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An attempt to extract common behaviour from heterogeneous results about mechanical alloying

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The first stages of the mechanical alloying process, fragmentation and welding, are analysed. In order to clarify the mechanisms of milling-induced diffusion, different interstitial solid solutions are examined. It is shown that diffusion of interstitial is mainly controlled by the stress field. In case of a substitutional solid solution, the mechanism of atomic transport is controlled by shear deformation. The consequence of the corresponding diffusion models are discussed. © *2004 Kluwer Academic Publishers*

1. Introduction

Since about two decades the rather easy deployment of the techniques necessary to achieve mechanical alloying (MA) and mechanosynthesis feeds avalanches of results and publications. Unfortunately, the complexity of the numerous elementary phenomena which are interplaying and interfering are made even more obscure by the ambiguity resulting from delicate and difficult characterization methods. Meanwhile, the driving forces which stimulate so many efforts devoted to mechanical alloying is far from being artificial: macroscopic scale mechanical impacts and the resulting nanoscale atom redistributions are likely to play an important role on biological cells, organic compounds, cosmic dust, welding, friction, new materials, new nanostructures, and technical applications.

Because mechanical phenomena taking place in solids usually do not obey state functions, thermodynamics may appear to be violated. In contrast with mechanochemistry devoted to reactions under hydrostatic pressure of gas, liquid or even solid phases, in the case of ball milling (BM) as well as of under severe plastic deformation (SPD), stress and strain in the elastic as well as in the plastic domains have to be taken into account. As observed during the last century for the understanding of mechanical behaviour of solids, the interpretation of MA may be delayed by the complexity of the role of lattice defects.

The aim of the present paper is to choose, among different results and articles, the arguments which support simple descriptions of the different steps involved in the process of BM and Mechanical Alloying (MA). Facing the innumerable results, interpretations and modelling which have been published, as well as some contradictions and the limit of our knowledge, the risk of a schematic description is taken in order to stimulate some simplification and clarification.

2. Results and discussion

Starting from the hypothesis that the complexity of BM and MA results from the interplay, interference, superposition of elementary phenomena it is attempted below to identify and describe the processes from the basic concepts of physical metallurgy and to discuss their relevance.

2.1. Cracks and fragmentation

It is well known that in ball mills (planetary, rotating, shakers, attritors, vibrating, etc.) the impact of balls submit powders particles of mean size d_p to a stress field σ_a which breaks these particles because σ_a is not hydrostatic. Classical concepts of fracture mechanics established that the resulting stress intensity factor $K \approx \sigma_a\sqrt{d_p}$ leads to fracture when K is larger than the critical value K_c which is characteristic of the materials but also depending of its microstructure, of the environment, of the temperature T and of the stress rate $\dot{\sigma}$.

In case the mean damage length is proportional to the size of the particle under stationary conditions, this size is expected to reach the asymptotic value: $d_p \approx K_c^2 \sigma_a^{-2}$.

As shown by the pioneering analysis of Griffith K_c varies as $\sqrt{E\gamma}$ the square root of the product of the Young modulus E by the surface energy γ. Because according to the composite model of nanomaterial, bulk and grain boundary [1, 2], E decreases with the grain size and with the amount of lattice defects and because γ varies with contamination likely to saturate frustrated chemical bonds at the surface, the stationary conditions may not to be satisfied and the asymptotic behaviour may be masked. The kinetics of mechanical alloying, of evolution of microstructure, of contamination and of fragmentation do not coincide. Therefore in systems for which K_c is very sensitive to composition of the powder, to defects, to grain size, to contamination, the expected asymptotic behavior becomes unlikely.

The variation of surface energy γ through chemisorption by chemical species unintentionally or intentionally present in the milling device contribute to the interpretation of the well established observation according to which the kinetics of the MB or MA reaction can change dramatically under the influence of additional agents, changing γ.

