

DILATOMETRIC STUDY ON LIQUID PHASE SINTERING OF Al-Ni POWDER COMPACTS

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Abstract

Compacts based on aluminium powder with mixed nickel powder in a quantity from 2.5 up to 20 at.% have been sintered in a dilatometer over the 550-750 °C temperature range. Owing to the heat generated during alloy forming, the temperature of sintered samples increases up to the melting point of the eutectic (640 °C), above which liquid phase appears as a result of contact melting. The dilatometric study has shown that formation of the liquid phase brings about shrinkage of the compacts without the preliminary growth that was observed in Al-Cr and Al-Ti systems. The main phase formed during sintering is the NiAl₃ compound. The influence of nickel concentration and sintering temperature on microstructure, porosity, and hardness of the sintered alloys has been studied.

Keywords: *liquid-phase sintering, microstructure, intermetallic compound, porosity, hardness*

INTRODUCTION

Aluminium has a considerable solubility in transition metals, especially if the concentration range of the existence of intermetallic compounds is included in the solubility limit, whereas the solubility of the transition elements in aluminium is low. For instance, the solubility of iron in solid aluminium does not exceed 0.9 wt.%, of titanium not more than 0.15%, of nickel about 0.05%. The solubility of these metals in liquid aluminium increases in accordance with temperature rise, and at high temperatures it can be comparatively high [1]. During sintering of binary powder mixtures of aluminium with iron, titanium, nickel, and chromium, respectively, intermetallic compounds and solid solutions based on these metals are formed [2]. However, in the course of the formation of the solid solutions and intermediate compounds, the predominant mass transfer is directed from aluminium into the transition metals both during solid state and liquid phase sintering.

As results of previous research [3] have shown, during solid state sintering of powder mixtures of the Ni-Al system, the formation of intermetallic compounds due to diffusion of aluminium atoms into the nickel particles is accompanied by emission of heat due to the exothermal reaction. This is also known from production of nickel aluminides by reactive sintering [4-7], which however was not the aim in the work described here. Upon rapid heating of compacts due to an intense heat release, the liquid phase originates at a temperature in the furnace that can be 150°C lower than the melting point of the eutectic alloy [3]. Therefore, the exothermal reaction in solid state is capable to heat a sample to the starting temperature of the contact melting (640°C) and, probably, even above the melting

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point of aluminium (660°C), while the temperature in the furnace remains noticeably below 640°C. The consequent wetting and spreading of the melt over the surface of the solid phase particles produces a substantial extension of the area of interaction between the components. As a result, a sharp increase of diffusion mass transfer of aluminium in nickel is accompanied by a fast growth in volume of the sample and a sudden rise of its temperature.

At the same time, the existence of a solubility of intermetallics in liquid aluminium indicates the capability of densification of powder bodies after formation of intermediate compounds on the surface of the nickel particles. This shrinkage is caused by dissolution of intermetallic compounds and the process of rearrangement of solid phase particles in the melt. As well as in the case of Al-Cu, Al-Ti systems and some others, a high exothermicity of this system allows one to conduct liquid-phase sintering of aluminium based powder bodies at furnace temperatures below the melting point of the eutectic.

The process of liquid-phase sintering of the Al-Ni system has been studied in this work. The phase diagram of the Al-Ni system is shown in a Fig.1. As follows from the diagram, in the Al-rich part of the system there is a eutectic containing 5.7 mass.% Ni [2]. Because the interaction between aluminium and nickel in powder mixtures proceeds with the formation of intermetallic compounds and heat emission, the availability of the low-melting eutectic in this system can render an essential influence on the process of its sintering and, therefore, on the choice of its regime [8]. This article is devoted to analyzing the results of dilatometric measurements of linear dimensions of powder bodies, changes of their phase composition, microstructure, porosity, and hardness depending on the mixture ratio and sintering temperature.

