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Research article
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Features of formation of the Al–Ni–Zr system alloy structure obtained by reducing oxide compounds by aluminothermy using SHS metallurgy

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Abstract: This work is focused on establishing the regularity of the effect of zirconium (2.21; 3.29; 3.69 and 6.92 wt.% Zr) on structure formation, the nature of distribution of elements and the microhardness of structural components in the Al–Ni–Zr system alloys obtained by aluminothermy using the SHS metallurgy. Regularities of the formation of structural components and their microhardness depending on the content of zirconium in Al–Ni alloys (50 wt.%) have been identified and scientifically substantiated. Structural components were identified by the methods of electromicroscopic studies and *X*-ray microanalysis of elements. The structure of the initial alloy consists of Al_3Ni_2 (β′-phase) and Al_3Ni nickel aluminides. Zirconium doping of the alloy in the amount of 2.21 wt.% leads to crystallization of zirconium nickel aluminide $Al_2(Ni,Zr)$. With further increase in the content of zirconium (more than 2.21 wt.% Zr), complex alloyed intermetallic compounds crystallize – Zr, W, Si aluminides and Ni zirconides. A regularity was established in the decrease of the solubility of nickel in nickel aluminides Al_3Ni_2 and Al_3Ni and their microhardness as the zirconium content increases in the Al–Ni–Zr alloys from 2.21 to 6.92 wt.%. In nickel aluminide with zirconium $Al_2(Ni,Zr)$, this contributes to a decrease in the solubility of Ni, Al and increase in the concentration of Si and Zr. Zirconium doping of the Al–Ni alloy in the amount over 2.21 wt.% contributes to an increase in hardness (*HRA*), despite a decrease in the microhardness of the metal base (Al_3Ni_2, Al_3Ni and $Al_2(Ni,Zr)$). The main reason for increasing the hardness of the Al–Ni–Zr alloys is the crystallization of complex-alloyed intermetallides – Zr, W, Si aluminides and nickel zirconide, which probably have an increased microhardness. Thus, zirconium doping of the Al–Ni alloy makes it possible to obtain a plastic metal base from nickel aluminides Al_3Ni_2, Al_3Ni and $Al_2(Ni,Zr)$ and complex-alloyed intermetallides with high hardness.

Keywords: Al–Ni alloy, Al–Ni–Zr alloy, structure formation, *X*-ray spectral microanalysis, microhardness, hardness, nickel aluminides, SHS metallurgy.

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Особенности формирования структуры сплавов системы Al–Ni–Zr, полученных при восстановлении оксидных соединений алюмотермией с применением СВС-металлургии

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Аннотация: Настоящая работа посвящена установлению закономерности влияния добавки циркония в количестве 2,21, 3,29, 3,69 и 6,92 мас.% на структурообразование, характер распределения элементов и микротвердость структурных составляющих

в сплавах системы Al–Ni–Zr, полученных алюмотермией с применением СВС-металлургии. Установлены и научно обоснованы закономерности формирования структурных составляющих и их микротвердости от содержания циркония в сплавах Al–Ni (50 мас.% Ni). Методами электронной микроскопии и микрорентгеноспектрального анализа элементов идентифицированы структурные составляющие. Структура исходного сплава состоит из алюминидов никеля Al_3Ni_2 (β′-фаза) и Al_3Ni. Легирование сплава цирконием в количестве 2,21 мас.% приводит к кристаллизации циркониевого алюминида никеля $Al_2(Ni,Zr)$. При дальнейшем увеличении содержания циркония (более 2,21 мас.%) кристаллизуются комплексно-легированные интерметаллидные соединения – алюминиды Zr, W, Si и цирконида Ni. Установлена закономерность снижения растворимости Ni в алюминидах никеля Al_3Ni_2 и Al_3Ni и их микротвердости по мере увеличения содержания циркония от 2,21 до 6,92 мас.% в сплавах Al–Ni–Zr. В алюминиде никеля с цирконием $Al_2(Ni,Zr)$ это способствует уменьшению растворимости Ni, Al и повышению концентраций Si и Zr. Легирование сплава Al–Ni цирконием в количестве более 2,21 мас.% способствует повышению твердости (*HRA*), несмотря на снижение микротвердости металлической основы (Al_3Ni_2, Al_3Ni и $Al_2(Ni,Zr)$). Основной причиной повышения твердости сплавов Al–Ni–Zr является кристаллизация комплексно-легированных интерметаллидов – алюминидов Zr, W, Si и цирконида никеля, обладающих, вероятно, повышенной микротвердостью. Таким образом, легирование сплава Al–Ni цирконием позволяет получить пластичную металлическую основу из алюминидов никеля Al_3Ni_2, Al_3Ni и $Al_2(Ni,Zr)$ и высокотвердые комплексно-легированные интерметаллиды.