2.2. Welding and crack healing induced by ball milling

As quoted by many reviews and books devoted to BM and or MA a welding process of particles is competing with the fragmentation and fracture process. In a preliminary approach it was proposed that cold welding of solid surface supposed structural as well as chemical coherency [3]. Meanwhile these conditions appeared too restrictive, under intensive cold rolling of duplex Fe-Cu alloys it was shown [4] that cracks appeared during a first stage of rolling but also that, further cold rolling did lead to a refinement of the microstructure and to the complete healing of cracks. These observations have been confirmed on duplex stainless steel and more recently observed by in situ transmission electron microscopy on α-Fe [5].

As shown by many experimental results, as well as by different numerical simulations, the surfaces and interfaces of specimen submitted to SPD obtained, e.g., by equal angle extrusion, intensive low cycle fatigue, torsion, BM, are characterized by fractal dimension larger than 2 and are surrounded by an intense work-hardening zone spreading on the surface area S up to a depth e and characterized by an energy per volume unit W. Both of these observations suggest conditions of crack healing under a closure compression stress field, given by:

$$S(\gamma_{\mathrm{A}} + \gamma_{\mathrm{B}} + e_{\mathrm{A}} W_{\mathrm{A}} + e_{\mathrm{B}} W_{\mathrm{B}}) > S(e_{\mathrm{A}} + e_{\mathrm{B}}) W_{\mathrm{AB}}$$

where W_{AB} is the volume energy after welding. The kinetic conditions for transport of matter from the excess zone to the depleted one is likely to be achieved by a fast plasticity and recovery process under compression stress.

From the point of view of applications the described welding process should be promising by avoiding heating and the subsequent heat affected zone, and is therefore different from Friction-Stir welding and Friction-Stir Processing. Meanwhile in all cases two conditions have to be fulfilled; (1) Increase the microstructural, chemical, defect energy reservoir W in order to create a driving force for joining, (2) increase the kinetics of the process at low temperature.

Independently of its role on welding the nanostructured surface obtained by SPD, BM and MA surface work hardening present the ability of increasing some mechanical properties such as fatigue life [6].

In both steps of fragmentation and welding under BM, the role of plastic and mechanical properties of the reactants and of the influence of external parameters on these mechanisms is determinant.

2.3. Interstitial solid solutions and compounds: Selected results of BM and MA

Different reasons support the interest for MA of interstitial compounds: Carbides and Nitrides present interesting properties (high melting point, hardness, magnetic properties, etc.) and are in many cases difficult to synthesize by classical techniques; The nanostructure of some hydrides may favour some applications in hydrogen storage; and The fact that sources of interstitial elements H, C and N can be gaseous or liquid offers the possibility to study gas–solid and liquid–solid reactions under milling.

In the present case the main concern is diffusion under milling. The diffusion of foreign interstitial atom (FIA) does not need lattice defects to operate and is some orders of magnitude (typically 3 to 5) higher than substitutional atom diffusion. Thanks to ab initio calculations the parameters of diffusion and interactions related with FIA and point defects in α iron have been determined [7].

Hereafter we mainly refer to binary and occasionally ternary iron Nitrides and Carbides. The choice of iron as metallic host for N and C was inspired by the possibility to exploit one of the most pertinent probe for MA studies i.e. Mössbauer spectroscopy. Because most results have been already published elsewhere [8, 9] experimental details are not given here and only the main features are summarised hereafter: The Nitrogen source is either γ'-$\mathrm{Fe_4N}$ or ε-$\zeta\,\mathrm{Fe_2N}$ Nitride obtained by $\mathrm{NH_3/H_2}$ gas reaction; Mechanosynthesis has been performed with a SPEX 8000 mill, and a vial filled under nitrogen atmosphere; and Structural data are obtained by Mössbauer spectroscopy, X-ray diffraction, electron microdiffraction, differential scanning calorimetry.

