

Martensitic transformation and shape memory effect in Ni-Al based alloys

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Abstract. Ni-Al based alloys are considered to be attractive high temperature shape memory materials. Among proposed alloying in the present work, there are Fe, Zr and Co elements. High temperature of martensitic transformation ($M_s > 150$ °C) with full shape recovery is achieved due to Zr alloying. Complex doping of Zr and Fe/Co also makes possible to produce perspective high temperature shape memory alloys.

1 Introduction

Binary Ni-Al alloys undergo thermoelastic martensitic transformation (MT) [1, 2, 3] in temperature range of 0-900 °C depending on nickel content. According to [3, 4] they may be considered as a potentially high temperature shape memory alloys.

Ni-rich β Ni-Al alloys are promising materials for technical usage due to their high melting temperature, excellent oxidation resistance and advantageous heat conductivity [1]. One of the applications is to produce high-strength structural alloys for use at temperatures higher than possible presently in the case of conventional titanium and nickel based alloys [5]. Another possibility is Ni-Al based coatings with improved high temperature strength and service lifetime of devices [6].

Main drawbacks of Ni-Al alloys are both lack of ductility at low temperatures and poor strength at high temperatures [1, 5].

As well known, widely used way for changing material properties is alloying. Composition of alloy determines martensitic transformation temperatures. Detailed analyze of doping elements [1-3, 5] showed that it is possible to get Ni-Al based alloys with shape recovery at temperatures higher than 100 °C.

To reach this aim we have chosen two criteria of selection doping elements for Ni-Al alloys:

- ✓ the element shouldn't reduce martensitic transformation;
- ✓ it should to improve room temperature ductility of the alloy.

For the binary Ni-Al alloys in concentration range of (60-69) at.% of Ni M_s temperature depends on alloy composition as follows: $M_s = (124Ni - 7410)$ K [2]. Nickel content increases MT temperatures in binary alloys.

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A lot of doping elements (Co, Ni, Pd, Pt, Cu, Ag, Au [7-10]) promote rising start temperatures of martensitic transformation in Ni-Al alloys.

Platinum group of metals (Pt, Rh, Ir, Pd) is used as doping elements for manufacturing Ni-Al based coatings in order to improve strength, oxidation resistance, TBC adhesion and service lifetime of materials. Alloying with Pt doesn't depress martensitic transformation [3, 11].

Gallium makes better of Ni-Al ductility by changing stacking fault energies and leads to the deterioration of slip interface plane brittle cleavage [12, 13].

From the point of view of ductilization the best result was achieved due to Fe alloying [7]. This element promotes formation of the second phase with better ductile properties. However, at the same time Fe significantly decreases MT temperatures.

Influence of zirconia on the temperature range of martensitic transformation of $Ni_{64}Al_{36}Zr_x$ alloys (0.37-0.77 at.% Zr) has been studied in [14]. As was established, these alloys undergo transformation below room temperature. According to [15] Zr doping also leads to the formation of new phase and zirconia was observed to segregate on dislocations. This result supports the suggestion that the substantial increase in ductile-to-brittle transition temperature in Ni-Al-Zr alloys is caused by the pinning of dislocations by zirconium. However, it is difficult to conclude about mechanical properties of the materials obtained because mechanical tests were not provided in [14].

In the present work the Ni-Al-Zr, Ni-Al-(Zr+Co), Ni-Al-Fe, and Ni-Al-(Fe+Zr) alloys were studied with the $Ni_{65}Al$ and $Ni_{60}Fe_3Al$ base compositions in order to investigate the influence of Zr, Fe and complex doping on the martensitic parameters.

2 Experimental procedures

Bulk Ni-Al, Ni-Al-X (Zr, Zr+Co, Zr+Fe) alloys (Table 1) were produced from pure elements by arc melting under argon atmosphere. For homogenization the materials were remelted seven times. Next, the heat treatment was carried out by quenching from 1200^oC into room temperature water during 15 minutes.