Ключевые слова: сплав Al–Ni, сплав Al–Ni–Zr, структурообразование, микрорентгеноспектральный анализ, микротвердость, твердость, алюминиды никеля, СВС-металлургия.

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Introduction

The high oxidation resistance and thermal conductivity of nickel aluminide played a role in its selection as a material for high-temperature applications, especially in the aerospace, automotive and energy industries [1; 2]. In connection with recent research on fuel economy, the low density of this intermetallide is a huge added benefit. The intermetallic structure of NiAl promotes structural stability even at critically higher temperatures, which are of important engineering value. This is possible due to the special phase of the B2 structure which persists even to the melting point, making it ideal for high-temperature structural applications [3]. Unfortunately, a major obstacle to the versatile applicability of this intermetallide is its poor mechanical properties at room temperature, especially its ductility and fracture toughness. The lack of slip systems and the complexity of transferring them across grain boundaries have been identified as single "contributors" to the NiAl brittleness [4].

Various approaches to improve the restrictions of this intermetallide have been studied over the years. They are still being studied, in order to make the most of its versatility. Researchers have included ductile phases in the brittle system. They have also applied directional solidification pathways, refined grain sizes, studied heat treatment, added rare earth metals, and even recently integrated nanostructures into the NiAl matrices [5—10]. However, in the papers analyzed here, there is no information regarding doping of the Ni—Al system alloys with rare metals, such as Sc and Zr.

Meanwhile, the formation of coherent precipitates $L1_2$ was observed during aging in aluminum alloys with Sc [11; 12]. This showed high thermal stability, allowing the use of Al alloys with Sc at higher temperatures. The undesirable coarsening of phases was not identified in the structure which has a beneficial effect on strength increase at room temperature and heat treatment temperatures. Zirconium, while having a lower diffusion coefficient than scandium, also forms metastable coherent precipitate $L1_2$. The disadvantage of using Zr is in its even lower maximum solubility in Al than in Sc — only 0.078 at. % [12]. This limits the use of these alloying elements when implementing the traditional NiAl production technology.

The promising technology of self-propagating high-temperature synthesis (SHS), which has a number of economic advantages, can be a solution to the problem of obtaining NiAl [13]. This process allows the formation of reinforcing phases in the matrix alloy. The method is used to synthesize nickel aluminides which are the metal matrix in modern functional materials. A high temperature of endogenous processes makes it possible to obtain cast composite alloys according to a short flow diagram [14—21].

The use of high-temperature reduction processes for refractory metal oxides seems economically feasible [21—24]. The present study is a continuation of work [22] in which the Zr content in the Al—Ni—Zr alloy ranged from 0 to 3.52 wt.%.

Thus, the objective of this work was to obtain zirconium-doped nickel aluminides by their synthesis from nickel oxide compounds and baddeleyite concentrate from the Far East region by the SHS metallurgy method. Another objective was to study the effect of zirconium on structure formation, liquation processes and microhardness of structural components of the Al—Ni—Zr system alloy.

Methods and materials

The initial substances for the charge were:
— NiO (99.5 wt.%, TU 6-09-3642-74, OSCH 10-2);
— baddeleyite concentrate (Table 1);
— calcium fluoride CaF_2 (98.0 wt.%, TU 2621-007-69886968-2015 with amendment 1);
— $NaNO_3$ (C.P., GOST 4168-79);
— aluminum powder (98.0 wt.%, PA-4, GOST 6058-73).

The composition of the charge in fractional parts was as follows: Al : NiO : CaF_2 : $NaNO_3$: $ZrSiO_4$ = = 10 : 10 : 12 : 6 : X, where X = 1.5, 2.0, 2.5, 5.0 and 8.0 of $ZrSiO_4$ fractional parts.

Metallothermic smelting was carried out in heat-resistant metal crucibles lined with refractory material. The charge was prepared by mixing a 50 g weighed portion with ∅ 40 mm grinding balls in a Pulverisette3 planetary mill (Fritch, Germany). This is a sealed 0.5 L container, at a speed of 500 rpm for 15—20 min. The experiment was carried out in the open air. The charge was ignited at a bulk mass after vibration compaction. The reaction was initiated with an electric igniter from above. Then the reaction proceeded without external heating. As a result of smelting, 2 layers of products in the form of metallic and slag phases were formed. They were separated due to gravity separation and the presence of calcium fluoride in the charge, acting as a flux.

In order to determine the regularity and average the results obtained, 5 melts were carried out for each concentration of the baddeleyite concentrate.