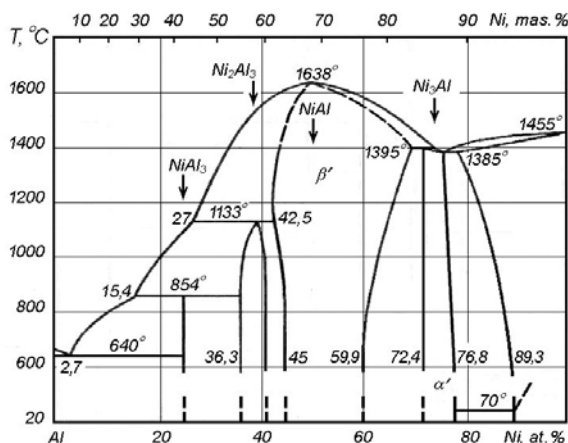


Fig.1. Phase diagram of the Al-Ni system [2].

EXPERIMENTAL PROCEDURE

Aluminium powder, designated PA-4 with particle size less than 100 μm (93% < 100 μm, irregular shape) was used as a base for preparation of the mixtures. Nickel powder PNC (carbonyl, the particle size is less than 10 μm) was used as an additive component. The nickel contents in the mixtures varied from 2.5 up to 20 at.%. From the powder mixtures, cylindrical compacts were prepared 10 mm in height and 10 mm in diameter and with an initial porosity of 20%. The compacting pressure was varied from 130

to 180 MPa depending on mixture composition. Before sintering, the compacts were annealed in a vacuum furnace for 1 hr at 500°C and a residual pressure of 10^{-2} Pa for removal of adsorbed gases.

Sintering of samples with the purpose of studying the changes of their linear dimensions was conducted for 30 min in a self-made pushrod-type vacuum dilatometer [9]. For controlling the temperature within the compacts, a narrow blind hole was drilled in them approximately at the center of the sample, in which the thermocouple was placed. The quartz tube of the dilatometer with the sample inside was put into the furnace preheated up to the selected temperature, which was maintained constant during the entire cycle of sintering. Owing to intermetallic compound formation accompanied by the heat release in compacts during sintering, there was a temporary increase of the compact's temperature that exceeded the temperature in the dilatometer tube.

During sintering in the dilatometer, the compacts were subjected to some strain at the stage of shrinkage under the action of the spring ensuring the reliable contact of the sample with the measurement system of the device, i.e. the pushrod. Therefore, dilatograms obtained during sintering describe the character of compact changes in volume mainly qualitatively and only partly quantitatively. To investigate the quantitative dependence of the final porosity of the alloys on the nickel concentration, the samples were sintered in a standard vacuum furnace over the temperature range of 550-750°C for 1 hour.

A LECO FR-3e hardness tester was used for hardness measurement of the sintered alloys. The phase composition of the alloys was determined on a Shimadzu 6000 X-Ray analyser with $\text{Cu}_{K\alpha}$ -radiation. The Powder Cell 2.5 program of full-profile analysis was used for processing the X-Ray pictures. The microstructural examinations were conducted using a scanning electron microscope Philips SEM 515 in a secondary electron mode.

EXPERIMENTAL RESULTS

Porosity of sintered alloys

The final porosity of alloys sintered at different temperatures as a function of nickel content in the mixture is shown in Fig.2. During sintering at low temperatures (550 and 575°C), samples do not exhibit noticeable volume changes except the compacts containing 17.5 and 20 at.% Ni, the porosity of which decreases at 575°C. With increasing sintering temperature, an intense shrinkage is observed for all nickel concentrations. The obtained results confirm that in this system, due to its high exothermicity, the process of liquid-phase sintering occurs more intensely than in the Al-Ti and Al-Cr systems [10,11].

