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ANALYSIS OF THE THERMODYNAMIC PROPERTIES OF SPECIAL-PURPOSE ALLOYS FOR CONDITIONS OF THERMOCHEMICAL PRESSING

АНАЛІЗ ТЕРМОДИНАМІЧНИХ ВЛАСТИВОСТЕЙ СПЛАВІВ СПЕЦІАЛЬНОГО ПРИЗНАЧЕННЯ ДЛЯ УМОВ ТЕРМОХІМІЧНОГО ПРЕСУВАННЯ

The objective of this research is to delve into the analysis of the thermodynamic characteristics exhibited by intermetallic systems incorporating Ni-Ti and Ni-Co-Al alloys, particularly under the specific conditions of thermochemical pressing. Moreover, it seeks to ascertain the grain size within these systems utilizing a sophisticated mathematical prediction model.

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

Робота спрямована на дослідження нових матеріалів для сучасних каталізаторів, гальванічних елементів та адитивних технологій в областях біоінженерії, які поєднують в собі високу каталітичну активність, низьку щільність, відносно не велику вагу та високі механічні властивості. Наше дослідження націлене на аналіз термодинамічних властивостей систем Ni-Ti та Ni-Co-Al у контексті термохімічного пресування. Також визначено розмір зерна за допомогою математичної моделі прогнозування. Під час синтезу під тиском відбувається подрібнення зерна за рахунок пластичної деформації та швидкого охолодження. Результати моделювання свідчать про можливість отримання продукту з визначеним розміром зерна при високотемпературному синтезі в умовах термохімічного пресування. Математичне прогнозування

за допомогою формули Ю.О. Бєлоконя дозволило визначити достатньо приближений до реальних умов експерименту розмір зерна.

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

Problem's Formulation

The study and use of intermetallic compounds is a hot topic in the field of materials science. Based on the results and technology of works [1, 2], in which the effect of temperature on the mechanical properties of intermetallics was systematically studied, the idea for this work was taken. Since the authors of the work focused on the development of semiconductor technologies, our work took as the subject of research a material for bioprosthetics and a potential material for electrical engineering. Due to the fact that one of the problems is considered to obtain the grain of the desired size and a certain lamellar or duplex structure, one of the objectives of this work was to solve this problem. To do this, we use a mathematical prediction model developed by Yuri Belokon for other alloy systems to obtain a grain size prediction.

Analysis of recent research and publications

When describing mathematical modeling, it is necessary to take into account thermokinetic data of the process, the speed of movement of the reagent and its macroscopic density.

We used special equations (kinetic formulas) to develop the process of creating intermetallic materials. These equations helped us predict how different factors would affect the final product. These factors include the temperature used, the degree of reaction completion, the density of the final material, the internal voltage, the degree of deformation and the size of the grains.

To make these materials, we started with a powder blend. For nickel titanium, it was just nickel and titanium powders. For nickel-aluminum, we used a mixture of nickel, cobalt and aluminum powders. We pressed these powders into a compact form and molded them. Then they quickly heated it under pressure. This caused a rapid reaction (a heat explosion) that compressed and deformed the powder. Once the workpieces were cooled to a certain temperature (Tk), the material became rigid and did not deform anymore.

It is important to understand the composition of these materials (nickel titanium and nickel cobalt aluminum). The chemical reactions that occurred during the formation and decay of these metal phases were studied. We used phase diagrams, which are similar to maps of the behavior of materials at different temperatures and formulations, to predict what product would be formed from temperature and a mixture of ingredients.

The activation energies and thermal effects of the reaction for each phase were theoretically determined, and the necessary data from studies of similar systems were taken for comparison. In the binary Ni-Ti system, the calculation was performed for the Ni_3Ti phase:(β-phase, Eβ = 75 kJ/mol), In the ternary Al-Co-Ni system, the calculation was performed for the Al_3Co phase (Eg = 57 kJ/mol) [3].

Formulation of the study purpose

The aim of this research is to determine the grain size using a mathematical prediction model developed by Y.O. Belokon.