Within the context of this work, samples with the size of the studied surface of about 1.5 cm^2 and 5 to 10 mm high were used. Marking was done with a permanent marker. In order to study the uniformity of element distribution in volume, the surface of the cross section was treated. The samples were fixed by hot pouring into the Rose's alloy. Abrasive grinding with abrasive paper on a rotating wheel was used with decreasing the grain size after each treatment.

In order to ensure a higher quality of the examined surface, abrasive polishing with a felt cloth on a rotating wheel and chromium oxide-based abrasive pastes with different abrasive particle sizes ranging from 9 to 1 μm were used. Ultrasonic cleaning in acetone medium was applied, in order to remove polishing products and other contaminants from the surface of the samples.

The following modern methods of research were used:

— *X*-ray phase analysis of alloys using a DRON-7 diffractometer;

— *X*-ray spectral microanalysis to determine the content of elements in different structural components of the alloys — on an analytical research complex based on FE-SEM SU-70 (Hitachi, Japan) with energy dispersive (Thermo Scientific Ultra Dry) and wave (Thermo Scientific Magna Ray) attachments;

— microhardness tests (H_{50}) by the standard method on the HMV-G21DT device (Shimadzu, Japan);

— assessment of porosity by hydrostatic weighing on AUW-220D analytical scales (Shimadzu, Japan);

— hardness tests by the standard *HRA* method on a Metolab 100 hardness tester (Russia).

Main results and their discussion

The alloy synthesis proceeds through the stage of reduction of the initial zirconium and nickel oxides, accompanied by the formation of intermetallides and can be summarized, with a certain degree of approximation, by the following equations of chemical reactions [13]:

$$^3/_4\,ZrO_2 + Al = {}^3/_4\,Zr + {}^1/_2\,Al_2O_3, \quad (1)$$

$$3Al + Zr = Al_3Zr, \quad (2)$$

Table 1. **Composition of baddeleyite concentrate, wt.%**
Таблица 1. Состав бадделеитового концентрата, мас.%

ZrO_2	CaO	SiO_2	Fe_2O_3	P_2O_5	TiO_2	WO_3	Impurities
72.83	0.86	10.28	0.89	10.19	0.25	2.35	1.35

$$3NiO + 2Al = 3Ni + Al_2O_3, \quad (3)$$

$$4Al + W = Al_4W. \quad (4)$$

The values of the Gibbs energy are ΔG_{1000K} = = –39 kJ/mol for reaction (1), –28 kJ/mol (2), –105 kJ/mol (3) and –254 kJ/mol (4).

The effect of variable zirconium content on structure formation and the nature of element distribution in structural components of the Al—Ni alloy (50 wt.% Ni) obtained by the SHS metallurgy method was studied. In all synthesized ingots, the vertical sections in the lower half showed a dense structure without pores, and in the upper half the porosity was about 20 %.

The diffraction patterns of all alloys (Fig. 1) have the same character and set of peaks. The difference is noticeable in the relative intensity of reflexes. This probably indicates unequal crystallization processes and the preferential growth along certain atomic planes. The $NiAl_3$ phase was identified. No compounds with zirconium were detected, due to the low concentrations of this metal in the initial mixture.

The following structural components are formed in the initial alloy during crystallization in the SHS process (Fig. 2). Nickel aluminide Al_3Ni_2 represents a β′-phase — solid solution of Ni in AlNi, located in the area to the left of the singular crystallization point of AlNi. Its crystals have a lighter hue and are multifaceted in the form of grains. The Al_3Ni crystals have a gray hue and occupy the main area in the thin section.

Figure 3 presents the microstructure and points of analysis in structural components of the Al—Ni—Zr alloy samples which contain 2.21, 3.29, 3.69 and 6.92 wt.% of zirconium. As its content increases, the alloy structure becomes more complex with a decrease in the total volume ratio of the Al_3Ni matrix alloy, and an increase in the density of reinforcing intermetallide phases with zirconium.