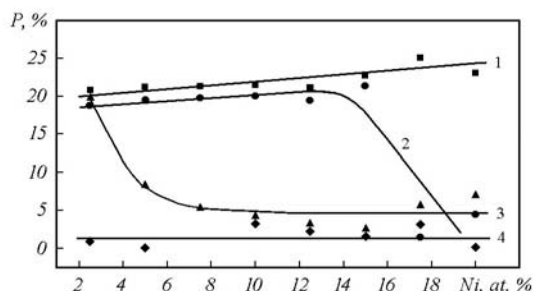


Fig.2. Porosity of sintered samples as a function of nickel powder content in the initial mixture. Sintering temperature, °C: 1 – 550, 2 – 575, 3 – 600, 4 – 700.

X-Ray phase analysis

The results of X-Ray analysis are given in Tables 1 and 2. Table 1 shows that all the nickel reacts with aluminium, since it cannot be found even after sintering at such a low temperature as 550°C, neither in the pure state nor as a Ni-Al solid solution.

Tab.1. Phase composition of Al-15 at.% Ni alloy sintered at different temperatures.

Sintering temperature [°C]	Phase [vol.%]			
	NiAl ₃	Ni ₂ Al ₃	NiAl	Al
550	2.5	18.4	0.8	78.3
600	50.6	1.5	1.8	46.1
700	71.1	–	0.2	28.7

Three intermediate phases: NiAl, Ni₂Al₃ and NiAl₃ form during sintering as a result of interaction between the components. The total content of intermetallic compounds in the alloy grows in accordance with the rise of sintering temperature at the same concentration of nickel in the mixture of 15 at.%. During sintering at 550°C, mainly the Ni₂Al₃ compound is formed, whereas the remaining phases make up only a minor part among all the intermetallics formed. With increasing sintering temperature the compound NiAl₃ becomes the main phase relating to its volume content in the alloys. So, as a result of sintering at 700°C, the Ni₂Al₃ phase cannot be found, while the content of the NiAl compound practically constitutes only a fraction of a percent.

Such regularity in sequence of formation of intermetallic compounds dependent on the sintering temperature confirms the diffusive nature of the reaction interaction of components. The intermediate compounds form due to the predominant diffusion of aluminium atoms into the nickel particles. The chemical equilibrium in the system is not reached at the low sintering temperature, when the diffusivity of atoms is comparatively low. Under these conditions the phase Ni₂Al₃ is formed, it does not correspond to the equilibrium state of the system containing 15 at.% Ni at the temperature of 550°C (Fig.1). The NiAl₃ compound, which meets the equilibrium state of the sintered mixture, becomes the main phase after sintering at 600 and 700°C.

The volume contents of phases that are formed in the Al-Ni system under conditions of sintering at 600°C are listed in Table 2 for various nickel contents in the powder mixture.

Tab.2. Influence of the nickel concentration in the mixture on the phase composition of the Al-Ni system alloys sintered at 600°C.

Concentration of nickel [at.%]	Phase [vol.%]			
	NiAl ₃	Ni ₂ Al ₃	NiAl	Al
5	11.1	10.5	-	78.4
10	17.1	6.4	0.3	76.2
15	50.6	1.5	1.8	46.1
20	63.7	13.0	6.4	16.9

Quite definite regularity is observed in the change of the NiAl, NiAl₃, and pure aluminium concentrations in sintered alloys. The higher the content of nickel in a mixture, the more the total quantity of the intermetallics formed during sintering, and the less free aluminium remains in the sintered composite. Such regularity is quite predictable, as the higher the nickel concentration in a mixture, the larger the quantity of Ni that should react with aluminium due to the increasing of the solid-liquid interface area.

Furthermore, as follows from the thermograph curves presented below describing the temperature variation inside the compacts during sintering, the more nickel contained in the mixture, the more the temperature exceeds the temperature maintained in the furnace. The data of Table 1 allows one to judge how the temperature rise of the sample due to its self-heating, as a result of heat release during formation of intermetallic compounds, influences the phase composition of the alloy. As to the Ni_2Al_3 phase, its content in the alloys does not obey any reasonable regularity; thus the results obtained for this compound have to be checked.

