Metastable Phase State During Mechanical Alloying

Yu.A. Skakov
Moscow State Steel and Alloys Institute (Technological University), Leninskii prospect. 4, Moscow, 117936 Russia

Abstract:

The interstitial mechanism of interdiffusion is effective under the conditions of powder treatment in high-energy ball mills. The major arguments to support this point of view are the following: (1) intermetallic phases are formed in sequences strictly determined by the asymmetry of the partial diffusion coefficients, the first to emerge being an intermetallic phase based on the low-mobile component; (2) the experimental evidence demonstrating the similarity of diffusion mechanisms in Mechanical Alloying (MA) and Solid State Reactions (SSR) in the course of annealing of diffusional pairs. The asymmetry of partial diffusion coefficients and the interstitial diffusion mechanism during annealing are determined by thermal activation, while in MA, the same is due to mechanical activation. Finally (3), our approach is based on the theory of Indenbom and Orlov explaining the plasticity mechanisms by the generation and movement of interstitial atoms under large or impact strains at low temperatures. The formation of certain phases during MA can be delayed due to the lack or insufficiency of vacancy mobility, if the thermodynamic driving force is much too low to be able to overcome the energy barriers for nucleation and growth. In the Cr-Ti system, formation of stable Laves-phase and amorphization occur during post-MA annealing.

Keywords: Diffusion, severe plastic deformation, point defects, interstitial atoms, Ni-Ti, Cr-Ti.

Introduction

Being able to predict the results of any material treatment (or production) method is essential for this method to become a real technology. For the mechanical alloying (MA) technology, such predictions have to be based on phase equilibrium diagrams and conditions for metastable phase formation, both general (as determined by the theory of phase formation) and peculiar to the given method.

The experimental evidence collected in a review on solid solutions obtained by MA methods [1] was compared with phase diagram data and results of the liquid quenching (LQ)
method. It was found that, in most of the systems studied, limiting solubility under the given extreme treatment was either equal or fairly close to the maximum solubility determined by equilibrium phase diagrams. Yet, in some systems, substantial deviations were observed, e.g., the extended solid solution of titanium in nickel [2, 3].

Since MA is markedly far from an equilibrium processing technique and because of the large thermodynamical driving forces involved in the component interaction, the probability of the formation of metastable phases is especially high. Connected with this, when one considers the role of diffusion and the level of thermodynamic stability of MA products, it would be more instrumental to focus on instances of correspondence between the synthesised products and the known equilibrium phases rather than on the cases of their miscorrelation. This is particularly important for phases, whose position on the phase diagram is theoretically substantiated. One example is the solubility limit of polyvalent elements in 1B group metals (i.e. the Hume–Rothery rule). The reviewed data [1] demonstrate that this rule is observed both under MA and under LQ. These correspondences enable one to view the cases of no correspondence with the equilibrium phase diagram as, above all, thermodynamically consistent (metastable) states. The phase-formation process affecting the component composition has to involve diffusion, i.e., directional movement of atoms under the chemical potential gradient. The key role of lattice diffusion in phase formation during MA was shown for some equilibrium intermetallics [3]. The present paper is devoted to the interplay between the deformation mechanism and interstitial diffusion as well as to the role of vacancies in the phase formation process.

2. Experimental

Mechanical alloying was carried out in a planetary-type ball mill (AGO-2U) with drum water cooling. The drum was rotated at 685 or 1000 rpm. The sample mass was 10 g and the ball mass (Cr-steel; diameter, 3–5 mm) 200 g. The ambient gas was air and, in some tests, argon. The ball temperature was estimated by computer simulation of ball motion [4] and, at 685 rpm, did not exceed 200°C. X-ray diffraction was carried out using a DRON-4 instrument, with Co Kα- (or Cu Kα-) radiation and a graphite single-crystal monochromator for diffracted beams. The powder morphology (Ti + Cr) was studied using a light microscope and micro hardness measurements.

3. Results and Discussion

3.1. The principal function of Severe Plastic Deformation in Mechanical Alloying

The MA course is determined not only by thermodynamic characteristics of the initial state and the final product but also by the kinetic conditions created by cold high-energy plastic deformation. These conditions include first of all the mechanism of plastic deformation itself, because it can account for a certain part of the overall mass transfer. To understand the mechanism of deformation responsible for the MA effect, one should consider side by side different processes of deformation able to give rise to such effects, including ball milling, shear under high pressure and deformation by explosion. It seems that the term high-energy cold deformation is applicable to all of them, so these deformation methods were classified as “specific and failing to be described by the existing theories of solid body deformation” [5]. Indeed, the conventional concepts of mechanisms of crystal plasticity (dislocation movement) and diffusion (through vacancies) do not explain convincingly the high process rates, supposed diffusion mechanism and bearing in mind that the temperature of the reacting material remains close to the room temperature [6].
In general, mechanical alloying results from the chemical interaction of components. Given that the new phase originates in a series of solid-state reactions proceeding at temperatures close to room ones, it is straightforward to suppose that these reactions occur at the interface of the initial component phases. The role of plastic deformation then would be limited to breaking of the initial material into small particles, roughening of contact surfaces and production of some mechanical activation. Despite the lack of clear-cut models of such activation, the notion of the crucial role of material grinding is quite widespread [7].

