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THE EFFECTS OF GRAIN SIZE ON MECHANICAL PROPERTIES OF Ni-Al INTERMETALLIC ALLOY

ВПЛИВ РОЗМІРУ ЗЕРНА НА МЕХАНІЧНІ ВЛАСТИВОСТІ ІНТЕРМЕТАЛІЧНОГО Ni-Al СПЛАВУ

The study demonstrates that employing the synthesis method in combustion mode, followed by pressure treatment until the product undergoes heating due to a chemical reaction, enables the production of an intermetallic $NiAl_3$ alloy with relatively high mechanical properties. The grinding of intermetallic alloy grains during the synthesis under pressure is a result of plastic deformation of the synthesis product and high cooling rates. Simulation results indicate that high-temperature synthesis of the Ni-Al intermetallic alloy in a powder mixture of pure elements, under conditions of thermochemical pressing during a thermal explosion with minimal external pressure on the mixture, allows for obtaining an intermetallic synthesis product with an average grain size ranging from 50 to 60 мм.

***Keywords**: modeling, thermokinetic analysis, intermetallics, thermochemical reaction, thermochemical pressing, activation energy.*

Для нового покоління сучасних каталізаторів необхідні матеріали, які поєднують високу каталітичну активність з низькою щільністю та високими механічними властивостями.

Великий інтерес викликають сплави на основі алюмінідів нікелю $NiAl_3$. У роботі показано, що методом синтезу в режимі горіння з подальшою обробкою тиском до розігрітого за рахунок хімічної реакції продукту вдається отримати інтерметалідний $NiAl_3$ сплав з доволі високими механічними властивостями. Подрібнення зерна інтерметалідного сплаву в процесі його синтезу під тиском відбувається в результаті пластичної деформації продукту синтезу та високих швидкостей охолодження. За результатами моделювання встановлено, що високотемпературний синтез інтерметалідного сплаву Ni-Al в порошковій суміші чистих елементів в умовах термохімічного пресування при тепловому вибуху при мінімальному зовнішньому тиску на суміш, дозволяє отримати інтерметалідний продукт синтезу із середнім розміром зерна 50...60 мкм. При кімнатній температурі середнє значення міцності при згинанні дорівнює 580 МПа, а при розтягуванні вона тричі нижча (190 МПа). Границя міцності при розтяжінні литого стехіометричного полікристалу $NiAl_3$ при 293 К складає близько 120 МПа, а міцність при згинанні порошкового $NiAl_3$, отриманого методом гарячого пресування — 250 МПа. Збільшення ступеня пластичної деформації синтезованого під тиском інтерметалідного продукту в умовах інтенсивної пластичної деформації дозволить на порядок знизити розмір зерна в кінцевому продукті і навіть сформувати в інтерметалідному сплаві субмікрокристалічну зернисту структуру. Проведені дослідження показують, що існують потенційні можливості підвищення пластичності та міцності цього матеріалу, наприклад шляхом спрямованого легування.

***Ключові слова**: моделювання, термокінетичний аналіз, інтерметаліди, термохімічні реакція, термохімічне пресування, енергія активації.*

Problem's Formulation

Intermetallic compounds exhibit special properties when compared to pure metals and solid solutions. The pressing of intermetallics was initially employed in works [1, 2], which systematically investigated the impact of temperature on the mechanical properties of certain intermetallics. The authors of work [3] focused on developing the technological process of pressing intermetallics for semiconductor technology. All these studies demonstrated that intermetallic-type chemical compounds exhibit the capability for significant plastic deformations at optimal temperatures and speeds. An elevation in temperature results in the creation of conditions fostering increased plasticity, though it is essential to consider the concurrent rise in oxidation as the temperature increases.

Analysis of recent research and publications

In the mathematical description of thermochemical pressing, it is essential to consider the thermokinetic characteristics of the process, the speed of movement of the reactant, and its macroscopic density. Therefore, alongside kinetic equations for the formation of the intermetallic structure, activation energy, and chemical transformation, rheological equations must be employed. These equations, used to describe rheodynamic models, enable numerical calculations of the kinetic dependencies of key parameters in the high-temperature synthesis pressing process, including synthesis temperature, completeness of chemical transformation, macroscopic density of the synthesis product, level of elastic stress in the product, rate of plastic deformation, and grain size of the final product.