Microstructure

The microstructure of alloys containing uniformly 15 at.% Ni and sintered at different temperatures is demonstrated in Fig.3. It can be seen that as a result of sintering at 550 and 600°C, the nickel particles under the action of aluminium diffusing in them are disintegrated at the surface into small-sized fragments which, apparently, are intermetallics. Sintering at 700°C results in full fragmentation of the initial nickel particles and a noticeable enlargement of the fragments, which are the NiAl_3 phase according to the data of Table 1. In all the samples small pores are present mainly in the aluminium binder, independent of the sintering temperature.

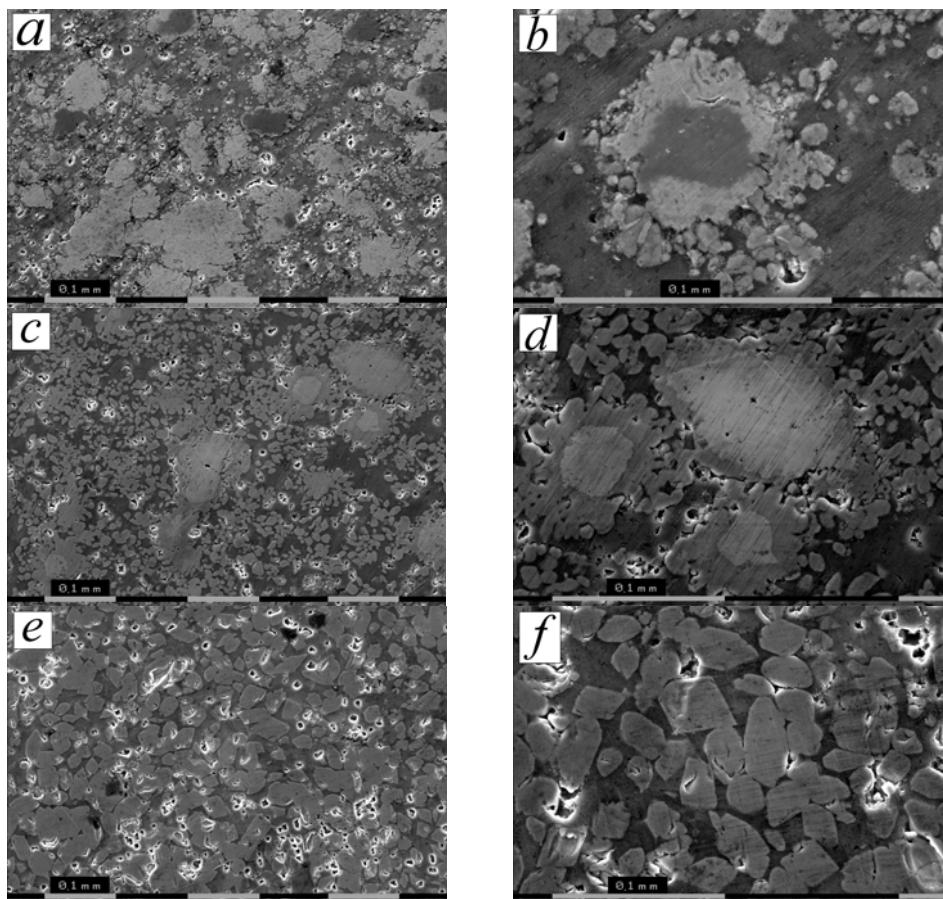


Fig.3. Microstructure of alloys containing 15 at. % Ni. Sintering temperature, °C:

