Non-Equilibrium Solid Solutions in Metal Systems Obtained by Mechanochemical Synthesis

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Abstract

Physicochemical properties of non-equilibrium solid solutions in metal systems obtained mechanochemically are investigated by means of high-resolution microscopy, X-ray diffraction and differential scanning calorimetry (DSC). It is demonstrated that nanocrystalline non-equilibrium solid solutions possess the excess free energy due to the presence of non-equilibrium non-stoichiometric defects and high density of interblock boundaries. The whole set of these defects creates synergetic effect in chemical activity.

INTRODUCTION

Modern industry needs new materials both with high chemical inertness and with high chemical activity. Highly active powders of metals and alloys are widely used in industry for the production of skeletal catalysts, diffusion-hardenable solders, metal cements, materials for hydrogen power engineering, *etc*. The excess free energy in such a system, resulting from an increase in the concentration of non-equilibrium defects, such as non-stoichiometry defects (substituent atoms, vacancies) or/and defects of plastic deformation (dislocations, intergrain boundaries), determines increased reactivity of the substance. Mechanochemical synthesis is the most promising method of obtaining non-equilibrium phases in which the defects of both types mentioned above are present. Intermetallides, solid solutions including supersaturated ones, obtained by mechanochemical synthesis always contain nanometer-sized blocks from which the particles of the final product are formed. The boundaries of these blocks have a very strong effect on thermodynamic characteristics of nanocrystalline materials. If we accept the boundary layer to be two atoms thick, then, for a material with coherent length of ~10 nm, about 15 % of atoms belong to boundaries. An increase in the width of boundaries of blocks as a result of strong deformation leads to an increase in the boundary layer, which affects both the thermodynamic characteristic and the reactivity of the material.

The goal of the present study is the investigation of some physicochemical properties of metal non-equilibrium solid solutions obtained by mechanochemical synthesis.

EXPERIMENTAL

The carbonyl nickel of PNK grade, aluminium of PA-4 grade, carbonyl iron PZhK, copper PMS-1, tin POE, gallium (TC 48–4–350–84), bismuth (TC 6–09–3616–82), semiconductor germanium were used in the investigation.

A ball planetary mill AGO-2 was used for mechanochemical synthesis. The drum volume was 250 cm^3, ball load 200 g, the amount of powder to be treated was 10 g. In order to avoid the oxidation of metals, all the experiments were performed in argon medium. Self-propagated high-temperature synthesis (SHS) was performed in argon at atmospheric pressure; initiation was performed with a firing composition ignited by the electric spiral made of Nichrome.

X-ray phase analysis was performed with DRON-3M and URD-63 diffractometers with CuK_{α} radiation. Electron microscopic studies were carried out with a JSM-T20 electron microscope, high-resolution electron microscopes JEM-2010 and JEM-400. Thermal analysis was made with the help of derivatograph of the Paulic-Paulic-Erday system. The heat of ordering of non-equilibrium solid solutions was determined by means of calorimetry with DSC-III (Seteram) and Perkin-Elmer DTF instruments in the DSC mode in argon medium.

The degree of aluminium extraction from intermetallides was calculated using the ratio of the amount of hydrogen evolved during the reaction of the samples with 20 % KOH solution to the amount of hydrogen that should be evolved on complete dissolution of aluminium present in the sample. The amount of hydrogen evolved in reaction was recorded automatically by DAGV-70-2M volumeter.

The reaction of gallium eutectics with solid solutions and copper-based mechanocomposites was monitored using changes in the intensity of diffraction reflections of intermetallide.

RESULTS AND DISCUSSION

Supersaturated solid solutions based on copper, nickel and iron were synthesized in the systems: Cu–Sn, Cu–In, Cu–Hg, Ni–Ge, Ni–Al, Ni–Bi, Ni–Sn, Ni–In, Fe–Sn. The high-resolution electron microscopy data suggest that solid solutions obtained by mechanochemical synthesis have nanometer-sized blocks of which the particles are composed. A micrograph of nickel-based solid solution of indium is shown in Fig. 1. The X-ray diffraction data evidence that the obtained phases conserve long-range order within 12–15 nm, too. According to Tarnball's classification [1], these structures in metal systems are called morphologically metastable structures; they possess excess free energy which in single-phase systems is usually con-

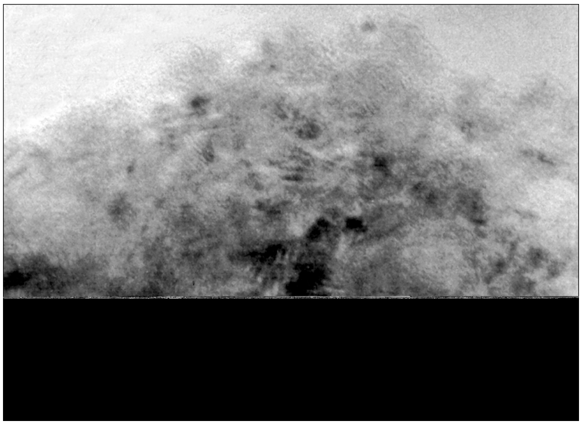

Fig. 1. High-resolution micrograph of Ni + In sample (In content 20 % mass) after mechanical activation for 20 min.

nected with high concentration of intergrain boundaries.