The starting material for synthesizing the *NiAl* intermetallic compound is a powder mixture of nickel and aluminum placed in the form of a briquette within a closed mold. The powder briquette is heated to a designated temperature and self-ignites in a thermal explosion mode when external pressure is applied, deforming the briquette. Plastic deformation halts when the synthesis product cools to temperature Tk, at which point it loses its plasticity.

To understand the formation of the structure of intermetallic *Ni-Al* alloys near the calculation point, it is crucial to consider the schemes of chemical reactions leading to the formation and decomposition of intermetallic compounds (metal phases). The state diagram of the mixture's components facilitates determining the corresponding phase of the reaction product based on the current temperature and the stoichiometry of the composition of the components near the calculation point (by the relative mass fraction of the components). Activation energy and thermal effects of the reaction for each phase were experimentally determined. For example, in the *Ni-Al* binary system, four intermetallic compounds are formed: $NiAl_3$ (*в*-phase, $E_в$ = 63 kJ/mol), Ni_2Al_3 (*г*-phase, $Eг$ = 75 kJ/mol), *NiAl* (д-phase, $E_д$ = 92 kJ/mol), and Ni_3Al (*е*-phase, *Ee* = 126 kJ/mol). Two phases form solid solutions based

on *Al* and *Ni* — *б*-phase and *ж*-phase, respectively. The state diagram of the *Ni–Al* system, as presented in sources [4, 5], indicates that Ni_2Al_3 and Ni_3Al compounds have relatively narrow regions of homogeneity, *NiAl* has a wide one, and the $NiAl_3$ phase corresponds to the formal composition. The formation and decay of phases, considering the thermal effects of the reaction according to the state diagram, are shown in Tabl. 1.

Table 1. Reaction diffusion in the system

Metallochemical reaction	Reaction temperature range
Formation of phases	
$3Ni + Al \rightarrow Ni_3Al + 157$ кДж	$T_{Al} \le T < T_\varepsilon$, $T_\varepsilon = 1380$ °C
$Ni_3Al + 2Al \rightarrow 3NiAl + 195$ кДж	$T_{Al} \le T < T_\delta$, $T_\delta = 1638$ °C
$2NiAl + Al \rightarrow Ni_2Al_3 - 64$ кДж	$T_{Al} \le T < T_\gamma$, $T_\delta = 1132$ °C
$N_2Al_3 + 3Al \rightarrow 2NiAl_3 + 58$ кДж	$T_{Al} \le T < T_\beta$, $T_\beta = 854$ °C

The structure of the interaction product layer confirms the complexity and ambiguity of the processes occurring at the interface of the components. Currently, there is no unified theory of diffusion interaction between solid and liquid metals. In [5], an approach is proposed that describes the growth kinetics of intermetallic phases within the meso-medium and is based on the following simplifying assumptions:

The formation of an intermetallic compound is limited by the diffusion of one component that moves more slowly.

Local thermodynamic equilibrium is quickly established at the interphase boundaries (the kinetics of the process are purely diffusional).

The dependence of diffusion coefficients on concentration is neglected.

The influence of interfacial surface tension and thermoelasticity effects is not taken into account.

Formulation of the study purpose

The objective of this study is to identify the patterns governing the mechanism for producing a densely compacted intermetallic alloy with a highly dispersed structure.

Presenting main material

Increasing the extent of plastic deformation in the pressure-synthesized intermetallic product, particularly under conditions of intense plastic deformation, can lead to a tenfold reduction in grain size in the final product. It may even facilitate the formation of a sub-microcrystalline granular structure within the intermetallic alloy. To model the influence of plastic deformation on structural-phase transformations in intermetallic *Ni-Al* alloys, the following equation is employed [6]:

$$D_k = \sqrt{D_\varepsilon^2 + \frac{c\rho_0\rho_c r_2 RT^2}{\chi_2 E_a (T_{a\partial} - T_0)} k_0 \exp\left(-\frac{E}{RT}\right)}. \quad (1)$$

It is evident from equation (1) that the ultimate grain size in the pressed product is influenced by several factors. These include the initial grain size of the product synthesized in the mold (D_0), the extent of deformation undergone by the synthesized product during pressing, the adiabatic synthesis temperature (T_{ad}), and its cooling rate. The cooling rate is contingent on the temperature of the mold (T_0), the radius of its cross-section (r_2), and the heat exchange coefficient between the synthesized product and the mold walls.