Table 1. Alloys compositions.

Alloy composition, at. %	Ni/Al ratio
Ni _{64.8} Al _{35.2}	1.84
Ni _{64.5} Al _{34.5} Zr ₁	1.87
Ni _{65.1} Al _{32.4} Zr _{2.5}	2.00
Ni _{63.5} Al _{33.6} Zr _{2.9}	1.89
Ni _{66.4} Al _{30.6} Zr ₃	2.17
Ni _{64.7} Al _{31.7} Zr _{3.6}	2.04
Ni _{66.2} Al _{29.8} Zr ₄	2.22
Ni _{59.8} Al _{37.4} Fe _{2.8}	1.60
Ni _{54.9} Al _{39.7} Fe _{4.5} Zr _{0.9}	1.38
Ni ₆₄ Al ₃₀ Zr ₃ Co ₃	2.13

Investigations of MT parameters by electrical resistivity method and three-point bending shape recovery test have been performed at temperature range of -196 +600^oC. The accuracy of temperature measurements of these methods is ± 5^oC.

Shape recovery (K_{sme}) is accessed by the ratio between the recovered strain observed after heating to the total strain at MT using three point bending test data (in percent).

Structural and microstructural investigations were also performed after mentioned heat treatment. The phase composition was analyzed by DRON 3M diffractometer with Cu-K α radiation. Microstructure analysis was done using light microscope Axiovert 40 MAT. The specimens were mechanically prepared and etched with Coparella's reagent (5 g ferric chloride, 2 ml HCl, 99 ml ethyl alcohol).

3 Results and discussion

3.1 Parameters of martensitic transformation

In the following section the influence of different alloying elements on the characteristic temperatures of martensitic transformation and shape memory effect in Ni-Al based alloys will be discussed.

The characteristic temperatures of MT (M_s , M_f , A_s , A_f) were measured by electrical resistivity method and three point bending shape recovery test.

Binary Ni_{64.8}Al_{35.2} undergoes MT with complete shape recovery at high temperatures: $M_s=200^o$ C, $A_s=130^o$ C (Fig. 1, Table 2). Analyze of tendencies in MT temperatures for binary Ni-Al alloys [3, 7, 14] and our own results show that the increase of Ni content causes M_s to rise, while the addition of third element may act in two different directions. Additions of Ti, V, Cr, Mn, Fe, Zr, Nb, Mo, Ta, W, and Si stabilize the parent β phase, thereby lowering the M_s temperature, while additions of Co, Cu, or Ag destabilize the β phase, increasing M_s temperature.

Table 2. Characteristic temperatures of martensitic transformation and shape memory effect in Ni-Al based alloys.

Alloy composition, at. %	M_s , °C	M_f , °C	A_s , °C	A_f , °C	K_{sme} , %
Ni _{64.8} Al _{35.2}	200	100	130	275	100
Ni _{64.5} Al _{34.5} Zr ₁	-125	–	–	-120	
Ni _{65.1} Al _{32.4} Zr _{2.5}	210	175	225	265	100
Ni _{63.5} Al _{33.6} Zr _{2.9}	150	20	125	225	100
Ni _{66.4} Al _{30.6} Zr ₃	150	20	30	170	100
Ni _{64.7} Al _{31.7} Zr _{3.6}	190	125	175	225	100
Ni _{66.2} Al _{29.8} Zr ₄	0	-110	-70	10	100
Ni _{59.8} Al _{37.4} Fe _{2.8}	200	100	115	230	100
Ni _{54.9} Al _{39.7} Fe _{4.5} Zr _{0.9}	-100	–	–	-90	100
Ni ₆₄ Al ₃₀ Zr ₃ Co ₃	190	135	160	220	100