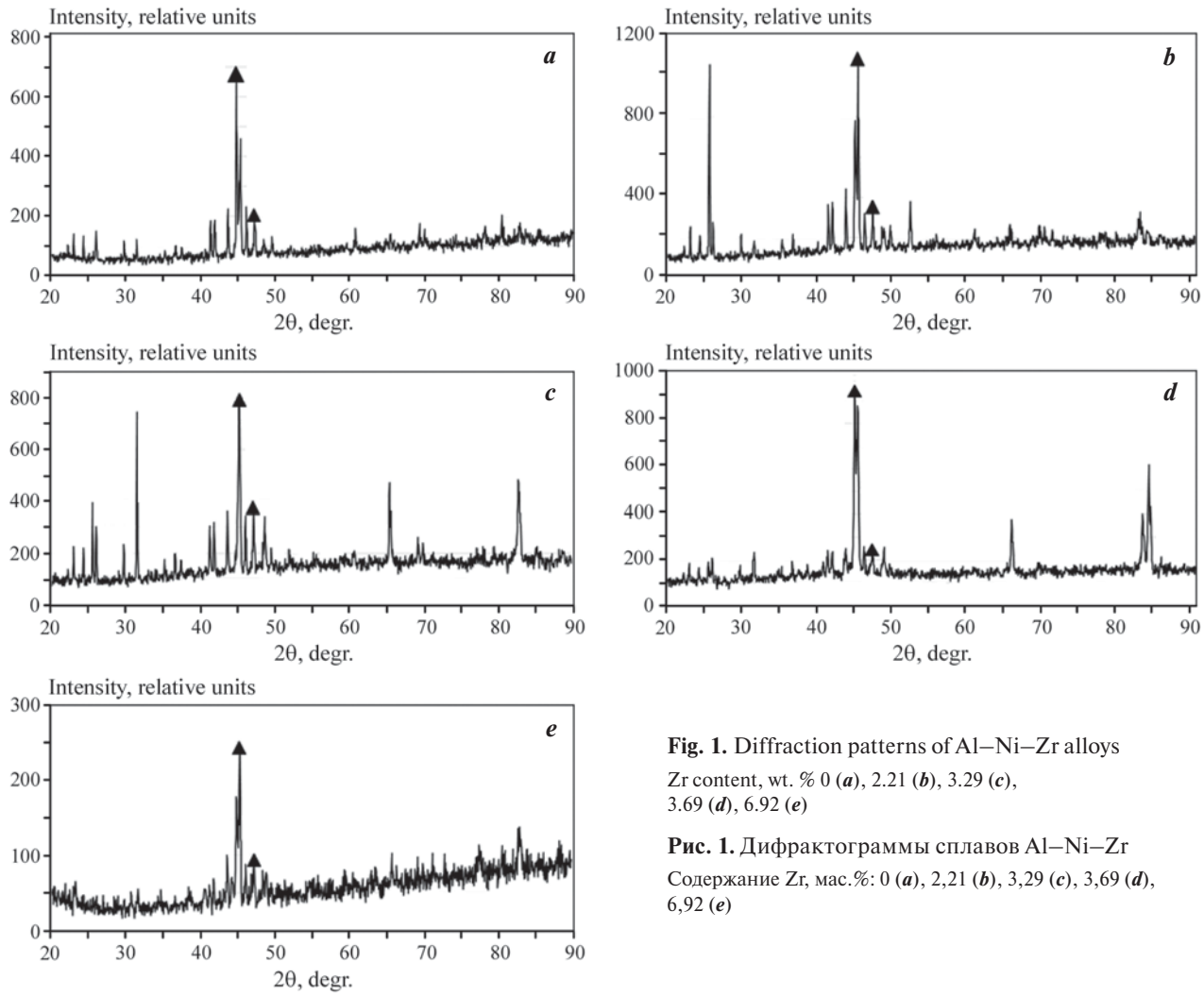
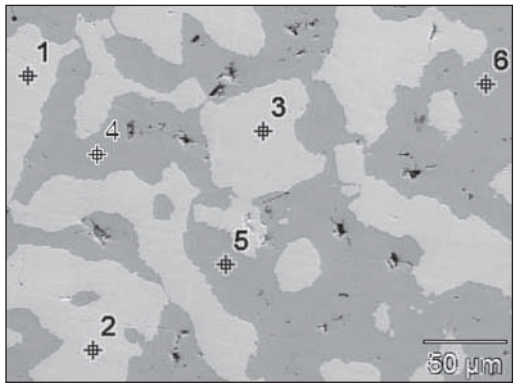


Fig. 1. Diffraction patterns of Al–Ni–Zr alloys
Zr content, wt. % 0 (***a***), 2.21 (***b***), 3.29 (***c***), 3.69 (***d***), 6.92 (***e***)

Рис. 1. Дифрактограммы сплавов Al–Ni–Zr
Содержание Zr, мас.%: 0 (***a***), 2,21 (***b***), 3,29 (***c***), 3,69 (***d***), 6,92 (***e***)



Points of analysis of the elements	Structural components	Content, at.%	
		Al	Ni
1–3	Al_3Ni_2	61.15	38.85
		$Al_{61.15}Ni_{38.95} = Al_{1.57}Ni = Al_{3.14}Ni_2 \approx Al_3Ni_2$	
4–6	Al_3Ni	74.56	25.44
		$Al_{74.56}Ni_{25.44} = Al_{2.43}Ni \approx Al_3Ni$	

