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Mechanochemical synthesis of intermetallic compounds

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Abstract. The current state of studies on the mechanochemical synthesis of binary metallic systems is considered. It is shown that this method is suitable for the preparation of intermetallic compounds and solid solutions in concentration limits of equilibrium diagrams of many binary systems. The mechanochemical approach is demonstrated to exhibit the most promise for preparing intermetallic compounds in systems characterised by large differences in the melting points and in the densities of the initial components as well as phases with nanometer grain sizes and metastable phases. The major factors, which influence the concentration limits of existence of non-equilibrium solid solutions prepared by the mechanochemical method, are revealed. Using numerous examples, it is demonstrated that the formation of solid solutions may involve several stages. At the first stage, nanosized layered composite structures are formed with simultaneous dispersion of the initial components (the formation of a large contact area). The second stage involves the synthesis of intermetallic compounds in nanosized layered composites. At the third step, the intermetallic compounds are dissolved in a metal solvent to give a solid solution. The bibliography includes 397 references.

I. Introduction

Intermetallic compounds can exist only in the crystalline state. Individual molecules cannot be distinguished in these compounds and they cannot be melted or dissolved without the loss of individuality and do not exist in the gaseous phase. In addition, the physicochemical properties of intermetallic compounds differ substantially from those of their components.[1–3] Intermetallides with a particular composition differ in the chemical properties not only from the constituent metals, but also from intermetallides, which are characterised by the same elemental composition, and yet contain the components in a different ratio.[4,5]

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Presently, a general theory, which would allow one to reveal factors stabilising particular intermetallic compounds, is lacking. A search for these factors was performed as follows. A group of systems in which the stability of intermetallic phases can be related to the effect of a particular factor was established after which the effect of this factor in other systems in which it was less evident was analysed. Three factors were revealed, *viz*., the ratio of the total number of valence electrons (e) to the total number of atoms per unit cell (a), the tendency for the maximum filling of space (*i.e*., for the formation of closest packing or structures with high coordination numbers) and the difference between the electronegativities of the components. The latter factor is of minor importance and is clearly manifested only in a small group of Zintl phases,[6] *viz*., in compounds of active metals (alkali metals, alkaline-earth metals, magnesium and aluminium) with germanium, tin, lead and bismuth.[7,8]

Hume-Rothery demonstrated[9] that phases with the same electron concentration (e/a) have similar crystal structures. In different systems, one of the following three types of structures is characteristic of phases with an electron concentration of 3/2, the so-called β phases: body-centred cubic (BCC) structures (the Cu – Zn, Cu – Al and Cu – Sn systems), structures of the β-Mn type (Cu – Si, Ag – Al and Au – Al) or hexagonal structures (Ag – Zn, Cu – Si and Ag – Sn). Phases with an electron concentration of 21/13 have complex cubic structures of γ-brass. In the case of $e/a = 7/4$, ε phases with hexagonal close-packed (HCP) structures are formed. The β, γ and ε phases have come to be known as electron compounds. In the case of a favourable dimension factor (more exactly, the number of electrons per unit cell), the electron concentration is of primary importance in the formation and stability of a particular crystal structure.

Compounds belonging to the $MgZn_2$, $MgCu_2$ and $MgNi_2$ structural types (the so-called Laves phases) are the most widespread intermetallides. For these compounds, the ratios between the atomic radii of the components (in addition to the above-mentioned stabilising factors) are also of great importance. The characteristic feature of Laves phases is that the smaller atoms (Zn, Cu and Ni) are grouped together to form tetrahedra linked to each other. The $MgZn_2$, $MgCu_2$ and $MgNi_2$ structures differ in the mode of arrangement of the tetrahedra. The bulkier magnesium atoms occupy the holes in the network of tetrahedra. As a result, very close packed structures are formed, the coordination number of the bulkier atoms being equal to 16. This value is larger than the coordination number (12) corresponding to the maximum density of packing of spheres of the same size. The

coordination numbers of the smaller atoms in these structure are equal to 12.[6]

The above-mentioned factors are responsible for the stability of solid solutions as one of the types of intermetallic compounds.[7] In the case of similar electronegativities of the elements and a favourable dimension factor, the electron concentration is the major factor affecting the limiting solubility. The quantitative theory of solubility of polyvalent elements in metals of the copper group is based on the concept of filling of the first Brillouin zone with electrons in the face-centred cubic (FCC) crystal structure.[8] Theoretically (taking into account the electron concentration), a solid solution can exist over wide concentration limits. However, the preparation of such solutions in these limits is determined primarily by the dimension factor. It was empirically established that if the atomic diameter of the element dissolved differs from the atomic diameter of the solvent by more than 14% – 15%, the dimension factor is unfavourable and the region of existence of the solid solution is limited.[9] No reliable theoretical explanation has been provided for the threshold value of 15%. Quantitative calculations were carried out within the framework of an elastic-sphere model. King [10] calculated the dimension factors for 469 substitution solid solutions and confirmed the above threshold value.

Therefore, the major factors influencing the formation and thermodynamic stability of intermetallic phases at equilibrium were revealed empirically.

Main procedures for the preparation of equilibrium intermetallic compounds involve alloying followed by homogenisation and sintering. Intermetallides with high formation enthalpies are generally prepared by the self-propagating high-temperature synthesis. Yet another procedure for the synthesis of intermetallic compounds, *viz*., the mechanochemical method, has been developed intensively in recent years. This method is promising in the synthesis of equilibrium and metastable phases, supersaturated solid solutions and amorphous phases and allows the preparation of intermetallides from components possessing high melting and boiling points (for example, $MoSi_2$) as well as from components characterised by large differences between these points (for example, the boiling point of magnesium in the Mg – Ti system is lower than the melting point of titanium). The mechanochemical procedure can be used for the introduction of the third component into a binary system to impart special properties to intermetallides.

Compounds prepared by the mechanochemical method are characterised by high dispersity (in most cases, nanosized particles are obtained), which affects the physicochemical properties of these compounds. Currently, one of the major problems with which researchers are faced in dealing with mechanochemical synthesis is to reveal the factors governing the formation and stability of phases prepared by this method.

In the present review, the experimental data on the problems of the mechanochemical synthesis in metallic systems published over the last 15 years are systematised. Earlier data, as a rule, are cited in the discussion of the general problems of metal deformation and mass transfer in the solid body.

II. Mechanochemical synthesis of intermetallic compounds and solid solutions at concentration limits of binary equilibrium diagrams

Analysis of the published data demonstrated that the mechanochemical method can be used for the synthesis of all major groups of intermetallic compounds, *viz*., of the following electron compounds: ε and β phases in the Zn – Ag [11] and Cu – Zn [12] systems, γ phases in the Cu – Zn system,[13] ε and η phases in the Cu – Sn system,[14] η (Cu_2Sb) and δ ($Cu_{4.5}Sb$) phases in the Cu – Sb system [15] and the Laves phases Fe_2Ti,[16] Mg_2Ni,[17–19] Mg_2Cu,[19] $MgZn_2$ [19] and Fe_2Tb.[20] The mechanochemical procedure for the synthesis of intermetallic compounds is most promising when the use of conventional metallurgical methods presents difficulties, in particular, in the synthesis of silicides of refractory metals. For example, the melting point of molybdenum (2620 °C) is virtually equal to the boiling point of silicon (2600 °C), whereas the densities of these elements differ by a factor of more than four (10.2 and 2.308 g cm^{-3}, respectively). In the case of silicon and tungsten, the difference between these parameters is even larger [T_{melt}(W) ≈ 3400 °C; ρ(W) = 19.35 g cm^{-3}]. Reactions of these elements can occur only through reactive diffusion at very high temperatures over a long period. However, it is very difficult to prepare monophase systems even under these conditions.[4]

Silicides of molybdenum,[21–27] tungsten [28] and tantalum [22,29,30] were synthesised by the mechanochemical method. The stoichiometric intermetallide $NbSi_2$ was prepared according to this method after continuous activation for 65 min.[31,32] The use of the mechanochemical method substantially simplified the preparation of iron silicides.[26,27,33,34] The boiling points of the first metals in the Mg – Ni, Mg – Ti, Mg – Si, Al – Nb, Al – Ru, Sn – Nb and Te – Cu binary systems are lower than the melting points of the second metals, but the mechanochemical approach allowed the preparation of the intermetallides Mg_2Si,[17,35,36] Mg_2Ni,[37] $NbAl_3$,[38] Nb_3Sn, Nb_6Sn_5,[39] AlRu [40] and Cu_2Te.[41]

Even more so, the synthesis of intermetallides according to conventional procedures presents technological problems due to a large difference between the melting points of the initial components. Hence, such intermetallides as FeSn, $FeSn_2$,[42–44] Ti_3Al,[38,45,46] TiAl,[45–51] $TiAl_3$,[41,45,46,52] AlPd,[53] Nb_3Ge, Nb_5Ge_2, $NbGe_2$,[39,54] ZrAl,[55] Ni_3Sn_2,[56] Ni_3Sn,[56] Ni_2Al_3,[57] NiAl,[57–65] VAl_3, V_5Al_8, V_4Al_2 and VAl_{10} [66] were prepared by the mechanochemical method.

The intermetallide Cu_7Hg_6, which is of practical importance, was prepared by mechanical alloying of copper with mercury.[67,68] These metals differ substantially in melting points. In addition, the vapour pressure of mercury at elevated temperature is very high.

Relushko *et al*.[69] studied the mechanochemical synthesis of iron aluminides in the Fe – Al system and revealed the sequence of formation of the Fe_2Al_5 and FeAl phases, *i.e*., the authors followed the stages of the synthesis of the intermetallides. The formation of the intermetallides in this system was also considered in more recent studies. Thus, Bonetti *et al*.[70] investigated Fe_3Al and FeAl and Morris and Morris [71] studied $FeAl_3$.

However, attempts to bring the mechanochemical synthesis to completion are not necessarily successful. In some cases, prolonged (during many hours) mechanochemical activation is required. It was found that mechanochemical treatment can substantially decrease the temperature of the subsequent thermal synthesis. Thus, preliminary mechanochemical activation of molybdenum and silicon powders for 2 h allowed the preparation of the intermetallide $MoSi_2$ at 800 °C.[72,73] After mechanochemical treatment of tungsten and silicon powders, the temperature of the synthesis of WSi_2 was 950 °C.[28] In the synthesis of β-$FeSi_2$, the duration of preliminary activation was decreased (50 h) by using brief mechanochemical treatment followed by annealing at 700 °C.[74] Conventional procedures for the synthesis required prolonged annealing at 982 °C;[75] however, the desired homogeneity of β-$FeSi_2$ was not achieved even in this case. Brief annealing of non-equilibrium systems obtained upon mechanochemical activation also afforded intermetallides, for example, Fe_3Al, FeAl, $FeAl_3$,[76] Fe_2Al_5,[76,77] γ-TiAl, $TiAl_3$ [51,52] and the corresponding compounds in the Co – Ti system.[78]

Systems characterised by large heats of formation of intermetallic compounds are worthy of particular consideration. Preliminary mechanochemical activation of these systems favours the subsequent self-propagating high-temperature synthesis. The new approach involving mechanochemical activation and self-propagating high-temperature synthesis extends the range of systems in which the latter can be performed,[79,80] expands the concentration limits of the synthesis and allows one to accelerate substantially the synthesis and to perform it in the solid-phase mode.[79,81] This approach was used for the preparation of the intermetallides NiTi,

NiAl, Ni_3Al, NiGe,[79–81] Ni_3Si,[82] $FeSi_2$,[75] $NbAl_3$,[83] FeAl[84–87] and $MoSi_2$.[86,88,89]

The mechanochemical method was employed for the synthesis of equilibrium solid solutions in systems characterised by continuous and very wide solubility ranges. Thus, Pavluykhin *et al.*[90] investigated the conditions of accelerated diffusion in binary metallic systems upon mechanochemical activation in centrifugal planetary mills and obtained solid solutions in the Fe–Cr system. Davis and Koch[91] were the first to examine the possibility of mechanical alloying of solid solutions consisting of fragile components. In the cited study, mechanical alloying of germanium with silicon (compositions containing 72 at.% and 50 at.% of Si) was investigated. Silicon and germanium are isomorphous and their unit cell parameters depend almost linearly on the concentration of the second element. The measured unit cell parameter of germanium was larger than that expected based on the Vegard rule, but this deviation virtually disappears in the case of specimens containing more than 72 at.% of Si. At lower concentrations of silicon, the deviation of the unit cell parameter persists even after annealing.