In metal systems, particle dispersion is limited by the high plasticity of the material [8]. On the other hand, because of the high affinity of metals for reciprocal dissolving, chemical interactions occur not only at the interface of adjacent particles but also within their volume. It is obvious that this phenomenon can take place only with a sufficiently high mobility of atoms.

In our papers published in 1992–1996 [9-10], a number of observations were made indicating that interstitial atoms are formed (in Ni- and Fe- powders) in the course of ball-milling. Thus, the lattice parameter of coarse-grained Ni powder was found to increase as a result of ball-milling under the conventional MA (without a second component). Having assumed that the reversible part of this increase in the lattice parameter could be accounted for by the formation of interstitial atoms in the course of deformation, which disappear after heating to 200°C (annealing), the concentration of interstitial atoms was estimated at 1–2%. It is worth noting that the lattice parameter of ultra fine-grained powder (70 nm) did not increase at all under ball-milling.

It followed from the studies by Golovin and Tyurin [11] and from those by Indenbom and Orlov [12,13] that mechanochemical synthesis could not be understood unless plasticity was viewed as a process of generation and movement of interstitial atoms or crowdions.

The well-known fact that alloying virtually stops together with the mill engine, was one of the major arguments in favour of such a view and actually it gave rise to our hypothesis that interstitial atoms were implicated in mass transfer and diffusion during MA. More than three decades ago, in a theoretical work, Indenbom and Orlov [11, 12] proposed a theory of generation and movement of interstitial atoms (or crowdions) as a mechanism of plastic deformation under large load or (high-rate strain) at low temperatures. The first experimental evidence for this mechanism was obtained in electron microscopy studies conducted shortly afterwards [14]. However this theory did not attract much attention until the late 1990s, when it was employed to analyze plastic deformation during micro-indentation. Quantitative data on time profiles of deformation and stored energy were obtained only recently in experiments involving concentrated loads (micro- and nanoindenting) [11].

The late appraisal of this theory could be explained by the lack of engineering interest. We will show that MA is the technology where the Indenbom-Orlov theory does work.

3.2. The Key Role of Lattice Diffusion. Interstitial mechanism of diffusion

An unambiguous answer to the effects of the diffusion mechanism among other kinds of mass transfer can be obtained by comparing the experimental mass transfer data with equations of the phenomenological diffusion theory. In the case of mechanochemical synthesis, however, the structural state of the material, the interface area, and the diffusion pathways are changed continuously by plastic deformation. All this makes obtaining quantitative data a hard task. A different approach for elucidating the role of diffusion is to rely on qualitative phase formation features. Thus, it was proposed [3] that the sequence of formation of intermetallics (IM) should be used instead of the numerical values of the diffusing component concentration variation to determine the direction of mass transfer as a function of the duration of treatment. The chemical composition of IM is known and so their
formation sequence will reflect the variation of the chemical composition at the diffusion front. If the partial diffusion coefficients are markedly different and the system allows the formation of more than one chemical compound, then the first to emerge will be the one deriving from the low-mobile component. This component (e.g., Ti in Ni+Ti- system) is diluted by atoms of a fast-moving component (here, Ni) until the concentration allowing for the formation of nuclei of the new chemical compound is reached; for the Ni-Ti system, this compound is NiTi₂. This is what was experimentally found in full agreement with the relationship of the partial diffusion coefficients available from high-temperature measurements: the diffusivity of Ni into Ti is at least two orders of magnitude greater than that of Ti into Ni [15]. If the concentration of the fast component in the initial powder mixture is larger than the homogeneity limit of the first IM, diffusion goes on and at some level of supersaturation, in accordance with the general theory of phase formation and the theory of reaction-diffusion; the next IM-phase nucleates and starts to grow. Diffusion of the fast-mobile component continues in the same direction (i.e., into the phase containing a low-mobile component).

We identified several two-component systems for which data were available on equilibrium phases, phase diagrams, synthesis products (our own data or borrowed from literature), and partial diffusivities, the latter obtained by conventional methods in interdiffusion studies, through high-temperature annealing.(mainly, from the Metal Reference Book, by C. Smithells)

This choice, of course, derived from an assumption that there was something common in the diffusion mechanisms at high (thermal activation) and low temperatures (additional mechanical activation). This common feature consists above all in the lattice nature of the diffusion, involving point imperfections. Whenever interstitial atoms play a significant part in diffusion, the partial diffusion coefficients have to be markedly different. In this work, a sequence of phases was studied for systems with the ratio of partial diffusivities ranging from \( \frac{D_A}{D_B} = 1.5 \) to ~100 (the Cr-Ti and Ni-Ti systems, respectively).

