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MECHANOCHEMISTRY OF INORGANIC SOLIDS

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ABSTRACT

Mechanochemical processes taking place during the mechanical treatment of solid samples are discussed in detail.

INTRODUCTION

One of the features of the mechanical treatment of solids is that it can be constant (continuous) or periodic. In the former instance the reactivity is changed owing to the constant field of stress that is applied to the solid (the Bridgeman anvil is an example). In the latter instance the stress is applied periodically by subjecting a solid to a sequence of powerful mechanical impulses (comminution in industrial mills, ball or vibration mills, attritors, etc., is an example).

A simplified scheme of such impulses in shown in Fig. 1. Each of the impulses can be characterized first by the formation of a stress field at the point of attack (the left side of the impulses) and second by its relaxation, which leads to various physical and physico-chemical after-effects (the right side of the impulses) [1,2].

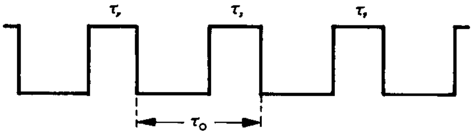

Fig. 1. The impulse character of mechanical treatment. τ_1 = time of interaction; τ_0 = the time interval between two impulses.

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Another feature of mechanochemical processes is its localization. Like many heterogeneous chemical processes, they do not proceed in the whole volume of a solid (or not at the whole surface) but at certain points. These points are usually the contacts between the particles of the solid or tips of moving cracks. These points are of special interest to many physicists nowadays, as very important and interesting information can be obtained concerning the stress field (so called "stress fabric"), shear deformation and the emergence of local high temperatures and pressures at these locations.

It is remarkable that as early as the 1920s the emergence of high temperature and pressure at the tips of moving cracks was reported by Griffits [3]. Their existence was subsequently supported by direct experimental data obtained in Cambridge, Karlsruhe, Leningrad and Novosibirsk. It was shown that the tip of a moving crack is surrounded by a field of increased temperature and pressure. The characteristics of the field depend on the velocity of crack propagation and on the physico-chemical properties of the solids in which the crack is propagated. About 15 years ago, in a paper dealing with the kinetic model of mechanochemical processes, I put forward a suggestion that if a reaction has two or more parallel channels, the mechanism of the reaction initiated in the tip of the moving crack will be different to a thermal reaction. The cause of this phenomenon is connected with the concentration of energy in the tip of the crack and with the impulse character of the process. Experimental support for this proposal has since

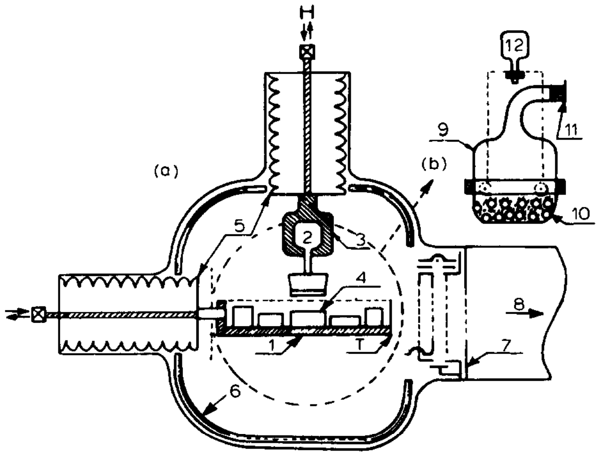

Fig. 2. Equipment for study of the mechanism of mechanochemical reactions in the tip of the moving crack. 1 = Sublayer for crystals; 2 = knife; 3 = knife holder; 4 = sample of alkali metal nitrate crystals; 5 = systems of sylphons; 6 = ionic source chamber; 7 = ionic source grid; 8 = drift space of the mass spectrometer.

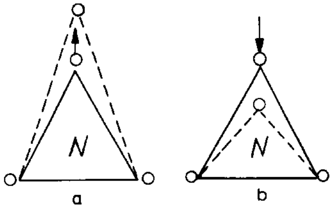

Fig. 3. Various kinds of deformation of nitrate ion leading to rupture of the bonds and decomposition of the ion. (a) Extension; (b) compression.

been found in various laboratories. An example of the data obtained is experiments on cleaving alkali metal nitrate single crystals directly in the ionic source of a time-of-flight mass spectrometer [4]. A diagram of the equipment that we have used is shown in Fig. 2.