Yurchikov *et al.*[92,93] studied the formation of intermetallic compounds and solid solutions in the Fe–Cr and Fe–Si systems under high pressure on doubled Bridgman anvils with a rotating central part. Neverov *et al.*[94,95] prepared a large number of solid solutions on Bridgman anvils.

In the Fe–Co system, solid solutions with body-centred cubic structures were formed on mechanical alloying of mixtures containing less than 80 at.% of Co, whereas solid solutions with face-centred cubic structures were formed in the case of 90 at.% of Co.[96–99] In this system, the sizes of blocks of the body-centred cubic and face-centred cubic phases were 10–30 and 40–70 nm, respectively. Monophase solid solutions were obtained in the Fe–Ni system with the use of a planetary ball mill.[100]

All phase compositions in the Fe–Mn system were obtained in a high-energy ball mill. However, the concentration limits of the regions of solid solutions were substantially extended compared to those observed in the equilibrium diagram. The particle sizes were 20–80 nm.[101]

The mechanochemical synthesis of nanocrystalline solid solutions with body-centred cubic structures using high-energy mills was reported.[102–106] It was suggested that a solid solution of aluminium in iron became partially ordered on prolonged activation. Nanocrystalline solid solutions of iron containing 4 mass % (8 at.%) of Al were prepared in a high-energy SPEX 8000 ball mill (USA) during intervals from 10 to 60 min.[107]

Therefore, analysis of the published data demonstrated that the mechanochemical synthesis of equilibrium intermetallic compounds is most efficient in the cases of large differences between the melting points and between the densities of the initial components, high temperatures of the synthesis and, if required, in the preparation of phases with nanosized grains.† This method is used more widely in preparation for the subsequent thermal synthesis or for the self-propagating high-temperature synthesis.

III. Mechanochemical synthesis of non-equilibrium phases in bimetallic systems with negative mixing enthalpies

The mechanochemical synthesis of non-equilibrium phases can successfully compete with such methods for their preparation as superfast quenching and precipitation from the gaseous phase. Practical interest in metastable compounds (*i.e.*, in systems with an excessive free energy) arises from their high reactivities. These phases find wide application. It is evident that chemical activity of metastable phases depends substantially on crystal structure imperfection, which, in turn, is determined by the degree to which the phase is in non-equilibrium. Therefore, the major problem of the preparation of metastable phases is to achieve the maximum concentration deviation from the equilibrium state with retention of the crystal structure of the initial phase. As mentioned above, in equilibrium systems, the maximum concentration of an alloying (dissolved) element in solid solutions is determined by the electron concentration and the difference between the atomic radii, which should be no higher than 15%. Analysis of the published data demonstrated that mechanochemical synthesis leads to changes of priorities and variations in the above parameters. First, the mutual correlation between the crystal structures of the components assumes great importance. Second, the dimension factor is shifted to the region of 15%–28% to attain substantial concentration deviations.

Binary metallic systems in which the course of mechanochemical synthesis of non-equilibrium phases is governed by the difference between the atomic radii are listed in Table 1. It can be seen that metastable solid solutions characterised by a substantial deviation of the concentration form the equilibrium state can be synthesised by the mechanochemical method in systems in which the solubility of one element in another is limited by the dimension factor and in which the difference between the atomic radii is 15%–25%. The concentrations of such solid solutions are higher than both the low-temperature (in all the cases under consideration) and high-temperature (Cu–Hg, Ni–Sn and Fe–Sn) equilibrium limits. For the Cu–Sn system, these concentrations are also higher than the concentrations of solid solutions prepared by fast quenching, (in the latter case, these values amount to only 8 at.% of Sn; Fig. 1). Tianen and Schwarz[56] prepared supersaturated solid solutions of tin based on α-nickel with the lattice parameter $a = 0.3699$ nm, which is 5% larger than that of pure nickel.

Table 1. Differences between the atomic radii (ΔR) and the concentrations of equilibrium (C) and supersaturated solid solutions (c) prepared by the mechanochemical method in different systems.

System	ΔR (%)	C (at.% of the second element)		c (at.% of the second element)	Ref.
		I	II		
Cu–Sn	19	11.25 (852°C)	~0	10	108–111
Cu–Hg	20	5 (657°C)	0	17	111–113
Cu–In	23	10.8 (574°C)	>1	11	114–116
Ni–Sn	21	10.4 (1130°C)	0	17.7	117–119
Ni–In	25	14.5 (908°C)	0	14.5	117–119
Fe–Sn	20	9.8 (900°C)	>2	32	120–124
Ni–Bi	30	0.5 (>500°C)	0	3	125, 126

Note. The following notations are used: I is the concentration at high temperatures and II is the concentration at room temperature.

The limiting non-equilibrium concentration decreases as the difference between the atomic radii increases further. In the Ni–Bi system in which the difference between the atomic radii is 30%, the enthalpy of formation of solid solutions calculated by the Miedema method[127–129] has a small negative value. According to the equilibrium diagram,[108] this system contained two intermetallic compounds with the bismuth contents of 78.08 mass % (NiBi) and 91.44 mass % ($NiBi_3$), the solubility of bismuth in solid nickel being no higher than 0.5 at.%.[125] Solid solutions of bismuth in nickel with bismuth concentrations of up to 3 at.% were synthesised by the mechanochemical method.[126]

In systems in which the limiting solubility is determined by the electron concentration, the content of the alloying element exceeding the value allowed in this crystal structure is very difficult to achieve. In the Cu–Al system, the difference between the atomic radii is 11%. Taking into account the electron concentration under equilibrium conditions at room temperature, the limiting

† The term 'nanosized grain' used in many modern publications is generally related to the sizes of coherent-scattering regions.

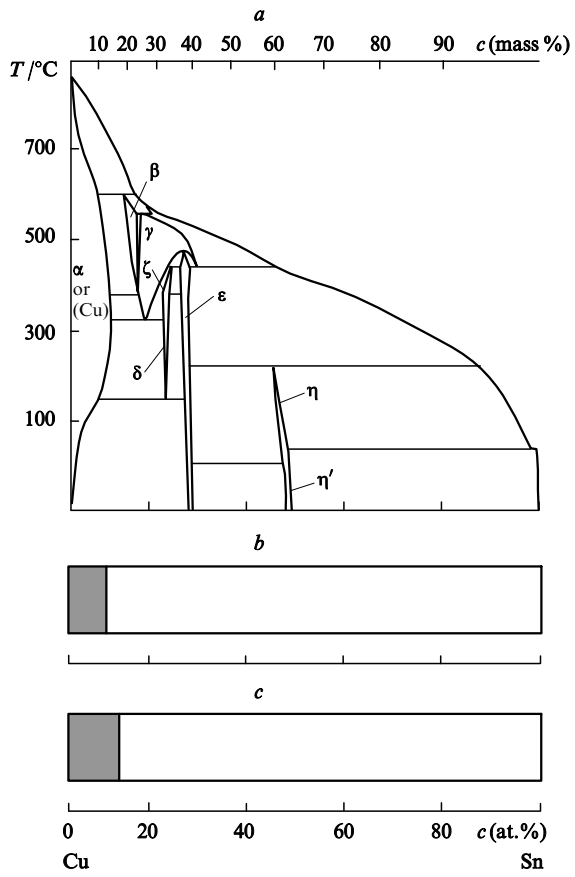


Figure 1. Equilibrium diagram of the Cu – Sn system (*a*) and the limiting concentrations of the solid solution prepared by fast quenching (*b*) and the mechanochemical method (*c*).

aluminium content in copper can be as high as 20 at.%. Solid solutions with a maximum aluminium content of up to 23 at.% were also prepared by the mechanochemical method.[111, 130, 131]

If there is structural compatibility between the metal serving as the solvent and the closest intermetallide and there is a favourable dimension factor, the resulting solid solutions are characterised by a very broad concentration range of supersaturation. In the Ni – Al system, the intermetallic compound Ni_3Al is structurally similar to nickel serving as the solvent.[132] According to the equilibrium diagram, the limiting solubility of aluminium in nickel is 13.5 at.% and 3.85 at.% at 1100 and 500 °C, respectively. At room temperature, the solubility is insignificant. The homogeneity region of the intermetallic compound Ni_3Al varies from 23 at.% to 27.5 at.% of Al.[108] Solid solutions of aluminium in nickel containing up to 28 at.% of Al were synthesised by the mechanochemical method.[111, 133]

The Ni – Ga system is characterised by an electron concentration identical to that observed in the Ni – Al system and by the favourable dimension factor ($\Delta R \simeq 10\%$).[134] The maximum gallium content in the equilibrium solid solution of gallium in nickel is 24.3 at.%. At the peritectic temperature of 1210 °C, the α' phase (Ni_3Ga) was formed. The solubility of gallium in nickel depends substantially on the temperature. For example, the solubility at 700 °C decreases to 15 at.% of Ga.[135] The system contained the β phase, *viz.*, the solid solution based on the intermetallide NiGa. The homogeneity region of the β phase falls in the concentration ranges of gallium from 36 at.% to 60 at.% and from 48.3 at.% to 53.3 at.% at high and low temperatures, respectively. At 1204 °C and a concentration of gallium of 29.4 at.%, the α' and β phases formed an eutectic. At 940 and 685 °C , two peritectoid reactions proceeded giving rise to new phases, *viz.*, γ and δ, respectively. The low-temperature γ' phase formed from the γ phases below 685 °C has the Ni_3Ga_2 composition and is characterised by a narrow homogeneity region. The Ni_3Ga phase (the Cu_3Au structural type) is structurally similar to β-nickel (the face-centred cubic structure). The succeeding Ni_3Ga_2 phase crystallises in the γ-Mn structural type, which can be described as a deformed structure of β-nickel, whereas the NiGa phase crystallises in the CsCl structural type (the body-centred cubic structure).[132] The mechanochemical method was used for the preparation of solid solutions of gallium in nickel with a Ga concentration of up to 50 at.%,[117, 133] *i.e.*, including the concentration range of existence of both structurally similar phases.

