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# THERMAL STABILITY OF SOLID SOLUTIONS OBTAINED BY MECHANICAL ALLOYING

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The heats of ordering for mechanochemically synthesized nano-sized supersaturated solid solutions were demonstrated for Ni–In, Ni–Sn, Ni–Al, Cu–Sn, Cu–Hg systems. It is shown that increasing concentration of doping element leads to decreasing of decomposition temperature and to increasing of decomposition enthalpy. The concentration heterogeneity of doping elements in mechanochemically synthesized supersaturated solid solutions was found. The reactivity of alloys Cu 20 mass % Sn for commercial powder and MA powder was investigated.

**Keywords:** *heat of ordering, mechanochemical synthesis, supersaturated solid solution*

## Introduction

The excess free energy is typical owing to a high concentration of non-equilibrium non-stoichiometric defects such as substituting atoms and vacancies. Moreover intermetallic compounds and solid solutions obtained by mechanical alloying (MA) usually have nano-sized grains and elevated concentration of grain boundaries. The thermodynamic characteristics of mechanochemically synthesized supersaturated solid solutions may be changed. This work is to investigate thermal stability of supersaturated solid solutions obtained by MA.

## Experimental

### *Equipment*

An AGO-2 water cooled planetary ball mill [1] in 250 cm$^3$ steel containers with 5 mm diameter balls was used for mechanochemical reaction in argon atmosphere.

DRON-3M and URD-63 powder diffractometers with CuK$_\alpha$ and CoK$_\alpha$ radiation were used for X-ray study.

PerkinElmer DTA 700 in the DSC mode was applied for the differential thermal analysis

Energy dispersive spectroscopy (EDS) was used for measurement of Sn concentration in mechanochemically synthesized solid solutions.

JSM-T20 scanning electron microscope, high-resolution electron microscopes JEM-2010 and JEM-400 were used for electron microscopic studies

### *Materials*

Ni, Cu, Sn, In powders and Hg (liquid) were used for mechanochemically preparation of solid solutions.

Conventional Cu 20 mass% Sn powder was used in order to study of the reactivity of equilibrium phases.

Liquid eutectic Ga 21.5 mass% In 16 mass% Sn was applied in order to study the reactivity of solid solutions.

## Results and discussion

### *Ni-In system*

The solubility of indium in nickel is negligibly small at room temperature (Fig. 1a), rises to 0.8 at.% by about 400°C and attained a maximum value of 14.5 at.% at 908°C. Mechanochemical synthesis yielded a series solid solutions with lattice parameters increasing with In content, attaining a maximum value *a*=0.36230 nm, which only slightly differs from the lattice parameter of equilibrium solid solution in the high temperature region. MA in the Ni–In system allows one to prepare solid solutions which are metastable with respect to the low-temperature part of equilibrium phase diagram (Fig. 1b). The high-resolution electron microscopy data suggest that solid solutions obtained by mechanochemical synthesis have nano-sized grains. A micrograph of nickel-based solid solution of indium is shown in Fig. 2. According to X-ray diffraction data evidence all phases obtained conserve long-range order within 12–15 nm, too. Following to Turnbull's classification [2], nano-sized supersaturated solid solutions in metal systems may be

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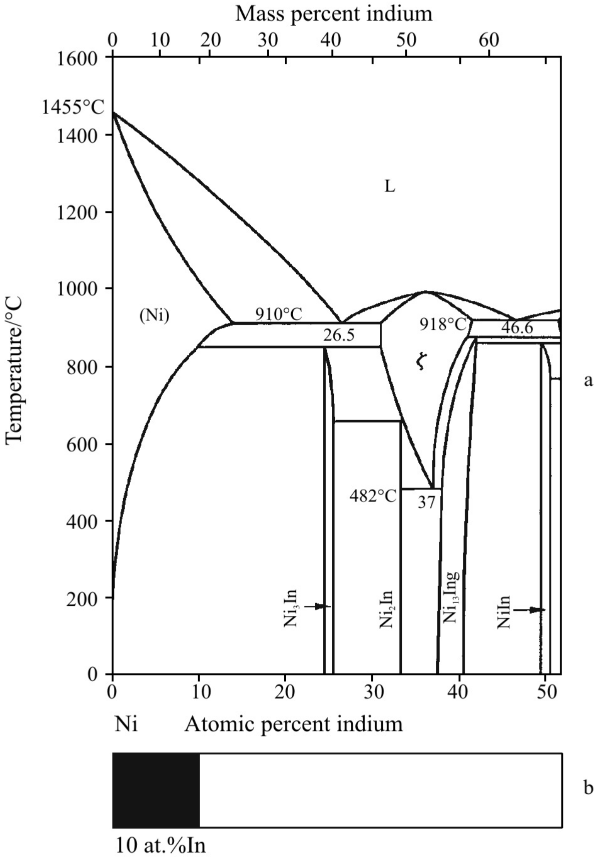

**Fig. 1** a – Equilibrium phase diagram and b – range of supersaturated solid solutions for nickel-indium system

called compositional and morphological metastable structures; they possess most excess free energy, which is usually connected with high concentration of non-equilibrium non-stoichiometric defects and intergrain boundaries.