Fig. 2. Microstructure and element distribution in structural components of the Al–Ni alloy

Рис. 2. Микроструктура и распределение элементов в структурных составляющих сплава Al–Ni

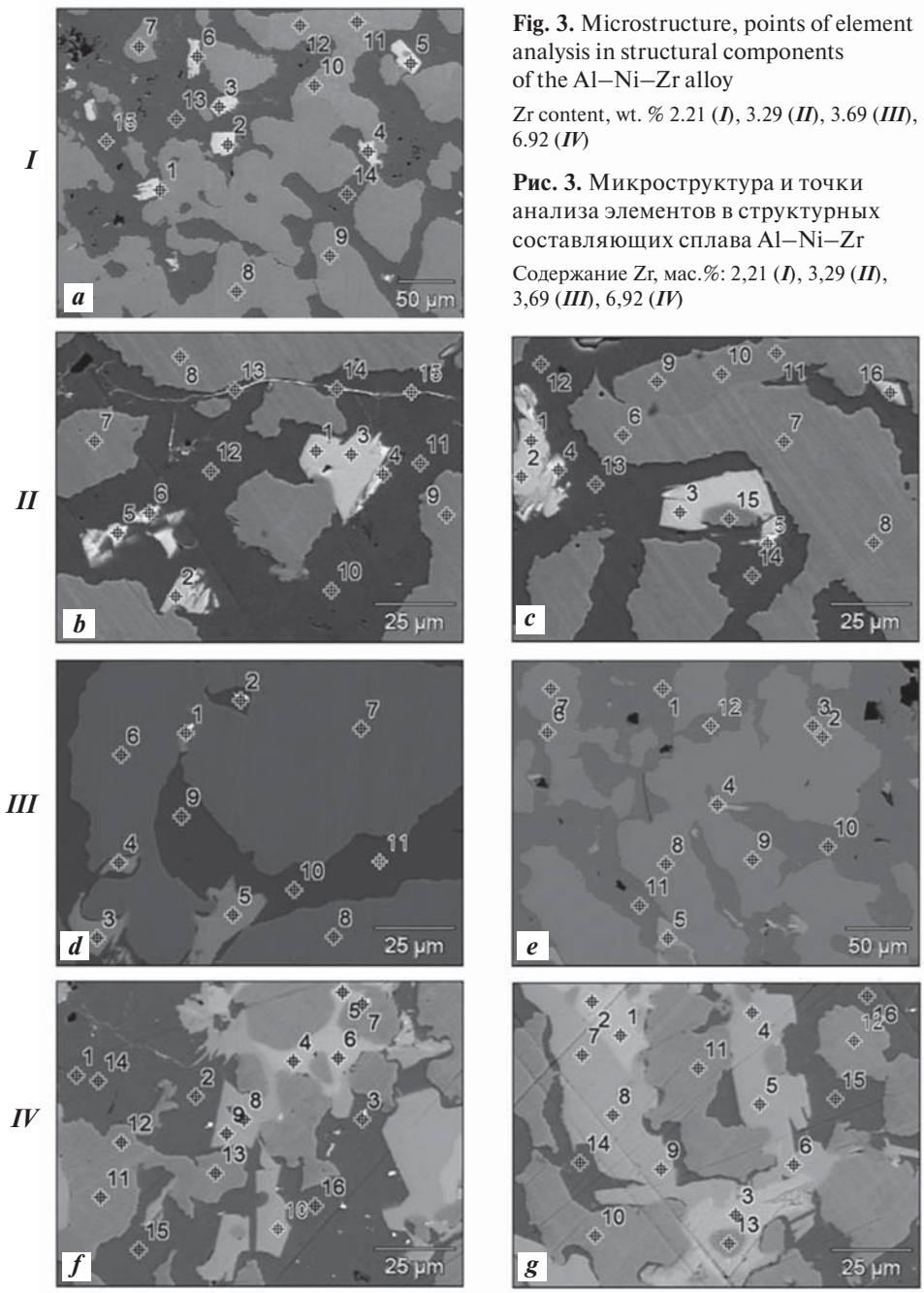


Fig. 3. Microstructure, points of element analysis in structural components of the Al–Ni–Zr alloy

Zr content, wt. % 2.21 (***I***), 3.29 (***II***), 3.69 (***III***), 6.92 (***IV***)

Рис. 3. Микроструктура и точки анализа элементов в структурных составляющих сплава Al–Ni–Zr

Содержание Zr, мас.%: 2,21 (***I***), 3,29 (***II***), 3,69 (***III***), 6,92 (***IV***)

Table 2. **Effect of zirconium additive on the content of elements (at.%) in structural components of the Al–Ni alloy and their distribution**

