ageing temperature to 773 and 873K, indicating that a new type of second phase in the aged Ni51Fe18Ga27Ti4 alloy was precipitated. Moreover, the results of Dong et al. [17] showed that adding 5 at.% Ti to Ni53Mn23.5Ga23.5 resulted in Ni3Ti phase precipitating in the aged samples. Therefore, the precipitates are identified as Ni3Ti type.

According to the XRD results, the crystal structure can be indexed as tetragonal martensite with lattice parameters a = b = 0.58881 nm and c = 0.5621 nm aged at 573K. While, the typical austenite peaks can be seen in samples aged at 673, 773, 873 and 973 K with cubic lattice parameters a = b = c = 0.581494 nm, 0.580597 nm, 0.584486 nm and 0.579833 nm, respectively.

Microstructure Observation

Fig. 2 shows the optical micrographs of Ni51Fe18Ga27Ti4 alloys aged at various temperatures. The sample aged at 573K has a martensitic microstructure with a small percentage of Ni3Ti precipitates, as shown in Fig. 2 (a). Some Ni3Ti precipitates remarkably emerged in the martensite structure as the ageing temperature increases to 673K Fig. 2 (b). At this ageing temperature, austenite phase starts to be appeared in the microstructure of this sample as it was emphasized by XRD, as shown in Fig. 1. In addition to the lath martensite phase, the cubic structure of austenite was found strongly in the microstructure of aged alloy at 773K; see Fig. 2 (c). In the same aged alloy, Ni3Ti particles significantly precipitated in both martensite and austenite phases. This aged alloy has the highest percentage of Ni3Ti among other aged alloys. Moreover, face centered cubic structure of phase is presented in the microstructure; see Fig. 2 (c). This phase precipitated at the grain boundaries between martensite and austenite phases. However, X-ray could not detect any peaks for phase because of its lower percentage in the microstructure; see Fig. 1. From Fig. 2 (d), the austenite phase percentage in the microstructure increases at the expense of the lath martensite phase. Where the predominant phase in this microstructure aged at 873K is the austenite. The Ni3Ti precipitates still exist in the microstructure at this ageing temperature but in lower content in comparison with aged alloy at 773K. It seems that the Ni3Ti precipitates re-dissolve in the microstructure again by increasing again temperature more than 773K. The reflection of these precipitates is observed at this ageing temperature (873K) in XRD patterns as shown in Fig. 1. The microstructure of the maximum ageing temperature at 973K consists entirely of pure cubic austenite structure, as shown in Fig. 2 (e). This austenitic microstructure was confirmed by the XRD patterns in Fig.1, where there is no any peak for the martensite phase. A small amount of Ni3Ti precipitates can be noticed in the austenitic microstructure of the aged alloy at 973K.

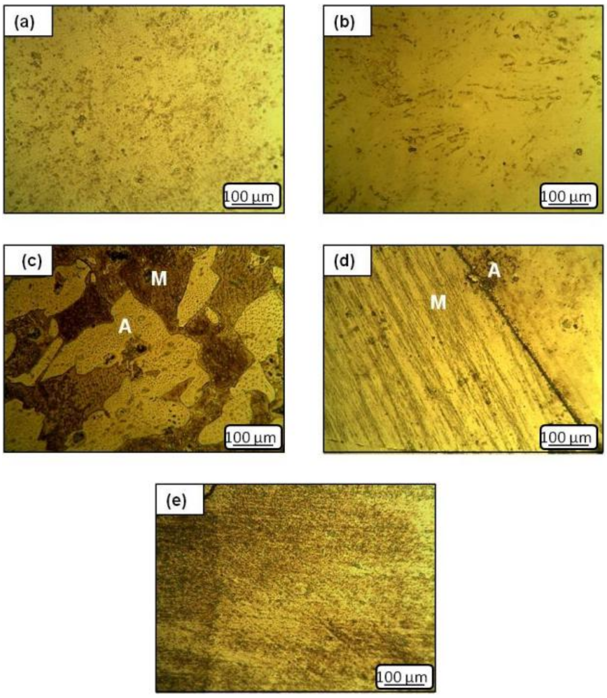

Figure 2: Microstructure of Aged Ni51Fe18Ga27Ti4 Alloy for 3 h at (a) 573 K (b) 673 K (c) 773 K (d) 873 K and (e) 973 K