It was shown that if the velocity of crack propagation is high, one of the primary gaseous products of the decomposition of a nitrate is not oxygen but nitric oxide. Similarly, during the fragmentation of an alkali metal bromate the primary product is also not oxygen but bromine.

Hence the products of mechanochemical decomposition of nitrates are different to those obtained by thermal decomposition of the same solids. A decrease in the velocity of crack propagation causes the disappearance of this effect and the usual thermal decomposition mechanism is realized. Recently we have observed the same effects on iodates and chlorates and applied this effect to the control of multiplication of cracks by the evolution of gaseous products [5]. The reason for the change in the mechanism of decomposition in the tip of a moving crack seems to be the excitation of various vibronic levels during the alteration of the velocity. When the velocity of crack propagation is high, the high-energy vibronic levels are excited, but when the crack propagates slowly, the low-energy vibronic levels are excited (similarly to the situation during thermal decomposition). To a first approximation, the main principle can be illustrated by Fig. 3. When low-energy vibronic levels (Fig. 3a), are excited, decomposition of the nitrate ion occurs via stretching of one side of the NO_3-ion triangle, resulting in the formation of oxygen. When we reach the next (higher energy) vibronic state of nitrate, there is probably another means of deformation of the triangle owing to its compression of it (Fig. 3b), the product of decomposition in this instance being nitric oxide.

The particular character of the rupture of chemical bonds by excitation of high-energy vibrons in inorganic solids can be detected by an ESR study of some persulphates of alkali metals [6]. The specific feature of the persulphate ion is the presence of a weak O–O bond (in addition to the strong S–O bonds etc.). The rupture of this bond causes the formation of two radicals with unpaired electrons, which can be observed by ESR. We have detected the appearance of these radicals during the mechanochemical

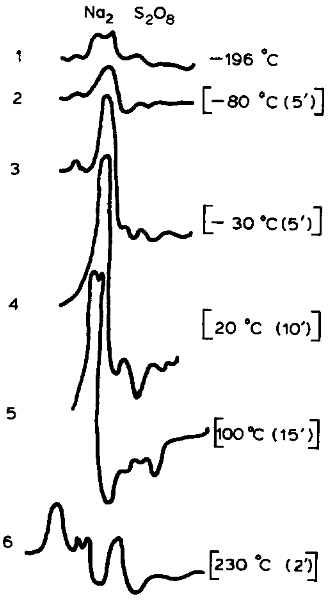

Fig. 4. ESR spectra of sodium persulphate ion during its mechanical treatment. 1, Milling in a vibromill immediately in the resonator of the ESR spectrometer at −196°C and subsequent 5 min annealing at −80°C; 2, the same, but annealing at −30°C; 3, annealing at 20°C (10 min); 4, annealing at 100°C (30 min), 1/3 real amplitude; 5, annealing at 200°C (15 min); 6, annealing at 230°C.

decomposition of sodium persulphate. Owing to the impulse character of the mechanical impact, the radicals formed can be preserved in the crystal matrix. Subsequent heating of the mechanically treated crystals gives new paramagnetic centres, which then disappear (Fig. 4).

The study of rapid changes in the structure of crystals during the mechanical treatment of solids is another important problem. The greatest difficulties are caused by the necessity to study local sites of the sample (ca. 0.1 mm^2) and by the short period during which the relaxation proceeds after a mechanochemical impulse (0.1–0.001 s). Until recently this problem was considered to be very complicated and for some kinds of metastable short-lived structures it could not be solved [7]. The difficulties can be overcome by using synchrotron radiation for diffraction analysis. As is well known, part of the energy is emitted as synchrotron radiation by shifting the wavelength of the electrons. The intensity of synchrotron radiation can be increased by application of various methods (for example, by using various types of wavelength shifter, multiple wigglers, magnets or undulators). By this means the intensity of the radiation can be increased to 10^{14} photon mm^{-2} s^{-1}, whereas for ordinary X-ray tubes the intensity is about 10^7 photon mm^{-2} s^{-1}.

This gives the possibility of taking an X-ray photograph and storing it in the memory of a computer within a very short time (ca. 10^{-5} s). For repeated processes this can resolve a point with an accuracy of 10^{-6} s (1 μs). Synchrotron radiation permits the study of fine X-ray line structures and gives the possibility of obtaining not only Debye diffraction patterns but also Laue diagrams.