In the Ni – Ge system, the difference between the atomic radii of the metals is small,[134] but the region of existence of the solid solution, which is determined by the electron concentration, is noticeably narrower than that in the Ni – Ga system. According to the equilibrium diagram, the limiting solubility of germanium in nickel is 13.8 at.% at 1161 °C.[125] The solid solution is followed by the β phase, which is a solid solution based on the intermetallide Ni_3Ge. The β phase is homogeneous in the concentration range from 22.9 at.% to 24.8 at.% of Ge and has the cubic structure of the Cu_3Au type similar to that of β-nickel. The following ε phase is a solid solution based on Ni_2Ge with the hexagonal structure of the nickel-arsenide type, which differs substantially from the structure of the preceding phase. The mechanochemical method was used for the synthesis of non-equilibrium solid solutions whose homogeneity region extends to a concentration of 25 at.% of Ge.[133]

It is known that a solid solution of aluminium in α-iron was formed in the Fe – Al system at concentrations of aluminium varying from 0 at.% to 25 at.% (quenched alloys).[132] The further addition of aluminium led to a gradual ordering of the solid solution. Under favourable conditions, for example, upon annealing, ordering started even at 18 at.% of Al. At 25 at.% and 50 at.% of Al, the intermetallides Fe_3Al and FeAl, respectively, were formed. Solid solutions of aluminium in iron with an aluminium content of up to 50 at.% were prepared by the mechanochemical method.[136 – 138]

Therefore, the mechanochemical method enables one to extend substantially the concentration range of existence of solid solutions toward the non-equilibrium region if the intermetallic compounds closest to the metal, which serves as the solvent, are structurally similar.

Metastable solid solutions can be prepared by the mechanochemical method from powders of metals in different systems among which are systems characterised by large differences between the melting points and between the densities of the initial components, by high melting points of the resulting intermetallic compounds and by narrow homogeneity regions of the equilibrium chemical compound. In the synthesis of supersaturated solid solutions, as in the synthesis of intermetallides, systems with very large differences between the melting points of the initial components attract particular attention. Among these are systems containing tungsten ($T_{melt} \approx 3400$ °C) and tantalum ($T_{melt} = 3015$ °C) whose melting points are higher than boiling points of many metals.

In the Ni – W system, the boiling point of nickel (2900 °C) is lower than the melting point of tungsten and hence compounds are difficult to prepare from these elements by conventional procedures. According to the equilibrium diagram, this system contained (*a*) the α phase, *viz.*, a solid solution of tungsten in nickel with a homogeneity regions from 0 at.% to 35 at.% of W at 900 °C and from 0 at.% to 41.5 at.% of W at temperatures from 1000 °C to the melting point, (*b*) the β phase, *viz.*, the intermetallic compound Ni_4W, and (*c*) the γ phase, *viz.*, a solid solution of nickel in tungsten containing ~4 at.% of Ni.[125] Solid solutions of tungsten in nickel were synthesised from a mixture of these metals by the mechanochemical method.[139]

An analogous ratio between the melting points of the initial components is observed in the Fe – W system. According to the

equilibrium diagram, the system contained two intermetallides, *viz*., Fe_2W and Fe_3W_2. At 1520 °C and at room temperature, the solubility of tungsten in iron is 33 mass % (13 at.%) and 8 mass % (3 at.%), respectively. At 1640 °C, the solubility of iron in tungsten in the solid state is only 0.8 mass % (2.6 at.%).[125] The solid-phase synthesis in this system was carried out by the mechanochemical method to produce solid solutions.[140]

In the Cu – Ta system, the mixing enthalpy is close to zero, the difference between the atomic radii is large (~ 25%), the initial components belong to different structural types, and the boiling point of copper is almost 600 °C lower than the melting point of tantalum. According to the published data,[108, 141] the solid-phase solubility of tantalum in copper is virtually absent. At 1200 °C, only 0.009 at.% of Ta was dissolved in copper and no other metallic compounds were formed. Supersaturated solid solutions of tantalum in copper were prepared by the mechanochemical method.[142]

In the Cu – Nb system, the difference between the melting points of the initial components is also large. According to the equilibrium diagram, the system contained only two phases, *viz*., solid solutions based on copper (α) and niobium (β). The solubility of niobium in copper at 1100 and 20 °C is 1.66 mass % (1.14 at.%) and 0.2 mass % (0.13 at.%), respectively. The solubility of copper in niobium at high temperatures and at 700 °C amounts to ~2 at.% and 0.07 at.%, respectively.[141] Solid solutions with concentrations of each component up to 10 mass % (7.05 at.%) were prepared by the mechanochemical method.[143, 144]

The limiting solubilities (~10 at.%) both of niobium in a solid solution of nickel (a face-centred cubic structure) and of nickel in a solid solution of niobium (a body-centred cubic structure) were achieved in the Ni – Nb system by the mechanochemical method.[145] For comparison, is should be noted that the equilibrium solubilities are 4.2 at.% of Nb (at 987 °C) and 3.5 at.% of Ni (at 1000 °C).[146]

Solid solutions of aluminium based on different metals are of particular interest in materials technology. These compounds differ sharply from the starting compounds in chemical properties. The concentration of aluminium introduced has a pronounced effect on the properties. Gerasimov *et al*.[147] observed the formation of supersaturated solid solutions based on α-titanium for the compositions $Ti_{100-x}Al_x$ (x < 60 at.%). The solutions were formed even if the equilibrium phases Ti_3Al and TiAl were used as the starting components. The authors believed that the intermetallides can decompose and tribochemical equilibrium was established in the course of mechanical alloying giving rise to metastable phases. Solid solutions in the Ti – Al system were prepared in a planetary ball mill using the Ti_xAl_{100-x} compositions (x = 75 at.%, 50 at.% and 35 at.%). In none of the compositions examined did amorphisation occur. In all cases, the formation of solid solutions was observed, *viz*., the hexagonal Ti(Al) solid solution in the cases of $Ti_{75}Al_{25}$ and $Ti_{50}Al_{50}$ and a mixture of hexagonal Ti(Al) and cubic Al(Ti) solid solutions in the case of $Ti_{35}Al_{65}$. Variations in the conditions of activation led to a change in the quantitative ratio between the hexagonal and cubic phases.[148]

It is known that the equilibrium concentration of aluminium in niobium is less than 10 at.% at 1000 °C.[149] The use of the mechanochemical method allowed an increase in the concentration to 30 at.%.[150]

Supersaturated solutions were formed in the Zr – Al system containing up to 15 at.% of Al, the lattice parameters a and c of zirconium being decreased from 0.3235 to 0.3200 and from 0.5196 to 0.5148 nm, respectively.‡ After mechanochemical activation for 12 h, the particle size was ~ 12 nm.[55]

‡ Here, the first and second values correspond to the lattice parameters of zirconium and of the solid solution of aluminium in zirconium, respectively.

Solid solutions with an Al content of up to 50 at.% were formed in the Al – Pd system in which the equilibrium solubility of aluminium in palladium is 15 at.%.[53]

The mechanochemical method was used for the synthesis of solid solutions Al – 10 at.% of X (X = Ti, Zr or Hf) from powders of the metals.[151] Supersaturated solid solutions containing up to 13 at.% of Sb with a grain size of 10 nm were obtained in the Cu – Sb system.[152] The maximum concentration of 2.1 at.% of Sb was achieved in the Fe – Sb system.[153] In the Fe – Tb system, the mechanochemical method made it possible to attain a solubility of 36 at.% of Tb.[20] Metastable solid solutions W – 25 mass % (25 at.%) of Re with nanosized grains were also prepared by this method.[154]

Systems in which the absence of solubility of one element in another one is associated neither with the difference between the atomic radii nor with the difference in the structural type, but is most probably determined by the electron concentration are a special case. For example, the difference between the atomic radii in the Ge – Sn system is ~ 12%.[134] The face-centred cubic structure of germanium is similar to the tetragonal structure of β-Sn.[125] However, the equilibrium concentration of germanium in solid tin falls in the concentration range of 0.001% – 0.1% (see Ref. 125) and the formation of intermetallides was not observed. Solid solutions with a substantial deviation from the equilibrium state containing 12 at.% – 24 at.% of Sn were synthesised by the mechanochemical method.[155] These concentrations of tin are substantially higher than its concentrations in solid solutions prepared by fast quenching.[156] The non-equilibrium solubility of germanium in tin is achieved if the particle sizes of germanium are no larger than 10 nm.

In the Ge – Al system in which the initial elements belong to the same structural type and the difference between the atomic radii is very small (only ~3%), no intermetallides are formed. At 424 °C and 54 mass % (30.3 at.%) of Ge, the eutectic consisting of two solid solutions appeared. The germanium content in a solid solution based on aluminium decreased from 5.1 mass % (~2 at.%) at the eutectic temperature to 0.3 mass % (> 0.1 at.%) at 20 °C.[125] Metastable intermetallic compounds were obtained by quenching from the liquid state.[42, 157] Structurally similar metastable intermetallides were also synthesised by the mechanochemical method.[158, 159]

Analysis of the experimental data demonstrated that systems in which the atomic radius of the alloying element is larger than that of the metal serving as the solvent are characterised by higher equilibrium solubilities than those observed in systems with other ratios between the atomic radii. For example, the solubilities of aluminium (R = 0.143 nm) in nickel (R = 0.124 nm), iron (R = 0.126 nm) and copper (R = 0.128 nm) amount to tens of atomic percent, whereas the solubilities of iron, nickel and copper in aluminium are close to zero. The use of the mechanochemical method allowed a substantial extension of the region of existence of such solid solutions. Thus, metastable solid solutions based on aluminium with Cu and Fe contents of up to 33 at.% (see Ref. 160) and 10 at.%, respectively, were prepared.[161 – 163] Pekala and Oleszak[164] prepared a solid solution with composition $Fe_{10}Al_{90}$ in a horizontal low-energy ball mill after activation for 200 h. The average size of crystallites of the solid solution was ~7 nm. It was found that the mechanochemical formation of the solid solution in the course of activation was preceded by the short-duration formation of the intermetallide $FeAl_3$ from powders of iron and aluminium. Dunlap *et al*.[165] compared the microstructures of supersaturated solid solutions of iron in aluminium synthesised by the mechanochemical method and fast quenching and demonstrated that alloys with composition $Al_{98}Fe_2$ prepared by fast quenching occurred as monophase supersaturated solid solutions. In the initial stage of the mechanochemical synthesis, a supersaturated solid solution whose microstructural properties are similar to those of quenched alloys was formed. Further activation led to a decrease in the grain size and gave rise to an amorphous phase.

Supersaturated solutions with a magnesium content of up to 45 at.% were synthesised in the Al – Mg system by the mechanochemical method. The particle sizes were in the range of 2 – 10 nm.[166]

In the case of intermetallides with low enthalpies of formation or with enthalpies close to mixing enthalpies, supersaturated solid solutions can be prepared not only by mechanochemical synthesis from powders of the initial elements, but also on mechanochemical activation of intermetallides resulting in disordering of the equilibrium intermetallic phases synthesised by other methods. For example, the intermetallides Nb_3Al,[167] V_3Ga,[168] Nb_3Au,[169 – 171] Ni_3V,[172, 173] $Cr_{53}Fe$ [174] and Fe_3Ge [176] were transformed into solid solutions with body-centred cubic structures, whereas $NbAl_2$ (see Ref. 172) and $TiAl_3$ (see Ref. 175) were transformed into solid solutions with face-centred cubic structures upon mechanochemical activation. As a result of disordering of equilibrium intermetallides, solid solutions also formed in the Ni – Al system.[177]

Supersaturated solid solutions of tin in iron characterised by a substantial deviation from the equilibrium state can be prepared using mechanochemical activation both of a monophase intermetallide and a mixture of intermetallic compounds.[178 – 180]

Therefore, the mechanochemical method allows the preparation of supersaturated solutions in systems with negative enthalpies of mixing of the components. For most systems, the degree of supersaturation depends on the difference between the atomic radii of the initial elements, their structural compatibility and the electron concentration.