High defect content in supersaturated solid solutions formed during mechanochemical synthesis is confirmed also by calorimetric investigations. Ordering temperature is known to be usually 0.6 of melting point. Ordering at lower temperatures is promoted by a 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. 3). In non-equilibrium solid solutions of aluminum in nickel (Al content 13 mass%), ordering should start at 700°C, while for mechanochemically obtained phases it starts at about 300°C [3].

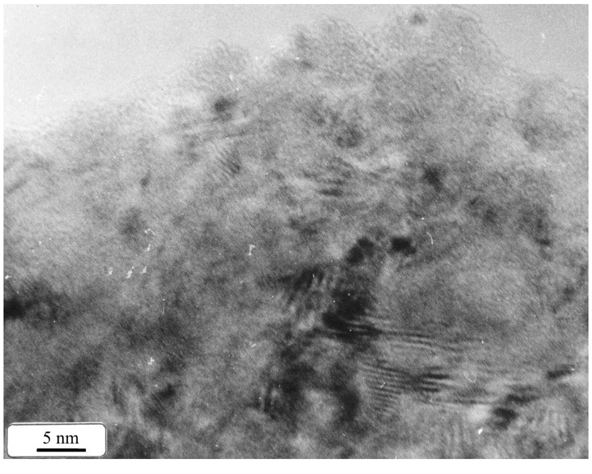

**Fig. 2** High-resolution micrograph of Ni + In sample (In content mass 20 %) after mechanical activation for 20 min

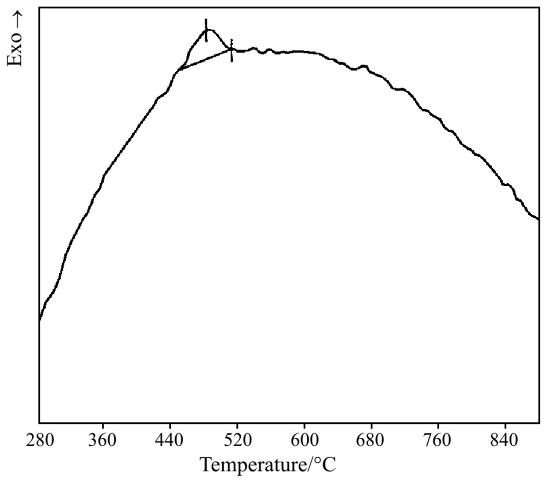

**Fig. 3** DSC trace of Ni 20 mass% In mixture after mechanical activation for 20 min

*Ni-Sn system*

In nickel-tin system, the difference in atomic radii is about 21%. The solubility of tin in nickel is close to zero at room temperature, attaining a maximum value of 10.4 at.% at 1130°C ($a$=0.36013 nm). Mechanochemical synthesis yielded a series of solid solutions with the lattice parameters increasing as a function of tin content: $a$=0.36010 nm at 10.4 at.% Sn, 0.3638 nm at 14.2 at.% Sn and 0.3659 nm at 17.5 at.% Sn. According to Vegard's law, a supersaturated solid solution with a maximum lattice parameter $a$=0. 3662 nm contained 17.7 at.% Sn. MA in Ni-Sn system yields metastable solid solutions, which are supersaturated with respect to both the high- and low-temperature part of the equilibrium phase diagram (Fig. 4). The difference between maximum lattice parameter of the supersaturated solid solution and the equilibrium lattice parameter reaches $\Delta a$=0.0058 nm for the high-temperature part, and $\Delta a$=0.0142 nm for the low-temperature part.

