YU. N. KOVAL*, G. E. MONASTYRSKY **, V.V. ODNOSUM *, T. CZEPPE***, YU. V. KUDRAYVTSEV *, A. V. YEFREMOVA *,
YU. V. NESTERENKO **, V.A.MOKHORT **

THE INFLUENCE OF THE ALLOYING WITH B AND Re ON NiAl BASED ALLOYS

WPŁYW DODATKÓW STOPOWYCH B I Re NA WŁASNOŚCI STOPÓW NA BAZIE FAZY NiAl

The investigations of the influence of the boron and rhenium additions to NiAl alloys with Ni content between 64 and 71 at.%, on the martensitic transformation and ductility are presented in the following paper. The 0.4 at.% of the boron addition, 0.8 at.% of the addition of rhenium when was added together with boron and 4 at.% of Re separately was used. The "as cast" and after solution treatment at 1000°C and water quenching alloys were investigated. The alloys revealed multiphase microstructure, containing, except β and γ'phases, martensite, Ni_5Al_3 phase, and in case of rhenium addition also Re- rich phases. The chemical composition and morphology of the phases was determined. Both boron and rhenium lead to the formation of the Ni- enriched zone along the grain boundaries. The characteristic temperatures of the martensitic transformation were determined with the use of electrical resistivity method. Except rhenium containing alloy all M_s temperatures revealed linear relation with the Ni to Al ratio. In the case of NiAlRe the relation between composition and M_s temperature remains unclear. The microhardness was measured along the grain boundaries, inside the grains and in the Re-rich precipitates. The grain boundary zones exhibited always higher hardness then internally the grains. The boron addition preferentially hardened grains boundary zone, but due to the Re-rich precipitates the average hardness of the NiAlRe alloy was found to be highest. The observations performed on the fracture surfaces of the boron and rhenium containing alloys suggest mixed trans- and intercrystalline modes of the fracture. The alloy containing both B and Re exhibited viscous mode of the fracture.

Keywords: NiAl, NiAlB, NiAlRe, martensitic transformation, ductility

W pracy zaprezentowano wyniki badań wpływu dodatków boru i renu do stopów NiAl o zawartości Ni pomiędzy 64 a 71%at. na przemianę martenzytyczną i plastyczność. Zastosowano dodatek boru 0.4%at., renu, w stopie z dodatkiem boru, 0.8% at. a indywidualnie - 4% at. Stopy badano po odlaniu i po homogenizacji w 1000°C i hartowaniu w wodzie. Stopy ujawniły skład wielofazowy, odlewnicze zawierały fazy β, γ', martenzyt i fazę Ni_5Al_3 oraz fazy bogate w ren. Skład chemiczny i morfologia faz zostały określone. Ren w nieznacznym stopniu rozpuszcza się w fazie macierzystej NiAl i głównie pozostaje w wydzieleniach. Zarówno dodatek renu jak i boru prowadzi do utworzenia strefy wzbogaconej w Ni na granicach ziaren. Temperatury charakterystyczne przemiany martenzytycznej określono metoda zmiany oporu elektrycznego. Za wyjątkiem stopu NiAlRe dla którego relacja miedzy składem a temperaturą M_s pozostała niejasna, we wszystkich pozostałych przypadkach relacja ta była linowa w zależności od proporcji Ni do Al. Mikrotwardość zmierzono w strefie granic ziaren, wewnątrz ziaren i ziaren wydzieleniach. Dodatek boru preferencyjnie umacnia granice ziaren, jednak w wyniku obecności wydzieleń bogatych w Re średnia twardość stopu NiAlRe okazała się najwyższa. Obserwacja powierzchni pękania pokazała, że w stopach z dodatkami występuje zarówno trans- jak i międzykrystaliczne pękanie, jednak typ lepkiego płynięcia zaobserwowano tylko w przypadku równoczesnego dodatku boru i renu.

1. Introduction

NiAl is an attractive material for a wide range of engineering applications. NiAl alloys have high melting temperature (1911 K), low density (6 g/cm³), excellent oxidation resistance up to 1573 K and good thermal conductivity. In addition to its attractiveness as an engineering material, Ni-Al also exhibits a range of interesting physical characteristics such as a highly ordered lattice, a wide composition range of stability, a variable defect structure, a reversible shape memory effect and anisotropy of plastic behaviour. However unsatis-

* INSTITUTE OF METAL PHYSICS NASU, 36 VERNADSKY BLVD., 03680 KIEV-142, UKRAINE
** NATIONAL TECHNICAL UNIVERSITY OF UKRAINE, PEREMOGA STREET 37, 03506 KIEV, UKRAINE
*** INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, REYMONTA 25 ST., 30-059 KRAKOW, POLAND

factory low-temperature mechanical properties make application of the NiAl problematical. Many attempts to improve poor ductility of the β NiAl phase by macro- and micro-alloying have been done. Results concerning the influence of different third element additions on the properties of NiAl alloys are presented in Table 1.