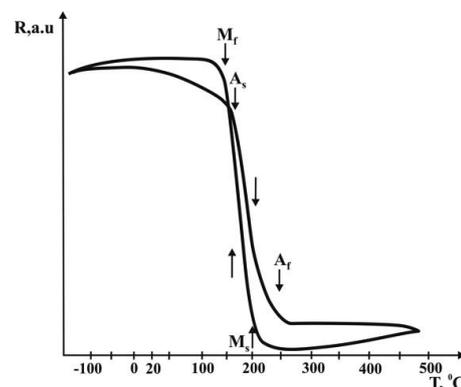


Fig.1. Temperature dependence of electrical resistance for the Ni_{64.8}Al_{35.2} alloy.

Nonlinear behavior of MT temperatures was observed as a result of zirconia alloying. Even small addition of Zr (1 at.%) significantly shifts characteristic transformation temperatures to lower temperature region up to $M_s =$

-125°C, in comparison with the binary alloy (Fig. 2). However another difference with the binary alloy is weak shape memory effect in Ni_{64.5}Al_{34.5}Zr₁.

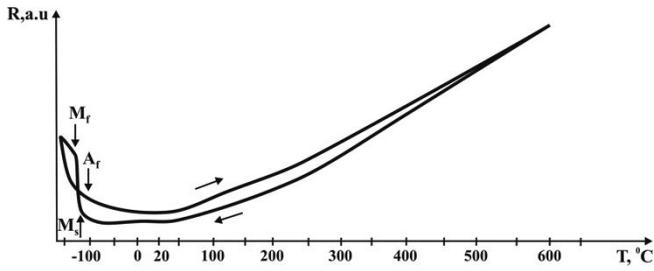


Fig. 2. Temperature dependence of electrical resistance for the Ni_{64.5}Al_{34.5}Zr₁ alloy.

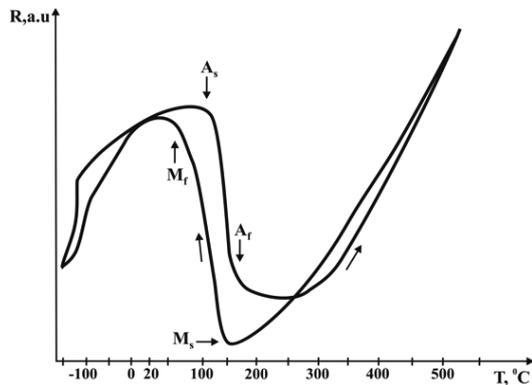


Fig. 3. Temperature dependence of electrical resistance for the Ni_{63.5}Al_{33.6}Zr_{2.9} alloy.

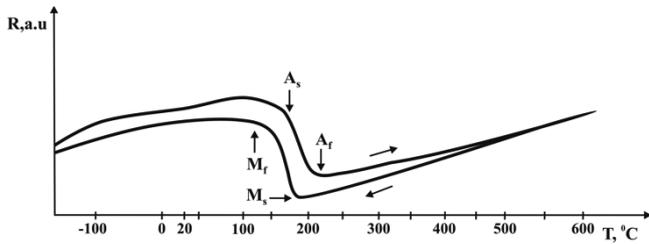


Fig. 4. Temperature dependence of electrical resistance for the Ni_{64.7}Al_{31.7}Zr_{3.6} alloy.

As was shown in work [14], additions of (0.37-0.77) at.% Zr lead to decrease of Ms temperature below room temperature. This tendency correlates with our results. However, in work [14] another base composition of binary alloy (Ni₆₄Al₃₆ with Ni/Al = 1.78) was used in comparison with ours (Ni_{64.8}Al_{35.2} with Ni/Al = 1.84).