It can be concluded that, as the ageing temperature increases the 100% martensitic microstructure found at 573K completely transforms gradually to 100% austenitic structure at 973K. Moreover, the amount of Ni3Ti precipitates enlarges at first in microstructure with ageing temperature from 573K to 673K. These precipitates reach its maximum percentages in the microstructure of aged alloy at 773K [13]. With further increase of ageing temperature to 873 and 973K, the Ni3Ti particles content decreases again by dissolving in the microstructure to lower percentages compared to 773K, as shown in Fig. 2.

Martensitic Transformation

The DSC curve of the aged alloy at 773k for 3 h is shown in Fig. 3, which illustrates that a one step martensitic transformation occurs upon cooling and heating. The forward martensitic transformation starts (Ms) around 294.9K and finishes (Mf) at 286.5 K, while the backward or reverse martensitic transformation (austenitic transformation) starts (As) and finishes (Af) at 320.8 and 327.9K, respectively. Phase transformation temperatures for other aged alloys are revealed in Table 1. Table 1 illustrates that the martensitic transformation temperatures decrease gradually as the ageing temperature increase.

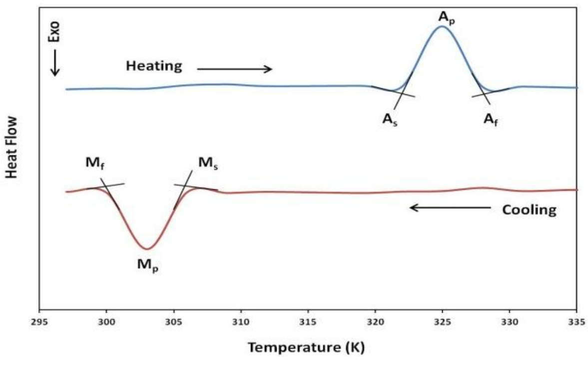

Figure 3: Martensitic and Austenitic Transformations at 773K for 3 h

As shown in Fig. 2, the microstructure of aged alloy at 773K for 3 h consists of martensite and austenite where the martensitic and austenitic transformation temperatures both are higher than room temperature. However, elevating ageing temperature to 973K for 3 h, leads to make the microstructure of this alloy has only austenitic matrix as shown in Fig. 1 and 2.

Table 1: Phase Transformation Temperatures for Ni51Fe18Ga27Ti4 Alloys Aged at 573-973K/3h. (all Temperatures are in Kelvin)

Ageing Temp.	M_f	M_p	M_s	A_s	A_p	A_f
573	310.9	318.3	323.4	329.1	337.6	345.2
673	306.7	310.6	315.7	325.4	331.8	338.8
773	299.8	302.4	306.2	320.8	324.4	327.9
873	287.6	294.2	304.5	312.7	317.3	321.0
973	267.3	275.6	283.7	298.3	306.8	315.4

Additionally, the precipitation of Ni3Ti particles can support the lowering of the martensitic transformation temperature. Where increasing ageing temperature up to 773K leads to enlarge the percentages of Ni3Ti precipitates in the microstructure, see Fig. 2 (c). The presence of these precipitates can hinder the shearing process. This phenomenon could partially responsible for the lowering of martensitic transformation temperature [8].

Magnetic Properties

The magnetization of the Ni51Fe18Ga27Ti4 alloys aged at different temperature were performed at room temperature under an applied field of 5KOe using vibrating sample magnetometer (VSM). The hysteresis loops of the investigated alloys were obtained as shown in Fig. 4. In the latter figure, the magnetization (M) as a function of applied field (H) was plotted for different aged alloys. While Fig. 5 displays the saturation magnetization (Ms), remnant magnetization (Mr) and coercivity (Hc) versus aging temperature.