Таблица 2. Влияние добавки циркония на содержание элементов (ат.%) в структурных составляющих сплава Al–Ni и их распределение

Figure	Zr, wt.%	Al_3Ni_2 or β′-phase	Al_3Ni	Al_2(Ni, Zr)	Al_2(Ni, Zr, V, Hf, Ti)	Al_3(Zr, Ni, W, V, Ti, Fe)	Zr_4(Al, Ni, Hf, Ti)	Zr_3(Al, Ni, Hf, Ti)	Al(Si, Ni, V, Mn, Cr, W)
2	0	61.15 Al 38.85 Ni (*1–3*)	74.56 Al 25.44 Ni (*4–6*)	–	–	–	–	–	–
3, *I*	2.21	61.68 Al 38.3 Ni (*7–12*, *a*)	75.23 Al 24.77 Ni (*13–15*, *a*)	67.78 Al 19.46 Ni 12.76 Zr (*1–6*, *a*)	–	–	–	–	–
3, *II*	3.29	61.0 Al 39.0 Ni (*7–9*, *b* and *6–11*, *c*)	74.4 Al 25.6 Ni (*10–12*, *b* and *12–14*, *c*)	66.85 Al 21.79 Ni 13.3 Zr (*1–3*, *b* and *c*)	64.6 Al 21.79 Ni 0.6 Ti, 0.75 V 0.7 Hf (*13–15*, *b*)	72.6 Al 4.05 Ni 0.28 Ti 0.835 V 21.19 Zr 0.32 Fe 1.0 W (*4–6*, *b* and *4–5*, *c*)	–	–	–
3, *III*	3.69	62.37 Al 37.63 Ni (*6–8*, *d* and *7–9*, *e*)	75.53 Al 24.47 Ni (*9–11*, *d* and *10–12*, *e*)	66.7 Al 19.3 Ni 13.24 Zr 0.78 Ti (*3–5*, *d* and *4–6*, *e*)	–	–	9.01 Al 7.92 Ni 0.94 Ti 79.27 Zr 2.93 Hf (*1*, *d* and *2–3*, *e*)	25.6 Al 11.45 Ni 0.56 Ti 59.76 Zr 2.63 Hf (*2*, *d* and *1*, *e*)	–
3, *IV*	6.92	62.5 Al 35.63 Ni 1.83 Si (*11–13*, *f* and *10–13*, *g*)	76.85 Al 22.87 Ni 0.25 Si (*14–16*, *f* and *g*)	65.0 Al 18.62 Ni 13.49, 2.87 Si (*4–6*, *f* and *1–3*, *g*)	–	52.56 Al 17.34 Ni 28.41 Zr 1.43 Hf 0.26 Ti (*1*, *f*)	–	–	39.06 Al 9.37 Ni 0.97 Cr 3.85 V 30.5 Si 0.75 Fe 1.0 Mn 12.95 W (*2–3*, *f*)

Note. The analysis points shown in Fig. 2 and 3 are given in brackets.

Table 2 shows the elementary and phase compositions of structural components of the synthesized alloys. As can be seen, the $NiAl_3$ and Ni_2Al_3 phases have been identified in all samples. Zirconium alloying complicates the phase composition of the alloy: the Al_2(Ni, Zr) phase is formed in all the samples, and with an increase in the zirconium additive over 2.21 wt.% — Al_2(Ni, Zr, V, Hf, Ti), Al_3(Zr, Ni, W, V, Ti, Fe), Zr_4(Al, Ni, Hf, Ti), Zr_3(Al, Ni, Hf, Ti) and Al(Si, Ni, V, Mn, Cr, W) are formed.

Figure 4, *a* shows that the increasing zirconium content in the Al—Ni alloy contributes to the extreme change in hardness with its minimum value at 2.21 wt.% Zr. In order to identify the reasons for this, the effect of zirconium on the microhardness of the Al_3Ni_2, Al_3Ni and Al_2(Ni,Zr) structural components was studied.

It was found that the Al_3Ni_2 (β′-phase) and Al_3Ni microhardness monotonically decreases to 6.92 wt.% Zr (see Fig, 4, *b*). This is due to the reduction of nickel solubility as the zirconium concentration increases (Fig. 4, *c—d*). The Al_2(Ni,Zr) compound has an increased zirconium content in addition to the low nickel content (Fig. 4, *e*). Moreover, their total Ni + Zr amount

