Mechanically Prepared Nanocrystalline Materials (Overview)

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We review recent results in new materials development by mechanical preparation techniques (mechanical alloying and milling) with an emphasis on research performed in Grenoble. Two general categories are considered: nanocrystalline and amorphous materials obtained by polymorphous (iso-compositional) transformations and mechanical alloying of highly supersaturated solid-solutions. We then consider nanostructures obtained on the path back towards equilibrium structures by nucleation and growth processes or by phase-separation. Design of new magnetic and mechanically attractive nanocomposites using amorphous precursors and metal-ceramic nanocomposites obtained by reactive milling are also considered.

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I. Introduction

Since the early use of milling devices for oxide-dispersion-strengthening⁽¹⁾, mechanical alloying (MA) or milling have become powerful tools for generation of nanostructures⁽²⁾⁻⁽³⁾. Indeed ball-milling generates large dislocation densities that precipitate to form nanograin boundaries. The heavy deformation conditions can favor metastable polymorphs over equilibrium phases, drastically increase solid-solubilities and generate nanocomposites in two-phase systems. In this paper we will provide examples of each of these processes of metastable nanophase formation. We will then consider the different materials and nanostructures that can be obtained as the metastable (or unstable) MA products undergo transformations towards equilibrium upon annealing.

II. Polymorphous Transformations under Heavy Deformation

Heavy deformation at high rates as experienced during cold-rolling, filing and ball-milling generates large dislocation densities that precipitate to form dislocation cell walls and form nanograin boundaries as revealed by TEM. Slip propagation from grain to grain occurs via stress concentrations generated at dislocation pileups. It has been suggested that this grain refinement mechanism becomes inoperative at a critical grain size $2r_c$. This critical size $2r_c$ is given by the distance of closest approach l_c between two mutually repulsive neighboring edge dislocations that the applied stress σ_a can impose:

$$2r_c > l_c \approx Gb / \pi(1 - \nu)\sigma_a \quad (1)$$

where G , b and ν are respectively the shear modulus, Burgers vector and Poisson's ratio⁽⁴⁾. However, the experimentally observed lower limit of 5 to 20 nm range, for grain size achievable by heavy deformation is system-

atically higher than values obtained by eq. (1) perhaps due to simultaneous grain growth leading to a "steady-state" grain size⁽⁵⁾. This is because grain growth rate dr/dt is known to be proportional to $1/r$ which diverges at very low grain sizes⁽⁶⁾ and is accelerated by the deformation induced temperature rise. Of course there is very little solid certainty about what occurs to the nanograins during impact. It has also been pointed out⁽⁷⁾ that presence of a component with very strong tendency towards surface segregation will stabilize the grain size just small enough for such atoms to cover the grain surfaces. Following this idea, one may also consider a similar influence of oxidation or other surface adsorbing elements. For example, oxygen has low solubility in aluminium but the free energy of formation of Al_2O_3 is strongly negative. One can therefore suppose that as the oxide forms during milling in presence of residual oxygen content it cannot segregate into particles due to the intense atomic-level fragmentation that accompanies heavy deformation. Thus, it is likely to form a monolayer at the grain boundaries in order to avoid dissolution into Al and will result in the stabilization of grain size r_c near

$$\begin{aligned} [4\pi(r/a_o)^2 / 4\pi(r/a_o)^3] &\approx (5/3)X_o \\ \Rightarrow r_c &\approx 3a_o / (5/3)X_o \end{aligned} \quad (2)$$

where a_o is an atomic diameter X_o is the oxygen atom fraction that can be related to its partial pressure in the vial before milling. For an O content $X_o = 3\%$ for example, we obtain $r_c \approx 20$ nm which is of the right order of magnitude. It thus appears that at least for now, theoretical derivations of steady-state nanograin size achieved by milling can be rigorously tested only in ultra-pure single component or non-segregating homogeneous systems.

1. Metastable polymorphs obtained by milling

When intermetallics are deformed at low temperatures, the passage of dislocations displaces the lattice atoms and generates anti-phase boundaries ultimately

resulting in the disappearance of long-range ordering as signalled for example by the disappearance of X-ray superlattice peaks or corresponding electron diffractions spots (for TEM observations of APB and SISF faults generated by milling see⁽⁸⁾). This process, which is accompanied by nanocrystallization, is more similar to the destruction of the superstructure by ion and electron irradiation⁽⁹⁾⁽¹⁰⁾ than to rapid quenching of the melt where the superstructure formation is suppressed⁽¹¹⁾.

