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Influence of low-energy mechanoactivation on the phase composition and microstructure of the 3Ni-Al intermallide-forming system

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Abstract. The application of low-energy mechanical activation (LEMA) of a 3Ni+Al powder mixture and its effect on the structure and elemental phase composition of mechanocomposites is studied in this work. The leading role of mechanical forces in the processes of deformation reorganization of the morphological structure of the powder composition is shown. A scheme of morphological transformations in the LEMA process in a 3Ni+Al powder mixture is proposed, which is divided into three successive stages: the formation of agglomerates consisting of nickel and aluminum particles; the formation of layered mechanocomposites consisting of layers of nickel and aluminum; formation of a homogeneous nickel-aluminum composition. It is determined that the degree of defects in the mixture increases only during the formation of agglomerates.

Keywords: low-energy mechanical activation, high-temperature synthesis, Ni3Al intermetallic compound, grain structure, mechanocomposit.

1. Introduction

Currently, the method of mechanical activation (MA) of chemical transformations is used to stimulate various solid-phase reactions [1–4]. Mechanochemical synthesis is also considered as one of the possible ways of "dry" technological processes in which the reaction is carried out without the use of solvents, thereby achieving a significant gain both in the cost of the process and in solving many environmental problems [5–8].

Despite the practical use of MA, the consistent study of mechanochemical reactions was developed only in the 20th century. The reason for this is the complexity of the phenomenon, the study of which requires knowledge about physics, chemistry and mechanics of condensed matter. Another reason is the lack of reliable and accurate tools and techniques for the direct study of chemical reactions under conditions of intense dynamic loads. Therefore, most of the modern knowledge about mechanochemical reactions is obtained indirectly. Currently, the mechanical method of activating chemical transformations is used to stimulate various solid–phase reactions [9-14].

The method allows to obtain many chemicals: intermetallides, oxides, sulfides, carbides and other compounds and their compositions. Mechanochemical synthesis of inorganic substances is carried out in an energetically stressed grinding device of various types. Planetary mills are most often used in this capacity. The initial components are powders of individual substances or chemical compounds.

In the process of MA, as noted in almost all studies, a significant dispersion of reagents occurs, their contact area increases and a new highly defective structure of reagents is created, characterized by an increased reserve of excess energy. The presence of excess energy increases the chemical activity of the treated system (activation itself).

At the same time, the opposite phenomenon may occur at MA – passivation – as a result of relaxation of structural defects and reduction of the reaction surface due to grinding of the mill material and grinding media, as well as a chemical reaction. Both types of relaxation are thermally activated, while the effective activation energy of relaxation processes depends on the amount of excess energy.

Another factor reducing reactivity may be phase transitions in reacting substances. The temperature of the phase transitions is achieved as a result of the dissipation of mechanical energy and heat release from chemical reactions. In this case, the change in the structure of the reagents is accompanied by a decrease in the excess energy accumulated during the MA process. Phase transitions are another possible channel for the relaxation of excess energy.

Thus, despite its proven effectiveness, machining in high-energy crushing devices often requires more careful selection of experimental conditions. Otherwise, it can lead to the formation of intermediate phases and contamination, which will complicate the subsequent synthesis of the product outside the mill [1, 9].

The results obtained in the article [15] on the mechanical processing of the 3Ni+Al composition in a low-energy mill and its subsequent thermal initiation showed that low-energy mechanical activation (LEMA) is able to significantly intensify the process of obtaining monophase intermetallic Ni3Al at the synthesis stage. Low-energy grinding may be more useful in certain cases than high-energy grinding. To confirm this, both experiments and theoretical calculations were used in [15] to identify and analyze the macrokinetic features of the low-energy mechanical activation process, which prepares a mixture of powder reagents for an explosive reaction, subsequently initiated by thermal action.

In this paper, a variant of low-energy mechanical activation (LEMA) of 3Ni+Al powder mixture [4] and its effect on the structure and elemental phase composition of the mechanocomposite particles formed from the components of the mixture are considered. The time of low-energy machining of the powder mixture varied between 0 and 30 hours.

2. Experimental procedure

Powders of aluminum ASD-4 (average size ~5 microns) and nickel PNK-UT4 (average size ~ 1 microns) were used in the work. Pre-mixing (2 hours), followed by low-energy mechanical activation and grinding of the 3Ni+Al powder mixture was carried out in an IBMT-30 ball laboratory mill (HT Machinery, Japan-Taiwan). Steel balls Ø25.4 mm in the amount of 15 pieces were used as grinders, the rotation speed of the drum was equal to 150 rpm. The weight of the powder mixture and the ratio of the mass of the balls to the mass of the mixture were, respectively, 50 g and 20:1.

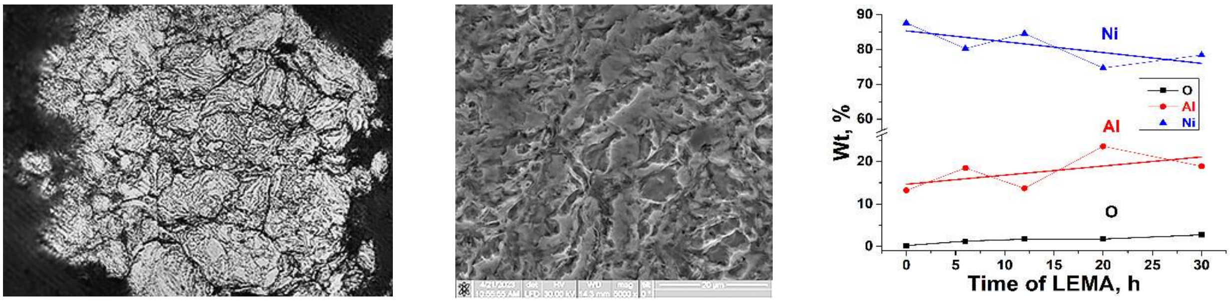
The duration of the treatment varied in the range of 0–30 hours, while in each individual case a fresh batch of powder mixture was processed. At specified intervals, the mill was stopped and measured: the amount of the substance involved in self-lining; the oxygen, nitrogen, and hydrogen content on the LECO-ONH836 device (USA).