Presenting main material

For assessing the possibilities of obtaining intermetallic alloys, particularly Ni-Ti and Ni-Co-Al, via the method of thermochemical pressing, thermodynamic analysis holds significant importance. Despite the fact that the topic of intermetallic compounds is not entirely new, the number of studies providing comprehensive information on them is extremely limited. The temperatures at which thermochemical pressing occurs are calculated taking into account adiabatic processes within the system.

The main calculated values that allow predicting the grain size of y were calculated using the following formulas. For unknown parameters, the data were taken from the literature. The heat capacity equation proposed in [4] was used for the calculations.

$$C_p\ (T) = a_0 + a_1 \cdot 10^{-3}T + a_{-2} \cdot 10^{5}T^{-2}. \quad (1)$$

To calculate the coefficients of melting temperatures of compounds and standard entropy values along with temperatures of polymorphic transformations $T_{пл}K$, we rely on thermodynamic data and phase diagrams.

Additionally, the coefficients were calculated using the equations proposed by Tsagareishvili and Gvelesiani. These equations provide mathematical models to estimate thermodynamic properties such as melting temperatures and standard entropy values based on experimental data and theoretical considerations. Utilizing these equations enhances the accuracy of thermodynamic analysis and facilitates the prediction of material properties and phase transformations.To clarify the data, the calculation was based on a comparison with the works [5,6] and the average value was taken

$$a = \frac{a_0}{n} = (5{,}95 - \frac{0{,}3C^{am}_{p298}\theta}{T_{пл}}); \quad (2)$$

$$b = \frac{a_1}{n} = \left(\frac{0{,}34C^{am}_{p298}}{T_{пл}}\right); \quad (3)$$

$$c = \frac{a_2}{n} = 0{,}9(a + b \cdot 298 - C^{am}_{p298}\ ). \quad (4)$$

Thermodynamic stability calculations of intermetallic compounds are based on the utilization of Gibbs-Helmholtz equations. These equations provide a framework for assessing the stability of compounds by analyzing changes in Gibbs free energy with respect to temperature and pressure. By applying Gibbs-Helmholtz equations, researchers can determine the conditions under which intermetallic compounds are thermodynamically stable or metastable, aiding in the design and synthesis of materials with desired properties.

$$\Delta G = \Delta H^{\circ}_T - T \cdot \Delta S^{\circ}_T, \quad (5)$$

ΔH°_T — enthalpy of formation, J/mol; ΔS°_T — entropy, J/mol; T — temperature, K; for the calculation of activation energy, the following formula was used:

$$E_a = \frac{R[lnk_2 - lnk_1]}{\frac{1}{T_1} - \frac{1}{T_2}}. \quad (6)$$

For calculating the equilibrium of chemical reactions in the investigated systems and estimating the equilibrium compositions of components, the constants of all independent reactions were determined:

$$\Delta G^{\circ}_T = -RT\ln k; \quad (7)$$

$$k_T = \exp\left(-\frac{\Delta G^{\circ}_T}{RT}\right). \quad (8)$$

The dependence of the grain size of the synthesized product on the degree of its deformation during pressing is described by an empirical relationship:

$$D_\delta = \frac{D}{\sqrt[3]{A\left(\frac{\varepsilon}{\varepsilon_{кр}}\right)^2}}. \quad (9)$$

With an increase in the degree of deformation of the pressurized intermetallic blank, especially under conditions of significant plastic deformation, the grain size is assumed to decrease by an order of magnitude. So it makes sense to use specific equations that consist of several parts responsible for different characteristics of the synthesis process. Modelling of the effects of plastic deformation using such an equation is as follows:

$$D_k = \sqrt{D_\varepsilon^2 + \frac{c\rho_0\rho_c r_2 RT^2}{\chi_2 E_a (T_{ad} - T_0)} k_0 \exp\left(-\frac{E}{RT}\right)}. \quad (10)$$

From equation (1) it is possible to distinguish individual parts that characterize the process and the final grain size in the compressed product depends on several factors: the initial product size (D_0), the degree of deformation of the synthesized product during compression, the temperature of adiabatic synthesis (T_{ad}) and its cooling rate. The cooling rate depends on the mold temperature (T_0), its cross-section radius (p_2) and the ratio of heat exchange between the synthesized product and the mold walls.