IV. Mechanochemical synthesis of supersaturated solid solutions in systems with positive mixing enthalpies

Of systems with positive mixing enthalpies, the Fe – Cu system has received the most study. If the concentrations of the components are equal to 50 at.% each, the mixing enthalpy calculated by the Miedema method [127 – 129] is 22 kJ mol^{-1}. It is believed that one of the reasons for the immiscibility of these metals in the solid state is the difference in their structural types. Thus, copper has the face-centred cubic (FCC) lattice and α-iron has the body-centred cubic (BCC) lattice. However, it is known that the structural type of iron changes as the temperature is increased: α-Fe (BCC) → β-Fe (BCC) at 770 °C → γ-Fe (FCC) at 920 °C. Hence, the possibility of dissolution is higher at high temperatures. At 1094 °C, the equilibrium solubilities of iron in copper and copper in γ-iron are 3.8 mass % (4.2 at.%) and ~8 mass % (~7.1 at.%), respectively.[108, 125] Solid solutions, which are non-equilibrium at room temperature, can be prepared by quenching from vapour or liquid phases. For example, solid solutions based on iron (BCC lattice) in the concentration range of up to 15 mass % (13.5 at.%) of Cu and based on copper (FCC lattice) in the concentration range of up to 20 mass % (22 at.%) of Fe were obtained from melts by quenching.[181] Supersaturated solid solutions in a wider concentration range were prepared by precipitation from the vapour phase *in vacuo* on a support at room temperature. It was demonstrated [182] that solutions had BCC structures if the copper content was lower than 50 mass % (47 at.%) and FCC structures if the copper content was higher than 70 mass % (68 at.%). Solutions with concentrations of copper in the range of 50 mass % – 70 mass % were not prepared. Supersaturated solid solutions in a wide concentration range were also synthesised by quenching from the vapour phase. Solid solutions based on iron existed up to 40 mass % (37 at.%) of Cu. Solid solutions based on copper with a FCC structure occurred up to 60 mass % (57 at.%) of Cu.[183]

Benjamin [184] was the first to report the results of mechanochemical alloying of the components in the Fe – Cu system. He obtained the homogeneous mixtures 80 mass % (82 at.%) of Fe – 20 mass % (18 at.%) of Cu and 50 mass % (24 at.%) of Pb – 50 mass % (76 at.%) of Cu in a high-energy laboratory mill. Metallographic studies of a specimen of the Cu – Fe system confirmed its homogeneity. It was also noted that the colour changed from red (the colour of copper) to grey (the colour of steel). Neverov *et al.*[94, 185] obtained solid solutions on a Bridgman anvil. The concentrations of copper in iron and iron in copper reached 40 mass % and 10 mass %, respectively. Gusev [186] demonstrated that solid solutions based on copper (FCC lattice) with compositions up to $Cu_{40}Fe_{60}$ and solid solutions based on iron (BCC lattice) with compositions up to $Cu_{30}Fe_{70}$ can be obtained in a centrifugal planetary ball mill. Kaloshkin *et al.*[187, 188] prepared supersaturated solid solutions $Fe_{100-x}Cu_x$ ($x = 20 – 80$) from powders of iron and copper in a planetary ball mill. The mechanochemical formation of solid solutions was completed in 30 min. It was also established that the FCC phase of the solid solution, the BCC phase of the solid solution and a mixture of these phases were formed at $x = 40$ at.% – 80 at.% of Cu, $x = 20$ at.% of Cu and $x = 30$ at.% of Cu, respectively. In studies of structural changes occurring in the course of mechanical alloying, Barro *et al.*[189] observed the formation of solid solutions in the Fe_xCu_{100-x} system ($x = 5$, 10 and 20). Uenishi *et al.*[190] performed mechanical alloying of the solid solution $Fe_{1-x}Cu_x$ and prepared also monophase compositions with BCC (if $x < 40$ at.%) and FCC (if $x > 40$ at.%) structures. Yavari *et al.*[191] confirmed that the lattice parameters in these compositions were increased. Eckert *et al.*[192, 193] prepared solid solutions Fe_xCu_{100-x} in a SPEX 8000 ball mill. It was demonstrated that monophases with FCC and BCC structures exist at $x \leqslant 60$ and $x \geqslant 80$, respectively, whereas solid solutions with FCC and BCC structures coexist in the range of $60 \leqslant x \leqslant 80$. The formation of solid solutions starts when grains reach nanometer sizes.

Jiang *et al.*[194, 195] also observed the formation of solid solutions in the Cu – Fe system and detected small amounts of γ-Fe (a FCC structure) in all specimens subjected to mechanochemical treatment for more than 10 h. Supersaturated solid solutions in the Cu – Fe system were also prepared in SPEX 8000 ball mills in more recent studies (see, for example, Refs 196 – 206). It was established by different methods that monophase supersaturated solid solutions were formed in mixtures containing more than 80 mass % or less than 60 mass % of copper, whereas two phases coexisted in the region with a copper content from 50 mass % – 60 mass % to 80 mass %.

Therefore, the mechanochemical method allows the preparation of supersaturated solid solutions throughout the concentration range of existence of a binary system with a high positive heat of mixing of the initial components (Fig. 2).

The Cu – Co system also has a positive mixing enthalpy (~20 kJ mol^{-1} for the equiatomic composition). According to the data reported by different researchers, the concentration of cobalt in a solid solution based on copper (β phase) at 1100 °C changes from 5.2 mass % to 8 mass % (from 5.6 at.% to 8.5 at.%) and the concentration of copper in a solid solution based on cobalt at the same temperature changes from 12 mass % to 14 mass % (from 11.2 at.% to 13.1 at.%). At temperatures below 500 °C, the mutual solubility of one element in another is no higher than 0.1%.[108] The low mutual solubility is attributable to the difference in the structural types of these elements. However, it is known that α-Co (the hexagonal close-packed structure) is transformed into β-Co at 350 – 470 °C. The latter, like copper, has a FCC structure. The high mutual solubility of these elements is quite possible due to the insignificant difference between their atomic radii. Fast quenching made it possible to dissolve up to 20 mass % of Co and less than 25 mass % of Cu in cobalt. The mechanochemical method was used for the preparation of solid solutions with FCC structures throughout the concentration range of existence of this binary system.[197, 199, 207 – 213] In a number of studies, it was found that phase transformations of cobalt occurred upon mechanochemical activation in ball mills.[214 – 216]

The Cu – Cr system is also characterised by a positive mixing enthalpy (~20 kJ mol^{-1} for the equiatomic composition). In this

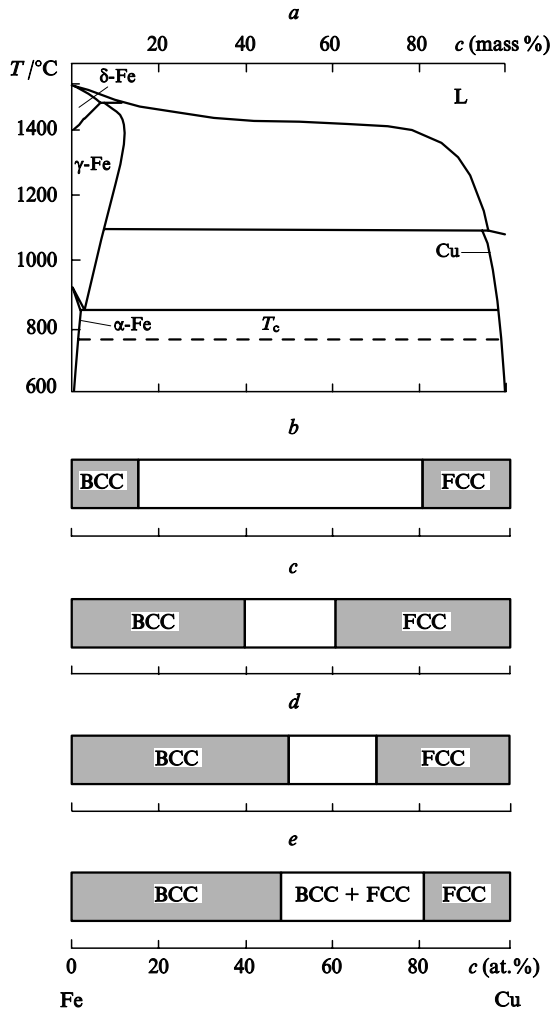


Figure 2. Equilibrium diagram of the Fe – Cu system (*a*) and the regions of existence of solid solutions synthesised by quenching from a melt (*b*), quenching from the vapour phase (*c*), precipitation from the vapour phase (*d*) and the mechanochemical method (*e*).

system, as in the above-considered one, the difference between the atomic radii of the initial metals is insignificant, but their structural types differ substantially (BCC and FCC structures, respectively). The solubility of chromium in copper varies from 1.25 mass % to 0.5 mass % (from 1.5 at.% to 0.6 at.%) at 1050 °C and it is less than 0.03 mass % at 400 °C. The solubility of copper in chromium is 0.16 at.% and 0.085 at.% at 1300 °C and 1150 °C, respectively.[141] Chromium has several crystal modifications, *viz*., α-Cr (BCC structure), β-Cr and γ-Cr. Supersaturated solid solutions characterised by substantial deviations from the equilibrium state were prepared by the mechanochemical method.[217–220]

In the Cu – V system, the atomic radii of the initial metals have close values, whereas their structural types are different (FCC and BCC structures, respectively). According to the equilibrium diagram, solid solutions based on copper (α) and vanadium (β) are formed in the system. The maximum solubility of vanadium in copper is 0.8 at.% at 1120 °C (0.1 at.% at 20 °C) and the maximum solubility of copper in vanadium is 8 at.% at 1530 °C.[141] A wide range was found in which the components in the liquid state were immiscible (the range from 4.0 at.% to 84.6 at.% of V). Solid solutions both with BCC and FCC structures were prepared on mechanochemical activation.[218,221] It was demonstrated [221] that the particle sizes of the components should be no larger than 30 nm for solid solutions to be prepared.