Typical examples of transformations into metastable polymorphs in cubic systems are the $L1_2$ (or γ') $\Rightarrow$ fcc (or γ) disordering which at equilibrium (higher T) is a first order transformation and $B2 \Rightarrow$ bcc which is second order at high T . While Cu_3Au is perhaps the most famous $L1_2$ system, experiments on disordering of Ni_3Al by filing⁽¹²⁾ and milling⁽¹³⁾ are of particular interest because its equilibrium order-disorder transition T_{od} is above the melting temperature (the intermetallic melts from the ordered state).

However, addition of a few at.% of certain elements such as Fe in Ni_3Al reduces the critical temperature T_{od} such that the equilibrium γ -phase appears below the liquidus⁽¹⁴⁾ although a two phase region of $\gamma + \gamma'$ must be crossed to obtain full disordering⁽¹⁵⁾. As such, ordering during cooling requires diffusion-controlled solute (Al) atom redistribution, a process that can be suppressed by rapid-quenching and allows the retention of the high- T disordered- γ state down to low temperatures as demonstrated in⁽¹¹⁾.

The γ' - $L1_2$ state of Ni_3Al is known to be ferromagnetic only at low temperatures but a few at.% Fe-addition raises the Curie temperature T_c very rapidly to several hundred degrees (K) as giant moments around Fe-atoms polarise the surrounding nickel atoms⁽¹⁶⁾.

Ferromagnetic $Ni_3Al + Fe$ alloys in their γ' -ordered state usually become paramagnetic before undergoing the order-disorder ($\gamma' \rightarrow \gamma$) transition as $T_c < T_{od}$ such that the equilibrium γ -phase was thought to be paramagnetic⁽¹⁷⁾⁽¹⁸⁾. However we found that the disordered γ -state produced by milling of the ordered state is ferromagnetic at room temperature⁽¹⁹⁾. While these alloys exhibit near Bloch-law behavior versus temperature, we found that theoretical models using Bragg-Williams nearest neighbor interactions⁽²⁰⁾⁽²¹⁾ overestimate their magnetic ordering energies.

As given in Table 1, the γ -state has Curie temperatures $T_c(\gamma)$ below those of the ordered state $T_c(\gamma')$. The giant moments of Fe-atoms is responsible for the magnetization of neighboring Ni atoms and since in the ordered state Fe preferentially substitutes for Al sites which have only Ni nearest neighbors, the magnetization is significantly lower in the disordered state with a lower number of Fe-Ni nearest neighbors.

While T_c 's of the disordered state are lower here, the ball-milled bcc metastable polymorphs of ordered intermetallics with a single magnetic moment-carrying species such as $FeAl$ ⁽²²⁾, $CoGa$ ⁽²³⁾, Co_2Si ⁽²⁴⁾ and many others have been found to possess T_c 's higher than the equilibrium ordered states because disordering increases the number

Table 1 Curie temperatures T_c and magnetization M of ordered (γ') and disordered (γ) $Ni_3Al + Fe$ alloys at 310 K and 2 kOe.

	$T_c(\gamma)$, K	$T_c(\gamma')$, K	$M(\gamma)$, emu/g	$M(\gamma')$, emu/g
$Ni_{71.6}Al_{20.8}Fe_{7.6}$	320 ± 10	350 ± 10	7	13.5
$Ni_{74}Al_{16}Fe_{10}$	415 ± 15	570 ± 5	30	45
$Ni_{75}Al_{12}Fe_{13}$	550 ± 5	725 ± 5	45	60

of moment-carrying nearest neighbor atoms.

As we shall now see, the study of reactions leading back to the equilibrium ordered polymorphs also has lead to new information applicable also to bulky crystals.

We developed compositions of $Ni_3Al + Fe$ whose $T_c(\gamma)$ and $T_c(\gamma')$ sandwich the T-range of observation of the reordering reaction such that $M(\gamma) = 0$ and the magnetization measured during isothermal ordering reactions yields directly the growing volume fraction $x(t)$ of ordered $L1_2$ phase.

Johnson-Mehl-Avrami analysis of isothermal measurements of M (and the transformed fraction x) in this range yield JMA plots (see Fig. 1) that are nearly linear, most show initial slopes $n \approx 1$ with slopes decreasing with time. It is significant that although some n values are below 1, they are never greater than 1. They can be compared to $n = 3$ or 4 corresponding to spherical (3-d) growth of nuclei. Lower n values have only been interpreted as indicative of solute atom diffusion-controlled or one or two dimensional polymorphous growth⁽²⁵⁾. If grain boundaries could act as sites for heterogeneous nucleation of the ordering reaction as for $bcc \Rightarrow B2$ in $CoFe$ ⁽²⁶⁾, the time dependence could simply correspond to quasi-linear growth of the ordered phase towards the still disordered grain interiors.