The following initial data were integrated for the calculation: H_0 = 50 mm, r_1 = 25 mm, r_2 = 15 mm, T_{ad} (*NiAl*) = 1911 K, T_0 = 300 K, c_0 = 0.6, c_{Ni} = 8907 kg/m^3, c_{Al} = 2700 kg/m^3, *м* = 0.14, c_{NiAl} = 5870 kg/m^3, c_{NiAl} = 600 J/kg·K, $Ea_{(NiAl)}$ = 92.048 kJ/mol, D_{Ni} = 100 мм. According to the simulation results, it has been determined that the high-temperature synthesis of the *Ni-Al* intermetallic alloy (Fig. 1) in a powder mixture of pure elements under the conditions of thermochemical pressing during

a thermal explosion, with minimal external pressure on the mixture, enables the acquisition of an intermetallic synthesis product with an average grain size ranging from 50 to 60 мм.

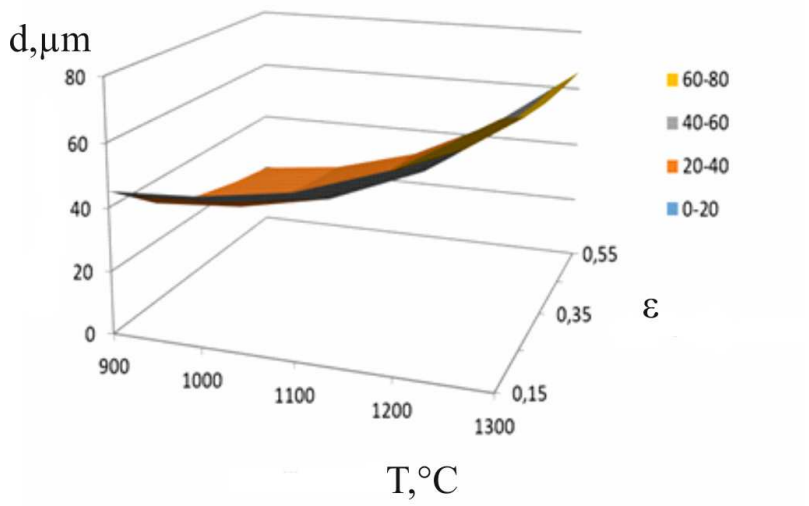


Fig. 1. Graph of the dependence of the final grain size of the Ni-Al intermetallic system on temperature and the degree of its deformation

The new generation of modern catalysts demands materials that combine high catalytic activity with low density and superior mechanical properties. Alloys based on nickel aluminides, particularly $NiAl_3$, are of significant interest [7]. Moreover, these alloys offer the advantage of being able to manufacture semi-finished products and complex-shaped items within a well-established technological process. The initial components used were pure nickel and aluminum powders with a dispersion ranging from 50 to 100 мм. The batch preparation involved dosing, mixing, filling the mold, pressing, and heat treatment. The pressing force varied between 2.5 to 5 tons, and initiation of the mixture was achieved using a tungsten spiral. The material's density, determined by the hydrostatic weighing method, is $4.71 \cdot 10^3$ kg/mi, aligning closely with the density of cast nickel aluminide ($4.73 \cdot 10^3$ kg/mi, as reported in [8]). The grains of $NiAl_3$ exhibit an equiaxed shape (Fig. 2), with an average size ranging from 30 to 40 мм.