The inputs were used for the calculation:(*Ni_3Ti):r_2*= 15 mm, T_{ad} = 1873 K, T_0= 298 K, ρ_0 = 0.6, ρ_{Ni3ti} = 7900 kg/m^3, c_{NiAl}= 22.4 J/kg·K, $Ea_{(Ni3Ti)}$= 75178 kJ/mol, D_{Ti} = 100 μm.; (*Al3Co*):r_2= 15 mm, T_{ad} = 1673 K, T_0= 298 K, ρ_0 = 0.6, ρ_{Ni3ti} = 6700 kg/m^3, c_{NiAl}= 24.38 J/kg·K, $Ea_{(Al3Co)}$= 57971 kJ/mol [7], D_{Ti} = 100 μm. The modeling results are shown in fig. 1 and 2.

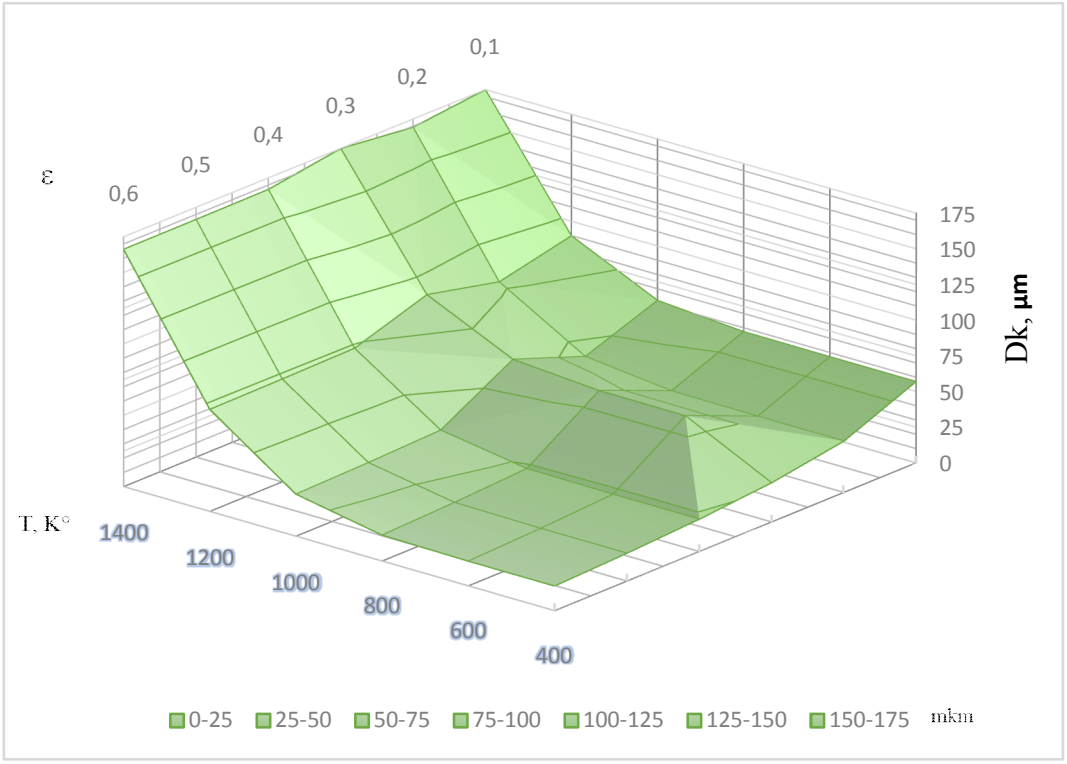

Fig. 1. Graph of the dependence of the final grain size of the Ni_3Ti phase *Ni-Ti* intermetallic system on temperature and the degree of its deformation