The phase composition of the mechanoactivated mixture and the final synthesis products was determined by X-ray diffraction analysis (DRON-4M (Russia) using CoKa radiation and software processing of the width of the reflexes at their half-height (FWHM)).

The morphology and microstructure of the activated mixture were studied by scanning electron microscopy using QUANTA 200 3d (USA) and Philips SEM515 (Germany) devices with the prefix EDAX, the sizes of aluminum inclusions in agglomerate sections were calculated by the random secant method using the ImageJ program. The parameter of the crystal lattices of nickel and aluminum was calculated using the extrapolation of the Nelson-Riley function.

3. Results

Analyzing the data obtained, it is possible to note (Fig. 1) the difference in the formation of the morphological structure of the powder mixture of aluminum and nickel during machining, depending on the energy intensity of the mill. If, during the machining of a powder mixture of nickel and aluminum in high-energy mills, dense layered mechanocomposites are formed with alternating metal strips of nickel and aluminum in their internal structure [9], then under relatively mild LEMA conditions, less dense agglomerates consisting of a nickel matrix with separate aluminum inclusions (a) are formed in the mixture.



(a) (b) (c)

Fig. 1. Microstructure of the cross-section of the agglomerate of the 3Ni+Al powder mixture after 30 hours of LEMA: optical image (a), SEM image (b) and elemental composition of the cross-section of mechanocomposites as a function of LEMA time (c).

The microanalysis showed that if at the initial stages of LEMA (up to 4 hours) separate agglomerates consisting of practically pure nickel are fixed, then after 6 hours of LEMA there are no areas with 100% nickel or aluminum content. Only areas with a predominant content of one or another component are recorded here.

After 30 h of LEMA, the internal structure of the agglomerate looks more torn and fibrous, without separate clearly formed layers (b). The distribution of the elemental composition in the section of the mechanocomposite indicates a slight increase in the mass concentration of oxygen in the mixture with an increase in the LEMA time to 2.86 wt.% (c). The mass concentration of aluminum in the section increases slightly (by 5.71 wt.%) due to a decrease of about the same amount (7.85 wt.%) nickel concentration.

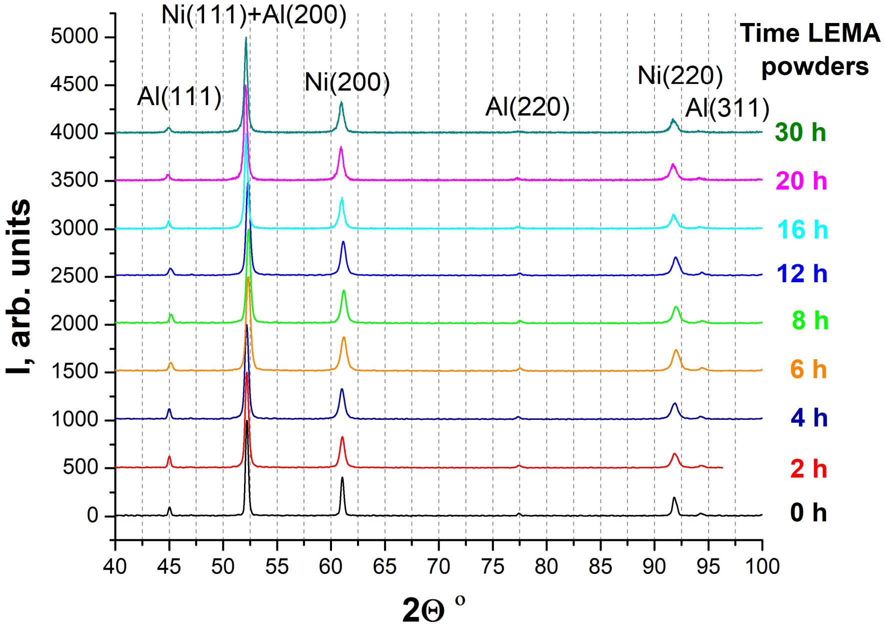


Fig. 2. X-ray phase analysis of the 3 Ni+Al powder mixture after different LEMA times.

It was revealed that the LEMA process of the 3Ni+Al powder mixture is carried out under conditions close to isothermal, self-linning of the activated mixture on the working surfaces of a low-energy mill is insignificant (does not exceed 9% of the mass of the starting substance). During the treatment period of 0–30 h, there are no mechanosynthesized phases in the mixture, since only nickel and aluminum reflex lines are present on the radiographs of the mechanoactivated 3Ni+Al powder (Fig. 2).

3. Conclusion

Thus, the leading role of mechanical forces in the processes of deformation reorganization of the morphological structure of the powder composition has been determined. The following scheme of morphological transformations in the LEMA process in a 3Ni+Al powder mixture is proposed, which can be divided into three main sequential stages: the formation of agglomerates consisting of nickel and aluminum particles; the formation of layered mechanocomposites consisting of alternating layers of nickel and aluminum; the formation of a homogeneous nickel-aluminum composition. At the same time, the degree of defects in the mixture increases only during the formation of agglomerates.

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