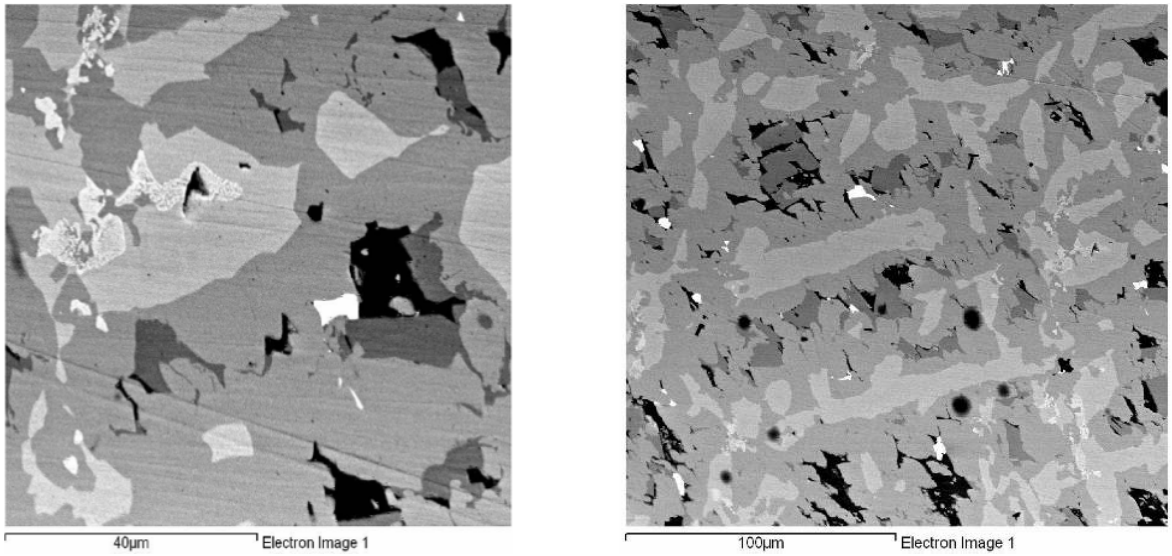


Fig. 2. The microstructure of nickel aluminide obtained by the method of synthesis in the combustion mode

To assess the mechanical properties of the intermetallic, various tests were conducted. Compression tests involved samples in the shape of a rectangular parallelepiped measuring 4Ч4Ч8 mm. Bending tests, utilizing a three-point scheme, used samples with dimensions of 5Ч5Ч35 mm. Torsion tests were performed on samples measuring 1Ч1Ч40 mmi. For tensile tests, heads were created on the samples, with a working part length of 20 mm and a cross-section of 5Ч3 mmI. All tests (with 5-7 samples for each point) were conducted on a UG-20 universal machine, utilizing special clamps, at temperatures ranging from 293 to 1273 K and a deformation rate of 10^{-3} s^{-1} [9].

For both bending and stretching at 293 K, the samples were elastically loaded up to failure, and no plastic deformation was recorded on the load curve. The strength values exhibited a scatter characteristic of brittle materials, with a coefficient of variation of about 5 %. At room temperature, the average bending strength is 580 MPa, while the tensile strength is three times lower at 190 MPa (Fig. 3). For comparison, the limit of tensile strength of cast stoichiometric $NiAl_3$ polycrystal at 293 K is approximately 120 MPa, and the bending strength of powdered $NiAl_3$ obtained by hot pressing is 250 MPa.