However various studies have claimed that grain boundaries in Ni_3Al stay disordered even for fully ordered grains⁽²⁷⁾⁻⁽³¹⁾. Furthermore a significant fraction of grain boundary Al atoms are usually oxidized thus rendering grain boundaries nickel-rich and γ -stabilized (even though Al may be the tensio-active element). In order to clarify these apparent contradictions, we performed direct observations of ordering on dark field images obtained with $L1_2$ -superlattice spots during in-TEM annealing on a hot plate⁽³²⁾. Since such observations are very difficult on nanocrystalline powders, we used melt-spun ribbons with micron-size grains. Saturation magnetization data show that melt-spun ribbons are always partially ordered (about 20%) while milling reduces the ordered fraction to less than 10%. As seen in Fig. 2, TEM images confirmed the presence of a dense dispersion of nanometer size ordered (bright) regions in the as-prepared films. Annealing was expected to result in growth (coarsening) of these spots or perhaps as reported for $fcc \Rightarrow L1_2$ ordering in Cu_3Pt alloys, growth of ordered regions from the grain boundaries inwards⁽³³⁾.

Figure 3 shows that a completely different ordering path is in fact followed: Ordering during in-situ annealing does not modify the volume fraction or size of the

Fig. 1 Modified JMA plots for the $\gamma \rightarrow \gamma'$ transformation showing slopes $n \leq 1$ in disordered nanocrystalline states of (left) $\text{Ni}_{74}\text{Al}_{16}\text{Fe}_{10}$ and (right) $\text{Ni}_{75}\text{Al}_{12}\text{Fe}_{13}$.

Fig. 2 Superstructure dark field images of melt-spun $\text{Ni}_{75}\text{Al}_{12}\text{Fe}_{13}$ showing nanometric-size ordered ($L1_2$) embryos in a micrometer diameter grain.

preexisting nanometer sized ordered domains. Instead, it occurs by the growth of such nano-zones that are behind moving grain-boundaries. Which grain-boundary moves depends on the energetics of interface or grain-boundary crystallographic orientations which are under consideration⁽³⁴⁾ but ordering occurs only behind advancing grain boundaries. The transformation therefore occurs via growth of preexisting ordered zones and the growth is uni-directional (one-dimensional) as can be seen by the nano-scale lamellar structure that it generates in dark field images. These observations are consistent with the

JMA exponent $n \approx 1$ determined from reordering kinetics as studied by isothermal magnetic measurements on nanocrystalline (ball-milled) samples⁽¹⁴⁾.

However the most significantly, the reordering mechanism observed in the TEM images of Figure 3 proves that the grain-boundaries themselves remain disordered otherwise ordered zones would not grow behind them but from them as observed for CoFe ⁽²⁶⁾. Thus the study of reordering kinetics in Ni_3Al -based alloys disordered by milling has lead to results indicating that grain-boundaries of ordered Ni_3Al remain disordered.

2. Polymorphous amorphization by milling

When amorphization of an alloy is obtained by rapid solidification, it is because of insufficient time for nucleation and growth of crystalline polymorphs from the liquid state. On the other hand, amorphization in the solid state occurs by the progressive destruction of the crystalline polymorphs by milling or irradiation and by the non-polymorphous processes of solid-state diffusion in multilayers and mechanical alloying. Nevertheless the respective amorphous states present many similarities and mechanically prepared amorphous alloys can even manifest a glass transition at T_g ⁽³⁵⁾. Polymorphous amorphization by milling occurs as increasing densities of defects are introduced into the powder by the heavy deformation until long range order crumbles by lattice instability⁽⁹⁾. The process in fact is not polymorphous if one considers topological (density) defects including vacancies as a component. In the systems with largely

Fig. 3 (top) TEM images of grains A and B below grain C; picture shows area of length about 5 microns; (bottom-left) dark field image of grain A on the left growing into grain C and lamellar ordered domains stretching behind the moving grain boundary; (bottom-right) dark field image of grain B on right growing upwards into grain C (and to the right) and lamellar ordered domains growing from the grain inside behind the moving grain boundaries.