2.3.1. $\gamma' \rightarrow \varepsilon$-$\mathrm{Fe_4N}$ transformation induced by grinding

Because of very unambiguous spectra, actual fingerprints of γ' and ε nitrides obtained by Mössbauer spectroscopy, it was shown that a short time grinding (2 h) transforms the γ' Perovskite-like structure into an ε hexagonal one. This result is consistent with the results of X-ray diffraction. Moreover, thermal ageing of ground ε-$\mathrm{Fe_4N}$ nitride (320 h at 463 K) restored the γ' structure and showed that neither appreciable nitrogen uptake nor loss had taken place during grinding. The studied phase transformations by grinding and ageing can be summarised as follows:

$$\gamma'\mathrm{Fe_4N} \underset{\xleftarrow{\text{Thermal Ageing}}}{\xrightarrow{\text{Congruent MA Transformation}}} \varepsilon\mathrm{Fe_4N}$$

The swift phase transformation induced by grinding of γ'-$\mathrm{Fe_4N}$, which becomes ε-$\mathrm{Fe_4N}$, corresponds to a shear mechanism and stacking fault formation, which transforms the fcc metallic sublattice into an hexagonal one. During this shearing, the nitrogen ordered distribution γ' is destroyed and becomes nearly random in ε. That thermal ageing of ε at 463 K restores the initial γ' nitride, shows that no appreciable nitrogen loss occurs during grinding, and, therefore, that the processes do not suppose thermodynamic equilibrium between the solid and the gas phases, or that the denitriding kinetics is slow.

The fact that the εFe_4N hexagonal phase is "kinetically" more "stable" under milling than the γ' phase suggests that the interstitial disordering favours slip phenomena (Stacking fault, dislocation glide, etc.). Similar phenomena to those described above have been observed in Fe_3C cementite, for which the prismatic sheet structure is partially disordered under milling. In analogy with the role of entropy and temperature (TS) a term such as—θS could be considered where θ would characterize the milling conditions.

2.3.2. *Conservation equations of MA reactions*

From the observed conservation of nitrogen content during grinding of Fe_4N, milling of powder mixture of Fe_4N or Fe_2N with α-iron was suggested. These experiments unambiguously showed that the product is single phased and obeys the following equations:

$$\mathrm{Fe} + \mathrm{pFe_qN} \rightarrow \mathrm{Fe_{(1+pq)}N}$$

The striking result that the amount of nitrogen initially dissolved in solid reactants is conserved in solid products in the same manner as with the former $\gamma' \rightarrow \varepsilon$ phase transformation.

These results, commented elsewhere [8, 9], appear specially interesting because the conservation equations are valid although the chemical potential of nitrogen in the reactants and in the products is much higher than in the gas phase. It can therefore be concluded that: (i) the temperature in the reacting zone of solid powder is not very high; (ii) the formation of N_2 molecule does not take place; and (iii) the transfer of nitrogen across interphase obeys a specific diffusion mechanism which depends on σ or(and) ε which will be discussed hereafter.

Once establishing the conservation of total nitrogen, it was temping to synthesize the metastable $\alpha''Fe_8N$ nitride discovered by Jack [10], which appeared to present very unique magnetic properties that did lead to the concept of "nitromagnetism".

α''-Fe_8N is obtained by ageing of α'-FeN_x martensite [11], precipitation in nitrogen supersaturated α ferrite, ageing of ε-$FeN_{0.2}$ [12] and molecular beam epitaxy. The most convenient way to describe the α'' crystallographic structure is to consider an ordering process taking place in the α'-FeN_x martensite. The Mössbauer spectrum of α'' present very well defined features, especially an environment with a very high hyperfine field (41 T). In the present case the Mössbauer spectrum of Fe_8N obtained by MA is very different from that of α''-Fe_8N. Large-Angle Electron Diffraction patterns unambiguously showed that the structure of the Fe_8N obtained by MA is cubic [13]. Therefore we called this solid solution $\alpha'''Fe_8N$, which can be considered as a "superferrite" in which the occupation rate of octahedral interstitial sites is random, the occupation of tetrahedral sites being excluded by the large energy difference determined by ab initio calculations between both sites [7].

Thanks to classical internal friction results it was proven that: (i) at room temperature the jump frequency of N or C under stress fluctuation is higher than 1 H_Z (SNOEK Effect); and (ii) the long range diffusion of interstitials is very sensitive to stress gradient (GORSKI Effect).