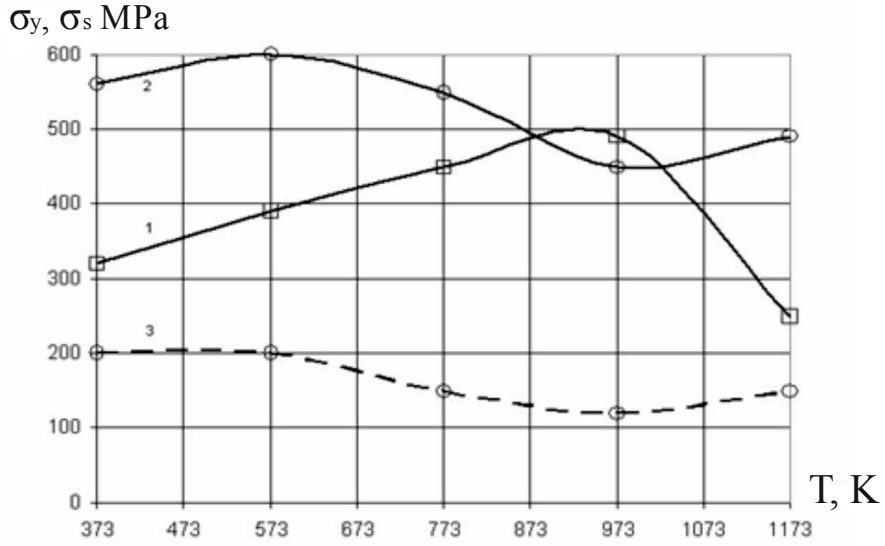


Fig. 3. Temperature dependence of the yield strength (1) and strength (2, 3) of $NiAl_3$ intermetallic during tests on compression (1), bending (2) and tension (3)

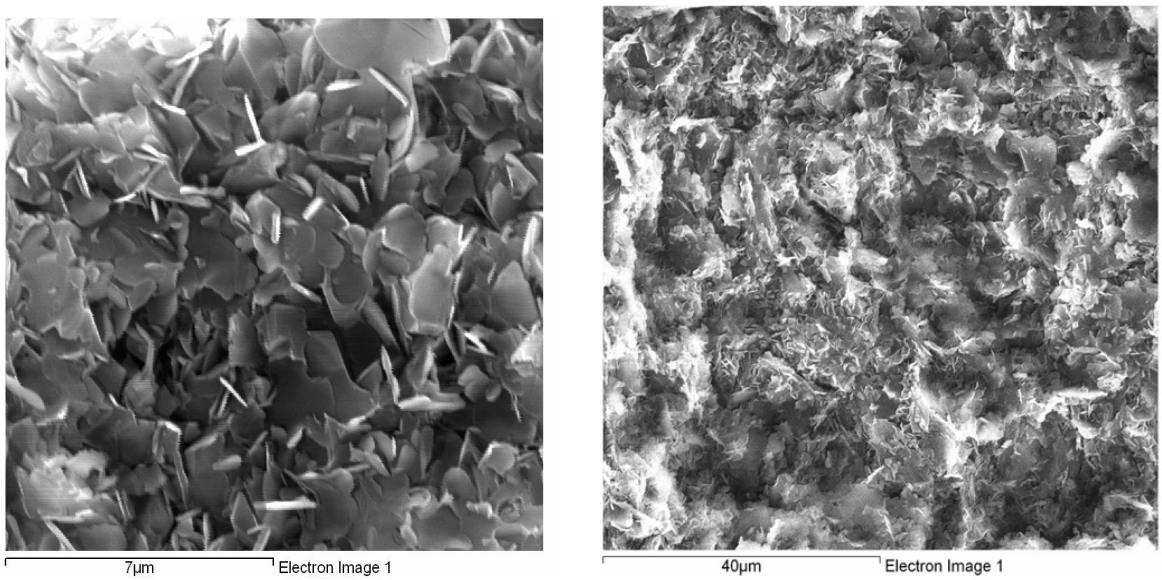
The higher strength of the synthesized material can be attributed to the structure formed during the manufacturing process, characterized by relatively small equiaxed grains. Casting methods typically do not yield such a structure. Up to temperatures of 1073 K, the destruction occurs primarily at the grain boundaries, with minimal plastic deformation of the grains (Fig. 3). At higher temperatures, a substantial proportion of plastically deformed grains emerges, and this proportion increases with the temperature of deformation. Nevertheless, the destruction remains predominantly intercrystalline.

In Fig. 4, (*a*) and (*b*) depict photographs of the microstructure of the surface of catalyst samples with different compositions. All samples exhibit a branched structure. A nanostructure, composed of hexagonal plates with a diameter of about 2 мм and a thickness ranging from 100 to 200 nm, forms on the surface of samples with manganese content. These plates are mainly oriented perpendicular to the substrate surface on which they grow, often developing along the edges to form star-like structures. There are also regions where the plates grow along the edges, creating long columnar structures.

