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MICROSTRUCTURE AND MARTENSITIC TRANSFORMATION OF $Ni_{50}Ti_{50-x}Er_x$ SHAPE MEMORY ALLOYS

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Abstract
The effect of rare earth element Er addition on the microstructure and phase transformation behavior of $Ni_{50}Ti_{50-x}Er_x$ $(x = 0, 1, 5)$ shape memory alloy was investigated experimentally. The results showed that the microstructure of $Ni - Ti - Er$ ternary alloys consist of the $NiEr$ precipitate and the $NiTi$ matrix. A one-step martensitic transformation was observed in all alloys. The martensitic transformation temperature M_s increased gradually with increasing Er content.

Keywords: Microstructure, Phase transformation, Shape memory alloy

1 Introduction

Near equiatomic $Ni - Ti$ based shape memory alloys ($SMAs$) have a unique shape memory effects and super-elasticity behavior and have been used in various fields, particularly in engineering and biomedical applications [1]. Current research interest on $SMAs$ mainly lies in controlling the martensitic transformation temperature and improving the shape memory effect for their applications. The effects of martensitic transformation, super-elasticity and shape memory effect have been widely studied by adding transitional elements to $Ni - Ti$ binary alloys. These elements include Fe [2], Hf [3], Pd [4],Pt [5], Cu [6], Au [7], Co [8] etc. The addition of Fe, Co to $Ni - Ti$ binary alloys decreases the martensitic transformation temperature. By contrast, but the addition of Hf and Pd can increase the martensitic transformation temperature of $Ni - Ti$ binary alloys.
Moreover, the microstructure and martensitic transformation temperature of the addition of La [9] [10], Ce [11], Pr [12], Nd [13] [14], Gd [15], Dy [16] to $Ni - Ti$ binary alloys have been studied using scanning electronic microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The addition of these rare earth elements to $Ni - Ti$ binary alloys was found to increase the martensitic transformation temperature and change the phase transformation sequence.
There, the effect of rare earth element Er addition to $Ni - Ti$ binary alloy on-microstructure and martensite transformation temperature remains unclear. In this work, Er content with atomic fractions of $0, 1\%$ and 5% added to $Ni-Ti$ binary alloys the microstructure and martensitic transformation were studied experimentally.

2 Experimental

The $Ni_{50}Ti_{50-x}Er_x$ $(x = 0, 1, 5)$ alloys were prepared by melting each $40g$ of raw materials with different nominal compositions (99.9 mass % sponge Ti, 99.7 mass % electrolytic Ni and 99.95 mass % Er) in a non-consumable arc-melting furnace using a water-cooled copper crucible. The alloys are denoted by $Er0$, $Er1$, and $Er5$ to refer to $Ni_{50}Ti_{50}$ $Ni_{50}Ti_{49}Er_1$, and $Ni_{50}Ti_{45}Er_5$ alloys, respectively Arc-melting was repeated four times to ensure the uniformity of composition. The specimens are spark-cut from the ingots and solution-treated at $850°C$ for an hour in a quartz tube furnace. Subsequently the specimens were quenched using water. Thereafter, the specimens are mechanically and lightly polished to obtain a plain surface.
The phase transformation temperatures of $Ni_{50}Ti_{50-x}Er_x$ alloys were determined by DSC using a $TAQ2000$ calorimeter. The temperature range of heating and cooling was from $-160°C$ to $150°C$, and the scanning rate of heating and cooling was $10°C\,\mathrm{min}$. SEM observations were conducted using a Hitachi $S3400N$ equipped with EDS analysis systems made by Oxford. An XRD experiment was performed a $D/MAX - 2500PC$ diffractometer using the software MDI Jade 5.

3 Results and discussion

3.1 Microstructure of $Ni_{50}Ti_{50-x}Er_x$ alloy

$Fig.1a$ shows the XRD curves of $Ni_{50}Ti_{50-x}Er_x$ $(x = 0, 1, 5)$ alloys at room temperature compared with $JCPDF$ cards (Nos. $65 - 0145$, $65 - 4572$, and

$19-0818$). The diffraction peaks are identified to be from $NiTiB1\acute{9}$ martensite phase, $NiTi$ $B2$ austenite phase, and $NiEr$ alloys. The detailed crystal plane indices are marked in $Fig.1b$ for $Er0$ at room temperature, $Fig1c$ for $Er5$ at room temperature, but the relative intensities of each XRD curve are quite different because of the differences in martensite phase fraction and austenite phase fraction. It can be seen that the diffraction intensity of martensite is evidently decreased with increasing Er fraction. The diffraction angle decreases with increasing Er fraction, which indicates that the lattice of the martensite expands with Er addition. Because the radius of Er is much larger than that of Ni and Ti, when Er atom is solubizilized in the matrix, the martensitic lattice is distorted certainly [11]. The Lattice parameters of alloys can be also calculated [17] by peaks position in XRD curves and shown in $Table1$. It is shown clearly that cell volume V expands for with Er addition to $Ni-Ti$ binary alloy from 0 at.% to 5 at.%.The observation can be confirmed in the following composition analysis.