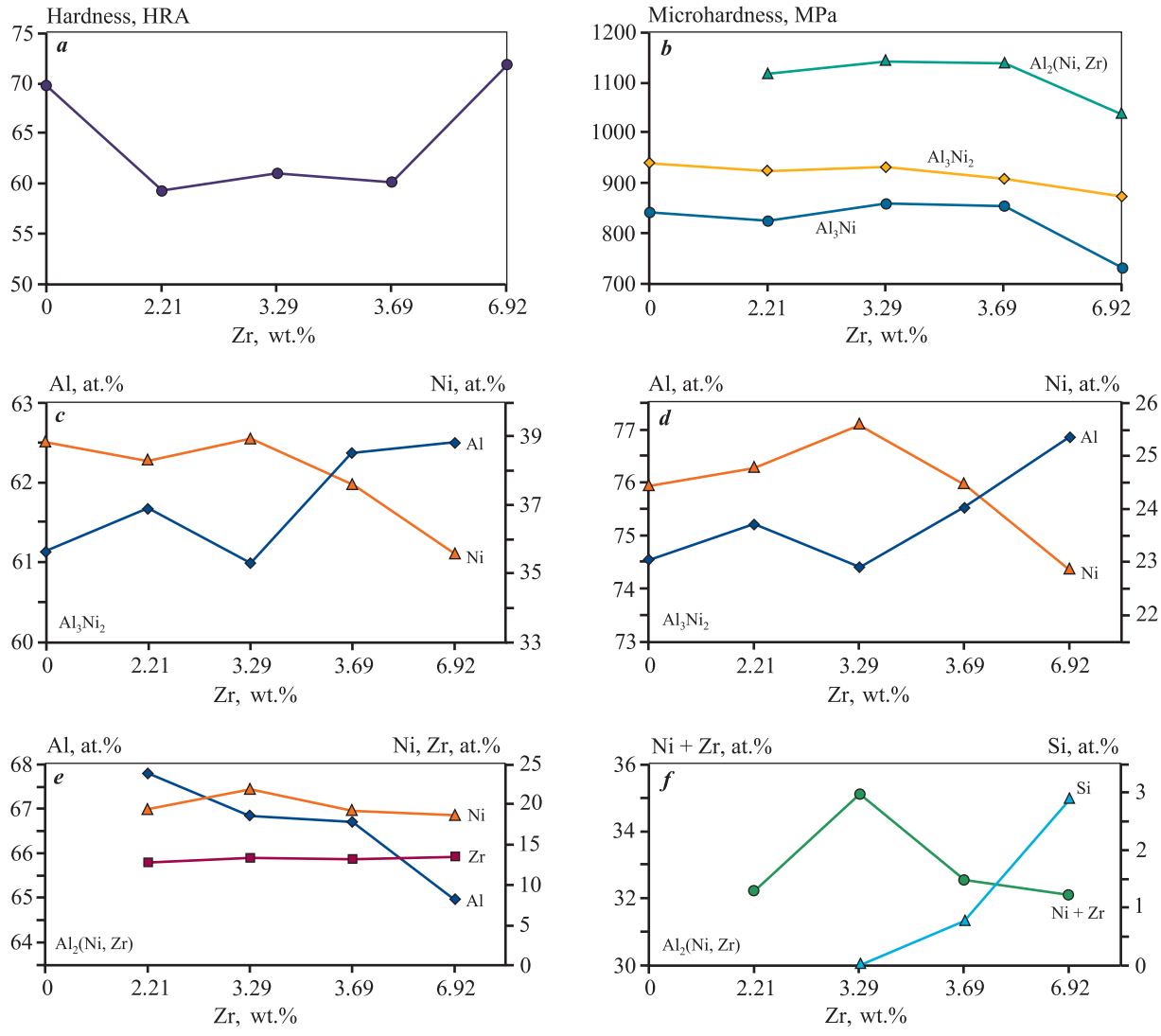


Fig. 4. Effect of zirconium on the composition and microhardness of nickel aluminides in Al–Ni alloys

a – hardness, ***b*** – microhardness of matrix phases, ***c*** – Al and Ni in Al_3Ni_2, ***d*** – Al and Ni in Al_3Ni_2, ***e*** – Al, Ni, Si in Al_2(Ni,Zr), ***f*** – Ni + Zr and Si in Al_2(Ni,Zr)

Рис. 4. Влияние циркония на состав и микротвердость алюминидов никеля в сплавах Al–Ni

a – твердость, ***b*** – микротвердость матричных фаз, ***c*** – Al и Ni в Al_3Ni_2, ***d*** – Al и Ni в Al_3Ni_2, ***e*** – Al, Ni, Si в Al_2(Ni, Zr), ***f*** – Ni + Zr и Si в Al_2(Ni, Zr)

decreases, and the concentration of silicon in $Al_2(Ni,Zr)$ increases significantly (Fig. 4, *f*).