X-ray investigation showed that upon heating all supersaturated solid solutions decomposed in agreement with equilibrium phase's sequence. Figure 5

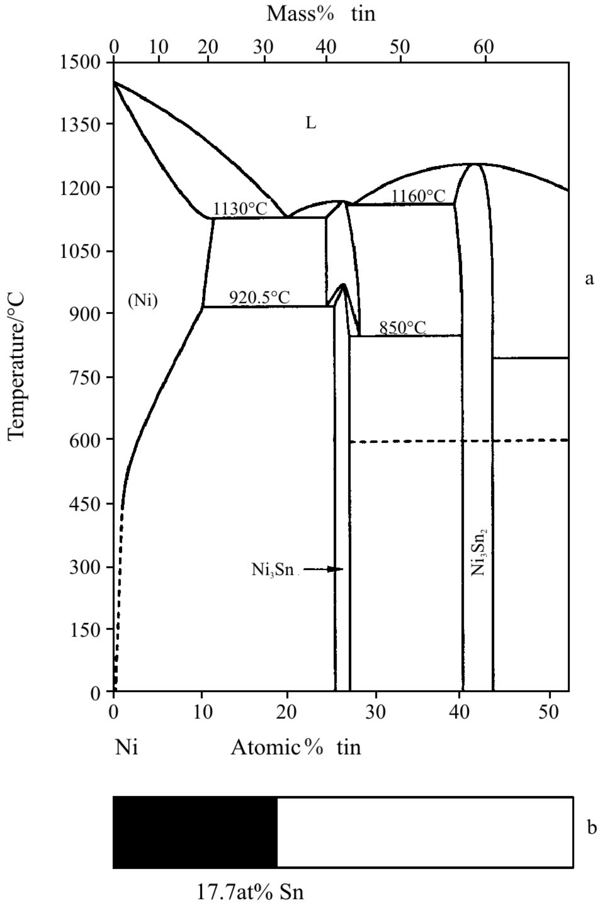

**Fig. 4** a – Equilibrium phase diagram and b – range of supersaturated solid solutions for nickel-tin system

shows DSC traces of Ni–Sn alloys. The endothermic effect is related to the melting of equilibrium phase. The heat of ordering for the sample with maximal concentration of tin in solid solution is 7.5 kJ mol$^{-1}$. It is typical that ordering temperatures are lower than 500°C for all samples; the starting temperature of ordering decreases substantially with an increase in the concentration of doping element: the difference is more than 100°C (Fig. 5).

### *Cu-Hg system*

A similar correlation between the decreasing of starting temperature of ordering process and an increase in the concentration of the second element was observed in the Cu–Hg system (Fig. 6). In this system, supersaturated solid solutions with Hg content up to 40 mass% were obtained [3]; 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 exothermal effects value also increases with increasing mercury concentration: it is 6.19 J g$^{-1}$ for Hg mass fraction of 10%; for 30%, it is 18.35 J g$^{-1}$ [5]. Thermogravimetry and other analysis technique was used for reaction mercury with rhodium and iridium [6, 7].

The thermal analysis of supersaturated solid solutions obtained by MA in other systems also shows that increasing concentration of doping element leads to decreasing of decomposition temperature and to increasing of decomposition enthalpy. For example, decomposition enthalpy of supersaturated solid solution zinc in iron increases from 1.2 to 3.5 kJ mol$^{-1}$ depending on zinc concentration [8, 9].

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 intergrain boundaries give their own contribution into heat effect.