Mechanochemically obtained supersaturated solid solutions, which are called composition metastable structures according to classification [1], possess much higher excess surface energy, which is due to the presence of defects of one more type, namely, non-equilibrium non-stoichiometric substituent atoms.

High defect content of supersaturated solid solutions formed during mechanochemical synthesis is confirmed also by calorimetric investigations. Ordering temperature is known to be usually 0.6 of melting temperature. Ordering at lower temperature is promoted by high defect concentration. For the mechanochemically obtained solid solutions, this process starts at substantially lower temperature. Ordering in the solid solution of indium in nickel should start at a temperature above 600 °C, while in such a solution obtained mechanochemically it starts at 460 °C (Fig. 2). In non-equilibrium solid solutions of aluminium in nickel (Al content 13 % mass), ordering should start at 700 °C, while in mechanochemically obtained ones it starts at about 300 °C [2].

Supersaturated solid solutions have been obtained in Ni–Sn system; the non-equilibrium concentration of the doping element in these solutions exceeds even the high-temperature solid-phase solubility of tin in nickel. The heat of ordering for the sample with maximal concentration of tin in solid solution is

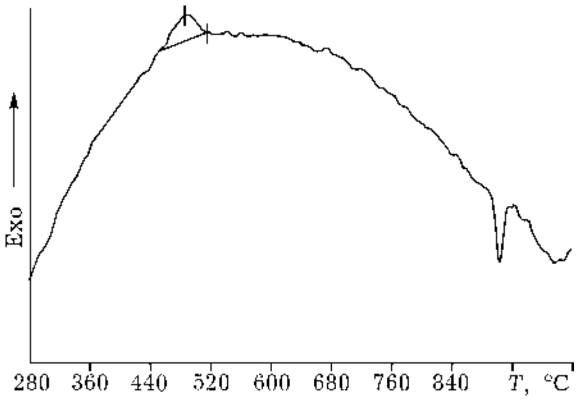

Fig. 2. Differential scanning calorimetry (DSC) of Ni + In mixture (In content 20 % mass) after mechanical activation for 20 min.

7.5 kJ/mol [3]. It is typical that ordering temperatures are lower than 500 °C for all the samples; the temperature of the start of ordering lowers substantially with an increase in the concentration of doping element: the difference is more than 100 °C (Fig. 3).

A similar correlation between the lowering of temperature of the start of ordering process and an increase in the concentration of the second element was observed in the Cu–Hg system (Fig. 4). In this system, supersaturated solid solutions with Hg content up to 40 % mass were obtained [2]; similarly to the case of Ni–Sn system, this value substantially exceeds the high-temperature equilibrium solubility which is ~5 % according to the equilibrium diagram of state [4]. The exoeffect value also increases with increasing mercury concentration: it is 1.48 cal/g for Hg mass fraction of 10 %; for 30 %, it is 4.39 cal/g [5]. For supersaturated solid solutions of germanium in nickel, exoeffect in the concentrational region of Ni_3Ge intermetallide is 6.3 kJ/mol (Fig. 5) [3].

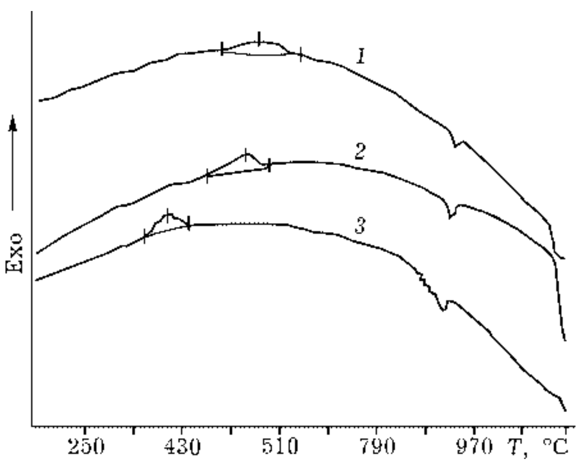

Fig. 3. DSC of Ni + Sn mixture after mechanical activation. Tin content, % mass: 10 (*1*), 15 (*2*), 20 (*3*).