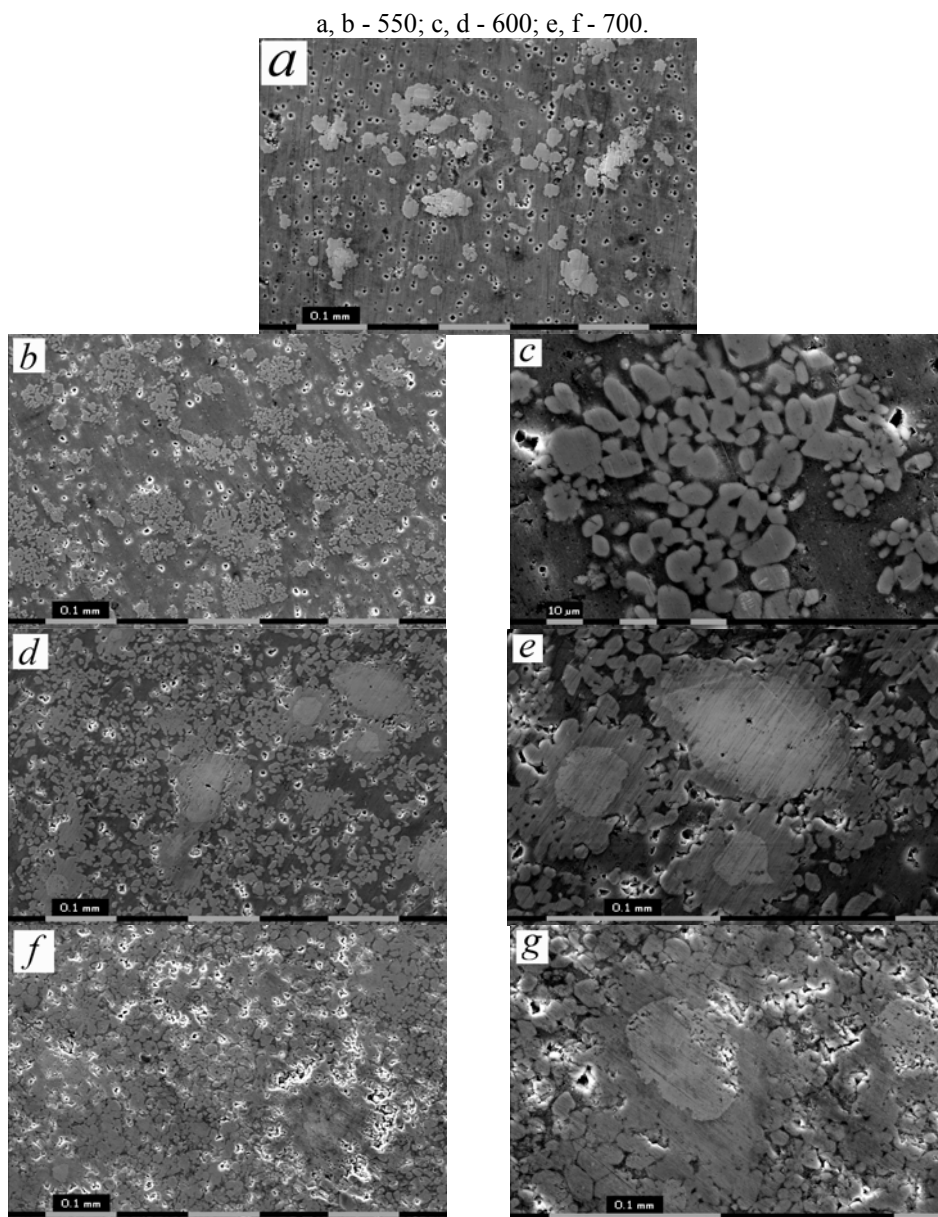


Fig.4. Microstructure of alloys sintered at 600 °C. Content of nickel in alloys, at. %:
a -; b, c - 10; d, e - 15; f, g - 20.

The influence of the nickel concentration on the microstructure of the alloys sintered at 600°C is shown in Fig.4. The higher the concentration of nickel in the mixture, the higher also the content of the second phase inclusions, small particles which probably are the NiAl_3 phase. The large particles of the second phase are former nickel particles. On their periphery are the intermetallic NiAl_3 forms. The NiAl_3 compound disintegrates at the interface with liquid aluminium during growth in the direction of the nickel particle centre.