In the Cu – Ag system, both components have FCC lattices, the difference between the atomic radii is ~11% and the melting points of the components have close values. However, according to the equilibrium diagram of this system, the components have limited solubilities in the solid state at the eutectic temperature (~780 °C). At this temperature, the solubility of silver in copper is 8.0 mass % (4.9 at.%) and the solubility of copper in silver is 8.8 mass % (14.1 at.%). Quenching at a rate of cooling of 10^7 deg s^{-1} afforded a continuous series of solid solutions. On cooling at lower rates, a continuous series of solid solutions was not detected. Depending on the conditions, solid solutions with different contents of the second element can be synthesised by the mechanochemical method throughout the concentration range of this system.[42,186,222–225]

In the Pb – Al system, both elements also have FCC structures, the difference between their atomic radii is ~18% and both metals are rather low-melting. However, the system is characterised by a positive mixing enthalpy. The metals do not form intermetallides and mutual solubility is absent. Supersaturated solid solutions were prepared in this system by the mechanochemical method.[226]

The Fe – Ag system is characterised by a very high positive mixing enthalpy, the initial elements have different structural types (BCC and FCC, respectively) and the mutual solubility of the components is limited even in the liquid state. The solubility of silver in solid iron is no higher than 0.01% and the solubility of iron in solid silver is 0.0006%.[125] Solid solutions are difficult to synthesise by the mechanochemical method.[227–230] Only very thin dispersions of iron in a silver matrix were obtained; the average radius of iron particles was equal to several nanometers.[230]

In systems with positive mixing enthalpies, a low mutual solubility of one component in another may be associated with a large difference between the atomic radii of the initial elements. For example, this difference in the Cu – Bi system is ~30% and the solubility of bismuth in copper in the solid state is only 0.003 at.% at 800 °C, the solubility of copper in bismuth being insignificant.[231] The formation of the metastable intermetallide with composition Cu_5Bi_2 was observed in this system.[232] The mechanochemical method was used for the preparation of supersaturated solid solutions of bismuth in copper with a concentration of bismuth of up to 4 at.%; the average grain size was ~10 nm.[233]

The Fe – In system is also characterised by a positive mixing enthalpy and the difference between the atomic radii of ~23%. In the equilibrium state mutual solubility is completely absent. Solid solutions of indium in iron with rather low concentrations of indium were prepared by the mechanochemical method.[234]

In solid solutions prepared by the mechanochemical method in systems characterised by positive mixing enthalpies and large differences between the atomic radii, the maximum solubilities of one element in another are rather low compared to those in systems in which the differences between the atomic radii of the initial elements are smaller and the elements can adopt similar structures due to phase transitions on mechanochemical activation.

The use of the mechanochemical synthesis for the preparation of intermetallides and solid solutions in immiscible systems with a large difference between the melting points of the initial components, in particular, in systems in which the melting point of one component is higher than the boiling point of another one, is of most practical interest. For example, the Mg – Ti system is characterised by a positive mixing enthalpy (12 kJ mol^{-1}). In this system, the difference between the atomic radii is ~9%, the components belong to the same structural type and the melting point of titanium is ~500 °C higher than the boiling point of magnesium. Hence, solid solutions are difficult to prepare by conventional methods (probably, they can be synthesised by precipitation from the vapour phase). Solid solutions of titanium in magnesium with concentrations of up to 20 mass % of Ti were synthesised by the mechanochemical method.[235] Moritaka *et al*.[236] examined the Ti – *x*Mg system (*x* = 10 at.%, 20 at.%,

30 at.%, 40 at.%, 50 at.%, 60 at.%, 70 at.%, 80 at.% and 95 at.%). Mechanical alloying was carried out in a Frich ball mill (P-7 type). Supersaturated solid solutions were detected at a magnesium content of $\geqslant 60$ at.%. In the range from 70 at.% to 80 at.% of Mg, the coexistence of solid solutions based both on titanium and magnesium was observed. The sizes of crystallites were larger and nonuniform distortions of the lattices of solid solutions based on magnesium were more substantial than those observed in the case of nanocrystalline solid solutions based on titanium.

The Cu–W system is characterised by a very high positive mixing enthalpy (35 kJ mol^{-1}). In this system, the difference between the atomic radii is $\sim 8\%$, the structural types of the initial metals are different (FCC and BCC, respectively) and the boiling point of copper is lower than the melting point of tungsten. Solid solutions were synthesised in this system by the mechanochemical method.[237,238] Raghu *et al.*[239] performed mechanical alloying in the systems Cu–5 mass % (1.9 at.%) of W and Cu–15 mass % (5.2 at.%) of W and demonstrated that nonequilibrium solubilities both of copper in tungsten and tungsten in copper occurred.

Therefore, the use of mechanochemical synthesis in systems which are immiscible in the equilibrium state allows the preparation both of metastable intermetallic compounds and non-equilibrium solid solutions. In systems in which the atomic radii of the initial components have close values and their structural types become similar due to phase transitions, the concentration ranges of existence of supersaturated solid solutions prepared by the mechanochemical method are extended most significantly compared to those of analogous solutions prepared by quenching. If the immiscibility in the equilibrium state is dictated by the difference between the atomic radii of the initial components, a substantially lower solubility is attained. In the latter case, rarely, if ever, can supersaturated solid solutions be prepared by quenching, whereas a particular solubility is achieved using the mechanochemical method, but this solubility is substantially lower than that in systems in which the difference between the atomic radii is small.

V. Quasicrystals and amorphous alloys

Follstaedt and Knapp[240] were the first to use solid-phase diffusion for the synthesis of icosahedral phases in the Al–Ru and Al–Mn systems. The melting point of ruthenium is substantially higher than that of aluminium and an alloy of these elements is difficult to prepare by quenching. Hence, the search for new procedures for the synthesis of these alloys is a topical problem. The formation of an icosahedral phase in experiments on heterophase diffusion signifies that nuclei of this phase are formed and grow more rapidly than the crystalline phase with the corresponding composition and a lower free energy in the solid state. This may be due to the fact that the fragments characterised by the short-range icosahedral order are more ordered in the crystal structure. Taking into account the results of experimental investigation of heterodiffusion and assuming that the mechanism of formation of amorphous alloys and supersaturated solid solutions on mechanical alloying is also associated with the process of heterodiffusion, Follstaedt and Knapp suggested that an icosahedral phase can also be prepared by mechanochemical alloying. Independently, Ivanov *et al.*[241] were the first to synthesise the icosahedral phases $Mg_{32}(Zn, Al)_{49}$ and $Mg_{32}(Cu, Al)_{49}$ from elements by the mechanochemical method and performed structural transformations of the corresponding Frank–Casper cubic phases into icosahedral phases by mechanochemical activation. The synthesis of the icosahedral phase $Mg_{32}(Zn, Al)_{49}$ from the elements involved an intermediate step giving rise to an amorphous phase. Apparently, clusters possessing short-range icosahedarl order were formed in this step. Then an icosahedral phase arose. This phase appeared to be rather stable and remained unchanged in the course of further treatment in a ball mill. The authors demonstrated that the synthesis of the icosahedral phase on mechanical alloying of metallic powders was accompanied by intermediate formation of an amorphous phase. Mechanochemical treatment of the cubic phase led to gradual broadening and then disappearance of a series of X-ray diffraction reflections belonging to this phase, whereas the remaining reflections were shifted so that they corresponded to the icosahedral phase. The X-ray diffraction reflections of the final product are broadened compared to those of quenched specimens. The metastable icosahedral phase was transformed into the cubic phase upon heating. According to the data of differential scanning calorimetry, this transformation was accompanied by three exothermic effects. The first of these effects most probably corresponds to annealing of defects in the icosahedral phase, which is confirmed by the fact that the X-ray diffraction reflections corresponding to this phase were narrowed after annealing of a specimen at the temperature of the first exothermic peak.

Eckert *et al.*[242] synthesised quasicrystals of $Al_{65}Cu_{20}Mn_{15}$ from the elements by mechanochemical activation in a planetary ball mill for 90 h. This phase also appeared to be stable to mechanochemical treatment. Thus, the X-ray diffraction pattern remained virtually unchanged in the course of grinding during 160 h. Unlike the authors of the above-considered study, Eckert *et al.* did not observe the formation of an intermediate amorphous phase and suggested that the formation of the icosahedral phase proceeded by a mechanism of heterodiffusion at the expense of heat, which was released upon dissipation of the kinetic energy of colliding balls. More recently (see, for example, Ref. 243), the icosahedral phase $Al_{70}Cu_{20}Fe_{10}$ has been synthesised from a mixture of metallic powders by the mechanochemical method. Local icosahedral symmetry was observed in alloys of aluminium with molybdenum after their mechanical grinding.[244]

The investigation performed by Schwarz and Johnson,[245] who demonstrated that amorphous alloys can be formed through heterodiffusion in a layered composite, has stimulated increased interest in the preparation of amorphous alloys in solid-phase processes. More recently, Schultz[246] has prepared a voluminous amorphous nickel–zirconium alloy by the annealing of a repeatedly rolled layered specimen. These facts suggested that the preparation of amorphous alloys by mechanical alloying occurred as a solid-phase process. During the last decade, a rich variety of amorphous alloys both in binary and multicomponent metallic systems, including systems characterised by large differences in the melting points and in the densities of the initial components, have been synthesised by mechanical alloying of powders of elements. For example, it was demonstrated that amorphous alloys can be prepared in the Ni–Mg system by the mechanochemical method (this process depends substantially on the blend composition). In addition, the formation of an amorphous alloy in magnesium-rich compositions was preceded by the formation of the intermetallic compound Mg_2Ni, whereas amorphous alloys were formed immediately from metallic powders in compositions with high nickel contents in spite of the fact that, according to the equilibrium diagram, the intermetallide Ni_2Mg existed in this concentration range.[247]

Nanosized amorphous alloys were also prepared in the Cu–Zr system.[248] The amorphous alloys Al_x-Zr_{100-x},[249] $Fe_{50}-Ta_{50}$,[250] Ni_xTa_{100-x},[251] Cu–Ti,[252] $Fe_{75}Zr_{25}$[253] and $Fe_{66.7}Zr_{33.3}$[254] were synthesised. In the Ti–Fe system, the formation of amorphous alloys was preceded by the formation of the supersaturated solid solutions β-Ti(Fe) and α-Fe(Ti) and the intermetallides FeTi and Fe_2Ti.[255] Amorphous phases were prepared in the systems Fe–6 mass % (11.3 at.%) of Si (see Ref. 256) and Se–As.[257] In the Fe–Cr system, amorphous alloys containing only 28 mass % (26.5 at.%) and 45 mass % (43 at.%) of Fe were prepared.[258] Multicomponent systems containing boron, phosphorus, silicon, carbon and other elements, for example, $Ni_{50}Pd_{40}Si_{10}$ (see Ref. 259) and YNi_2B_2C,[260] have received much consideration. In the latter system, the formation of nanocrystalline or amorphous phases is determined to a large extent by the

activation parameters (an amorphous phase appeared only after prolonged activation). Amorphous phases with composition $Cu_{86-x}Sn_xP_{14}$ ($x = 2-15$) can be prepared from powders of the initial elements, the time of the preparation of the amorphous phase depending on the tin content in the mixture. Thus, the duration of activation was 28, 20, 12 and 32 h at $x = 4, 5, 8$ and 10, respectively.[261] The alloy $Fe_{39}Ni_{39}Si_{10}B_{12}$ can be prepared both in the amorphous and nanocrystalline states.[262] An amorphous alloy with composition $(Zr_{0.65}Al_{0.075}Cu_{0.175}Ni_{0.1})_{100-x}Fe_x$ ($x \leqslant 20$) was synthesised from powders of the initial elements.[263]

Ermakov *et al.*[264–267] were the first to perform amorphisation of intermetallic compounds by the mechanochemical method. They carried out the structural transformation of the intermetallic compounds X–M, where X = Y, Gd or Tb and M = Fe or Co, from the crystalline to amorphous state in a wide concentration range by mechanical grinding. In the late 1980s, investigations of this process have been started by many researchers.[268–272] Amorphisation of intermetallides was examined in the Sn–Nb, Ge–Nb,[39,269] Cr–Ti, Cu–Ti, Fe–Ti, Mn–Ti, Co–Ti, Ni–Ti, Cu–Cr, Ni–Zr, Mn–Si[270] and Ni–Al[271,272] systems. Koch[13] was the first to initiate the process of amorphisation of intermetallides and called it 'mechanical grinding' rather than 'mechanical alloying' from the initial elements. In the last decade, this process has been studied intensively. Amorphisation of the Laves phases Fe_2Sc and Fe_2Y was investigated.[273,274] It was demonstrated that vigorous mechanical grinding of the intermetallide Fe_2Sc led initially to partial chemical disordering followed by amorphisation, whereas Fe_2Y was transformed into the amorphous state without preliminary disordering. Amorphisation of the intermetallides $Ni_{10}Zr_7$ and $NiZr_2$ was also studied.[275–277] Skakov *et al.*[278] investigated the process of amorphisation in the Ni–Nb system. An amorphous phase with composition $Fe_{78}P_{22}$ was prepared by mechanical grinding.[279] Poon *et al.*[280] succeeded in transforming supersaturated solid solutions based on titanium into amorphous phases.