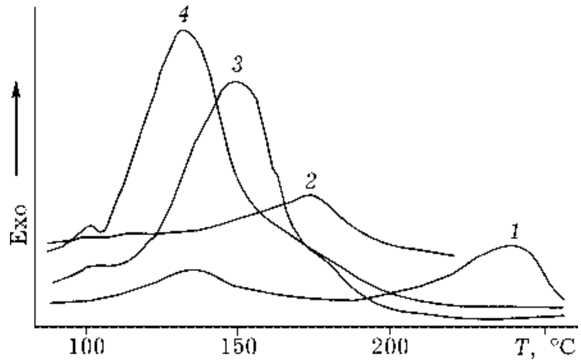

Fig. 4. DSC of the samples of solid solutions of mercury in copper. Mercury content, %: 10 (*1*), 20 (*2*), 25 (*3*), 30 (*4*).

All the non-equilibrium solid solutions obtained mechanochemically get separated under annealing into the equilibrium phases characteristic of a given concentrational region. However, it seems impossible to distinguish the heat effect related only to non-equilibrium non-stoichiometric defects, because these solid solutions have nanometer-sized blocks of which the particles are composed; high concentrations of interblock boundaries give their own contribution into heat effect.

Systems with excess free energy possess higher reactivity. This is clearly demonstrated by the reactions of supersaturated solid solutions of the Cu-Sn system with liquid gallium eutectics. In this system, nanocrystalline supersaturated solid solutions have been obtained. They decompose with exothermal effect under annealing (Fig. 6). The phase composition of these solid solutions at the temperature of 473,

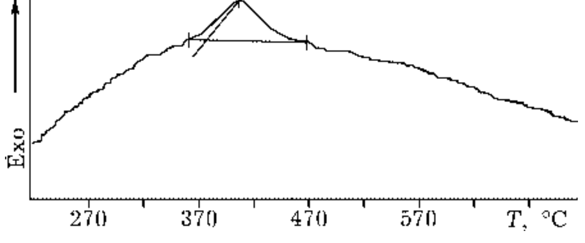

Fig. 5. DSC of Ni + Ge mixture (Ge content 25 % mass) after mechanical activation.

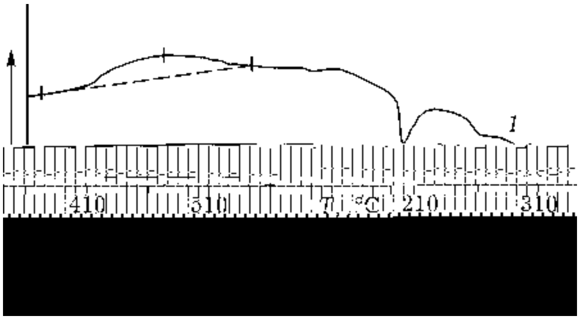

Fig. 6. DSC of Cu + Sn alloys with Sn content 20 % mass: *1* – obtained mechanochemically; *2* – commercially available.

563 and 643 K was investigated. At elevated temperature, the intensity of the diffraction peaks of annealed samples increases while their width decreases. With increasing the annealing temperature, the diffraction reflections are observed to shift toward the equilibrium concentrations of solid solution. Supersaturated solid solutions annealed at 643 K decompose to form a solid solution with lattice parameter $a = 0.3613$ nm, which corresponds to the mass (atomic) fraction of tin ~10.1 (5.67) %, and Cu_3Sn intermetallide. The Ga–In–Sn eutectics with In and Sn mass fraction 21.5 and 16 %, respectively, and melting point of 283.7 K, was used to investigate the rate of its interaction with various Cu–Sn alloys in the concentration region of high-temperature solid solution:

$$\underset{\text{Eutectics}}{\text{Ga–In–Sn}} + \underset{\text{Solid solution}}{\text{Cu (Sn)}} \rightarrow CuGa_2 + \beta\text{-InSn}$$

Assuming that the change of the integral intensity of diffraction reflections of $CuGa_2$ intermetallide is proportional to reaction rate, we monitored this change in order to follow the reaction. X-ray phase analysis was performed every 15 min for 24 h starting from 1 h after mixing the alloy powder with liquid eutectics. Initially, X-ray diffraction analysis revealed diffraction reflections of copper, $CuGa_2$ and amorphous phase, which is most likely liquid eutectics. The intensity of peaks corresponding to $CuGa_2$ increases with time, while the intensity of reflections of copper and amorphous phase decreases. After 24 h, in experiments with mechanochemically obtained alloys, the amorphous phase disappears completely; in the solidified sample, the main phase is $CuGa_2$ intermetallide. The rate of $CuGa_2$ formation observed using the changes in the intensity of the diffraction peaks of intermetallide is shown in Fig. 7. The reaction rate is substantially higher for the mechanochemically obtained non-equilibrium solid solutions than for the alloys of equilibrium composition in the concentration range of high-temperature solid solution, for which the reflections of the amorphous phase are still observed after 24 h.