A similar pattern of particle disintegration at the interface with aluminium melt during formation of intermetallic compounds was observed in the Al-Ti system [12]. This phenomenon is explained by the generation of tangential tensile stresses, the intensity of which grows from the centre to the periphery. In the central part of large inclusions, intermetallic compounds with smaller contents of aluminium, that is Ni_2Al_3 and NiAl presumptively, are formed. With enrichment by aluminium due to its diffusion from the melt, step-by-step they turn into the NiAl_3 compound.

Dilatometric studies

Dilatograms for sintering at 600°C of the pressed powder mixtures with the contents of nickel powder from 2.5 up to 20 at.%, are shown in Figs.5 and 6. It is possible to see that there is definitely no growth stage preceding shrinkage during the sintering of this system. However, such a growth stage is observed for the Al-Ti and Al-Cr systems [10,11], which also form intermediate chemical compounds like the Al-Ni system.

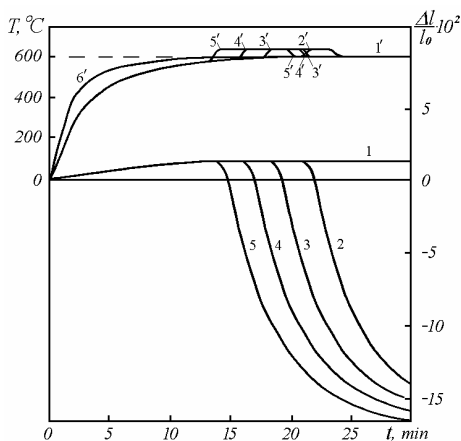


Fig.5. Dilatometer curves for dimensional change (1-5) and temperature ($1'$ - $5'$) during sintering of Al-Ni alloys at 600°C . Content of Ni, at. %: 1, $1'$ - 2.5; 2, $2'$ - 5; 3, $3'$ - 7.5; 4, $4'$ - 10; 5, $5'$ -12,5; $6'$ - temperature in dilatometer tube.

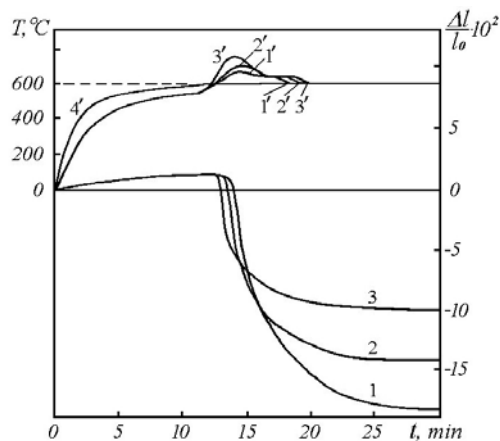


Fig.6. Dilatometer curves for dimensional change (1-3) and temperature ($1'$ - $3'$) during sintering of Al-Ni alloys at 600°C . Content of Ni, at %: 1, $1'$ - 15; 2, $2'$ - 17.5; 3, $3'$ - 20; $4'$ - temperature in dilatometer tube.

During sintering, the compact with the content of 2.5% nickel only undergoes a thermal expansion which is not accompanied by the subsequent densification, as the sintering process proceeds under conditions when both components are in solid state (Fig.5, curve 1). Owing to the small content of the additive component, the amount of heat emitted during formation of the intermetallic compounds as a result of diffusion interaction of the components is apparently not sufficient to reach the eutectic melting point of 640°C (Fig.5, curve $1'$). As mentioned above, at this temperature the liquid phase may be formed by the contact melting of nickel and aluminium

At 5 at.% Ni content the heat emitted during the reaction to form intermetallic compound becomes sufficient to heat up the sample to the eutectic melting point, at which there is an intense shrinkage of the powder compact (Fig.5, curve 2). In the temperature curve, a rather fast increase of its temperature up to 640°C is observed after 20 minutes of

heating the sample. This temperature remains constant for 2-3 minutes and then decreases to 600°C, which is the temperature in the dilatometer tube (Fig.5, curve 2').