For some systems, amorphisation upon mechanical grinding occurred as a cyclic process. For example, investigations of the structural evolution of powders of elements upon mechanical grinding of the $Co_{75}Ti_{25}$ and $Co_{50}Ti_{50}$ mixtures[281–283] demonstrated that the formation of amorphous alloys with these compositions occurred rather rapidly, but these alloys were transformed into Co_3Ti and CoTi (both compounds have BCC structures) on further mechanical treatment. These intermetallides were thermally stable and were not transformed into other phases upon heating to 1300 K. However, further grinding again afforded the amorphous compositions $Co_{75}Ti_{25}$ and $Co_{50}Ti_{50}$. Surinach *et al.*[284] observed the transformation of an amorphous phase into a nanocrystalline phase in the $Fe_{77.5}Cu_1Nb_3Si_{9.5}B_9$ system and determined the activation energy of the nanocrystalline transformation.

Amorphous structures can also be prepared according to the mechanochemical method by grinding intermetallides together with metallic powders. Thus, an amorphous phase in the Cu–Cd system was prepared by grinding the equilibrium δ phase together with a copper powder.[285] It should be noted that attempts to obtain an amorphous structure in this system either by mechanical alloying of powders of copper and cadmium or by grinding of the single δ phase failed.

Amorphous phases in the Mg–Ni and Mg–Ni–V systems were synthesised upon mechanical grinding of the Mg_2Ni alloy with powders of nickel and vanadium, respectively.[286] An amorphous phase was formed by mechanical grinding of the intermetallide $EuFe_2$ as well as by its grinding with powders of europium and iron.[287] More complex amorphous phases were also synthesised in such a manner. The amorphous compositions $Mg_2Ni_1M_{0.1}$ (where M = Ni, Ca, La, Y, Al, Si, Cu or Mn) can be prepared by mechanochemical grinding of the binary system of the intermetallide $Mg_2Ni_{0.9}M_{0.1}$ and a powder of nickel.[288]

The regions of existence of amorphous alloys synthesised by the mechanochemical method were calculated and determined experimentally in a large number of studies (see, for example, Refs 289–295).

VI. Phase and structural transformations in the mechanochemical synthesis of intermetallic compounds

Benjamin[184,296,297] considered mechanical alloying of metallic powders in attritors as a repeated process of cold welding under pressure and grinding. He believed that a metal particle is flattened upon its initial collision with balls, *i.e.*, the ratio of the surface area of the particle to its volume increases, surface films of adsorbed impurities being disrupted. Flattened metal particles contact with each other through the freshly formed surfaces giving rise to a layered composite of powdered particles (Fig. 3). The layers in this composite become thinner as welding and grinding are continued. The formation of layered composites was detected in many systems.[13,230,247,298,299] There are five typical stages of evolution of a mixture of powders of two plastic metals (Fig. 4).

The formation of layered composites from mixtures of metallic powders is accompanied by their intensive dispersion as evidenced by the results of investigations on deformation of metals. Initially, the so-called elementary structure of slip bands appears upon deformation of pure metals even without the use of activators and mills.[300] This band consists of thin slip lines, which

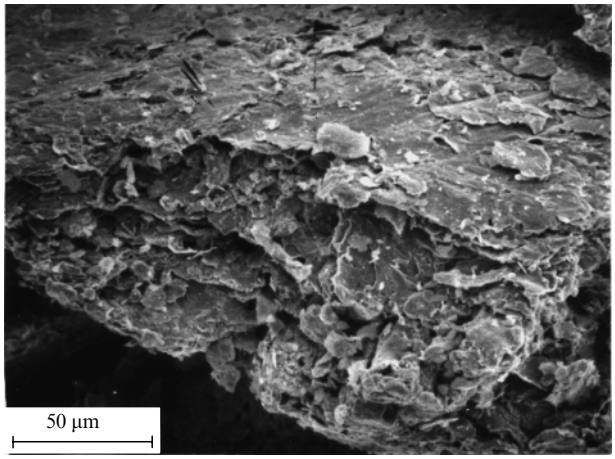


Figure 3. Microphotograph of a cross-cut cleavage of the layered composite (the system Ni–14 at.% of Al, mechanochemical activation for 30 s).[80]

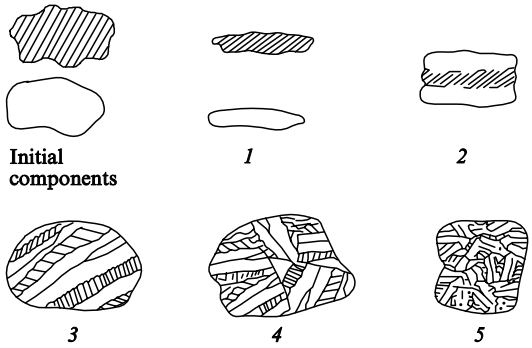


Figure 4. Typical stages of evolution of plastic powders in the course of mechanochemical activation;[84]
(*1*) plastic deformation of the initial particles (flattening), (*2*) the formation of new contacts between the initial elements, (*3*) accumulation of dislocations and breakage of layers into blocks, (*4*) and (*5*) subsequent stages of mixing and diffusion giving rise to the product.

cover the crystal surface uniformly. As plastic deformation is developed, packets of slip bands arise and deformation is distributed less uniformly throughout the bulk of the crystal. More in-depth investigation demonstrated that crystals were broken up into blocks, which were slightly disordered with respect to each other, even in the initial stage of deformation. At this stage, the appearance of dislocation networks was observed in studies of a thin foil by electron microscopy. Further development of plastic deformation led to roughening of the dislocation network to form an irregular cellular structure, the density of dislocations at the interface of the cells being substantially higher than the average density throughout the bulk. At this stage, the growth of disordered blocks was observed.[300] The mechanism of formation of the cellular structure is not entirely known. However, it is assumed that processes of polygonisation associated with dislocation climb and rearrangement are of great importance in this mechanism. Since dislocation climb can occur only under the action of very large stresses or through diffusion inflow of point defects,[301] the formation of the cellular structure is estimated taking into account these factors. At rather high temperatures (close to the temperature of recrystallisation), the formation of a cellular structure is promoted by a high rate of migration of vacancies. The concentration of vacancies in plastically deformed metal is also high. Thus, it is believed that this concentration and the equilibrium concentration of point defects at temperatures close to the melting point are of the same order of magnitude. According to van Bueren,[302] after low-temperature deformation, which leads to a change in the linear dimensions of the specimen by only 10%, the concentration of point defects reaches $10^{19}-10^{20}$ cm^{-3}. Apparently, the high concentration of point defects upon low-temperature deformation is responsible for the formation of a cellular structure. In addition, low-temperature deformation is favourable for a decrease in the cell dimensions.[303] Rapid deformation also influences the cell dimensions, *viz*., it causes the formation of extremely small cells.[303, 304] The formation of cellular structures characterised by the disordered arrangement of the adjacent cells and substantial deformations were observed for chromium,[303] iron,[305] copper,[306] tantalum,[307] molybdenum and its alloys [308–312] and for a number of other metals and alloys.[313–316]

Therefore, domains of the crystal lattice are rearranged in the course of plastic deformation. This effect was revealed both for metals and their alloys in wide ranges of temperature, stresses and rates of deformation. The fragment-boundary angles depend on the degree of deformation and can be as large as several tens of degrees. The boundaries are either small-angle walls and networks or grain boundaries of a deformation nature.

Plastic deformation arising under the joint action of high pressure and shear on mixtures of metals leads to a decrease in the dimensions of coherent-scattering regions compared to the analogous regions for individual compounds treated analogously.[317–321] Positron studies of structural defects in metals subjected to high pressure and shear deformations demonstrated that vacancy clusters with sizes of up to 0.5 nm were formed in these specimens. In addition, specimens were intensively saturated with dislocations as the degree of deformation increased.[319]

Therefore, plastic deformation leads to the formation of non-equilibrium point defects and their clusters and to a high density of dislocations. As the degree of deformation increases, a cellular structure is developed followed by fragmentation. In the case of plastic deformation of heterogeneous mixtures, blocks become smaller and interactions at the boundaries of dissimilar blocks occur.

Processes of grinding and formation of layered composites occur more vigorously in planetary ball mills because rapid shear deformations are realised on collisions in such mills. The dynamics of grinding, the microstructure and the sizes of the particles formed depend both on the conditions of mechanical treatment and on the properties of metals as exemplified by copper, nickel, iron and germanium.[320–326]

The process leading to a decrease in the grain size in ball mills involves three steps.[326]

1. Initially, deformation is localised in slip bands consisting of a series of high-density dislocations.

2. When a particular degree of deformation is achieved, annihilation and recombination of these dislocations take place within small-angle grain boundaries separating individual grains. The grain sizes thus obtained are 20–30 nm.

3. The orientation of individual crystalline grains with respect to the adjacent grains becomes totally random.

These stages are typical of deformation processes, which involve metals with BCC lattices and intermetallic compounds and which occur at high rates of deformation.

Eckert *et al*.[327] found that the minimum grain size of nanocrystalline metals (generally, 6–22 nm) is achieved if two competitive process take place, *viz*., substantial plastic deformation caused by mechanical treatment in a ball mill and relaxation of the material. Moreover, it was found that the minimum grain size of metals with FCC lattices is in inverse proportion to the melting point.[328, 329] Fecht *et al*.[328] demonstrated that the average grain sizes of metals with BCC lattices and hexagonal close-packed lattices are decreased to 9 and 13 nm, respectively.