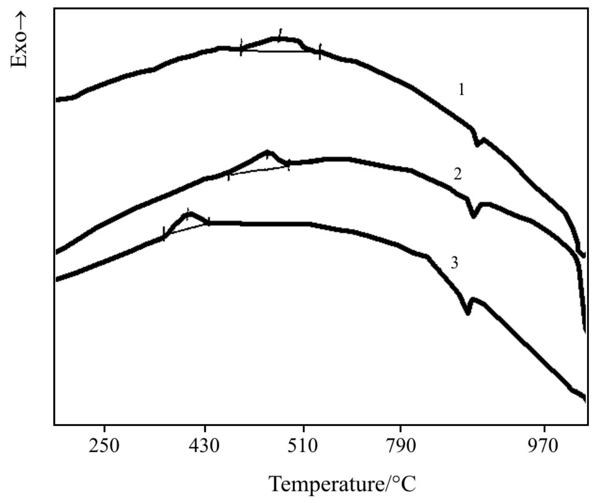

**Fig. 5** DSC-traces of MA system nickel-tin. Sn content, at.%: 10 (1), 15 (2), 25 (3)

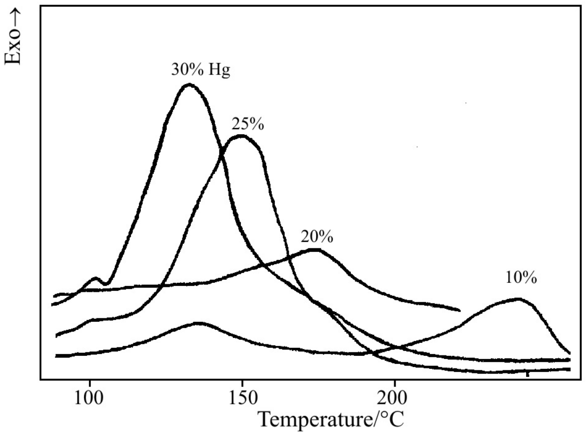

**Fig. 6** DSC-traces of the samples of solid solutions of mercury in copper

The features of structures and properties of supersaturated solid solutions were well studied for quenched alloys. A large body of research of quenched supersaturated solid solutions revealed that high concentration of vacancies (~$10^{-4}$) provides high non-equilibrium concentration of doping elements. Dislocation concentration of quenched supersaturated solid solutions significantly exceeds the usual concentration. Moreover, excess of vacancies in a quenched alloy also provides increasing in the density of dislocations. For example, the quenched solid solution Al 16 mass% Ag has great number of dislocation loops, which were formed by excess vacancies and helicoidal dislocations. The increasing doping element concentration leads to a growth of the fraction of vacancies on this type of dislocations [10].

Dislocations are responsible for segregation of dissolving atoms and formation of a new structure. Ginje-Preston zones are the main type of such structures in the quenched supersaturated solid solutions and zone concentration is about $10^{17}$ zones cm$^{-3}$ [11]. Vacancies play a crucial role in formation of Ginje-Preston zones. Vacancies form the transition region between zone nucleus and matrix and create conditions for decreasing energy of coherent tension. Ginje-Preston zone size depends on temperature and time annealing. For example, quenched supersaturated solid solution Al 4% Cu after 10 months at 25°C has Ginje-Preston zone size ~5–6 nm, but after 3 months at 100°C it increases to 10–12 nm [12]. It is believed that decreasing of decomposition temperature of quenched supersaturated solid solutions with growth of the doping element concentration depends on the formation of Ginje-Preston zones, which are initial stages for the separation processes to equilibrium phases.

The majority of authors noted that plastic deformation before annealing increases the decomposition rate, and speculated that the resulting dislocations at plastic deformation are active centers of formation of other phases [13, 14]. The formation of equilibrium phases in these conditions occurs at 0.3 of their melting points [15–17].

The different quenching regimes are realized in the high energy ball mills [1], and elevated concentrations of vacancies and dislocations are formed during mechanical treatment [18–21]. The dislocations create the prerequisites for subsequent formation of Ginje-Preston zones. Moreover, the intensive plastic deformation of metal alloys during mechanical activation also leads to the formation of Ginje-Preston type defects. Additionally nano-sized mechanochemically synthesized a supersaturated solid solution provides high concentration of grain boundaries and large volume fraction of atom on grain boundaries in these ultra-fine materials also may be served as a base for the Ginje-Preston zones.

So, Ginje-Preston zone type defects in mechanochemically synthesized supersaturated solid solutions may be created due to quenching regimes in high energy ball mills, intensive plastic deformation and nanometer grain size.

The low temperature decomposition of supersaturated solid solutions obtained by MA may be explained by the high concentration of Ginje-Preston zone type defects, which creates the concentration heterogeneity of doping elements. The concentration distribution of doping element in mechanochemically synthesized supersaturated solid solutions was studied by EDS method for Cu 20 mass% Sn system. It was shown that the local tin concentration in the same sample varied from 8 to 22 mass%. It is believed that the grain boundaries of mechanochemically synthesized supersaturated solid solutions contain the most concentration of doping element.

Indirect proof of a high concentration of defects at the boundaries may serve the kinetic of the interaction mechanochemically obtained supersaturated solid solutions with external reagents. 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. 7). The endothermic effects are related to the melting of equilibrium phases. The phase composition of these solid solutions at the temperature of 473, 563 and 643 K was investigated. The diffraction patterns reveal an increase in peak intensities and a decrease in peak widths for the annealed samples, reflecting the crystalline grain growth and strain release that occurred during heating. With increasing annealing temperature, the patterns show a shift in peak positions towards those of the equilibrium phase composition. Annealed at 643 K, the MA solid solution decomposed into a mixture of equilibrium solid solutions, with a lattice parameter of 0.3673 nm, corresponding