The high time resolution of synchrotron radiation permits precise measurements of the development of the distortion of solid structures during mechanical deformation and the relaxation of this distortion. Owing to the high intensity of synchrotron radiation, it is possible not only to increase the time resolution of the measurements but also to detect structural changes in a very small volume of the sample. Good examples of the application of synchrotron radiation to the study of mechanical activation have been obtained in our Institute. Thus the structural changes in the initial stages of deformation of some solids [8] were studied. For instance, during the cutting of metallic tin single crystals it was established that in the local region (ca. 0.01 mm^2) under the ruby cutter, immediately cutter had passed the usual stable α-modification of the tin was transformed into the tetragonal form. This form is stable at pressures of about 100 kbar. After the load has been released, the pattern of the tetragonal modification disappears. Similar experiments were carried out with silver and aluminium single crystals; here the metastable modifications were not detected, although strong but rapidly vanishing distortions of the initial structure were observed.

In addition to the study of relaxation structural changes (i.e., processes that proceed on the right side of the mechanical pulses shown in Fig. 1), synchrotron radiation diffractometry can be applied to the investigation of phenomena accompanied by the formation of a stress field (i.e., the left side of the pulses). As an example, Fig. 5 shows the results of measurements of the intensity and half-width of the X-ray line in the diffraction pattern of deformed lithium fluoride single crystals. It can be seen that the formation of a stress field does not occur immediately but a few milliseconds later.

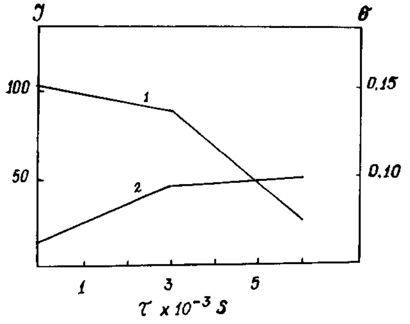

Fig. 5. Decrease in intensity of the X-ray line (1) and its broadening (2) during deformation of lithium fluoride detected by a diffractometer on synchrotron irradiation.

The study of the effect of preliminary mechanical treatment is, as we have previously mentioned, another basic direction of investigation into the mechanochemistry of solids. This subject is essentially one of after-effect field stress relaxation, but these after-effects are of long duration.

DISCUSSION

There is a common opinion that the main reason for the reactivity changes as a result of preliminary mechanical treatment in fragmentation of a solid and therefore the formation of a new surface. In spite of this opinion, it has been noted that the generation of various defects during the treatment might be one of the main reasons for the reactivity changes. In this instance the formation of defects is characterized by the interesting feature that they are formed in non-equilibrium concentrations. Therefore, the solid after treatment should be regarded as metastable. It follows that the treatment of a solid by short but powerful mechanical pulses can be regarded as one of the methods of producing an "active" or "metastable" state of solids [9–11]. It is well known that a metastable state is formed as a result of energizing and then quenching of a solid and a metastable solid has some excess free energy. This excess can be lowered by localized atomic rearrangements. The morphological, structural and compositional changes in the crystals of solids correspond to the quenched excited states in solids.

There are many methods for the production of metastable solids. The energization might consist of irradiation, melting, evaporation or accumulation of energy by a chemical reaction with subsequent quenching, which is normally characterized by a cooling rate. The plastic deformation of a solid can be regarded as one of the methods of energy storage in solids and therefore can be recommended as one of the methods of producing metastable states.

As can be seen from Table 1, the mechanical methods of producing the metastable state of solids can give three basic types of metastability: morphological, structural and compositional. The use of these methods provides the accumulation of a large excess of energy (ca. 0.2–0.8 RT_{m}) (where T_{m} = temperature of melting).

There are two approaches to evaluating the effect of the preliminary mechanical treatment of the reactivity of solids. The first takes account of the integral increase in the free energy of solids owing to the increase in both enthalpy and entropy terms during the treatment. The alteration of the isobar-isothermal potential (or free energy if the sample is a solid) can be determined using the equation suggested by Hüttig:

$$\Delta G_T^* - \Delta G_T = \Delta A_T^x$$

TABLE 1

Methods of production of metastable states

Method	Type of metastability c-compositional s-structural m-morphological	Rate of freezing ($K\ s^{-1}$)	RT (T_m = melting temperature)
I. Freezing of the melt or crystals	cs	10^3–10^5	0.4–0.9
(a) Freezing of the melt on the cool surface			
(b) Laser melting		10^{12}	
II. Condensation (Hindered synthesis of crystal structure)			
(a) Condensation of vapours	c	10^{12}	0.9
(b) Electrochemical condensation	c		
(c) Chemical or topochemical reactions	m		
(d) Cross-beam condensation			
III. Irradiation of solids			
(a) by heavy charged particles (e.g. fission products)	c	10^{12}	0.5
(b) ion implantation			
IV. Effect of mechanical impulse Treatment in mechanical activators:			
(a) Free collision (shock)	csm	10^9	0.2–0.9
(b) Shear deformation			
(c) Shock + stress			
Shockwave treatment		10^{13}	

The change in free energy also results in variation of the equilibrium constant:

$$\Delta G = -RT \ln K_\alpha$$

This leads to a change in the rate that is proportional to the deviation of the system from equilibrium. The energy stored in solids as a result of treatment can be determined either by using calorimetric methods (e.g., by measuring heats of solution) or by the DTA method as the difference between the enthalpies of activated and non-activated solids. The determination of the excess energy stored in a solid by DTA involves the measurement of the area of the peak on DTA curves [12–14]. This peak is usually connected with the annealing of the defects arising during mechanical treatment. The application of DTA methods to the study of the mechanism of the mechanical activation can be exemplified by the results in papers [15,16] describing studies of the main channel of relaxation of energy stored in crystals of

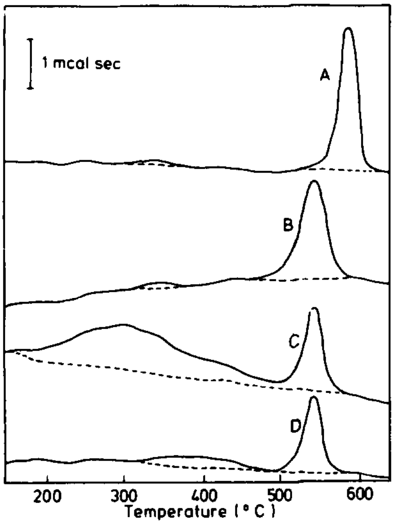

Fig. 6. DSC curves for mechanically treated samples of γ-Fe_2O_3: (A) without treatment; (B) compressed at 4000 kg/cm^2; (C) vibromilled for 3.0 h; (D) vibromilled for 3.0 h and annealed at 200°C for 24 h.

γ-iron(III) oxide after treatment in a vibration mill. The thermograms were recorded by using differential scanning calorimetry (Fig. 6). The results of the experiments showed that the energy stored during mechanical treatment has two main effects on the DTA curve. The first is a shift of the exothermic peak corresponding to the phase transition to the low temperature region. Another is evolution of heat before phase transition, which corresponds to annealing defects. Depending on the kind of treatment, the relationship between these two effects might be different. If, for example, a specimen of γ-Fe_2O_3 is compressed up to a pressure ca. 4000 kg cm^{-2}, the treatment influences mainly the phase transition temperature. In contrast, treatment in a vibration mill for 3 h results in an increase in the energy evolved on heating to 250°C, giving a second peak on the DTA curve.

Similar results were obtained in the DTA of ammonium perchlorate [17,18]. Whereas three-dimensional loading of the specimen up to 200 kg cm^{-2} caused a shift to the right of the endothermic peak, which corresponds to the transformation of the rhombic modification of ammonium perchlorate into the cubic form, the exothermic peak, which corresponds to the thermal decomposition of ammonium perchlorate, shifted to the left (i.e., in the low-temperature region from 330 to 310°C). When the pressure is above 300 kg cm^{-2} the mechanical activation is stopped. In contrast to what has been said above, even some passivation takes place. Shock wave treatment affects ammonium perchlorate in a different manner owing to the simultaneous action of the pressure component and shear stresses. The exothermic peak corresponding to the thermal decomposition shifted to the left to such an extent that thermal decomposition started below the phase transition temperature. Meanwhile, no shift in the phase transition temperature occurred. These examples show that methods of thermal analysis might be used both for the evaluation of stored energy and for the study of channels by which stored energy might be relaxed.

