MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5411–5415

On the analysis of mechanism of supersaturation of metal powders with interstitial impurities during mechanical activation

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The paper discusses the mechanisms of formation of nanostructure, chemical and phase composition, and dispersity of the particles of metal powders obtained in the process of mechanochemical activation and of mechanical alloying. It has been shown that the processes of plastic deformation and disintegration of the particles are realized via macrodislocations, which are the linear defects of nanostructure. The moving macrodislocations create around themselves the clouds of impurity atoms, the transfer of which determines the mechanism of strong supersaturation with impurities and the structural-phase composition of the powders obtained.

The mechanisms of the mechanical alloying of iron with carbon have been studied. A model has been proposed for the nucleation and growth of cementite via the formation of the nonequilibrium interstitial phases. Carbon segregations have been investigated, the distribution and density of which are mainly non-uniform and are fully determined by the interstitial phase structures. Within the frames of the model proposed the existence of an amorphous iron phase in a special "cluster-isolated" state has been predicted.

1. Introduction

The effective practical application of mechanochemical techniques requires the knowledge of the mechanisms that determine the formation of the main physicochemical characteristics of the material produced (dispersity, structural-phase composition, magnetic characteristics, etc.). The present paper is the review of the results of our investigations of mechanisms of the formation, plastic deformation, and destruction of nanostructures as well as those mechanisms that limit the dispersity of the powders obtained during mechanical disintegration. With the Fe-C system taken as an example, the mechanisms of particle saturation with interstitial impurities are discussed along with the features of formation of structural-phase composition during mechanical activation (MA).

2. Mechanism of nanostructure formation in metal powders during MA

One of the specific features of the MA method is that a powder particle is subjected to an impact loading. The time of action τ_1 is determined by the rate of rotation of the mill and lies within 10^{-3}–10^{-6} s. Owing to severe plastic deformation, particles suffer strong dynamic hardening and their temperature can increase up to the melting temperature T_m. At $T \leq 0.4T_m$ hardening results in the formation of a cellular dislocation structure with subsequent prerecrystallization polygonization. As the temperature exceeds $0.4T_m$, the processes of primary recrystallization, the centers of which are mainly formed at defect pileups, become dominant. Within the time τ_1 grains have no time to grow significantly, since after the termination of the action a particle is sharply cooled in a surrounding medium to temperatures close to room temperature. Thus, the structure of the particles contains numerous isolated nanograins. In the remaining part of the particle, accumulation of further generations of nanograins takes place until the entire particle acquires a nanocrystalline (NC) structure. In addition, the particles can be saturated with impurities that are the products of the decomposition of the milling medium [1]. The above scheme of the formation of NC structure (Fig. 1) appears to be quite general and is applicable to many plastically deformed materials [2].

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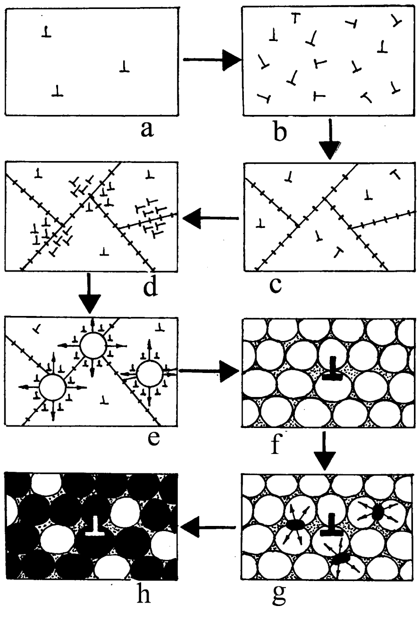

Figure 1 Formation of nanostructure and phase composition of powders: (a) initial defect structure of an isolated crystallite; (b) increasing dislocation density in the beginning of the process; (c) formation of substructure in a crystallite by polygonization at high temperatures; (d) appearance of recrystallization zones in the form of microregions supersaturated with dislocations; (e) formation and growth of isolated nanograins; (f) completion of recrystallization processes, formation of nanostructure with mobile macrodislocations (symbol $\perp$ denotes the site where the center of the macrodislocation core is located; (g) supersaturation of grain boundaries with impurities, nucleation and growth of grains of a new phase; (h) multiphase nanostructure after long-term disintegration.