To investigate the material's behavior upon reaching the yield point, torsion tests were conducted in the temperature range from 293 to 573 K. The samples were subjected to prior electrolytic polishing. In these tests, the sample was twisted to a specified angle using a reverse torsional pendulum setup, then unloaded, and the residual strain ($г_{ost}$) was determined. The shear modulus value of 66 GPa was employed in stress calculations.

The nature of the dependence of flow stress on residual deformation at room temperature in the microdeformation region (Fig. 5, *a*) mirrors that of cast materials, particularly those with the LI2

superstructure [10, 11]. The stress-strain curves (Fig. 5, *b*) exhibit no peculiarities compared to cast materials. The flow stress increases with rising test temperature. It was observed that at temperatures of 293 K and 573 K, the plasticity is 12 %. Generally, the reduction of intermetallic plasticity with increasing temperature is a well-known phenomenon [12, 13], with the minimum occurring at 873 K. The material undergoes destruction through chipping at an angle of 45° to the axis of the sample.



а *б*

Fig. 4. Fracture surfaces of $NiAl_3$ intermetallic samples tested for tension: *a* — at a temperature of 293 K, *б* — temperature of 1173 K

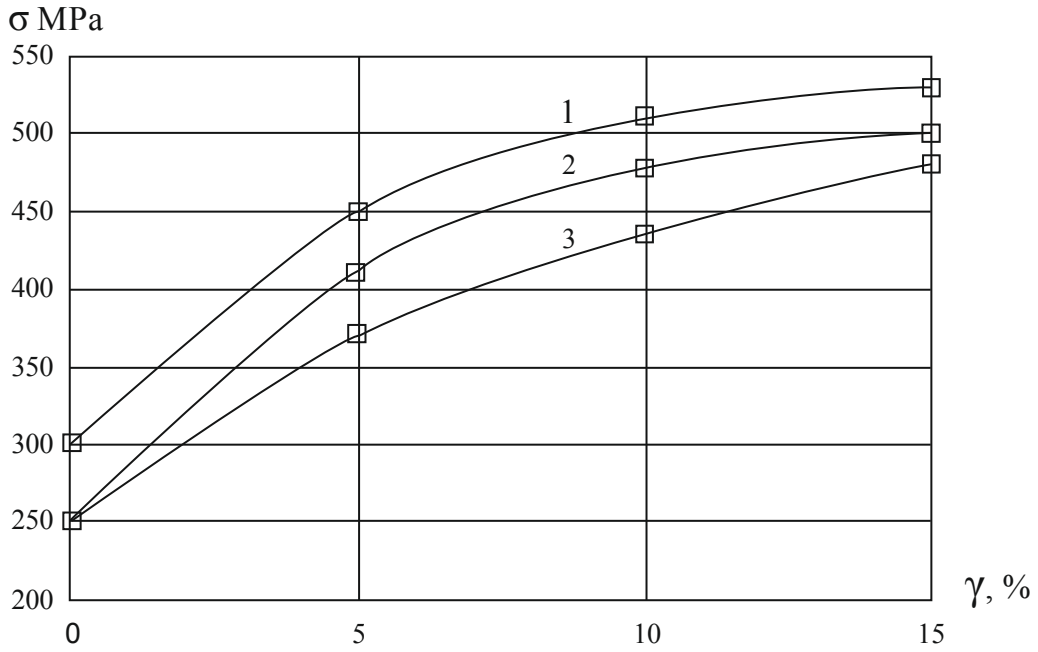


Fig. 5. Dependence of the shear stress on the residual deformation of $NiAl_3$ intermetallic in the area of macrodeformation: 1 — at a temperature of 873 K, 2 — 573 K, 3 — 293 K

Conclusions

In conclusion, the synthesis of an intermetallic $NiAl_3$ alloy using the combustion synthesis method followed by pressure treatment until the product is heated due to a chemical reaction allows for the production of a material with relatively high mechanical properties. The conducted studies indicate potential opportunities for enhancing the plasticity and strength of this material, such as through directional alloying.

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