3.2 Morphologies and compositions of $Ni_{50}Ti_{50-x}Er_x$ alloys

$Fig.2$ depicts the back-scattering SEM images of $Ni_{50}Ti_{50-x}Er_x$ $(x = 0, 1, 5)$ alloys. For $Er0$ alloy, there are two different morphologies, namely, black phase and matrix, can be identified in the SEM image ($Fig.2a$). The black phase is in irregular shape and distributed randomly in the matrix. For $Er1$ and $Er5$ two different morphologies, namely, white phase and matrix, can be identified in the SEM images. Some white particles that are nearly round in shape and up to $3\mu m$, and $10\mu m$ in diameter with a white thin curving area can be found to be distributed in the matrix in $Fig.2b-c$.

To identify the phase structure, EDS analysis was conducted in SEM. The compositions of the white phase and matrix are shown in $Table2$. The $Ti : Ni$ ratio in the matrix is observed to be near 1. Thus, the matrix can be concluded to consist of $Ni-Ti$ phase. The EDS results show that the $Er : Ni$ ratio in the white phase is near 1 and can be regarded as the $ErNi$ intermetallic compound with minimal Ti solid-solution inside. The amount and size of the $ErNi$ phase increase with increasing Er fraction.

3.3 Phase transformation of $Ni_{50}Ti_{50-x}Er_x$ alloys

$Fig.3a$ depicts the DSC curves of the $Ni_{50}Ti_{50-x}Er_x$ $(x = 0, 1, 5)$ alloys. Each DSC curve of $Er0$,$Er1$ and $Er5$ shows only one peak during the heating and cooling process, which indicates a one-step $B2 \longleftrightarrow B1\acute{9}$ phase transformation. $Fig.3b$ shows the effect of Er concentration on martensitic transformation start temperature M_s. As observed, the martensitic transformation start temperature M_s increases with increasing Er fraction. Moreover, all martensite transformations finished at a temperature M_f in DSC curves, higher than room temperature at $20°C$. Thus, martensite transformation cannot finish fully at room temperature, which indicates that both the austenite phase and the martensite phase exist in the $Ni-Ti-Er$ alloy.