3. Mechanisms of plastic deformation of NC materials

One feature of NC state is that the bulk of nanograin is virtually defect-free. In this case, dislocations present in the bulk of grains emerge onto grain boundaries, ensuring the forming of an amorphous-like thin-film state of the substance on them. Thus, powder particle can be represented as a set of close-packed nondeformable spheres bound by a liquid-like medium at the boundaries.

To such a material, we can apply a theory of macrodislocations developed in [3]. The heart of the model is the assumption that in such materials, plastic deformation is effected via macrodislocations, which are linear defects of a regular packing of nanograins. This model is schematically shown in Fig. 2. If NC materials were built as regular packing of nanograins, in planar section they would look what is shown in Fig. 2a. The existence of liquid-like medium at nanograin boundaries would give a pattern shown in Fig. 2b. A regular packing of grains can contain such defects as demonstrated in Fig. 2c. The existence of liquid-like medium on NC boundaries leads to the appearance of macrodislocation shown in Fig. 2d. Under the effect of mechanical action, these macrodislocations will move, effecting plastic deformation via inter-grain sliding.

The measure of yield point σ_Y for the materials where macrodislocations are the main carrier of plastic deformation is given as follows [3].

$$\sigma_Y = \frac{2G}{1-\nu} \exp\left(-\frac{4\pi\xi}{b}\right), \tag{1}$$

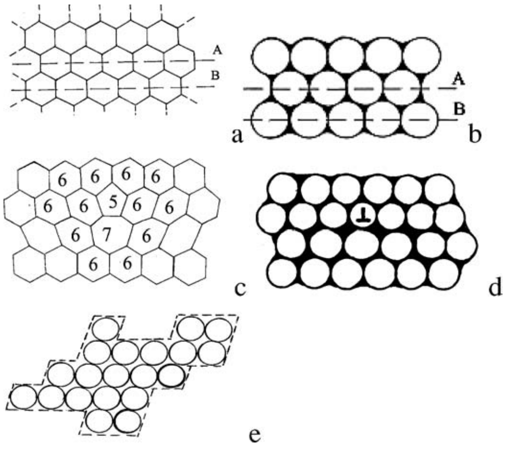

Figure 2 Model of plastic deformation of NC material.

where G is a shear modulus of a medium, ν is Poisson's ratio, b and ξ are Burgers vector and macrodislocation width, respectively.

Since flow in thin liquid layers is realized via diffusion initiated by shear stresses, for the shear modulus G the following expression can be obtained:

$$G = \frac{1}{3}\left\{K_l\left[\frac{R}{V_l^2\left(R + 4\sqrt{\frac{D\Omega\delta K_l}{12kTRv_d}}\right)} - V_l\right] - K_S V_S\right\}, \tag{2}$$

where K_l and K_s are the moduli of compression of the liquid-like and solid phases, respectively; V_l and V_s are the volume fractions of these phases; D is the self-diffusion coefficient in the liquid-like phase; Ω is the atomic volume; δ is the grain-boundary thickness; k is the Boltzmann constant; T is the temperature; and v_d is the velocity of movement of macrodislocations, R is the radius of NC.

It follows from (2) that the shear modulus of G tends to zero if $v_d \to 0$, $R \to 0$ or $T \to T_m$. This implies that under certain conditions a transition into superplastic state is always possible for NC materials.

It should be noted that a macrodislocation is a structural defect that represents a carrier of plastic deformation on meso- and macrolevels. Its role as carrier of plastic deformation becomes of more importance with the decrease (for some reason) of the number of ordinary dislocations, which are the carriers of plastic deformations on microlevel. It is just the situation that is observed in NC and amorphous materials [3, 4].