The same temperature plateau at the level of 640°C, the eutectic melting point, is observed for the compacts containing 7.5; 10 and 12.5 at.% Ni (Fig.5, curves 3'-5'). In this case, the more nickel introduced into the mixture, the longer becomes the period at this temperature and the earlier the temperature is attained. Such regularity is explained by the fact that the higher content of nickel in the mixture provides a higher amount of released heat, which in turn, ensures faster self-heating of the sample and formation of a large amount of liquid phase. The stabilising of the temperature at the same level coinciding with the contact melting temperature may be explained in such a way that all the heat remaining after heating the samples to 640°C is spent for the melting of aluminium which is in contact with nickel particles. It is the origin of the compact shrinkage caused by rearrangement of the solid phase particles that confirms formation of the liquid phase at the moment of the appearance of the horizontal part in the temperature curve.

During further increase of the nickel content in the mixture from 15 to 20 at.%, the heat emitted is so large that the temperature of the compact, as a result of its self-heating, noticeably exceeds the eutectic melting point (Fig.6). After the exothermal effect caused by alloy formation during sintering, in the course of spontaneous cooling of the samples of the above compositions, a temperature plateau at 640°C appears again on the temperature curve. However, as distinct from the temperature plateau due to the melt formation, in this case the appearance of an isothermal part of the graph is connected with the solidification of the eutectic liquid.

From Figure 6 it also follows that the degree of linear shrinkage of the compact with 15% Ni appears to be the largest in comparison with the other samples. The increase of nickel content in the mixture reduces the degree of the compact shrinkage. This event confirms an increase of the volume fraction of the intermetallic compounds which forms a stiff skeleton of a sintered powder body on the one hand, and a lower amount of the liquid phase appearing on the other hand.

Hardness of alloys

Figure 7 shows the results of hardness measurements of alloys sintered at different temperatures. With an increase of the nickel content and the sintering temperature, the hardness of the samples grows. This fact can be linked to the formation, in increasing volume proportion, of intermetallic phases of higher hardness than that of the aluminium matrix. The results of microstructural observations (Figs.3 and 4) and X-Ray analysis (Tables 1 and 2) confirm an increase of volume content of the intermetallic phases.

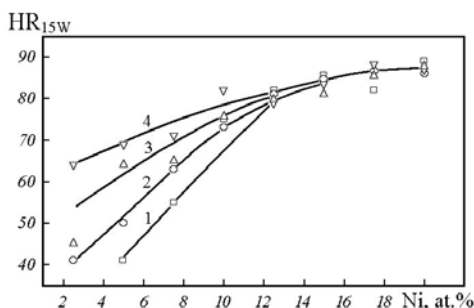


Fig.7. Hardness of alloys sintered at different temperatures as a function of the nickel

content, °C: 1 – 600, 2 – 650, 3 – 700, 4 – 750.

CONCLUSIONS

- Compacts based on aluminium powder containing from 5 to 20 at.% nickel powder can be subjected to exothermal reactive sintering without loss of the initial sample's shape. This sintering seems to be possible as a result of the liquid phase formation due to a contact melting of the components.
- Compacts with nickel contents from 5 to 20 at.% increase their density after sintering at temperatures of 550°C and higher. Thus, the initial porosity of green compacts, i.e. 20%, is reduced to below 10%. The hardness of sintered alloys with 10-20 at.% Ni is within the interval of 70-90 HR_{15W}.
- As a result of the exothermal reactions occurring in the Al-Ni system the intermediate compounds NiAl, Ni₂Al₃ and NiAl₃ are formed and additionally the liquid phase appears. The main phase formed during sintering is the intermetallic NiAl₃, that is in chemical equilibrium with the aluminium melt.
- The matrix of the alloys with 5-10 at.% Ni content sintered at temperatures of 600°C and higher is aluminium, which contains intermetallics in the form of inclusions. At the contents of nickel 15 and 20% in the mixtures, the base of sintered alloys predominantly consists of intermetallic compounds, between the particles of which there are pores and remains of nonreacted aluminium.

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