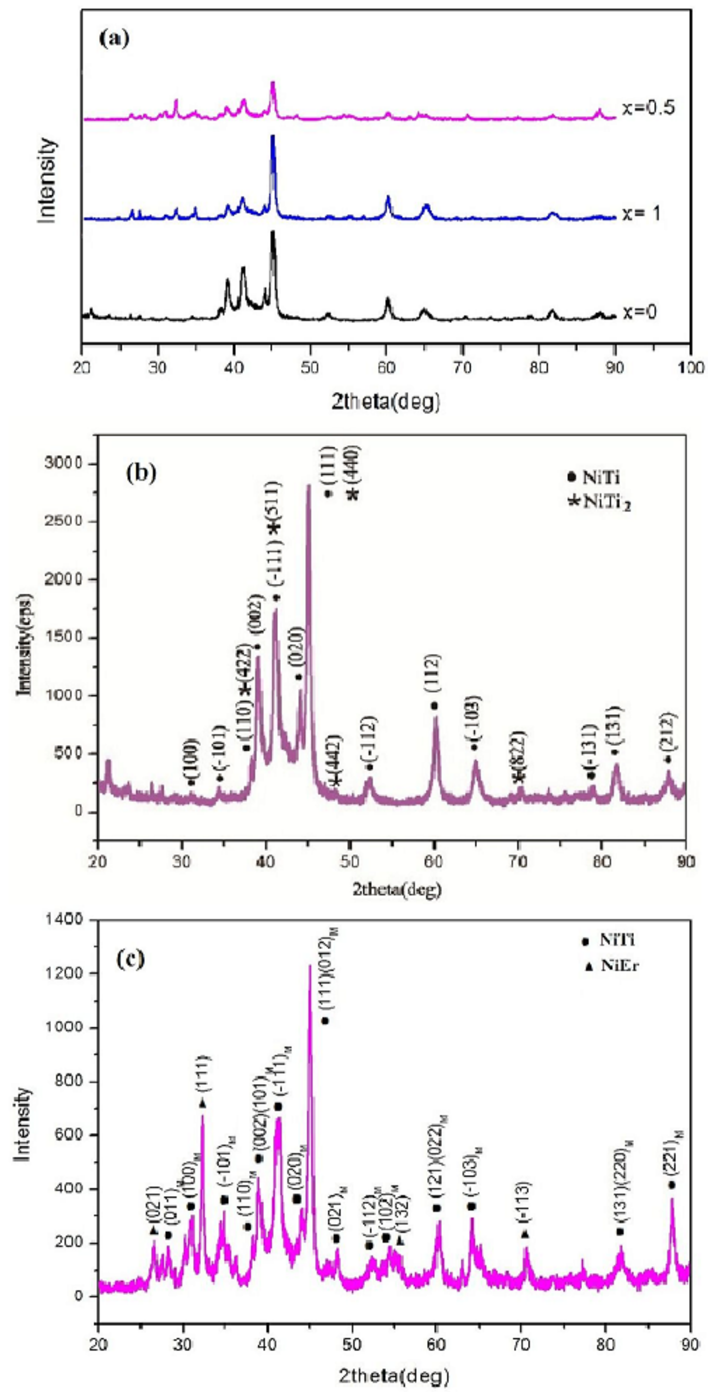

Figure 1: Fig. 1 XRD curves of $Ni_{50}Ti_{50-x}Er_x$ ($x = 0, 1, 5$) alloys:
(a) XRD curves of $Ni_{50}Ti_{50-x}Er_x$ alloys; (b) Indexed diffraction peaks $Ni_{50}Ti_{50}$;
(c) Indexed diffraction peaks $Ni_{50}Ti_{45}Er_5$.

Table 1: Lattice parameters of $Ni-Ti-Er$ alloys

Alloy	Phase	$a(nm)$	$b(nm)$	$c(nm)$	$\beta(°)$	$V(nm^3)$
$Er0$	M	0.2898	0.4121	0.4619	97.86	0.05464
$Er1$	M	0.2905	0.4121	0.4622	98.72	0.05534
$Er5$	M	0.2939	0.4129	0.4648	98.87	0.05640

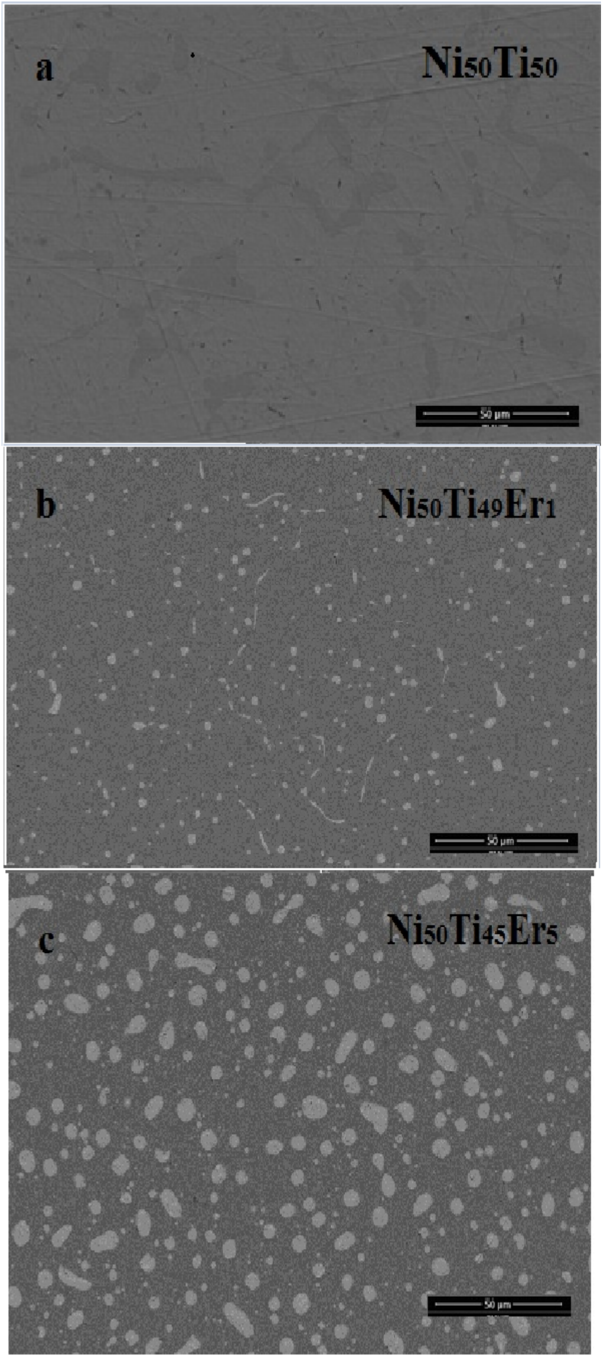

Figure 2: Back-scattering SEM images of $Ni_{50}Ti_{50-x}Er_x$ ($x = 0, 1, 5$) alloys: (a)$Ni_{50}Ti_{50}$; (b)$Ni_{50}Ti_{49}Er_1$; (c) $Ni_{50}Ti_{45}Er_5$.