4. Mechanisms restricting dispersity of powders during mechanical disintegration

If metal powders are to be milled in a surfactant that gives interstitial impurities, dispersity of powders can be restricted by a superplasticity effect [2]. In this case the value of modulus G (formula (2)) is insignificant and macrodislocation mobility is high since it is fully determined by mass transfer along grain boundaries. At the same time, surfactants can drastically decrease the energy barrier of macrodislocation migration to an outer surface. As a result, macrodislocations can freely realize any plastic deformations without causing any destruction. In this case powder dispersity will stay unchanged, and particles will have shapes of discs with a low thickness-to-diameter ratio.

When macrodislocations emerge onto the external surface of a particle, steps are formed similar to those shown in Fig. 2e by dashed lines. It is important that the height of the steps is to be multiple to the average size of nanograin. This fact was studied experimentally on Fe powder samples, obtained by milling in the presence of surfactants [1]. X-ray diffraction showed that the particles had NC structure—the size of grains after 1-h milling was $(2.4 \pm 0.4) \times 10^{-8}$ m. To investigate the microstructure of surface, we used atomic force microscopy (AFM). The width of the steps in Fig. 3a is about 2×10^{-8} m and corresponds to the size of a single grain. In Fig. 3b width of steps is 10^{-7} m and is multiple to five grain sizes.

At sufficiently low temperatures, high nonuniformity of the NC structure, or at low mobility of atoms at grain boundaries, the conditions necessary for the effect of superplasticity to occur may not arise. In this case, blocked dislocation pileups will arise, which are sources of high stresses capable of causing fracture. As a result, the particle will disintegrate until its size becomes less than the size of a macrodislocation pileup capable of providing fractures. This condition permits us to estimate the minimum dimensions of powder particle obtained by MA.

The minimum (in length) pileup can consist of two macrodislocations; therefore, the minimum dimension of particle cannot be smaller than the size of such a pileup. It is known from the theory of dislocation pileups that their length l is unambiguously related to the number of dislocations and to the blocking stress σ. The expression for a pileup of two dislocations is as follows

$$l = \frac{bG}{2\pi(1-\nu)\sigma}. \tag{3}$$

The minimum length can be obtained by setting $\sigma = \sigma_u$ (fracture stress):

$$l_{\min} = \frac{bG}{2\pi(1-\nu)\sigma_u}. \tag{4}$$

The ratio G/σ_u is usually about 10–10^3 [2]. With the middle values in this range being $G/\sigma_u \sim 10^2$ and $v \approx 0.5$, Equation 4 gives $l_{\min} \approx 30b$.

The size of grains in particles obtained after 99 h of milling is 4×10^{-9} m; therefore, the minimum size of particles is about 1.2×10^{-7} m. The experimentally measured minimum size of particles is $(1.5 \div 2.0) \times 10^{-7}$ m (Fig. 3c), which is in a good agreement with theoretical calculations.

5. Mechanism of saturation of NC powders with interstitial impurities

Strong supersaturation of metal powders with interstitial impurities in conditions of ball milling has been observed in many papers [1,4, for example]. Theoretically it has not been explained yet. The search for the new mechanisms of the convective transfer of impurities along material boundaries can be made much easier if some close features of interaction of dislocations and macrodislocations with impurities are considered. A moving macrodislocation can attract impurity atoms similarly to the ordinary edge dislocations. The macrodislocation nucleus sizes are several orders larger than those of the lattice dislocation nuclei. As a result, an impurity cloud around macrodislocation nucleus is much larger than ordinary Cottrell's atmospheres. These characteristics enable macrodislocations to be an efficient carrier of grain-boundary impurities throughout NC material.

In general, the process of impurity buildup by powder particles is demonstrated in Fig. 4. During MA particles are subjected to almost periodical short dynamic loadings resulting from the mechanical effect of balls (Fig. 4a, curve 1). Let τ_1 be the mean time of particle impact, and τ_2 the mean time of mechanical effect cycle. Then τ_1–τ_2 is the time when a particle stays unaffected. The impurity buildup can take place only during mechanical impact, while in the period τ_1–τ_2 a particle relaxes into some equilibrium state without supersaturation (Fig. 4a, curve 2).