TABLE 1

Influence of the alloying elements on the phase composition of the NiAl alloys

Alloying element	Influence on the phase composition
Cr, W, Re, V	pseudobinary eutectic forms [2, 3, 4, 5]
Fe, Co, Cu	γ phase (fcc structure) stabilizes [6, 7, 8, 9]
Ti, Hf	ternary intermetallic phases are formed [10]

The best ductility was achieved for the alloy of Ni-25Al-27.5Fe (in at%). Elongation of the sample in ductility tests achieved 5–6% [10]. In this case best ductility resulted from dendritic two-phase ($\beta + \gamma$) microstructure. It was found that in the case of alloying of stoichiometric NiAl alloy with B, a thin layer of B along the grain boundary and islands-like precipitates inside the grains are formed [11, 12]. Such a thin layer of a boron -rich phase may improve the resistance of grain boundaries against cracking during the compression [12]. However this effect was lost at temperatures high enough - 1000°C and 1300°C [12]. The influence of the alloying with W, Re and V are not completely clarified. The purpose of this study was to investigate the influence of alloying of NiAl with B and Re on the martensitic transformation, microstructure and fracture mode. Martensitic transformation was described in some earlier papers [8, 13], but the influence of the alloying on it is not completely understood [14, 15, 16].

2. Experimental procedure

NiRe and NiB master alloys were used for the preparation of NiAlRe and NiAlBRe alloys. Alloys were prepared by melting in the arc-melting furnace under argon gas atmosphere. The nominal addition of B was up to 0.4 at.%. The samples were cut with diamond saw on rectangular prisms of the 20×4×0.15 mm size. The alloys were investigated "as-cast" and after solution treatment at 1000°C during 15min in argon gas atmosphere followed by water quenching. The chemical composition of alloys is presented in Table 2. Temperatures of martensitic transformation were determined by the temperature dependence of electrical resistivity measurements. As well dilatometry was applied in order to find martensitic transformation characteristic temperatures and resulting volume effect.

TABLE 2

Chemical composition of the alloys

Alloy	Chemical composition
NiAl	$Ni_{71} Al_{29}$
NiAlB	$Ni_{63.5} Al_{36.1} B_{0.4}$
NiAlBRe	$Ni_{69.1} Al_{29.7} B_{0.4} Re_{0.8}$
NiAlRe	$Ni_{64} Al_{32} Re_4$

Mechanical properties were investigated by the measurement of the microhardness. To investigate microhardness of the material, samples were mechanically and eloctrolytically polished, to enable observation of the indentation marks. Metallographic investigations were performed with the scanning electron microscope REMMA-101A. Samples for electron microscopy were prepared using standard grinding and polishing procedures, after etching with use of the Caparella's reagent (5g ferric chloride, 2 ml HCl, 99 ml ethyl alcohol). Phase composition analysis was performed with use of X-ray diffractometer URS-2.0.

3. Results and discussion

The phases identified by the X-ray phase analysis in the "as-cast" alloys are presented in Table 3. The coexistence of four or fifth phases was found in all cases. The presence of the following phases in the "as-cast" samples was noticed: β (NiAl), γ'(Ni$_3$Al), martensite (M) of L1$_0$ structure, Re-rich and Ni$_5$Al$_3$. (Presence of the last phase was not completely certain).

TABLE 3

Phase composition of the as-cast alloys

Alloy	Phases identification
NiAl	β(NiAl), γ'(Ni$_3$Al), Ni$_5$Al$_3$, M
NiAlB	β(NiAl), γ'(Ni$_3$Al), Ni$_5$Al$_3$, M
NiAlBRe	β(NiAl), γ'(Ni$_3$Al), Ni$_5$Al$_3$, M, Re
NiAlRe	β(NiAl), γ'(Ni$_3$Al), Ni$_5$Al$_3$, M, Re