The initial step of the mechanical synthesis in metallic systems involves the formation of layered composite structures accompanied by simultaneous dispersion of the initial components to nanosized grains. The formation of such layered composites results in an increase in the contact area between the initial components. It is known that heterogeneous solid-phase reactions can proceed only at the regions of tight contacts of the reacting phases. At these regions, a layer of the product arises and the further course of the reaction depends on the mechanism of diffusion of the reacting compounds through this layer. Solid-phase compounds are transferred primarily through diffusion whose rate depends on the mobility of lattice defects (their mobility is particularly high at the crystal surface even at low temperature).[330]

Pavlyukhin *et al*.[90] studied the formation of solid solutions in the Fe–Cr system and demonstrated that accelerated diffusion can proceed in binary metallic mixtures upon their mechanical activation in centrifugal planetary mills. Based on the results of Mössbauer spectroscopy, the authors estimated the diffusion coefficient (D) for the system containing spherical particles of radius R under conditions of activation. The determined value $D \simeq 10^{-5}-10^{-7}$ cm^2 s^{-1} is seven orders of magnitude larger than the diffusion coefficient of chromium in iron at 1600 K ($10^{-12}-10^{-14}$ cm^2 s^{-1}). A change in the microstructure of the alloy, which is generally observed in the initial step of mechanical alloying, was ignored in calculations. However, since the thickness of layers changes substantially in the course of mechanical alloying, the radius of the initial species is not the only factor determining the diffusion path.

In the case of plastic deformation of metals, diffusion can be substantially accelerated due to destruction and generation of dislocations [331] along which the rate of diffusion in metals is several orders of magnitude larger than along other directions.[332–339] In addition, it was demonstrated [340–345] that the diffusion coefficient is linearly proportional to the rate of deformation. Therefore, solid-phase dissolution of elements can be substantially accelerated on rapid plastic deformation. If this process is accompanied by the formation of layered composites, mass transfer can be promoted, on the one hand, due to short diffusion distances, and, on the other hand, due to acceleration of diffusion upon rapid plastic deformation.

Clemens [346] found parallels between mechanochemical synthesis and solid-phase transformations in layered film systems. He believed that the role of mechanical activation consists in the formation of a composite from disperse particles of the initial components and promotion of diffuse mixing due to generation of non-equilibrium defects.

Hellstern and Schultz[347] considered phase formation taking into account solid-phase diffusion. In the cited study, mechanical mixing of pure powders of iron and chromium was performed in a ball mill under argon. The authors believed that mechanical treatment afforded a layered microstructure consisting of two elements and the layers became thinner in the course of treatment. Since this system possesses a substantial chemical driving force, which favours diffusion between layers, the process occurs through the mechanism of a solid-phase diffusion reaction. An analogous viewpoint was also followed in a more recent study.[348] In the latter study, it was demonstrated that particles with a typical layered structure were formed in Ni–Zr and Fe–Zr systems at the initial stage of mechanical treatment of initially crystalline powders in a mill. Further mechanical treatment afforded composites consisting of ultrathin layers in which solid-phase diffusion proceeded. Samwer suggested[349,350] that amorphous alloys are formed in the course of solid-phase diffusion and this process occurs at low temperature due to rapid diffusion of one component into another one. As a result of mechanical treatment, particles of the components adopt a 'multilayer-sandwich' form and a negative heat of mixing is the driving force for the process. Koch *et al.*[271] also believed that mechanochemical reactions are accompanied by the formation of ultradisperse composite particles, solid-phase diffusion occurs in these particles and a negative mixing enthalpy is the driving force for diffusion.

Most researchers attributed fast mass transfer in mechanochemical reactions characterised by negative mixing enthalpies to a large contact area and a high rate of solid-phase diffusion at high rates of plastic deformation of metals.

A large number of experimental studies of spontaneous diffusion arising when particles of the initial components (which are in intimate contact) become nanosized, have been carried out in recent years.

In many systems, non-equilibrium solid-phase solubility of one element in another one is readily realised when grains become nanosized. It was found that extremely high diffusion rates are characteristic of highly disperse nanosized particles.[351–353] It was found that copper immediately dissolved in nanosized gold particles at room and lower temperatures.[354] Fast spontaneous alloying afforded the intermetallides $AuSb_2$, InSb and AlSb.[355–357] It was demonstrated that every pair of elements is characterised by its own critical grain (particle) size at which spontaneous alloying starts at room temperature. The critical size of the initial particles increases as the heat of alloy formation increases. In the Au–Cu,[358] Au–Zn[353] and Au–Al[359] systems, the mixing enthalpies are negative and spontaneous alloying takes place even in the case of a rather large critical particle size. In the Au–Ni system, the enthalpy is positive and spontaneous alloying at room temperature occurs only if grains are very small. In the In–Al system, the mixing enthalpy is substantially larger than zero and hence, spontaneous alloying was not achieved (Fig. 5). Phase diagrams for systems consisting of nanosized particles differ substantially from standard diagrams and the solid-phase solubility of one element in another increases essentially (reaches several tens of percent) even if the elements virtually do not form solid solutions.[361] It was assumed that relaxation of lattice distortions, which may be caused by a dissolved atom, proceeds much more readily in nanosized particles than in bulkier particles because the lattice becomes more mobile (Fig. 6).[362,363]

Therefore, mass transfer in layered composite structures containing nanosized grains, which are formed in the first step in metallic systems with negative mixing enthalpies, proceeds through spontaneous diffusion. This diffusion can take place at room temperature because the critical grain size at which it starts depends on the mixing enthalpy, *viz.*, the larger the (negative) mixing enthalpy the larger the appropriate grain size. In systems in which intermetallides with high heats of formation (or, at least, in which the heats of formation of intermetallic compounds are substantially larger than the heats of mixing of solid solutions), these intermetallic compounds are formed first. Examination of

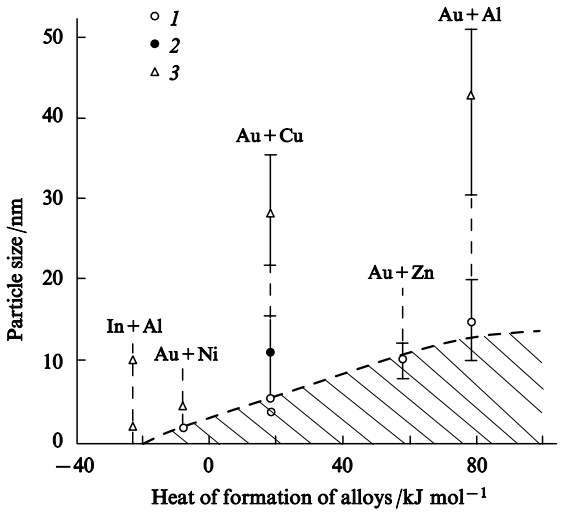


Figure 5. Dependence of the critical sizes of the initial particles on the heat of formation of alloys in different systems at 300 K;[360] (*1*) complete spontaneous alloying at 300 K, (*2*) partial spontaneous alloying, (*3*) alloying does not occur.

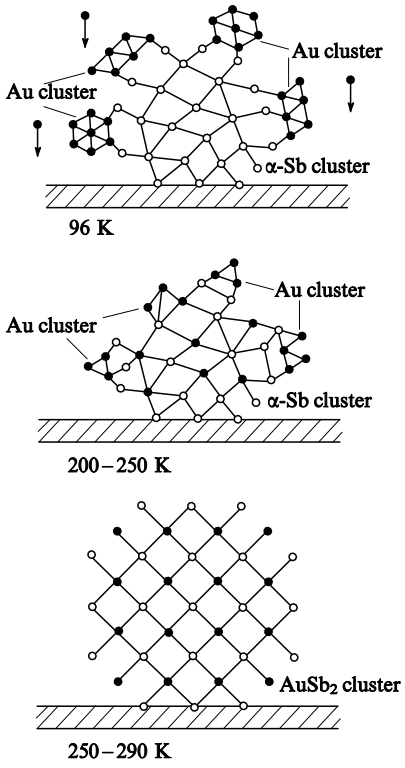


Figure 6. Scheme of spontaneous alloying of gold and antimony particles.

the mechanochemical synthesis of solid solutions demonstrated that in layered composites, intermetallides are actually formed first. In the second step of the mechanochemical synthesis, intermetallides characterised by a high heat of formation and a high content of the alloying element arise in the Ni–Ge, Ni–Al, Ni–Si, Ni–Bi, Ni–Sn, Ni–In, Ni–Ga, Cu–Sn, Cu–In, Cu–Ga and Fe–Sn systems.[111,113,115–119,121–124,126,132,364] X-Ray diffraction data corresponding to the phase formation in the course of the mechanochemical synthesis of solid solutions of bismuth in nickel are shown in Fig. 7. In this system, two intermetallic compounds, *viz.*, NiBi (78.8 mass % Bi) and $NiBi_3$

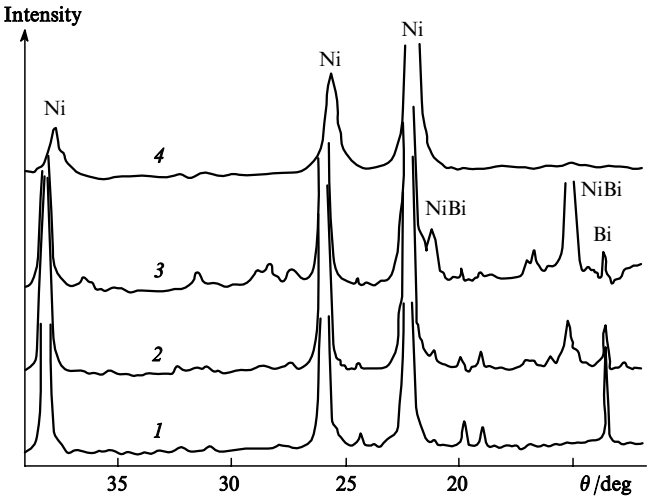


Figure 7. X-Ray diffraction patterns of the products of mechanical alloying of nickel with 10 mass % of bismuth. The activation time (min): (*1*) 1, (*2*) 3, (*3*) 10, (*4*) 90.[126]

(91.44 mass % Bi), exist.[108] The enthalpies of formation of these compounds calculated by the Miedema method[127–129] are approximately -4 kJ mol^{-1} for NiBi and -2 kJ mol^{-1} for $NiBi_3$. In the course of the mechanochemical synthesis of solid solutions in this system, the formation of layered composites is followed by the formation of the intermetallide NiBi (see Fig. 7). It is worthy of note that the above-mentioned phase can be formed under equilibrium conditions only if the bismuth content is 78 mass % and the mixture subjected to mechanical activation contains only 10 mass % of Bi. As the time of activation was increased, the intensities of reflections of the NiBi phase increased (see Fig. 7, curves *2* and *3*), the lattice parameter of nickel remaining the same. The growth of the NiBi phase proceeded until the bismuth was completely consumed. Only further activation of the resulting intermetallide with unconsumed nickel led to a decrease in the intensities of reflections of the intermetallide NiBi, broadening of the diffraction peaks of nickel and their shift to the small-angle region (see Fig. 7, curve *4*), which is indicative of the formation of a solid solution. Analogous changes in the diffraction patterns were observed for other systems. The dynamics of changes in the phase composition of the mixture can be followed using the Fe–Sn system as an example (Fig. 8). Thus, the amount of the intermetallic compound $FeSn_2$ increased and then decreased upon mechanochemical dissolution of $FeSn_2$ in iron to form a solid α-solution of tin in iron. Mechanochemical activation led to a decrease in the grain size of α-Fe to 10–20 nm and the resulting intermetallide $FeSn_2$ also contained nanosized particles (Fig. 8 *b*). It should be noted that the intensive formation of the solid solution α-Fe(Sn) was observed only if the grain sizes of the phases α-Fe and $FeSn_2$ reached 3–8 nm. These values agree well with other data on the mechanochemical synthesis of solid solutions in this system.[122]