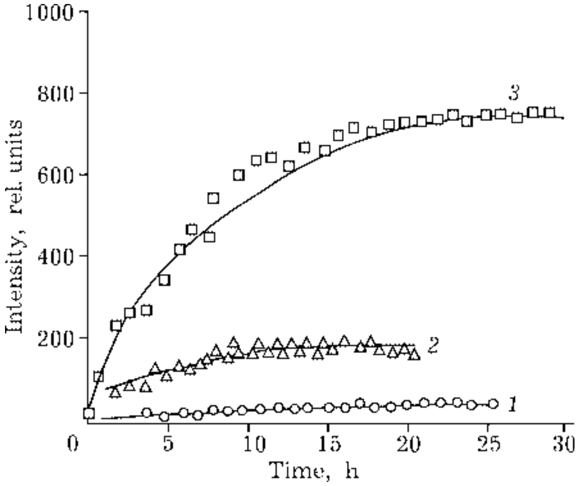

Fig. 7. Interaction of Cu + Sn alloys (Sn content 20 % mass) with gallium-tin eutectics. Samples are obtained pyrometallurgically (*1*) and by mechanical alloying in Spex mill for 200 (*2*) and 480 min (*3*).

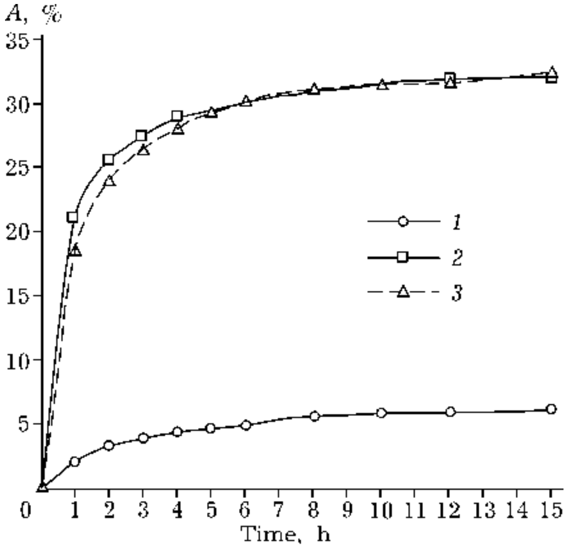

Fig. 8. Leaching curves of Ni_2Al_3 intermetallide: *1* – obtained by SHS; *2* – obtained by SHS after mechanical activation for 3 min; *3* – obtained mechanochemically for 25 min (sample composition: Ni + 60 % at. Al).

It may be assumed that high reactivity of the non-equilibrium solid solutions obtained mechanochemically is conditioned both by the presence of non-equilibrium non-stoichiometric defects and by the presence of nanometer-sized blocks formed as a result of intensive plastic deformation of a mixture of metal powders under mechanical alloying.

Similar changes are observed also in supersaturated solid solutions based on intermetallides. It is known that the Ni_2Al_3 intermetallide can be transformed by disordering of the vacancies into the supersaturated solid solution based on NiAl [6]. The micrometer-sized well-crystallized Ni_2Al_3 intermetallide obtained by SHS is transformed mechanochemically into the solid solution of subtraction based on NiAl; its coherent length is ~10 nm [6]. Chemical activity of this phase is much higher than that of the equilibrium phase (Fig. 8).

CONCLUSION

Thus, nanocrystalline non-equilibrium solid solutions obtained by mechanochemical synthesis possess excess free energy which is due to both the non-equilibrium non-stoichiometric defects and high density of interblock boundaries. The entire set of these defects creates synergetic effect in chemical activity.

REFERENCES

1 D. Turnbull, *Metallurg. Trans.*, 12 A (1981) 695.
2 T. F. Grigorieva, Ph. D. Thesis, Novosibirsk, 1988.
3 T. F. Grigorieva, A. P. Barinova, V. V. Boldyrev, E. Yu. Ivanov, *Solid State Ionics,* 101–103 (1997) 17.
4 M. Khansen, K. Anderko, Struktury dvoynykh splavov, Metallurgizdat, Moscow, 1962.
5 E. Ivanov, Proc. 2nd Intern. Conf. on Structural Applications of Mechanical Alloying, Vancouver, 1993, pp. 171–176.
6 T. F. Grigorieva, M. A. Korchagin, A. P. Barinova, N. Z. Lyakhov, *Metally*, 4 (2000) 64.