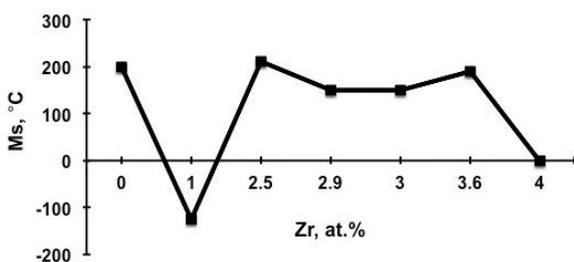


Fig. 5. Ms dependence from Zr content in Ni-Al-Zr alloys.

Tendency of Ms and As to rise with further increase of Zr content is noticed (Table 2, Fig. 5). For example, Ni_{63.5}Al_{33.6}Zr_{2.9} and Ni_{66.4}Al_{30.6}Zr₃ alloys undergo martensitic transformation at Ms=150°C, lower temperature than in case of binary Ni_{64.8}Al_{35.2} alloy (Ms=200°C).

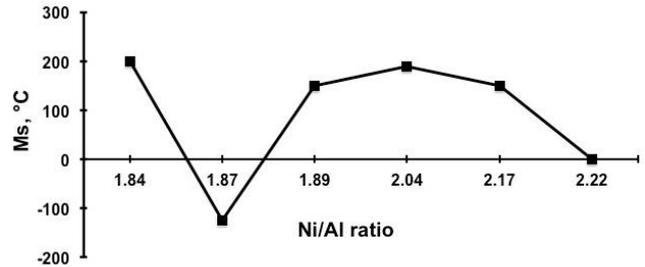


Fig. 6. Ms dependence on the Ni/Al ratio in Ni-Al-Zr alloys.

The important factor controlling characteristic temperatures of MT is also Ni/Al ratio in Ni-Al based alloys. As shown in Figs. 5, 6, Ms significantly decreases with small Zr additions but together with the increasing of Ni/Al ratio. Rising of Ni/Al ratio (to 2.17) as well as Zr content (up to 3.6 at.%) promotes increasing of MT temperatures. However, further rising of these parameters shows the tendency to lower MT temperatures.

Interesting fact is that increasing Ni/Al ratio from 1.84 for Ni_{63.5}Al_{33.6}Zr_{2.9} to 2.16 for Ni_{66.4}Al_{30.6}Zr₃ compositions, preserving fixed Zr content decreases As by 100°C (from 125 to 30°C, Table 2).

As shown in Table 1, Ni_{64.8}Al_{35.2}, Ni_{64.5}Al_{34.5}Zr₁, and Ni_{63.5}Al_{33.6}Zr_{2.9} alloys have the same Ni/Al ratio (1.84-1.87). However, their characteristic temperatures of MT are completely different. The first alloy is binary one with Ms=200°C. Small zirconia addition lowers Ms to -125°C, but further increasing of Zr content increases Ms to 150°C. In this example the “pure” zirconia influence on MT temperatures is clearly seen.

As established, all considered Ni-Al-Zr alloys with >1.at.% Zr demonstrate full shape memory effect (K_{sme} = 100%, Table 2).

Small addition of Zr decreases MT temperatures. This tendency may be reversed due to the increase of Ni/Al ratio. Consequently, it may be concluded that in the case of small Zr additions (2.5-3.5 at.% Zr) it was possible to achieve high MT temperature, with Ms 210°C in a result of both controlling factors Zr content and Ni/Al ratio close to 2 properly chosen.

Replacing Ni by Fe in Ni_{59.8}Al_{37.4}Fe_{2.8} alloy doesn't change MT temperature range in comparison with the binary Ni_{64.8}Al_{35.2}. This alloy reveals complete shape recovery. However, increase of the Fe content together with small Zr addition (0.9 at.%) caused significant shift of MT temperatures to the lower temperature range (Table 2).

Complex alloying with Zr and Co only slightly decreased MT parameters and kept complete shape recovery in case of investigated alloy composition (Table 2).

3.2 Structure and microstructure investigations of Ni-Al based alloys.

The structural analysis of Ni-Al and Ni-Al based alloys has been performed at room temperature.