When dealing with other approaches, one should take into consideration the connection between the properties of different types of defects originating in the solid sample during treatment and the particular characteristic features of the chemical reaction mechanism. It has been shown that the problem of the increase in the solid-state reaction rate does not only involve the simple accumulation of the integral energy by solids; it is necessary to know the kind of defects by which this energy is stored. Depending on the reaction mechanism and its rate-determining step, the chemical reaction rate in solids may be affected by different types of defects [19]. Therefore, the most important consideration is to study the kinds of defects to which a particular reaction is especially sensitive. Bearing this in mind, one can recommend a method of preliminary treatment in which the concentration of the given defects in solids is maximal.

Using such an approach, we could not only deal with the measurement of integral values as excess heat of solution, broadening of X-ray lines, etc.; it is necessary now to acquire direct information concerning the essence of the processes that occur during mechanical treatment and the defects formed as a consequence.

The results of our experiments on the study of the effects of preliminary mechanical treatment on the reactivity of solids towards liquid reagents (e.g., leaching) might be used as a good example of such research. If the solubility of a solid in liquids is low, the rate-determining step of the overall process is not the usual transport of the fluid reagent to the interface but the chemical reaction on the surface of a solid. The mechanism of this reaction usually involves the formation of a complex compound between the cations and anions of the lattice and the ligand molecules present in solution (or water molecules when we are dealing with aqueous solutions). Whether the ion is extracted from the lattice or is left in the lattice and the process is limited by the adsorption of the liquid on the surface depends on the relationship between the energy of complex formation and the energy of the crystal lattice. Of the two components, we can control only the energy of ion extraction from the lattice (if, of course, the composition of a liquid has to be kept constant). This can be done by forming defects in the crystals which will loosen the chemical bonds in the lattice. Dislocations, boundaries and point defects will be most probable defects. Therefore, the treatment of solids by high-power mechanical impulses can be used as one of the methods for increasing the rate of solution of solids.

For example, the reactivity of tricalcium phosphate could be increased as a result of preliminary mechanical treatment. The increase in reactivity

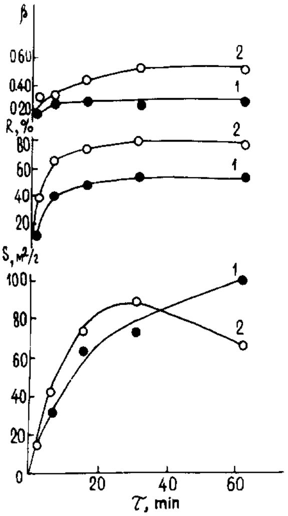

Fig. 7. Effect of mechanical treatment on the change in surface area, broadening of X-ray line and reactivity of kola apatite. 1, Wet treatment; 2, dry treatment.

could not be explained as a simple result of enlargement of the specific surface area of phosphate due to fragmentation of the crystals. A comparison of the increase in specific surface area and broadening of X-ray lines with changes in the reactivity of apatite (natural tricalcium phosphate) during mechanical treatment is shown in Fig. 7.

The reactivity of apatite has been defined as the amount of phosphate dissolved in aqueous ammonium citrate solution (so-called Pitterman probe) [20]. It can be seen that there is a correlation between the change in the half-width of the X-ray line and reactivity and no correlation between reactivity and specific surface area (Fig. 8). The lack of correlation between reactivity and specific surface area, the lack of change in ionic conductivity during mechanical activation and the state of phosphates to be annealed led to the conclusion that the principal defects formed during mechanical treatment are dislocations [21], and these are responsible for activation. If this is the case, mechanical treatment should be performed so as to obtain as many dislocations as possible. Therefore, the mechanical treatment should not be carried out in the commonly used mills but in specially designed apparatus that can result in the plastic deformation of phosphates, i.e., the so-called mechanical activators. The feature of mechanical activators is an increased power of mechanical impulses inside them. The increase in the solubility of natural phosphates in weak organic aqueous solution enables us to recommend an improved method for producing phosphorus fertilizers without using acid treatment for phosphates [22,23]. Agrochemical testing of apatites and phosphates after mechanical activation has shown that they can be used as good fertilizers for soya beans, wheat, buckwheat, etc. The

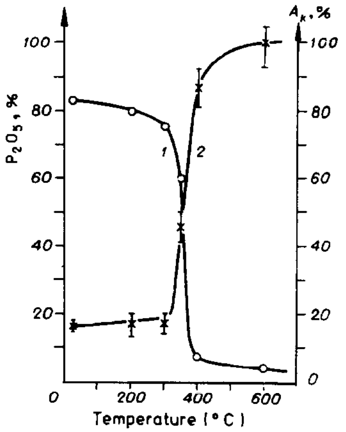

Fig. 8. Changes in solubility of kola apatite in 5% ammonium citrate aqueous solution (1) and half-width of X-ray line (2) after heating of a sample at various temperatures.

fertilizing properties of mechanically activated phosphate are comparable to those of commercial superphosphate [23,24].