Therefore the mean square deplacement $\langle X \rangle$ of N or C during MA which may be approximated by $\langle X^2 \rangle = p \cdot f \cdot t \cdot a^2$, where f: frequency of ball impacts; p: probability for one powder particle to be submitted to impact; t: time of milling; a: lattice parameter. With $p = 5 \cdot 10^{-2}$ volume fraction of powders compressed $f \sim 10^2\ s^{-1}$; $t = 3600$ s; $a \sim 2.810^{-10}$ m, a mean square deplacement of about 30 nm is obtained which can be compared with the grain size of the different phases (nitrides and ferrite) inside the powder particle.

Ball milling of carbon steel perlite led to very similar results. The above discussed results, as well as those obtained by ball milling of carbon steel perlite, also leading to a carbon interstitial enriched ferrite, suggest that the parameters which favour the formation of a phase are: (1) a fast diffusion under milling conditions; and (2) the possibility of a large degree of disorder.

3. Specific diffusion mechanisms and their consequences

The analysis presented above established that under impact of balls the displacement of foreign interstitial atoms (FIA) results from the variation during time of the stress field $\dot{\sigma}$ and from the stress gradient $\overrightarrow{\mathrm{grad}}\sigma$. Meanwhile the role of plastic deformation is indirect because although lattice defect are not needed for the diffusion of N or C to take place the stress field around the defects also contribute to the displacement of FIA.

The concept of ballistic diffusion is used to describe the displacements of knocked atoms under neutron irradiation and the formation of cascades. Sometimes atomic diffusion during MA is referred as ballistic diffusion, but in the present case we suggest that this term may be misleading.

In contrast with FIA the displacement of substitutional atoms is much slower and kinetics of mixing much longer as shown by ball milling of elements such as Mn, Cu, Ag, Au, etc. with iron nitrides and ferrite for which new compounds have been obtained but for milling times much longer as for binary nitrides [14, 15]. In comparison with interstitials, substitutional atoms have also a much smaller activation volume for stress-induced diffusion, therefore the mechanism of diffusion under milling is different. Because the stress field is not hydrostatic under BM or SPD the shear stress and consequently the shear deformation can be very high.

That in substitutional solid solutions MA and in some case SPD lead to a mechanical mixing through diffusion mechanisms which are neither thermal nor chemical nor ballistic nor induced by stress in contrast with the case of FIA is proven by the extension of solubility domains shown in many binary systems such as Ag-Cu, Au-Fe, Fe-Cu, Nb-Cu, etc. [16, 17]. It is therefore clear that diffusion of substitutional atoms is induced by the micromechanisms originating plastic deformation of nanostructured alloys. Although many evidences suggest that the plastic deformation of nanomaterials results from the competition between perfect and partial dislocations slip, twinning [18], grain boundary sliding [19], grain rotation [20], etc. These mechanisms are not antagonist. If only shear is taken into account the interaction of gliding dislocations with interfaces and interphases originate on these boundaries additional defects which in analogy with "Terrace-ledge-kink" model of surface create specific atomic environments.

In case the crystal structures of two metals A and B are similar the description of the MA process is proposed to result from the superposition of the successive translation displacements $\vec{b}_\mathrm{i}$ in the glide planes P_j which are crossing an ideal planar phase boundary separating the two A-B phases (Fig. 1). The succession of slip displacements creates new atomic environments defined by the number and the nature of neighbouring atoms, for example environment $E^{\mathrm{ijk}}_{\mathrm{ABC}}$ is characterized by i atoms A, j atoms B, k atoms C, etc. neighbours. In the bulk of A and B environments are $E^{\mathrm{Z}}_{\mathrm{A}}$ and $E^{\mathrm{Z}}_{\mathrm{B}}$. On each sides on the terrace are environments T defined by $E^{\mathrm{Z-t}}_{\mathrm{A}}$ and $E^{\mathrm{Z-t}}_{\mathrm{B}}$, t is the number of AB bonds resulting from the vicinity of the planar interface. When a ledge is created at the intersection with a slip plane environments L appear or $E^{\mathrm{Z-l}}_{\mathrm{A}}$ and $E^{\mathrm{Z-l}}_{\mathrm{B}}$ for which l bonds are broken, then K when a kink is formed $E^{\mathrm{Z-k}}_{\mathrm{A\,resp.\,B}}$, then K_2 for double kink, X when an extrusion is formed and finally S when an atom A (resp. B) is separated from the interface (Fig. 1). This displacement of an atom results from the collective successions of shear drifts of amplitude $\vec{b}_\mathrm{i}$, therefore this type of atomic transport can be qualified as "drift diffusion". In case all glide systems of a cubic symmetric system have the same probability to operate the Einstein equation should be valid to describe the mean square displacement: $\langle X^2 \rangle = \Sigma f_\mathrm{i} \cdot b_\mathrm{i}^2 \cdot t$, where f_i is proportional to the frequency for the translation $\vec{b}_\mathrm{i}$ to take place.