Thus, the microhardness of Al_3Ni_2, Al_3Ni and $Al_2(Ni,Zr)$ decreases as the zirconium content in the Al—Ni alloy increases because the solubility of Ni and Ni+Zr decreases.

The main reason for increasing the hardness of the Al—Ni—Zr system alloys during alloying with 2.21—6.92 wt.% Zr is the crystallization of additional intermetallide compounds (Zr, W, Si aluminides and nickel zirconides) possessing high microhardness (Table 3).

Table 3. **Crystallization of intermetallide compounds depending on the content of zirconium in Al–Ni–Zr alloys**

Таблица 3. Кристаллизация интерметаллидных соединений в зависимости от содержания циркония в сплавах Al–Ni–Zr

Zr, wt.%	Compound	Composition, at.%
3.29	Al_3(Zr, Ni, W, V, Ti, Fe)	72.6 Al 4.05 Ni 0.28 Ti 0.835 V 21.19 Zr 0.32 Fe 1.0 W
3.29	Al_2(Zr, Ni, V, Hf, Ti)	64.6 Al 21.79 Ni 11.55 Zr 0.6 Ti 0.75 V 0.7 Hf
3.69	Zr_4(Al, Ni, Hf, Ti)	9.01 Al 7.92 Ni 0.94 Ti 79.27 Zr 2.93 Hf
3.69	Zr_3(Al, Ni, Hf, Ti)	25.6 Al 11.45 Ni 0.56 Ti 59.76 Zr 2.63 Hf
6.92	Al_2(Si, W, Ni, V, Ti, Mn)$_3$	39.06 Al 9.37 Ni 0.97 Cr 3.85 V 30.5 Si 0.75 Fe 1.0 Mn 12.95 W 1.58 Ti
6.92	Al(Zr, Ni, Hf, Ti)	52.56 Al 17.34 Ni 28.41 Zr 1.43 Hf 0.26 Ti

The main reason for increasing the hardness of the Al—Ni—Zr system alloys during alloying with 2.21—6.92 wt.% Zr is the crystallization of additional intermetallide compounds (Zr, W, Si aluminides and nickel zirconides) possessing high microhardness (Table 3).

Thus, by doping the Al—Ni alloy with zirconium (more than 2.21 wt.%), it is possible to obtain a plastic metal base of Al_3Ni_2, Al_3Ni, $Al_2(Ni,Zr)$ and high-hardness intermetallide phases of Al_2(Ni, Zr, V, Hf, Ti), Al_3(Zr, Ni, W, V, Ti, Fe), Zr_4(Al, Ni, Hf, Ti), Zr_3(Al, Ni, Hf, Ti), Al(Si, Ni, V, Mn, Cr, W) which increase the hardness of the Al—Ni—Zr system alloy.

Conclusion

1. The structural components in alloys of the Al—Ni—Zr system containing 2.21, 3.29, 3.69 and 6.92 wt.% Zr have been identified by electron-microscopic studies and *X*-ray spectral microanalysis of elements.

2. Regardless of the zirconium content, Al_3Ni_2 (β′-phase), Al_3Ni and $Al_2(Ni,Zr)$ crystallize in the Al—Ni—Zr alloy. In addition to these, various intermetallide compounds differing in stoichiometry and chemical composition crystallize in the alloy studied. They include zirconium, tungsten, silicon aluminides and nickel zirconide.

3. The solubility of nickel in Al_3Ni_2 (β′-phase) and Al_3Ni, as well as nickel with zirconium in $Al_2(Ni,Zr)$ has been found to change with increasing zirconium content in the Al—Ni—Zr alloy:

— the amount of nickel in Al_3Ni_2 and Al_3Ni decreases;

— the concentrations of Ni, Al and Ni + Zr in $Al_2(Ni,Zr)$ decrease;

— the silicon content increases on the contrary.

4. The regularity of Al_3Ni_2, Al_3Ni and $Al_2(Ni,Zr)$ microhardness decrease depending on the zirconium content in the Al—Ni—Zr alloy has been established.

5. Doping of the Al—Ni alloy with zirconium (more than 2.21 wt.%) promotes increase of hardness in spite of decrease of microhardness of the Al_3Ni_2, Al_3Ni and $Al_2(Ni,Zr)$ metal base.

6. The main reason for increasing the hardness of Al—Ni—Zr alloys is the crystallization of complex intermetallide phases — Zr, W, Si aluminides and Ni zirconides. Thus, the structure corresponding to the Charpy principle is confirmed.

7. Due to the structure developed and phase composition, as well as the increased hardness, it can be assumed that the alloys with the addition of 6.92 wt.% Zr are the most heat-resistant and wear-resistant of the synthesized alloys. This in turn, can be used in the conditions of increased wear and high temperatures.

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