Except the martensite phase, similar phase composition was found after the solution treatment (Tab. 4). Taking into account X-ray results for NiAlBRe and NiAlRe alloys one can concluded that Re was not completely dissolved in NiAl matrix. The microstructures of the NiAlB, NiAlRe and NiAlBRe alloys are presented in Figs. 1-3. The microstructure of NiAlB alloy (Fig. 1) consisted of equiaxial and long grains. Grain boundaries in NiAlB and NiAlBRe were coarsened (Fig. 1, 3). The chemical composition of coarsened grain boundary zones for NiAlB alloy is Ni$_{66}$Al$_{34}$ with traces of B while composition of matrix is Ni$_{60 \div 62}$Al$_{38 \div 40}$. Traces of B

Phase composition of the samples after the solution treatment

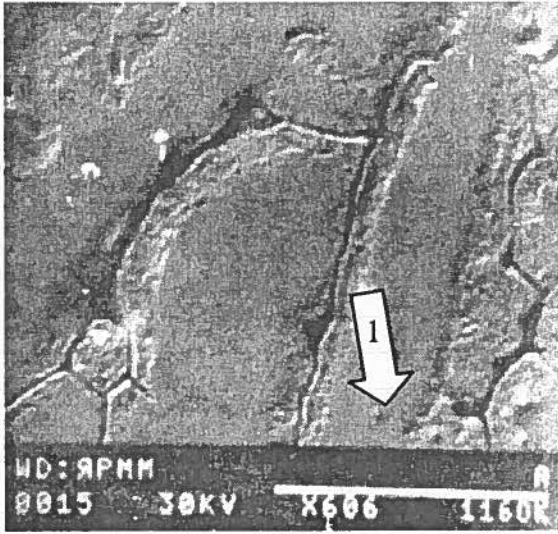| Alloy	Phases identification
NiAl	β(NiAl), γ'(Ni$_3$Al), M
NiAlB	β(NiAl), γ'(Ni$_3$Al)
NiAlBRe	β(NiAl), γ'(Ni$_3$Al), Re
NiAlRe	β(NiAl), γ'(Ni$_3$Al), M, Re

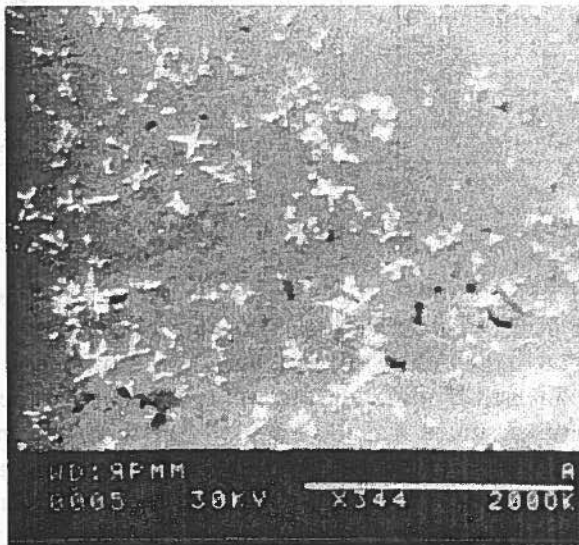Fig. 1. SEM micrographs of typical structure NiAlB after solution treatment (×606)

Fig. 2. SEM micrographs of typical structure NiAlRe after solution treatment (×344)

were found in islands- type precipitations with composition close to Ni$_{62}$Al$_{38}$ with traces of B (arrow 1 Fig.1). Concentration of Ni at grain boundary zone increase in comparison with inner part of the grain in NiAlB alloy. Composition of the matrix was Ni$_{60\div61}$Al$_{39\div40}$Re$_{0.1-0.2}$ but the grain boundary composition was close to Ni$_3$Al with traces of B content. Traces of B were observed

at the grain boundary zones both for NiAlB and NiAlBRe alloys. In NiAlBRe alloy precipitations of a Re-rich phase (white zones in the figures 2, 3) were also observed. The chemical composition of this precipitates was determined by EDS system in SEM, and was about Ni$_{21}$Al$_{15}$Re$_{64}$B for NiAlBRe and Ni$_{13}$Al$_{19}$Re$_{69}$ for NiAlRe alloy (in at.%).
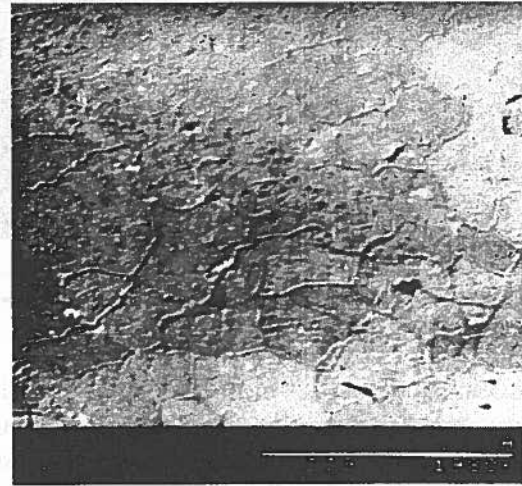