In general, the magnetization curves exhibited the typical characterization of ferromagnetic materials due to the deviation from rectangular form and according to their lower coercivity. The magnetization of the aged Ni51Fe18Ga27Ti4 alloys increases gradually with the elevating in aging temperature from 573K up to 773 K. The latter ageing temperature has the highest value of magnetization among other ageing temperatures. With further increase in aging temperature to 873 and 973K, the magnetization decreases slightly with 873K and dramatically at 973K, as shown in Fig. 4. The lowest value of magnetization obtained with ageing temperature at 973K. In aged Ni51Fe18Ga27Ti4 alloy, the Ni3Ti precipitates and the matrix have a certain coherent relationship. With increasing aging temperature, the quantity and size of the Ni3Ti precipitates increases, as shown in Fig. 2, and hence the relationship between the precipitate phase and matrix changes, which in turn altering the magnetization of the alloy. Increasing ageing temperature up to 773K increases the volume fraction of Ni3Ti precipitates leading to continual reduction in Ti content in the matrix. This depletion in the matrix Ti percentage resulting in the partial Fe atoms ferromagnetically couple with the neighboring Fe atoms, which increases the saturation magnetization, as shown in Figs. 4 and 5. It is reported that increasing the Fe content effectively increases the saturation magnetization [18].

In the same direction the decrease in Ti content in the matrix could change the structure of the martensitic matrix then affecting positively on the saturation magnetization [19, 20]. Where Ti additions to Ni51Fe22Ga27 alloy at the expense of Fe content changes the structure of five–layered martensite, ferromagnetic phase, to non-modulated martensite, which is paramagnetic phase [15].

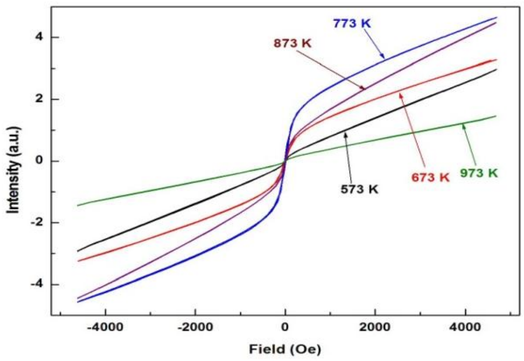

Figure 4: Magnetization Saturation of Aged Ni51Fe18Ga27Ti4 Alloys

From the XRD results, the martensite phase transforms to austenite phase as the aging temperature increase, see Fig. 1. When the ageing temperature exceeds 773K, the austenite phase became the predominant phase in the microstructure. Additionally, It is well known that the saturation magnetization of austenitic phase is lower than that of martensitic phase [21, 22]. Thus by increasing the ageing temperature to 873k and to 973K the transformation from martensite phase (ferromagnetic) to austenite phase (paramagnetic) decreases Ms, Mr and Hc, as shown in Fig. 5. The Ni51Fe18Ga27Ti4 alloy aged at 973 K aged temperature has the lowest values for these measured magnetic properties among other alloys due to that the matrix consists of only single phase of austenite, and the magnetization decreases sharply.

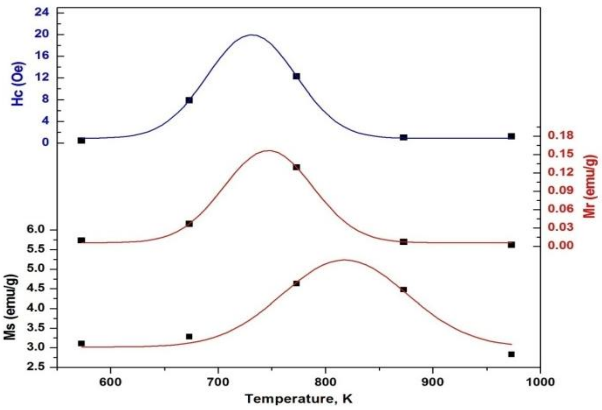

Figure 5: Effect of Ageing Temperature on the Saturation Magnetization (Ms), Remnant Magnetization (Mr) and Coercivity (Hc) of Ni51Fe18Ga27Ti4 Alloys