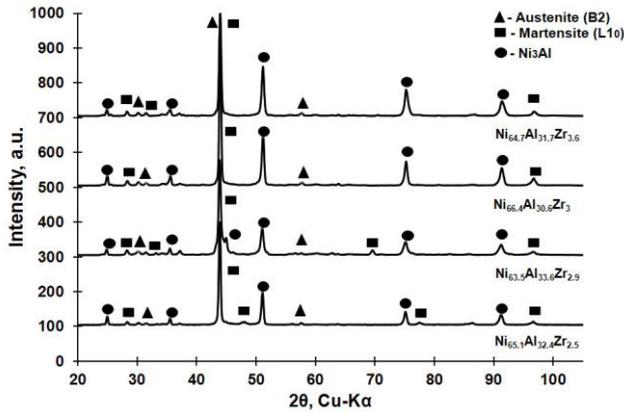


Fig. 7. X-ray diffraction pattern for Ni-Al-Zr alloys.

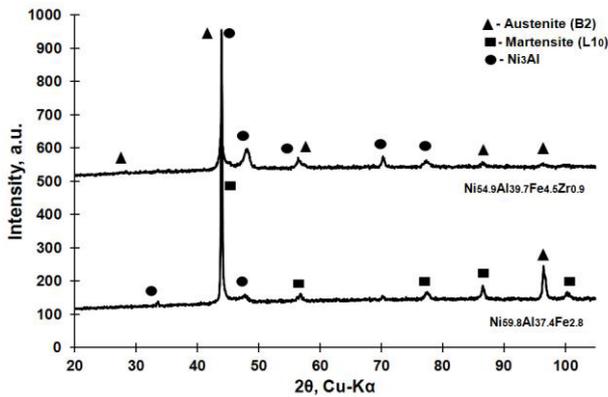


Fig. 8. X-ray diffraction pattern for Ni-Al-Fe, Ni-Al-Fe-Zr alloys.

Binary alloy contains B2 parent phase, Ni₃Al (γ) and L₁₀ type ordered martensite as well as Ni-Al-Zr ones (Fig. 7).

Iron doping and complex alloying by Co and Zr (Ni_{59.8}Al_{37.4}Fe_{2.8} and Ni₆₄Al₃₀Zr₃Co₃, Fig. 8) doesn't show changes in quantitative phase composition comparing with binary alloy. However, only B2 and Ni₃Al (γ) phases are presented at room temperature in Ni-Al-Zr-Fe alloy.

Ni-Al alloys are known from its brittleness. Elements like Zr, Co, Zr+Co, and Zr+Fe are potentially perspective-additions for the grain refinement.

Microstructural investigations show that large grains in binary Ni-Al alloy (Table 3) are reduced after zirconia alloying (Table 3, Fig. 10). Accordingly with the estimated average grain sizes for different alloys, the refinement increases with increasing Zr content in alloy. For maximum Zr content (4 at.%) grains dimensions were eight times reduced. So, addition of Zr (more than 1 at.%) leads to decrease grain size of conventionally casting alloys and Zr seems to be good candidate for the production of the rapidly quenched Ni-Al-Zr alloys.

As was reported in [16], Ni-Al-X ribbons with X: Co, Cu, Cr, Zr, Co+Zr were produced. As it was found, Ni-Al-Zr and Ni-Al-(Co+Zr) ribbons were of the best

quality. Other alloying elements caused poor quality of the ribbons with pores or flakes.

Table 3. Average grain sizes of Ni-Al based alloys.

