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# Isothermal oxidation study on NiMnGa ferromagnetic shape memory alloy at 600–1000 °C

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ABSTRACT

Oxidation behavior of NiMnGa alloy has been investigated under isothermal temperature by thermo gravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy equipped with an energy dispersive X-ray (SEM–EDX) spectroscope systems. The Ni–28.5Mn–20.5Ga alloy (composition in atomic percent) was exposed to oxygen atmosphere isothermally, i.e., between 600 °C and 1000 °C, for 1 h. A gravimetric method was used to determine the oxidation kinetics; weight gain per unit area as a function of time. It was determined that the oxidation constant increases significantly with isothermal temperature. Activation energy of the oxidation was found to be 152 kJ/mol. X-ray diffraction patterns of the heat-treated samples contain oxide peaks, mainly belonging to $Mn_3O_4$. X-ray analyses demonstrate that the amount of the oxide increases with isothermal temperature while that of martensite phase decreases. The scanning electron microscopy equipped with an energy dispersive X-ray (SEM–EDX) spectroscope analysis also gives the same result. According to magnetic measurements, the saturation of NiMnGa alloys decreases with rising isothermal oxidation temperature.



## 1. Introduction

Oxidation of shape memory actuators is unavoidable when they exposed to air for a long period. This oxidation causes significant changes in the microstructure of the shape memory alloy, e.g., destabilization of martensite phase, and as a result of this, the shape memory effect of the alloy diminishes in time [1]. In contrast to other alloys, shape memory alloys need to be heat-treated for rearrangement of the crystal structure. However, similar to other metallic alloys, such heat treatment procedures cause oxidation of the surface in the shape memory alloys [2]. Oxidation is advantageous as it improves the wear resistance of these alloys [3].

In ferromagnetic NiMnGa alloys, martensite transformation temperature, crystal structure and magnetic properties of the alloy are affected by the composition. Thus, these properties are controlled by adjusting the composition. Another approach to improve these properties is the application of an isothermal heat treatment procedure [4–6]. It is much easier to control the martensite transformation temperature by heat treatment rather than adjusting the proper composition. For this reason, instead of addition of a new element or adjusting the compositions of Mn, Ni and Ga, heat treatment is a suitable and widely used technique to improve the martensite transformation temperature, Curie temperature, crystal structure and magnetic properties of the alloy. However, as depicted before, heat treatment atmosphere results in oxidation of the NiMnGa alloy, which is used as a sensor or actuator. There is no detailed research in the literature on oxidation of NiMnGa alloy at isothermal heat treatment conditions.

In this study, oxidation behavior of NiMnGa alloy in oxygen atmosphere at temperatures between 600 °C and 1000 °C was investigated by means of TG/DTA, XRD and SEM–EDX analyses.

## 2. Experimental

Ni–28.5 at%Mn–20.5 at%Ga alloy was used to investigate the oxidation behavior. Samples with identical surface areas were obtained by machining and cutting a large piece of this alloy. Roughness of these specimens was minimized by grinding while acetone is used to clean them. To determine oxidation behavior of alloys, nonisothermal TG/DTA measurement were done at the heating rate of 10 °C/min in air atmosphere by Perkin Elmer Pyris TG/DTA thermal analysis system. Isothermal oxidation experiments were performed by Perkin Elmer Pyris TG/DTA thermal analysis system,

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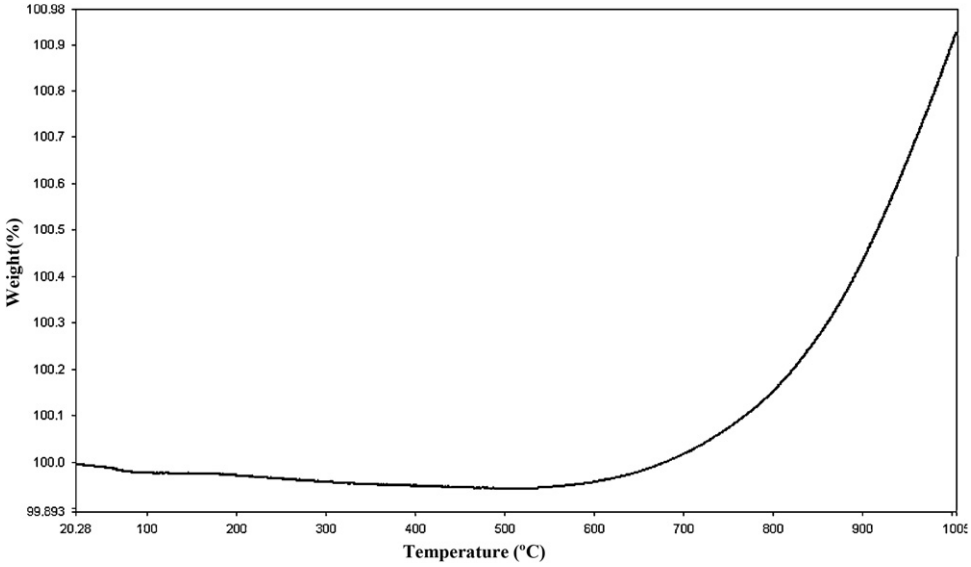