Mechanical Properties

The effect of ageing heat treatment on the mechanical properties of Ni51Fe18Ga27Ti4 alloy was investigated. The mechanical properties of the aged Ni51Fe18Ga27Ti4 alloy was studied through the hardness measurements. Figure 5 represents the relationship between ageing temperature and the hardness values of Ni51Fe18Ga27Ti4 alloys. The hardness of the investigated alloys gradually increases as the temperature of ageing treatment increase. This increment in hardness measurements from 573K until 773K, through 673K, could be related the presence of Ni3Ti precipitates. As the ageing temperature increases the percentage of Ni3Ti precipitates increases in the matrix of martensite, until the temperature of 773K, which in turn influences the hardness value. The maximum value of hardness was obtained at the ageing temperature of 773K, as shown in Fig. 5. At this ageing temperature, the austenite phase (soft phase) in a reasonable amount appeared accompanying the lath martensite phase (hard phase) in the microstructure. According to the presence of the austenite phase in the microstructure, the hardness should be decreased. However the hardness value increased and not decreased as expected that could be related to the existence of the maximum contents of Ni3Ti precipitated phase in that microstructure, at 773K. It seems that there was a competition between austenite phase and the precipitated Ni3Ti phase and the latter won this competition. By increasing ageing temperature to 873K, the mount of austenite phase enlarges in the microstructure and at the same time the Ni3Ti precipitates amount decreased again, that leads to dramatically decrease in hardness value. By further increase in ageing temperature to 973K, the microstructure transforms entirely from martensite to austenite and in the same direction the volume fraction of Ni3Ti decreases as well, which in turn decreases the hardness measurements. The aged Ni51Fe18Ga27Ti4 alloy at this highest ageing temperature (973K) has the lowest value of hardness, as shown in Fig. 6.

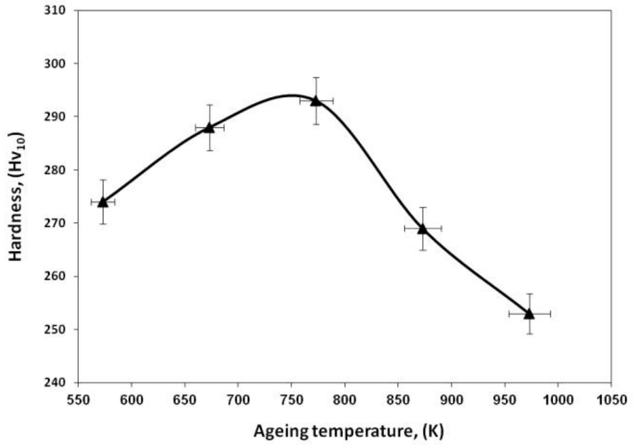

Figure 6: Hardness Measurements versus Ageing Temperature

CONCLUSIONS

The effect of ageing temperature on the microstructure, martensitic transformation, and magnetic and mechanical properties of Ni51Fe18Ga27Ti4 alloy was investigated. The results can be concluded as follows:

1. The microstructure gradually transformed from fully martensitic at 573K to entirely austenitic at 973K. In addition, the volume fraction and size of Ni3Ti precipitates increases in the microstructure firstly with increasing ageing temperature up to 773K. Then decreased again by dissolving in the matrix by elevating temperature more than 773K.
2. Martensitic transformation temperature has an inverse relation with ageing temperature. This could be due to the precipitation of Ni3Ti phase, which in turn hindered the martensitic transformation. AT 973K, the martensitic transformation temperature became under the room temperature.
3. The continual depletion in the matrix Ti content as the ageing temperature increases leads to enhance the saturation magnetization, remnant magnetization and coercivity up to 773K. Further increase in ageing temperature made the austenite as a prevailing phase in the microstructure, which is a paramagnetic phase and negatively affect the magnetic properties.
4. The presence of hard Ni3Ti particles in the microstructure increases the hardness measurements especially at 773K, where at this temperature the Ni3Ti phase has its highest volume fraction in the microstructure.

However, the hardness value significantly decreases due to the existence of the soft austenite phase with higher percentages in the microstructure at elevated ageing temperatures.

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