The results of this study unambiguously showed that the formation of phases in all the systems considered (Ni-Ti, Ni-Nb, Al-Ti, Cr-Ti, and Fe-Sn) was determined by lattice diffusion, given that the first phases to emerge were IMs based on the low-mobile component (Ti, Nb, Sn) in accordance with the known ratio of partial diffusivities [3]. Under the conditions of powder treatment in a high-energy ball mill, the mechanism of lattice diffusion by means of continuously generated interstitial atoms is the most likely, if not the only one, plausible.

This conclusion is confirmed by comparing the orders of magnitude of the Ni-diffusion coefficients in the mechnanochemical synthesis of NiTi₂ [10] and in the amorphization reaction of the Au/La diffusion pair [16]. For the latter system, not only the partial Au -diffusion coefficient was known but also the interstitial diffusion mechanism was definitely shown to be active.

The order of magnitude of the diffusion coefficient under mechanical activation was estimated from the expectation time (ball-milling duration) for the first particles of the NiTi₂ intermetallic to appear. To be more accurate, from the appearance time of a Bragg reflection at the site of the strongest line of NiTi₂ (115). Bearing in mind the sharpness of the line, the particle size of the new phase (and the diffusion path) was estimated at 100 nm. The treatment duration before the appearance of the reflection was 1–5 min. Assuming it to be 100 s, we found \( D \sim 10^{-12} \text{ cm}^2/\text{s} \). A similar order of magnitude of \( D \) was obtained from data on the diffusion annealing of an Au + La composite with a layer width of ~10 nm, at the temperature \( T = 50–80 \) °C [16]. temperature ranges in both cases are roughly equal, and so it can be supposed that, both under thermal (Au diffusing into La) and mechanical activation (Ni diffusing into Ti), diffusion proceeds by means of interstitial atoms.

Experimental evidence to support the proposed mechanism of synthesis reactions under thermal and mechanical activation can be found in [17], where the similarity of these
two processes was convincingly shown. In this work, amorphization of the Ni + Zr mixture under mechanical activation was carried out up to a given degree of transformation upon which the powder was placed in a DSC apparatus and heated at a steady rate. The authors show that amorphization of the part of the mixture that failed to react in the drum (until the mill was stopped) continued inside the calorimetric cell under heating, that is under thermal activation.

Fig. 1 Schematic representation of the diffusion currents in a diffusional A/B pair for a high-mobile component A and a low-mobile component B \((D_{A\rightarrow B} >> D_{B\rightarrow A})\) assuming formation of point defects near the A/B interface under thermal activation. The difference between the atomic radii of A and B is one of the most important parameters characterizing diffusional pairs with anomalously high diffusion mobility for one from components (for example Au/La).

A common feature of all the three systems mentioned above is a marked asymmetry of component diffusivities under normal conditions (particularly so, for Au-La), which is typical for the diffusion involving interstitial atoms (Fig.1). This asymmetry can, apparently, become more prominent under mechanical activation or significant, if it was not manifested
under thermal activation [18]. This fact explains the potential applicability of the MA technology to a wide range of systems.

### 3.3. The transformation under annealing conditions after mechanical alloying

With some systems, subsequent heating of the MA product brings its phase state closer to equilibrium. Hence, the question arises concerning the reasons for which this equilibrium state is not reached in the course of MA. The first necessary condition for any system—the sufficient diffusion mobility—is provided by the continuous production of interstitial atoms. There is, however, another important condition: a sufficiently strong thermodynamical driving force to overcome the energy barriers for nucleation and growth of a new phase [18].

It is known that intermetallics with complex crystal structures fail to nucleate without the participation of vacancies. For this reason, a new phase does not form in MA, particularly for low values of the Gibbs energy and under a weak thermodynamical driving force. The formation of IM (i.e., its precipitation from a supersaturated solid solution) can occur under thermal annealing after mechanochemical synthesis, at a point when the concentration and mobility of vacancies become sufficient (e.g., Cr₂Ti at 650-750 °C).

The major barrier at low temperatures and widely different specific volumes of the original and new phases is associated with the elastic deformation energy. If the new phase has a smaller volume, the elastic deformation is compensated by the inflow of interstitial atoms. On the other hand, the formation of a phase with a larger volume than the matrix phase is facilitated due to the inflow of vacancies. If the thermodynamical driving force is too low the process can not occur during MA but becomes possible under heating to temperatures at which elastic deformations can be compensated by the inflow of vacancies possessing increased mobility.