Investigations demonstrated that the dynamics of formation of intermediate intermetallic compounds in the second step of the mechanochemical synthesis of solid solutions in metallic systems characterised by negative enthalpies of formation correlates with the enthalpies of formation of equilibrium intermetallic compounds.[365–368]

Comparative studies of mechanochemical synthesis from a mixture of metallic powders and from a mixture of a metal serving as the solvent and intermetallic compounds, whose phase compositions are identical to those of substances which are formed in the intermediate stage of the mechanochemical reaction of the metallic powders, demonstrated that the dynamics of formation of the solid solution is virtually the same in both cases.[369]

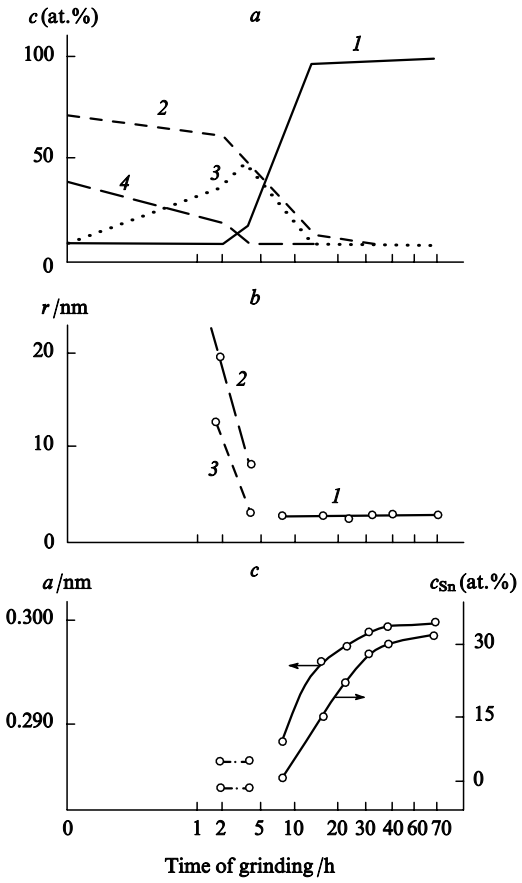


Figure 8. Dependences of the phase composition (*a*), the average size of crystallites (*b*), the lattice parameter of the resulting BCC phase and the concentration of tin (*c*) on the time of grinding in a Pulverizette-5 mill;[123] (*1*) α-Fe(Sn), (*2*) α-Fe, (*3*) $FeSn_2$, (*4*) β-Sn.

Therefore, the synthesis of solid solutions in metallic systems characterised by negative mixing enthalpies may involve the following stages.

1. The formation of layered composite structures with simultaneous dispersion of the initial components to nanosized particles (a sharp increase in the contact area between the initial components).

2. The formation of intermetallic compounds in nanosized layered composites.

3. Dissolution of intermetallic compounds in the metal acting as the solvent to form a solid solution.

Most of researchers assumed that the process of formation of amorphous alloys from metallic powders involves two steps. In the first step, layered composites containing nanosized grains are formed. The formation of an amorphous alloy in the second step proceeds through diffusion in a heated specimen. It is believed that the specimen is heated at the expense of the energy of collision of balls and the temperature increases to hundreds of degrees, but it does remain inadequate to attain crystallisation of an amorphous alloy. This point of view was confirmed by Petzoldt *et al.*[370] The authors observed amorphous interlayers between layers of nickel and niobium by electron microscopy. These interlayers are analogous to those between layers of nickel and zirconium observed by Meng *et al.*[371] in experiments on annealing of sputtered films.

In a number of studies, the formation of intermetallic phases before amorphisation was detected. This fact seems to be quite reliable because amorphous alloys in many systems were prepared by mechanical grinding of intermetallides. The formation of intermetallic compounds involves, most probably, two steps

because intermetallides can arise immediately in layered composite structures.

In layered composite structures, which are formed in metallic systems, spontaneous diffusion of the initial compounds can proceed at room temperature due to the thermodynamic driving force for the process. In analogous layered composites formed in systems characterised by a positive mixing enthalpy, this driving force is absent. It can be suggested that the formation of solid solutions under conditions of mechanochemical activation proceeds, most probably, through quenching from the liquid state because, first, the temperatures of phase transitions, including the solid phase → liquid phase transition, sharply decrease compared to those in a bulky material as the sizes of the initial particles decrease to several nanometers,[372–376] and, second, sharp local increases in temperature and pressure can take place in activators.

Bowden *et al.*[377–379] gained experimental evidence for the existence of local heating and revealed their sites, which arise at the contacts between particles of solid compounds on their mechanical treatment. The authors established that the area of heating sites is, on the average, 10^{-2} cm^2, the time of their existence is 10^{-5}–10^{-3} s and the temperature jumps at the sites of heating can be as large as 800–1000 K and sometimes even larger. According to the hypothesis proposed by Dubnov, Sukhikh and Tomashevich,[380] individual dislocation pairs with antiparallel Burgers vectors in the regions of intensive shear can annihilate with restoration of a perfect structure and liberation of the dislocation energy, which, according to estimates made by Cottrell,[381] is ~1 eV. Since the atomic forces act only through very short distances, the region of energy liberation is limited to a radius of about one interatomic distance. In this case, local heating is $\sim 10^3$ K.

Avvakumov[321] also concluded that local sites of heating limited by the melting point of particles being treated can arise in the mechanochemical processes.

Urakaev and Avvakumov[382] calculated the thickness of the molten zone. They believed that this value can reach 5×10^{-7} cm if the size of rubbing particles is $\sim 10^{-4}$ cm and the sites of local heating (taking into account the possibility of melting of particles treated) are limited by their melting points. Kopylov *et al.*[383] suggested that intermetallic compounds can be synthesised in a planetary mill due to short-period local heating on friction of the particles. Based on the results of calculations, it was concluded[384–387] that high local temperatures and pressures can arise in the course of mechanochemical activation.

Dannik[388] solved the problem of collision of two particles taking into account frictional forces on interaction of rigid bodies. Based on Dannik's equations, Urakaev[389] calculated the temperatures at the contacts between inorganic particles rubbed in drums of centrifugal planetary mills. The maximum local temperature at the rubbing surface of the particles is ~1030 K and the lifetime of this temperature is 10^{-9} s.

Ermakov, Yurchikov and Barinov[390] also considered the problem of the effect of the temperature on processes occurring in mechanochemical activators. They believed that substantially heated and rapidly cooled local regions (hot spots) can appear at the surface of the particles. The lifetime of hot regions of sizes 1–10 nm 'heated' almost to the melting point is 10^{-3}–10^{-6} s. The authors also estimated the rate of cooling of these regions at 10^6–10^9 deg s^{-1}. The appearance of hot sites has also been observed in more recent studies. For example, the intermetallide SnTe was synthesised at room temperature by repeated cold pressing of granulated tin and powdered tellurium.[391] The system consisted of the initial elements until the pressing action provided an adequate mechanical energy. Hot regions of diameter 1–2 nm were observed at the metal surface with particle sizes of 10–15 nm. In these regions, 0.25%–0.35% of the total deformation energy was accumulated after 30-fold pressing (1.25 g of a mixture of Sn and Te, 343 MPa).

Eckert *et al.*[392] also calculated the high local temperatures arising at contact sites. The experiments were carried out using a 'Pulverizette-5' planetary ball mill (Frich, Germany) at the ball rates of 2.5, 3.6 and 4.7 m s^{-1}. The temperatures at the contact sites, which are shifted with respect to each other due to deformation caused by colliding balls, were calculated as described by Schwarz and Koch.[393] The following values were obtained: at the rate of 2.5 m s^{-1}, $\Delta T = 80$ deg; at the rate of 3.6 m s^{-1}, $\Delta T = 167$ deg; at the rate of 4.7 m s^{-1}, $\Delta T = 287$ deg. The authors believed that the average temperature of the drum, which was 50, 80 and 120 °C, respectively, in the case of the above-mentioned rates, should be added to the temperature developed due to collisions.

Zalkin[394] concluded that molten zones can arise at temperatures, which are substantially lower than the melting point of a low-melting element; in this case, diffusion has virtually no effect on the onset of melting.

Experimental investigations aimed at direct measurement of local temperatures are many fewer in number compared to studies in which local temperatures were calculated. Changes in the temperature are sometimes determined on vibrating mills with the use of thermocouples. A thermocouple is attached to the outer wall of the drum and the temperature can be monitored throughout the process. In this case, it is assumed that the temperatures of the drum, balls and the material under treatment are equal or differ insignificantly. Kimura *et al.*[395] used this procedure for the measurements of the temperature of the drum wall depending on the rate of the stirrer of the attritor and demonstrated that the temperature of powders reached 573 K.

The AGO planetary ball mills are characterised by very high energies and the input power of ~1 W per cm^3 of the drum volume.[396] The temperature of balls can amount to 500 °C increasing very rapidly.[397] Hence, not only dispersion of the initial components, but also substantial temperature jumps, which arise upon contact of the material treated with balls, should be taken into account in mechanochemical synthesis in high-energy mills.

Analysis of the published data demonstrated that mechanochemical synthesis of non-equilibrium solid solutions in metallic systems characterised by a positive mixing enthalpy involves two steps. In the first step, layered composite structures containing nanosized grains of the initial components are formed. In the second step, solid solutions arise. The second step can proceed through quenching of the liquid phase in which, apparently, mixing of the components occurs. The liquid phase is formed both due to a sharp decrease in the temperature of phase transition to the liquid state when grains become nanosized and due to local temperature jumps in the contact region at the instant grinding particles collide.

In the case of metallic systems with a positive mixing enthalpy, it seems reasonable to speak about mechanical alloying rather than about the mechanochemical synthesis of non-equilibrium solid solutions. Unfortunately, the term 'mechanical alloying' is assigned in the literature both to systems in which chemical reactions proceed and to systems in which components are only mixed.

The formation of intermetallic compounds upon liquid-phase contact interaction in metallic systems, which are characterised by a negative mixing enthalpy and which contain a low-melting component, should also be taken into account. The presence of layered composites in metallic systems containing nanosized grains in which the melting temperature is sharply decreased with simultaneous existence of rather high temperature jumps at sites of contacts with grinding particles can ensure contact melting of the components and their chemical reaction in the liquid phase.

Presently, there is no agreement regarding the nature of mechanochemical synthesis, *viz.*, the question of whether it is a solid-phase process or it proceeds in the liquid phase remains open. A large number of calculations and experimental studies available in the literature indicate that substantial temperature jumps can occur in activators. However, the direct mechanochemical synthesis from components with high melting temperatures and the fact that mechanochemical synthesis can be performed on

Bridgman anvils and in low-energy ball mills in which high temperatures are difficult to attain provide evidence in favour of the solid-phase nature of the processes.

In the present review, various opinions as to the mechanisms of processes occurring in mechanochemical synthesis in metallic systems are surveyed. It should be noted that most researchers consider the preparation of amorphous alloys and supersaturated solid solutions by the mechanochemical method as the process of disordering of equilibrium phases.

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