Different conditions are likely to bring severe perturbation to this model: non isotropic distribution of glide systems—large difference of A and B atom sizes—large difference of mechanical properties etc. Meanwhile when A and B are not too different and even immiscible in usual conditions a quasi regular solid solution should be obtained by MA process. This supposes that the chemical driving force towards equilibrium is quenched. The hypothesis of a temperature of O K leads to assume that the chemical diffusion is made inefficient.

Although conditions to obtain a complete solid solution $\mathrm{A}_{1-x}\mathrm{B}_x$ in all cases are rather restrictive the trend of MA is to lead to a peritectoid—like reaction producing a "quasi regular solid solution" (QRSS) at least if the heat resulting from the adiabatic conditions is not sufficient to initiate ageing of the specimen. That such a QRSS may result from a "drift diffusion" process got some start of experimental support by the Mössbauer hyperfine parameters distribution identified as "quasi–universal" by Le Caër [21]. When the correspondence between the hyperfine field and the environment can be established, the experimental environment distribution can be compared to the QRSS distribution given by binomial expressions $P_\mathrm{i} = C^{\mathrm{i}}_{\mathrm{Z}}(1-x)^{\mathrm{i}}x^{\mathrm{Z-i}}$. The formation of the QRSS distribution is obtained asymptotically and progressively and by no means correspond to an homogeneous kinetics, more precisely