**Fig. 1.** Nonisothermal TG/DTA measurement of Ni–28.5 at%Mn–20.5 at%Ga alloy.

too. First, the alloy was heated up to the previously determined oxidation temperature at a rate of 50 °C/min in nitrogen atmosphere and then kept isothermally at this temperature for 1 h while pure oxygen was purged over sample continuously at a rate of 100 ml/min. The mass gain of samples as a function of time was measured via thermogravimetric analyzer. Isothermal oxidation temperatures were selected as 600, 700, 800, 900 and 1000 °C. In order to identify the possible formation of oxide structures, X-ray diffraction (XRD) measurements were carried out in the range of 20–80° by using Cu Kα as incident beam (Rigaku RadB-DMAX II). Surface characterization of the oxidized specimens was performed by using SEM (JEOL JSM 7001F) equipped with an energy dispersive X-ray (EDX) spectroscope. Physical property measurement system (PPMS) (Quantun Dizayn PPMS 7) was used to determine the magnetic properties by applying an external magnetic field. The magnetization measurements were taken at room temperature for the interval of −30.000 Oe (−3*T*) to +30.000 Oe (+3*T*).

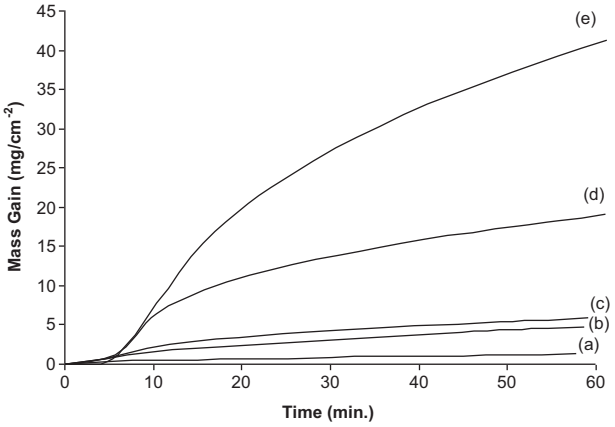


**Fig. 2.** Mass gain of the samples exposed to isothermal heat treatment for 1 h at different temperatures (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C and (e) 1000 °C.

## 3. Results and discussion

### 3.1. Isothermal oxidation kinetics

Depending on oxidation, the weight gain were divided two part by Li et al., one weight gain occur linearly, other occur parabolic [7]. As seen in Fig. 1, the weight gain change parabolic between 500 and 1000 °C temperature intervals. According to these result, chosen oxidation temperatures of our study fit parabolic oxidation Laws [8,9]. Furthermore, Fig. 2 shows the curves giving the mass gained by samples with time of isothermal heat treatment for the studied temperatures, i.e., 600, 700, 800, 900 and 1000 °C. According to these graphs, the amount of oxidation increases parabolic with time accompanied by a significant increase in the mass of the specimens. Oxidation constant of the alloy at different temperatures was calculated by using the parabolic equation.

$$\left(\frac{\Delta W}{A}\right)^2 = K_p t \quad (1)$$

where $\Delta W/A$ is the mass gain per area of the specimen, $K_p$ is the parabolic oxidation constant and t is the duration of the heat treatment at which the sample is exposed to oxygen [3,9]. Here, the value of $K_p$ is equal to slope of the time ($t$) vs. $(\Delta W/A)^2$ curve [10]. The calculated oxidation constants and their correlation values for different temperatures are given in Table 1. High correlation constant values, i.e., $R = 0.98–0.99$, point out that the oxidation behavior of the studied NiMnGa alloy obeys the parabolic law.

According to the values of the calculated oxidation constants, the amount of oxidation increases gradually with increasing temperature. So, initial oxidation rate so low. This is common in most of the metals as they are prone to oxidation in oxidizing atmospheres [11]. Peruman et al. applied heat treatment to NiMnGa alloys under pure argon atmosphere at 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C. According to this study, the samples heat-treated up to 1000 °C had the shape memory behavior while the optimum heat treatment temperature was determined as 800 °C. The authors attributed the loss of shape memory effect for sample treated at 1000 °C to the

**Table 1**
The oxidation constant values of the studied NiMnGa alloys between 600 and 1000 °C.

| Temperature (°C) | $K_p$ (mg$^2$ cm$^{-4}$ s$^{-1}$) | $R$ (correlation coefficient) |
|---|---|---|
| 600 | $5.22 \times 10^{-4}$ | 0.98 |
| 700 | $6.79 \times 10^{-3}$ | 0.99 |
| 800 | $1.01 \times 10^{-2}$ | 0.99 |
| 900 | $1.05 \times 10^{-1}$ | 0.99 |
| 1000 | $5.18 \times 10^{-1}$ | 0.99 |