Table 2: The compositions of $Ni_{50}Ti_{50-x}Er_x$ alloys

		$Ti(at.\%)$	$Ni(at.\%)$	$Er(at.\%)$	Phase
$Er0$	matrix	49.39	50.61	0	$NiTi$
	black phase	66.99	33.01	0	$NiTi_2$
$Er1$	matrix	49.24	50.21	0	$NiTi$
	white phase	2.92	49.84	47.19	$NiEr$
$Er0$	matrix	49.99	50.01	0	$NiTi$
	white phase	4.31	47.72	47.97	$NiEr$

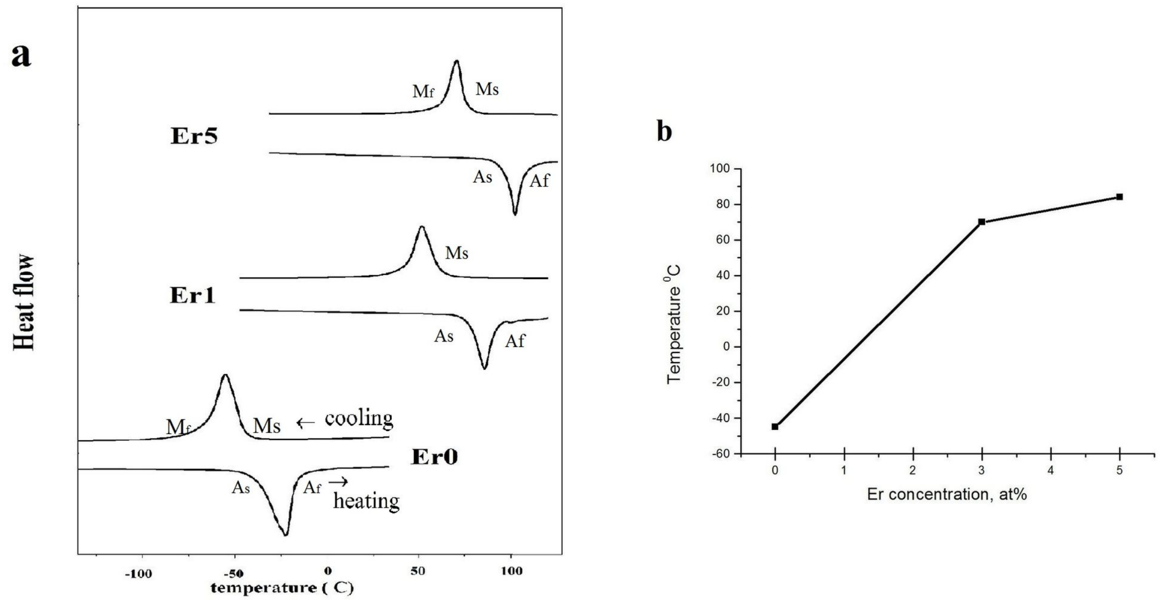

Figure 3: DSC curve and martensite transformation temperature of $Ni_{50}Ti_{50-x}Er_x$ alloys: (a) DSC curves; (b)M_s curve.

4 Conclusions

In summary, the effect of RE element Er addition on the microstructure and martensitic transformation behavior was investigated by SEM, XRD, and DSC. The microstructure of the $Ni_{50}Ti_{50-x}Er_x$ alloys consists of $Ni-Ti$ matri and $Ni-Er$ alloy with a small amount of Ti solute.
The lattice of $NiTi$ matrix is expanded by Er addition. The $Ni-Ti-Er$ alloy one-step martensitic transformation, increasing the Er fraction, the martensitic transformation start, temperature M_s increases gradually.

Author Contributions

M.Dovchinvaanchig designed microstructure, XRD measurements and phase transition analysis, Ya.Gangantogos performed microstructure analysis, B.Munkhjargal measured DSC. M.D. wrote the paper.

Conflict of Interest

The authors declare no conflict of interest.

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