The delay in the formation of the amorphous phase and its precipitation under heating (at 550-650 °C) was observed in the Ti-Cr system. An amorphous phase was formed from a matrix with a BCC lattice under a relatively small thermodynamic driving force, when the supply of vacancies is needed. This example is interesting not only because it explains the so-called "spontaneous amorphization" under heating but also because it provides reliable (even if indirect) evidence for the immobility of vacancies at low temperatures in mechanical alloying by ball milling. This, in turn, confirms the interstitial nature of the diffusion process in MA.

### 4. Conclusions

1. The deformation conditions in a high-energy ball mill, i.e. heavy loading and high strain rates, at temperatures close to room temperature are similar to the ones under which according to the Indenbom–Orlov hypothesis, the mechanism of plastic deformation involving interstitial atoms could be effective. Under the conditions of powder treatment in a high-energy ball mill, the mechanism of lattice diffusion by means of continuously generated interstitial atoms is the most likely, if not the only one.

2. The prevailing diffusion of one of the components undergoing deformation in a high-energy ball mill is observed even with elements having close positions in the Periodic table and roughly similar diffusivities at elevated temperatures (in the Ti-Cr system, the fast element is Cr). Consequently, in addition to the usual thermal activation, diffusion can also be activated by mechanical treatment in a high-energy ball mill due to generation of interstitial atoms (mechanical activation).

3. An amorphous phase does not form during the MA process of the Ti-Cr system
(amorphous modification of the Laves phase) because of the large difference between specific volumes of the amorphous phase and crystal matrix. In order to compensate the elastic deformation, a supply of vacancies must be provided, and, for this reason, amorphization can occur only under annealing after MA (the effect of "spontaneous amorphization"). This effect provides evidence for the absence of sufficient mobility of vacancies under MA conditions.

References


Резюме: Известное для ряда металлических систем явление аномально быстрой диффузии одного из компонентов диффузионной пары, которое связывается с движением такого компонента по междоузлиям, распространено на диффузионный процесс при механическом сплавлении (МС). Диффузия по междоузлям оказывается эффективной в условиях обработки порошков в высокоэнергетической мельнице. Главные аргументы: (1) образование интерметаллидов происходит в строгой последовательности, которая
определается соотношением парциальных коэффициентов диффузии, первым является интерметаллид на основе малоподвижного компонента; (2) успешное прогнозирование первого продукта МС при использовании соотношения парциальных коэффициентов измеренных обычными способами при высокотемпературном отжиге говорит о близости механизмов диффузии (или о совпадении основного механизма). Известно, что при высокотемпературном отжиге таким механизмом является решеточный механизм по вакансиям (термическая активация), а в ходе деформации пориста в шаровой мелочи при МС (температура не сильно превышает комнатную) также основным может быть решеточный но по междоузлям (механическая активация); (3) последнее положение вполне согласуется с теорией Инденбома-Орлова, которые для больших нагруженей и достаточно низких температур предложили механизм пластической деформации путем генерации и движения точечных дефектов. Проведен анализ причин задержки образования некоторой стабильных интерметаллидов в ходе МС (например, фаза Лавеса в системе Cr-Ti) накрп после МС приводит к образованию такой фазы благодаря повышению концентрации и подвижности вакансий. Эти наблюдения косвенно говорят об отсутствии заметного участия вакансий в диффузионных процессах в ходе МС (низкая температура!).

Ключевые слова: Диффузия, пластическая деформация, точечные дефекты, внедренные атомы, Ni-Ti, Cr-Ti.

Содержание: Интерметаллни механизм лежащие в основе диффузии являться эффективным у условий диффузии в высокуглеродистых меловитах. Главные аргументы которые подрываются в протекании приведены следующие: (1) интерметаллические фазы формируются в эвтектике которые существуют строго определенные асими́трии парциальных коэффициентов диффузии, после которых интерметаллические фазы состоянны на малоподвижной компоненте; (2) экспериментальные доказаны которые убедительные диффузионные механизмы за механической активацией и реакциях в результате фазы током одгрева фазы. Активация парциальных коэффициентов диффузии и интерметаллических диффузионных механизмов током одгрева фазы одре́денный по теплоте активации, пока́же, точные коэффициенты одговорны за механическое легирование; (3) наш приступ был засвидетельствован на теории Инденбома-Орлова, подтверждающий механическое образование и крепление интерметаллических атомов под условиями таких или ударных напряжений на высоких температурах. Формирование одре́денных фаз током механического легирования возможно за обложением због недово́льные покрета за вакансию атома, который вентом допустимой энергетической бариере для нуклеации и распада зерна. В систему Cr-Ti формирование стабильных Лавесовых фаз и аморфизация одновременно после механического легирования.

Ключевые речи: диффузия, пластическая деформация, тачкасти дефекты, интерметаллические атомы, Ni-Ti, Cr-Ti.