Alloy composition, at.%	Lengthwise size	Cross out size
Ni _{64.8} Al _{35.2}	488.8	205.4
Ni _{64.5} Al _{34.5} Zr ₁	187.7	57.4
Ni _{65.1} Al _{32.4} Zr _{2.5}	78.2	22.3
Ni _{63.5} Al _{33.6} Zr _{2.9}	72.3	24.4
Ni _{66.4} Al _{30.6} Zr ₃	66.8	15.1
Ni _{64.7} Al _{31.7} Zr _{3.6}	61.1	16.9
Ni _{66.2} Al _{29.8} Zr ₄	57.9	16.3
Ni _{59.8} Al _{37.4} Fe _{2.8}	517.2	283
Ni _{54.9} Al _{39.7} Fe _{4.5} Zr _{0.9}	208.1	103.9
Ni ₆₄ Al ₃₀ Zr ₃ Co ₃	23.9	10.5

Martensitic relief is seen in binary Ni_{64.8}Al_{35.2} (Fig. 9) and Ni_{59.8}Al_{37.4}Fe_{2.8} after heat treatment (Fig. 11) at room temperature. In both cases average grain size is quite large. It becomes clear that Fe is not acting as grains refiner.



Fig 9. Microstructure the Ni_{64.8}Al_{35.2} alloy.

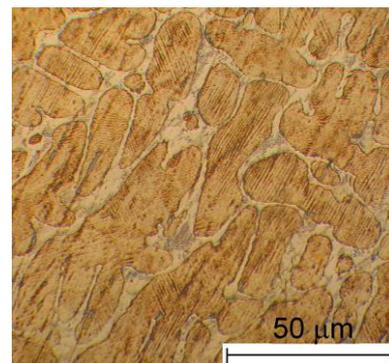


Fig.10. Microstructure of the Ni_{66.4}Al_{30.6}Zr₃ alloy.

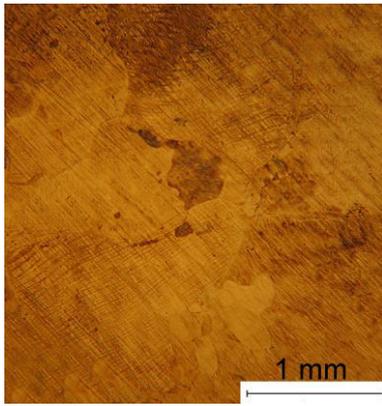


Fig.11. Microstructure of the Ni_{59.8}Al_{37.4}Fe_{2.8} alloy.

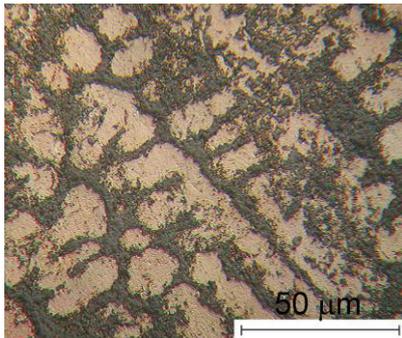


Fig.12 Microstructure of the Ni₆₄Al₃₀Zr₃Co₃ alloy.

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4 Conclusions

Analyze of influence of different alloying (Zr, Fe, Zr+Fe, Zr+Co) on martensitic parameters in Ni-Al alloys from point of view of producing high temperature shape memory alloys with small grain size has been performed.

- ✓ All considered doping elements do not depress martensitic transformation.
- ✓ Zr doping of Ni-Al alloys as well as Zr+Fe and Zr+Co significantly decreases grain sizes in Ni-Al based alloys.
- ✓ Ni-Al-Fe (Ni_{59.8}Al_{37.4}Fe_{2.8}), Ni-Al-Zr (Ni_{65.1}Al_{32.4}Zr_{2.5}, Ni_{64.7}Al_{31.7}Zr_{3.6}) and Ni-Al-Zr-Co (Ni₆₄Al₃₀Zr₃Co₃) demonstrate high temperature shape memory effect.
- ✓ Increasing of Zr content causes of the same influence on martensitic start temperatures (Ms, As) as increasing Ni/Al ratio.
- ✓ Zr as well as (Zr+Co) and (Fe+Zr) are perspective alloying elements for producing alloys by rapid solidification methods.

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