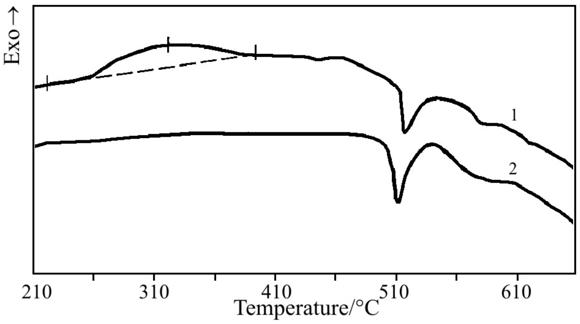

**Fig. 7** DSC-traces of Cu 20 mass % Sn alloys: 1 – obtained mechanochemically; 2 – commercially available

to 10.1 mass% Sn in solid solution, and a small amount of $Cu_3Sn$. Figure 7 shows DSC traces for Cu 20 mass% Sn commercial powder and MA powder. The ternary eutectic Ga 2l.5 mass% I6 mass% Sn, with a melting point of 283.7 K, was used to react with Cu 20 mass% Sn. The paste was made by mixing the alloy powder with the liquid alloy. Ternary or quaternary phase diagrams for the systems Cu–Sn–Ga, Cu–In–Ga, and Cu–In–Ga–Sn are not found in the literature. In this work results were obtained at room temperature, where the formation of the intermetallic compounds $CuGa_2$ is responsible for solidification.

Based on the assumption that the reaction may be described in terms of the formation of $CuGa_2$, the reaction rate was determined to be proportional to the integral intensity of $CuGa_2$ reflections. XRD was conducted every 15 min for 24 h, beginning 1 h after initially mixing the liquid and solid. Initially diffraction patterns revealed the presence of copper, and due to the liquid alloy, an amorphous phase was also observed. With increasing time, the intensity of peaks corresponding to $CuGa_2$ increased and the amount of amorphous phase decreased. After 24 h the amorphous phase was no longer visible. $CuGa_2$ was the main phase present in the fully solidified samples. Figure 8 shows the reaction rate of samples: the commercial alloy and powder mechanically alloyed. The mechanically alloyed powders had enhanced reactivity. An amorphous phase was observed 24 h after mixing a paste containing commercial Cu 20 mass% Sn alloy powder, indicating that the reaction occurred at a much slower rate than the paste containing MA powder. The reaction rate of pure copper with the liquid alloy was also investigated, and was found to be undetectable. Particle size analysis indicated that the particle size distributions of the MA powder and the commercial powder were very similar, however the crystalline grain sizes obtained by XRD revealed a much smaller grain size for the MA powder.

The reaction rate of paste made from as-received commercial powder was compared with that from commercial powder which underwent SPEX milling for 8 h in argon atmosphere. Particle size analysis of the two powders revealed a similar average particle size, while diffraction patterns indicated that the milled powder was much larger than that of the as-received powder. The smaller crystalline size translated into a faster reaction rate, indicating that mechanical alloying can be used to increase the reactivity of these solid solutions.

An additional point to emphasize is that the sharp increasing of rate of the interaction between mechanochemically synthesized nano-sized supersaturated solid solutions and liquid eutectic at the initial stage of process (Fig. 8) may serve as the proof of elevated concentration of defects at the grain boundaries.

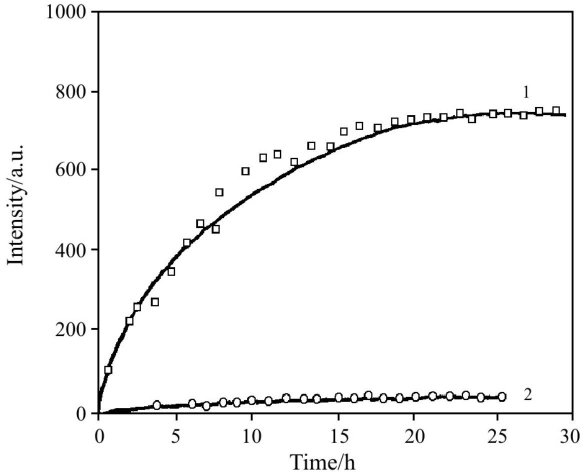

**Fig. 8** Reaction rate of Cu 20 mass % Sn: 1 – MA alloy, 2 – commercial alloy

## Conclusions

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 the high density of intergrain boundaries. However, it is impossible to distinguish the heat effects related only to non-equilibrium non-stoichiometric defects and only to grain boundaries.

It is shown that increasing concentration of doping element leads to a decrease of the decomposition temperature and to an increase of the decomposition enthalpy. The concentration heterogeneity of doping elements in mechanochemically synthesized supersaturated solid solutions was found.

The considerable distinctions between rates on initial stage of chemical interaction of liquid eutectics with conventional alloy and mechanically synthesized nano-sized alloy were demonstrated. This fact may be explained by the high concentration of defects at the grain boundaries.

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