In contrast to the mechanical activation of apatite, the activation of ferrites proceeds via the formation of their metastable state via the redistribution of bi- and trivalent cations between the octa- and tetrahedral positions.

Studies in our Institute [25] have shown that if the capacity of the mechanical impulse is large, mutual shifts of planes in the oxygen sublattice could be achieved. The displacement in the (111) direction is especially important, for here the planes can shift in a vector that is smaller than that typical of the oxygen sublattice in a spinel structure. As a result, the long-range order in the oxygen sublattice is disturbed whereas the close packing of oxygen atoms is preserved. The resulting oxygen lattice might be a hybrid of cubic and hexagonal sheets. As a consequence, the number of neighbouring octahedral sites that are responsible for the cation–anion–cation bond is modified [26] (Table 2, Fig. 9). In particular, the pairs of super-exchanged cations appear with a bond angle different from 90° (usual for the ferrite structure). As a result, the magnetic properties of ferrites are changed. As during mechanical activation amorphization of the structure occurred, the model of the structure of such solids is a random packing of rigid spheres [27]. According to this model, the most probable sites in the oxygen sublattice to be occupied by cations are octahedral sites [28,29].

Mössbauer spectroscopic data support this point of view. From these data it follows that during mechanical activation of ferrites all the cations that previously occupied tetrahedral sites move into octahedral positions. The physical consequence of this is an increase in magnetic ordering during the treatment. This result is striking in itself, but it also has a chemical

TABLE 2

Dependence of the number of octahedral sites nearest to cations with various cation–anion–cation bond angles on the type of oxygen sublattice A-cation

Type of oxygen sublattice	No. of octahedral sites, corresponding to cation–anion–cation bond angle			
	71°	90°	132°	180°
Cubic ABCABC	0	12	0	16
Hexagonal ABAB	2	6	12	0
Hybrid BABC	1	9	6	3

after-effect. For example, the order of leaching of cations from spinels is changed after mechanical treatment. It is well known that zinc cations pass into solution first by acid leaching of zinc ferrite, followed by iron(III) cations. In the leaching of mechanically activated zinc ferrite with hydrochloric acid the reverse occurs: iron(III) ions pass into solution first, and only then are zinc ions leached. In this way, mechanical activation of solids makes it possible to develop new methods of producing amorphous spinels. The advantage of the method is its simplicity and the possibility of carrying out the amorphization of spinel in stages. Each stage can be controlled by selecting the kind and number of mechanical impulses.

Mechanical treatment by power impulses carried out on other types of compounds with structures similar to spinels (e.g., chalcopyrite) has given analogous results: after mechanical treatment and amorphization the coordination of the iron(III) cation is changed from tetrahedral to octahedral [30]. The process known as mechanical alloying can be cited as a good example of mechanochemical reactions. Mechanical alloying involves the production of metal powder with a controlled microstructure by repeated welding, fracturing and rewelding of a powder mixture under the action of mechanical impulses [31]. In contrast to conventional ball milling, the rates of two

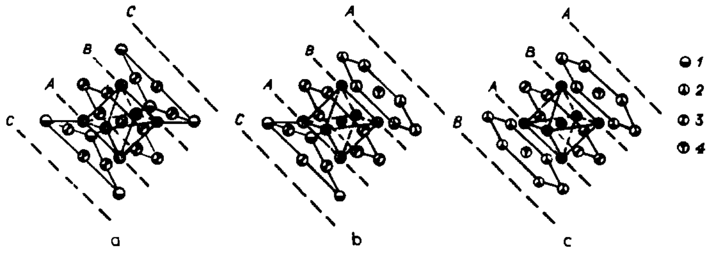

Fig. 9. Possible distribution of ions in two nearest coordination spheres of a given cation by different kinds of anionic sublattice symmetry. a = Cubic; b = hybrid; c = hexagonal. Oxygen octahedra are singled out. The possible positions of cations in the second coordination sphera are denoted by the cation–anion–cation angle: (1) 180°; (2) 132°; (3) 90°; (4) 71°.

competing processes: fracture and welding during mechanical alloying are balanced.