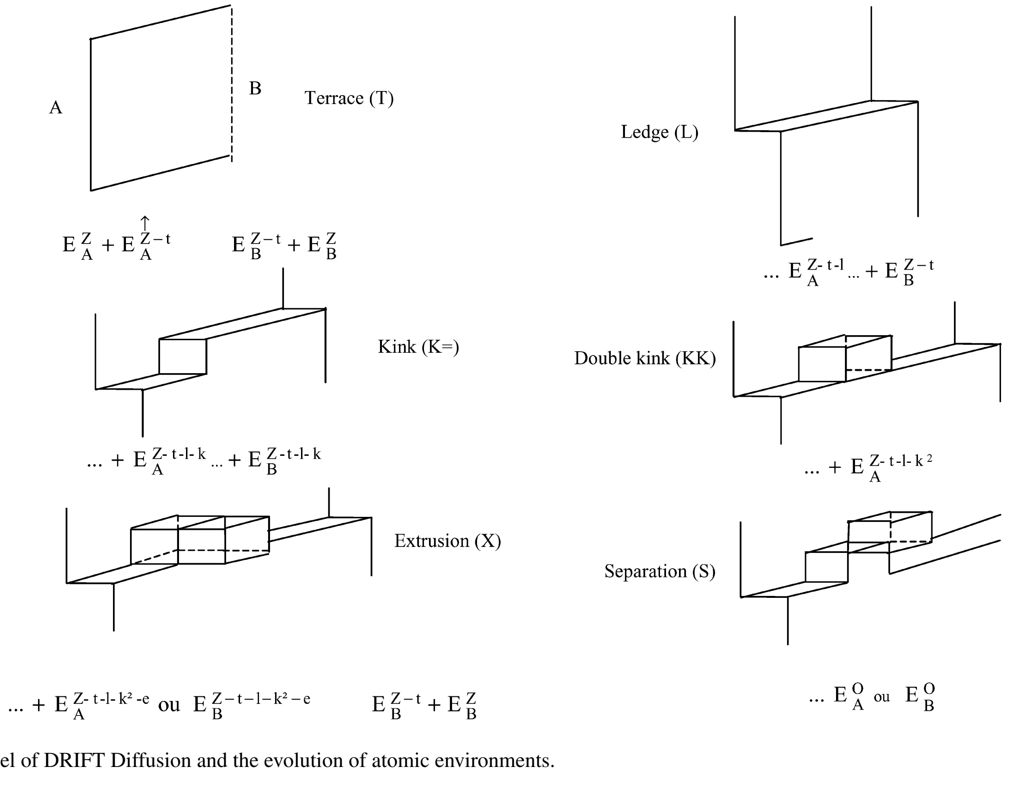

Figure 1 Model of DRIFT Diffusion and the evolution of atomic environments.

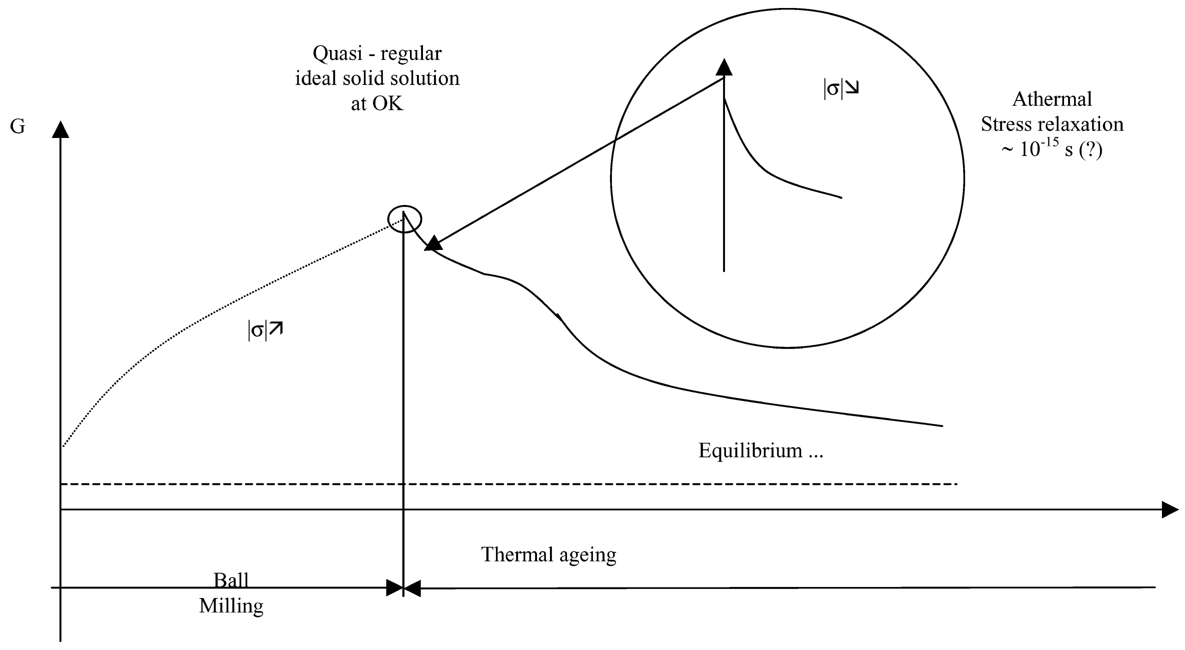

Figure 2 Variation of the G function during impacts of BM and Thermal ageing.

T environments appear first as resulting from fragmentation and welding, L environments when for each nanograin the primary slip system is activated, K when slip lines or shear bands intersections are formed, ... Therefore the kinetics of formation of environment S is the slowest as shown by the hyperfine parameters distribution.

At the mesoscopic scale of the particle two main stages are to be distinguished (i) increase of stored energy by impacts, after each impact a very fast athermal stress relaxation takes place, and (ii) thermal ageing (Fig. 2) [9].

When the ensemble of particles is considered during MA these two stages overlap. The way to minimize the overlapping is to keep the processing temperature as low as possible in order to quench the quasi regular solid solution.