Calculations made in [5] demonstrate that during MA (in a planetary ball mill with drum radius of 0.02 m, angular rotation speed of 76 rad./s, drum rotation circumference radius of 0.1 m, $\tau_1 = 0.7 \times 10^5$ s, $\tau_2 = 25$ s) of iron powder with a particle radius of $R_p = 10^{-5}$ m and NC radius of $R = 3 \times 10^{-9}$ m in the presence of carbon,

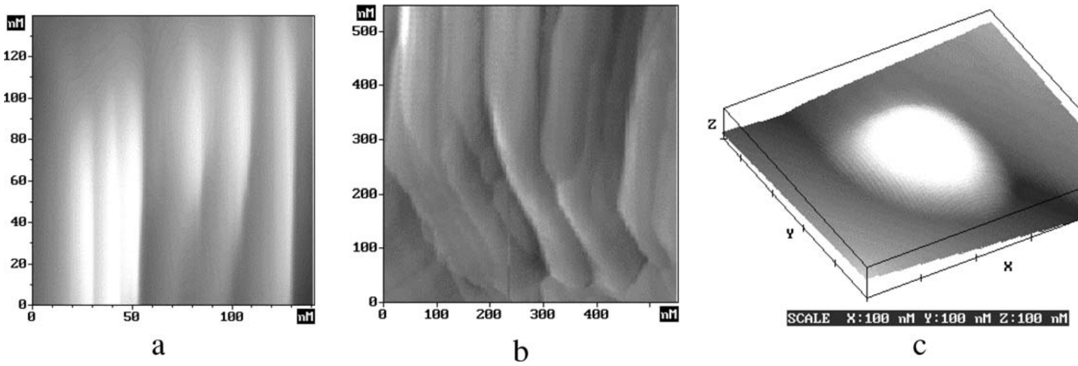

Figure 3 (a and b) AFM images of steps and (c) image of the finest particle.

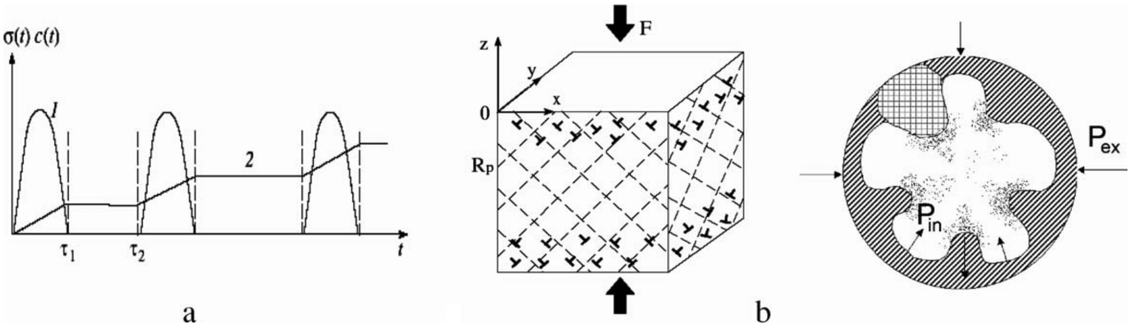

Figure 4 (a) Conditional representations of the dynamic mechanic loading $\sigma(t)$ on a particle (1) and the process of the accumulation of impurity $c(t)$ in particle (2); (b) the conditional representation of the macrodislocation accumulations in a particle at the moment of impact; (c) probable structure of nanocrystallite.

the number of macrodislocations introduced into a particle during one impact is equal to 400 and they cover an average distance of 2.5×10^{-8} m (Fig. 4b). In this case, MA for 21 h is enough to reach complete saturation of NC boundaries with carbon impurities. Although these data are in a good correlation with experiment [4], it should be mentioned that so high supersaturation of α-Fe boundaries is prohibited when taking into account an equilibrium phase diagram for Fe-C.

X-ray diffraction analysis and Mössbauer spectroscopy experiments have shown that NC boundaries are free from both pure carbon and an equilibrium chemical compound (cementite) if concentration of carbon in the initial mixture is no more than 15 at.% [1, 4]. It has been found that α-Fe in close vicinity of NC-boundaries is present in some amorphous state. This enabled us to propose a hypothesis, according to which in conditions of strong carbon saturation interstitial phases of non-stoichiometric composition $Fe_{2-x}C$, $x \in \langle 0, 1 \rangle$ can be formed on intercrystallite boundaries of α-Fe [4]. The hypothesis can be explained as follows.