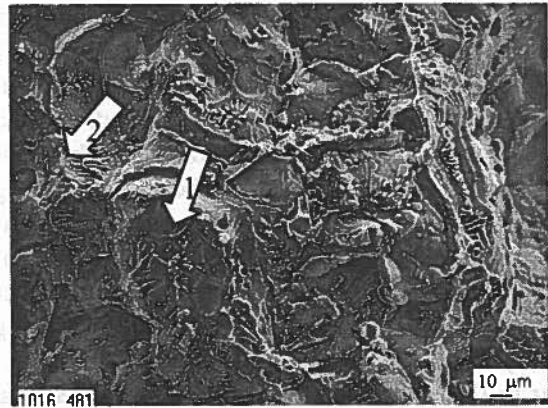Fig. 3. SEM micrographs of typical structure NiAlBRe after solution treatment (×339)

Fig. 4. Micrograph of the fracture surface for NiAlBRe1.5 after solution treatment

The chemical composition of the matrix in NiAlRe alloy was Ni$_{59\div60}$Al$_{38\div40}$Re$_{0.2-0.3}$. Only small part of Re dissolved in NiAl matrix. Needle precipitations (Fig. 3) reveald composition of Ni$_{63\div69}$Al$_{31\div37}$. Composition of grain boundary zones in NiAlRe alloy is close to the needle precipitations.

The micrographs of the fracture surfaces of the NiAlB and NiAlBRe alloys are presented in Figures 4 and 5 respectively. The observations suggest that mixed fracture mode (transcrystalline mode (arrow 1) and intercrystalline mode (arrow 2) fig. 4, 5) took place. Partially viscous fracture mode was observed in NiAlBRe

alloy (Fig. 4, arrow 3). The NiAlB alloy did not show viscous fracture mode at all. The NiAl and NiAlRe alloys fracture surfaces demonstrated also inter+transcrystalline fracture modes.
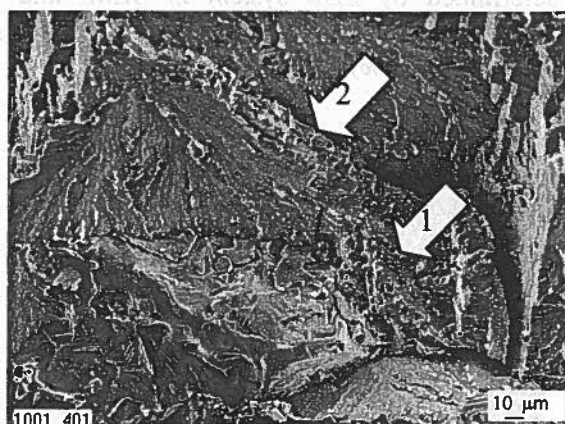

Fig. 5. Micrograph of the fracture surface NiAlB after solution treatment

Mechanical properties of the alloys were studied by the measurements of the microhardness. Microstructure investigations allow to distinguish three main zones of different properties in the alloys: a.)grain boundary zone, b.) zone inside the grains, c.) white precipitations (the last one for the Re containing alloys). Results of the local and average microhardness are presented in Table 5 and at Fig. 6. The grain boundary zone showed approximately the same hardness like zone inside the grains in NiAl alloy (Table 5). Average hardness of NiAlB was much higher than of NiAl and the grain boundaries exhibit higher hardness than inside the grains (Table 5). Probably the presence of B changes the structure of grain boundary zone. Also, NiAlRe was harder than NiAl but in this case the hardness at the grain boundaries and inside the grains were approximately equal to each other. A correlation between hardness of NiAlBRe at the grain boundary zone and at the zone inside the grains was similar to that for NiAlB. It may be concluded that the B addition strengthens grain boundaries in NiAl alloy (Tab. 5). Influence of Re is not completely clear but it increases average hardness of NiAlRe alloy. Re-rich precipitates revealed similar hardness in NiAlRe and NiAlBRe alloys. In case of the NiAlBRe alloy this precipitates are harder than the matrix. It is probable that B not only influences grain boundary zones but also affects the zone inside the grains and the Re-rich precipitates. Different hardness of the grain boundary zone and inside the grains was observed in NiAlB and NiAlBRe alloys, in NiAlRe and NiAl the hardness is approximately the same. The reason of this may be high concentration of B at the grain boundary zones.