The above attempt to describe the specific diffusion mechanisms involved in BM and MA processes suggests many questions or remarks among which the following ones:

(1) When interstitial ternary alloys such as Fe C Si steels where studied by L. Darken, he showed that the driving force for chemical diffusion is not the concentration gradient but the chemical potential gradient (uphill diffusion) in the case of the formation of $\alpha'''\mathrm{FeN}_{0.1}$ by MA the diffusion induced by milling is driven by concentration gradient and appears to work against the chemical potential gradient. Meanwhile it is not completely excluded that the compression stress during ball impact reaches the high yield stress of high nitrogen steel typically $2 \cdot 10^3$ MPa (corresponding to a pressure of $2 \cdot 10^4$ atmospheres) and is sufficient to lead to the extremely high chemical potential in the reaction zone (Fig. 3). By the way the maximum stress applied to the powder during milling is depending of the mechanical characteristics (hardness, yield stress, hardening coefficient, etc.) of the device parts (vial, balls) and not simply of the kinetic momentum of balls.

(2) In contrast with other experimental results showing (splitting of diffraction peaks) the formation of α' martensite in Carbon or Nitrogen steel, the established formation of the α''' highly supersaturated ferrite [13], confirmed by the Mössbauer study of the ageing of α''' raises the question of the high sensitivity of the product to experimental conditions, which are extremely difficult to define and therefore to keep under strict control. In case a too high temperature would be reached during milling the formation of austenite could be possible and therefore of martensite by cooling.

(3) That the stress (mainly normal stress) and deformation (mainly shear) induced diffusion shows a strong trend to lead to a peritectoid-like transformation and to a single phase product reduces the theoretical interest of studies devoted to MA of systems having a negative enthalpy of mixing. Therefore many diagnostic experiments are devoted to the case of strongly positive enthalpy of mixing such as Ag-Cu; Ag-Fe; Au-Fe; Cu-Fe; Cu-Nb, etc. In this case an unambiguous extension of the solubility domain is observed which corresponds to a specific MA milling phenomenon in contradiction with demixing and spinodal decomposition (Fig. 4). Therefore when an ageing process interferes with the mechanical mixing an eutectoid-like transformation resulting from adiabatic nature of the process contributes to forbid the complete solubility to take place. Meanwhile it was underlined that in this case as well as for an amorphous-crystal transformation the necessary nucleation stage obeys to conditions on the concentration gradient [22].

(4) When chemical and deformation energies are released by an ageing process which lead to a multiphase system with different concentration domains, further milling is likely to induced an oscillating behaviour of mixing and demixing stages.