The equilibrium interstitial phases of carbon form in metals under the condition $a_c/a_{Me} \leq 0.590$ (a_c is carbon atom diameter, a_{Me} is metal atom diameter). Since for an equilibrium bulk state of iron $a_c/a_{Fe} = 0.606$, no areas of interstitial phases exist on equilibrium phase state diagram of Fe-C. On polycrystal boundaries $a_c/a_{Fe} \approx 0.583$, which complies with the condition of interstitial phase existence. In NC-iron, the contribution of boundaries into the total quantity of atoms is comparable with a bulk contribution. This is why the possible existence of interstitial phases with carbon in NC-iron cannot be ignored. In the bulk iron, interstitial phases are unstable, this is why they can transform into cementite when the thickness of their layers will be large enough to locate a large cementite molecule.

Based on theoretical and experimental results, one can draw a conclusion that by the moment of cementite nucleation the most probable internal structure of nanocrystallites will be similar to that indicated in Fig. 4c. Here, the external NC boundary is conditionally pictured as sphere of radius R. Under the boundary a rough layer of interstitial phases is located (shown by single hatch-lines), with cementite growing in its widest places (diced area).

The internal volume of nanocrystallite consists of the solution of carbon in iron, which is considerably segregated in the vicinity of crests (shown by corresponding increase and decrease of density of dots). Since small particles are always characterized by the presence of external Laplace pressure $p_{ex} = 2\sigma_{ex}/R$(σ_{ex} is the surface energy of the external boundary), carbon content in both phases depends exponentially on the NC size:

$$c(R) = c_0 \exp\left(-p_{ex}\frac{\delta V}{kT}\right). \tag{5}$$

Here c_0 is impurity content in a phase at $R = \infty$, δV is the change of volume under the effect of an impurity atom.

Such values of impurity content correspond on average to the central areas of α-solution in NC. Assuming that $\sigma_{ex} \approx 1$ J/m^2, $\delta V \approx 10^{-29}$ m^3, $R \approx (10^{-9} \div 10^{-8})$ m, $T \approx 300$ K, we will obtain $p_{ex} \approx (10^9 \div 10^8)$ Pa and $c(R)/c_0 \approx (10 \div 1)$. These data indicate considerable differences between chemical compositions of nanocrystallite and coarse-grained materials.

Local internal Laplace pressure (p_{in}), which arises in different areas of a rough surface, can have different signs. Hence, areas of local extensions of an α-phase (near ridges) should contain carbon atom aggregations, while areas of local compression (near pits) will have an α-phase virtually clean from impurities. An additional factor to sustain this situation is the effect of the elastic repulsion of an impurity from the boundary of material with a larger shear modulus. Therefore, NC-powder can have an essentially non-uniform local chemical composition, promoted by the Laplacian pressure, surface roughness of interstitial phases layer and elastic effects of interaction between impurities and polycrystal boundaries.

Furthermore, it should be noted that at $R \approx (1.0 \div 1.5) \times 10^{-9}$ m and average thickness of an interstitial phase layer in the order of 0.5×10^{-9} m, an average radius of a NC α-Fe nucleus is equal to $(0.5 \div 1.0) \times 10^{-9}$ m. These values virtually coincide with the radii of clusters in the bulk phase of solid amorphous iron or melt. This suggests that because of the inevitable scatter of R values a mechanically activated iron powder will always contain a certain amount of amorphous α-iron in a special "cluster-isolated" state.

6. Conclusion

A good deal of experimental and theoretical material has been accumulated by now, which makes it possible to explain some mechanisms of formation of physicochemical characteristics of NC powders obtained by MA. The theoretical interpretation of these mechanisms is easily performed through the use of the motion of macrodislocation, which is a linear defect of regular packing of nanocrystallites.

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Received 11 September 2003
and accepted 27 February 2004