Analysis of the microhardness measurements show that mechanical properties of different phases in NiAl and NiAlRe alloys are similar. Alloying with B leads to the increase of hardness at the grain boundary zones. NiAl is less hard, NiAlBRe exhibits middle hardness and NiAlRe is the hardest one. Main conclusion concerning the alloying with B is that this addition increases hardness at the grain boundaries, while the influence of Re appears in increasing of hardness in the matrix, due to hard Re-rich precipitates.

Measurements of the temperature dependence of electro-resistivity allowed to determine starting temperature of the martensitic transformation (M_s). Alloying with B and Re do not suppress martensitic transformation. The results are presented in Table 6.

TABLE 5

Results of the hardness investigations

Alloy	HV of the grain boundary zone,	HV inside the grains	HV of the Re-rich precipitates	average Vickers hardness
NiAl	382	367	–	367
NiAlB	624	511	–	512
NiAlRe	554	532	557	553
NiAlBRe	482	448	584	457

TABLE 6

Characteristic temperatures of martensitic transformation

Alloy	Ms [°C]	Mf [°C]	As [°C]	Af [°C]	Ni/Al ratio
NiAl	18	-50	-30	74	2,4
NiAlB	-120	-140	-130	-100	1,75
NiAlRe	70	-120	-70	250	2
NiAlBRe	-50	-100	-100	-40	1,9

Results of the dilatometric measurements are presented in Table 7. It is shown, that there exists the meaningful difference between characteristic temperatures of the martensitic transformation measured by this method and by electrical resistivity. This difference can be explained by different sensitivity of the equipments. Authors assumed that the resistivity method was more precise. A volume contraction effect during martensitic transformation was about -0.3%. Data shown in Table 6 suggest that temperatures of martensite transformation are sensitive to Ni/Al ratio but this dependence is not simply linear. In case of NiAlRe (Ni:Al = 2,4) with M_s = 70°C and NiAl (Ni:Al = 2) with M_s = 20°C the dependence is not evident. Probably a part of Re dissolves in NiAl matrix but the influence of Re on M_s is complicated. In the case of NiAl, NiAlB and NiAlBRe alloys M_s temperature depends only on Ni:Al ratio (see also Tab. 6).

<div style="text-align:right">TABLE 7</div>

Results of the dilatometric investigation

Alloy	Ms [°C]	Mf [°C]	As [°C]	Af [°C]	Volume effect, %
NiAl	5	-15	5	20	-0.33
NiAlBRe	-60	-85	-60	-50	-0.31

4. Conclusions

1. After the solution treatment at 1000°C NiAl and NiAlB alloys contained NiAl and Ni_3Al phases. NiAlBRe and NiAlRe alloys contained also Re-rich phase of the compositions: $Ni_{21}Al_{15}Re_{64}$ for $Ni_{69.1}Al_{29.7}B_{0.4}Re_{0.8}$ alloy and $Ni_{13}Al_{19}Re_{69}$ for $Ni_{64}Al_{32}$ Re_4 alloy (all in at.%). In the case of $Ni_{71}Al_{29}$ and $Ni_{64}Al_{32}Re_4$ alloys martensitic phase was observed additionally. Alloying with B was a reason for the grain boundaries coarsening and hardening. Alloying with Re leads to the increase of the hardness both at grain boundary and the matrix.

2. The hardness at the grain boundaries zone and inside the grains was different in $Ni-63,5$ $Al_{36.1}B_{0.4}$ and $Ni_{69.1}Al_{29.7}B_{0.4}Re_{0.8}$ due to microalloying with B. It is assumed that this differences is the reason for the transcrystalline fracture observed in $Ni_{63.5}Al_{36.1}B_{0.4}$ and $Ni_{69.1}Al_{29.7}B_{0.4}Re_{0.8}$ alloys. Alloying both with B and Re lead to the observed traces of the viscous fracture mode in $Ni_{69.1}Al_{29.7}B_{0.4}Re_{0.8}$ alloy.

3. All the investigated alloys were undergoing martensitic transformation. A volume effect of the transformation was about -0.3%. M_s temperature depended on the Ni/Al ratio.

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