Mechanical alloying gives the possibility of producing metastable structures with morphological and compositional instability, which results in increase reactivity of the alloy obtained.

Omitting the well-known physical and metallographical consequences of mechanical alloying, we can point out here some interesting chemical consequences. The formation of so-called super-corroding alloys for hydrogen production is a good example of an increased reactivity as a result of mechanical treatment [32].

The reactivity towards hydrogen of the mechanically alloyed mixture $2Mg + Ni$ was compared with that of the Mg_2Ni alloy prepared by melting and sintering. It was found that mechanically alloyed MgNi has an increased reactivity towards hydrogen, but the explanation of this increased reactivity as being due only to an increase in the reaction surface seems to be inadequate when one bears in mind the experimental results of the authors themselves and the data obtained in our laboratory on the formation of a special electronic excited state between nickel and magnesium.

It should be emphasized that on going from a commonly used system based on homodesmic metals or alkali metal halide ionic compounds to more complicated, heterodesmic systems, the mechanisms of plastic deformation will be completely different. The dislocations in composite heterodesmic compounds (e.g., aluminosilicates) have much higher Burgers vector. Part of the chemical bonds in these compounds are covalent, e.g., directed. As a result of the heterodesmic structure and covalent bonds, the amorphization proceeds very easily on mechanical treatment. During amorphization solids are enriched by a large number of free dangling bonds.

The mechanical activation of silicon dioxide (silica) can be regarded as a good example. The lattice of silica consists of SiO_4^{4-} tetrahedra linked through oxygen bridges with an O : Si ratio of 2 : 1, every oxygen being shared by two silicon atoms. Each silicon atom is surrounded by four oxygen atoms forming tetrahedra.

There are two kinds of bonds in silica: strong covalent bonds between silicon and oxygen atoms and weak pseudo-covalent bonds between silicon atoms. In contrast to the metals, where the movement of dislocations is important, in plastic deformation the deformation of silica is basically determined by the number of the broken bonds between silicon and oxygen atoms and their subsequent relaxation. As a result, amorphization occurs in the form of a lens orientated in some preferential crystallographic directions [33]. As the rupture of silicon–oxygen bond proceeds mostly irreversibly, the formation of paramagnetic centres, occurs which can be detected by ESR [34,35].

Similarly, amorphization occurs during the action of mechanical power impulses on other compounds with covalent bonds (or with mixed ionic and covalent bonds). It can be observed by the plastic deformation of the feldspar, plagioclarse and other frame silicates and aluminosilicates. For sheet silicates (amphiboles) amorphization manifests it to a smaller extent [36]. The features of amorphization processes in this instance are strongly determined by crystallographic orientation [37]. This orientation correlates well with the positions of silica–oxygen chains in crystals. With spodumen and lepidolite we have shown that amorphization detected by X-ray line broadening is strongly anisotropic. Just like amorphous spinel formation, amorphization of silica and silicates does not occur until the mechanical impulse has some critical power level.

This is one of the main reasons why mechanical treatment in apparatus with high-power mechanical impulses (planetary mills, attritors, vibration mills, etc.) results in amorphization and the formation of paramagnetic centres in silica, whereas milling in the usual mills (ball mills, rollers, crushers) merely leads to trivial fragmentation.

Thus, as we have seen from the examples given, for activation to occur it is necessary to have a given power of the mechanical impulse. Hence mechanical treatment with the aim of activation must be carried out in the corresponding regime. Because of this, a high power of mechanical treatment and an impulse character are essential for activation to be achieved. For example, the effectiveness of activation in a vibration mill is dependent on the amplitude of the vibration and there are only weak correlations between effectiveness and frequency in a mill.

Hence dry treatment with chiefly plastic deformation in the contact zone as the main physical results of treatment turns out to be much more effective than wet milling, where the main channel relaxation of stress field is fragmentation. From this point of view, possible effects connected with the packing of solid particles during their presence in apparatus for activation should be evaluated: the distribution of loading between particles that undergo the treatment, the type and value of deformation on contact between the particles, etc.

Thus one should expect (and we have experimental evidence of this) mechanical activation to proceed not at the initial moment of comminution when the major part of the energy will be spent on fragmentation, but some time later when the particle size reaches some critical value.

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