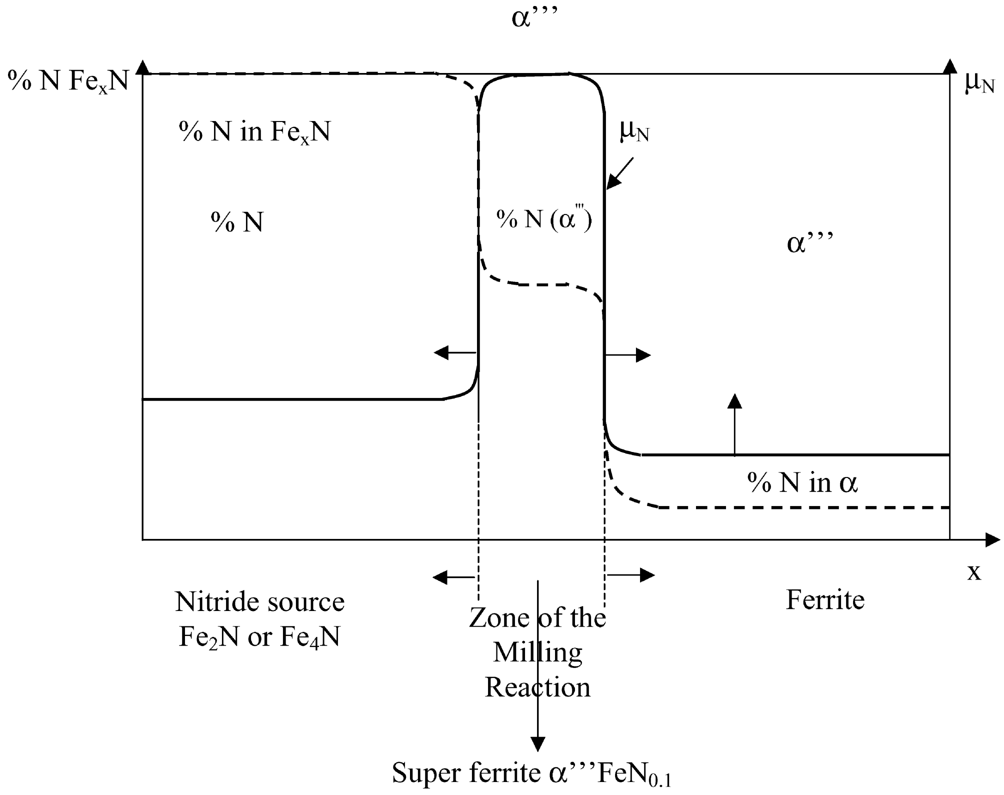

Figure 3 Variation of C_N% and μ_N from reactants to the α'' MA product (arbitrary units).

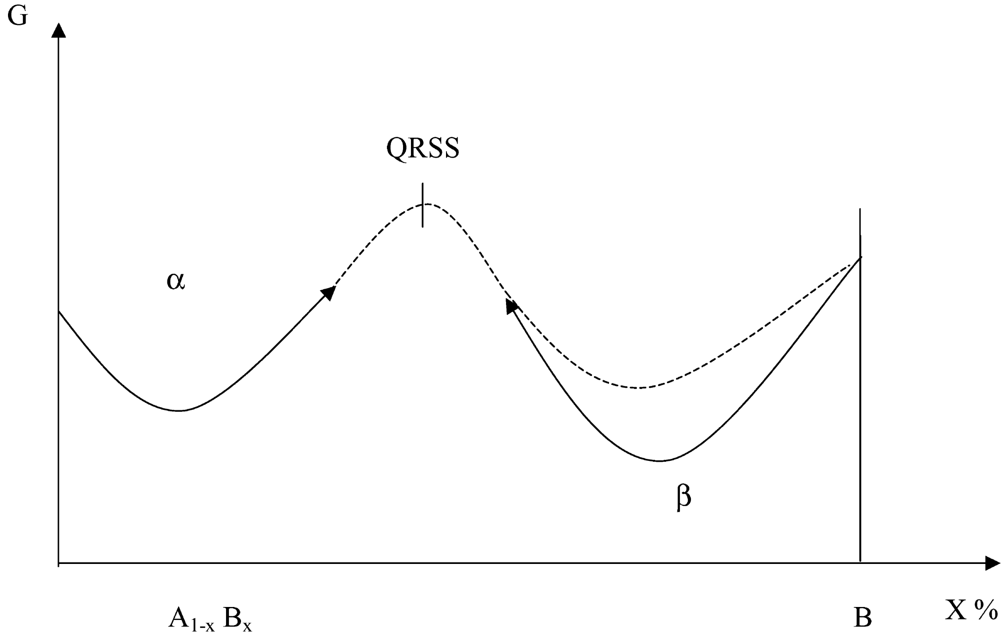

Figure 4 BM induces a specific mechanism of "Shear-Drift" diffusion which favors the formation a Quasi Regular Solid Solution (QRSS) in the structure for which ordering is the lowest and diffusion the easiest. BM opposed spinodal transformation: $\alpha + \beta \rightarrow$ QRSS.

4. Conclusion

After two stages corresponding to fragmentation and welding under milling of reactants elements, mechanical mixing takes place. The specific diffusion mechanisms involved in this process are examined and discussed in both cases of interstitial and of substitutional alloys. In the case of interstitials the diffusion is proposed mainly to be stress controlled. In substitutional alloys the diffusion results from shear deformations interacting with interphase boundaries.

When experimental conditions allow the MA process to take place at low temperature the final product shows a highly disordered distribution of atoms resulting from a specific mechanism of "drift diffusion" induced by plastic deformation which is mainly controlled by the concentration gradient.

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