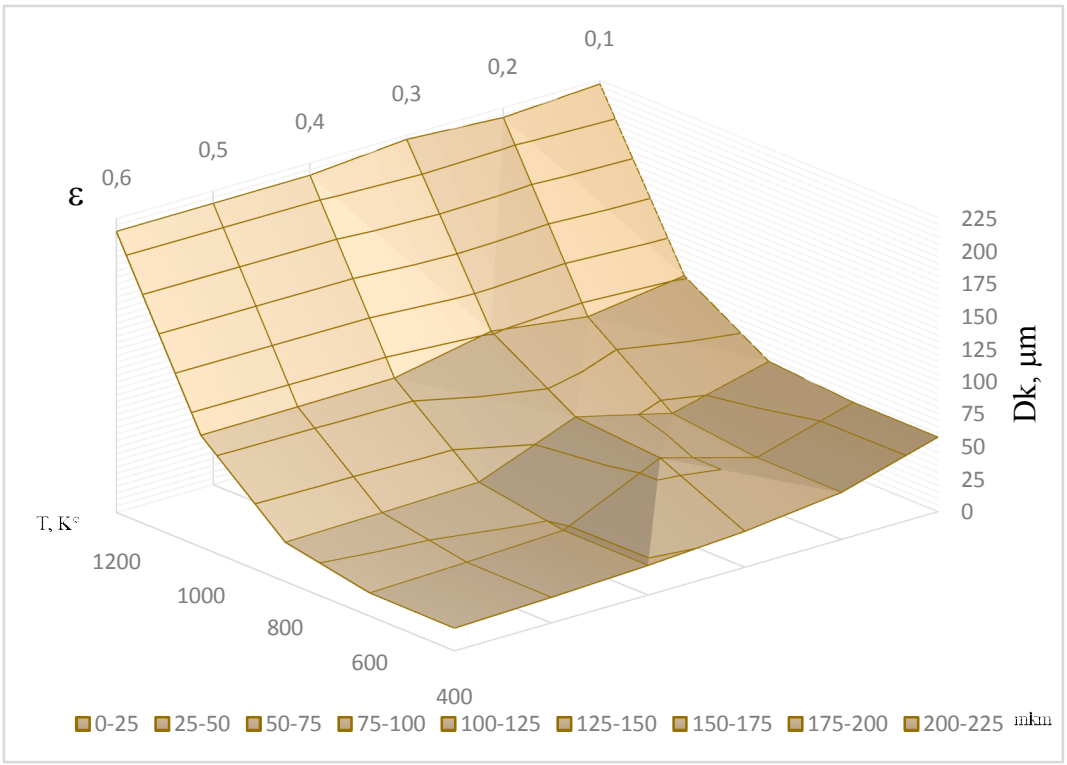

Fig. 2. Graph of the dependence of the final grain size of the Al_3Co phase *Al-Co-Ni* intermetallic system on temperature and the degree of its deformation

The results of modelling and using the Belokon equation (Fig. 1,2) showed similar results to the work [1,2]. When using the established law, synthesis allows to produce a product of inter-metallic synthesis with an average grain size of 25 to 50 μm, which cores with an average grain value of 50-60 in other works, taking into account the difference of systems and their components.

The modeling process is characterized by the participation of the kinetics equation in the general law and the participation of the deformation law. In this study, the original method, which does not include fundamental changes, was used to calculate the grain size of individual systems for thermochemical pressing processes.

A number of papers demonstrate the analysis and study of similar systems using the CALPHAD method, the data from which were used in this work [7,8]. The result was compared with the calculated one and had good convergence.

Conclusions

Modeling the synthesis of intermetallic alloys by combustion synthesis followed by pressure treatment is an effective method for predicting the alloy grain size and, consequently, mechanical properties. Our studies indicate potential opportunities to increase the ductility and strength of this material, for example, by means of directional alloying.

It is also proposed to use a more complex deformation model for the used model to improve the accuracy of calculations.

The formula used theoretically allows modeling for more complex systems, including cantor alloys.

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