negative heats of mixing and large atom-size differences between the components such as in $L1_2$ type Zr_3Al , the defects contributing most to the raising of the crystal lattice energy and to amorphization are anti-site defects or atoms of one species forced onto the sublattice of the other. In chemical terms we may consider that anti-site defects and APD boundaries generate “wrong bonds” such as A-A and B-B bonds when A-B bonds have the lowest energy. The consequent enthalpy increases due to “elastic mismatch” and other factors have been reviewed in the literature⁽³⁶⁾. These contributions and others such as the lattice stability term for each crystalline polymorphs⁽³⁷⁾⁽³⁸⁾ can be used to construct free energy versus concentration curves for the amorphous and the increasingly deformed crystalline phases. However these considerations neglect the role of grain boundaries generated by precipitating dislocation cell walls that lead to nanocrystallization. Indeed, amorphization during milling is accompanied by nanocrystallization. The energy surplus due to grain boundary free energy per unit area γ_{gb} is approximately $\Delta G_{gb} = 1.5\gamma_{gb}V_m/r$ while the free energy of polymorphous melting is approximately $\Delta G_{ls} = \Delta H_{ls}(T_m - T)/T_m$ where ΔH_{ls} is the enthalpy of melting at the melting temperature T_m and V_m is the mo-

lar volume. This effect alone would lead to spontaneous amorphization for grain radii $r_c < 1.5\gamma_{gb}V_m/\Delta G_{ls}$. For a reduced undercooling $(T_m - T)/T_m = 0.5$ typical of a glass former and other typical values such as $\gamma_{gb} = 1000$ mJ/m², $V_m = 10$ cm³ and $\Delta H_{ls} = 10$ kJ/mol, we obtain $r_c = 3$ nm⁽⁵⁾. In this simplistic approach, amorphization will not occur via ball milling if the mechanically determined lower-bound to the nanocrystal size as for example given by eqs. (1) and (2) is superior. However amorphization leads to the disappearance of most anti-site or wrong-bond type defects especially because atomic diffusion in an amorphous alloy is generally easier than in its crystalline polymorphs and this effect contributes increasingly as the heat of mixing becomes increasingly negative with $-\Delta H_{mix} \gg -\Delta H_{ls}$ such that anti-site defects (superstructure defects) become much more costly than the heat of melting due to the disappearance of topological long range order. Spontaneous amorphization should therefore occur at higher radii than the critical grain radius $r_c \approx 1.5\gamma_{gb}V_m/\Delta G_{ls}$ in systems with $-\Delta H_{mix} \gg -\Delta H_{ls}$. For example consistent with $\Delta H_{mix}(Zr_3Al) < \Delta H_{mix}(Ni_3Al) < 0$, Zr_3Al seems to amorphize with grain size well above 10 nm⁽³⁹⁾, while isostructural Ni_3Al cannot be amorphized by milling.

III. Supersaturated Solid-Solutions and Mechanically Prepared Alloys of Immiscible Elements

Since several years ago mechanical alloying has been shown capable of achieving highly supersaturated (amorphous and crystalline) solid-solutions. As mentioned earlier, milling results in nanocrystallization with nanograin sizes typically of the order of 10 nm. The free energy of a phase increases with interfacial area and energy. The free energy increase per mole of B particles of radius r within A may be written as $\Delta G_{\text{interface}} = 3\gamma_{\text{AB}} V_m / r$. This change in free energy for nanometric B component in the A matrix is schematically drawn in Fig. 4 and it is seen that the common tangent with the G-curve of the A-phase is displaced to higher B contents. Such supersaturation enhancement is common in nanocrystalline systems. For example, mechanically alloyed Ni-Ge dissolves 23 at.% or more of Ge in the fcc phase⁽⁴⁰⁾.

Furthermore, amorphous or crystalline solid-solutions were reported for usually immiscible Cu-Ta, Cu-V, Cu-Fe and others. (see⁽²⁾). While some such alloying may be due to contaminants, the case of fcc-CuFe alloys first obtained by MA in Kyoto⁽⁴¹⁾ clearly indicated that through a mechanism to be determined, milling generates a driving force even when the enthalpy of mixing ΔH_{mix} is strongly positive. Since alloying in a two-component nanocrystalline system liberates $\Delta G_{\text{interface}}$, it was natural for most researchers to compare $\Delta G_{\text{interface}}$ for the typical MA nanograin-size $2r$ of about 10 nm to the positive free energy of mixing $\Delta G_{\text{mix}}(\text{AB}) \gg 0$ of immiscible components and conclude it to be insufficient to force the dissolution. The phenomenon thus remained quantitatively unexplained.

However, when the mechanical properties of two elements A and B are very different, heavy co-deformation generates nanometer-size fragments of the hard (say B) phase⁽⁴²⁾⁽⁴³⁾ and almost all the reports of MA of immisci-

Fig. 4 Free energy curves G_A of the A matrix and G_B of the particulate B-phase raised by $\Delta G_{\text{interface}} = 3\gamma_{\text{AB}} V_m / r$.

ble components concern co-deformation of high melting often bcc elements with ductile copper and fall in this category.

In this context it should be noted that the “average” nanocrystal size D derived from X-ray diffraction is only the center of a size distribution (for example Cauchy) and when $D=10$ nm, of the order of one volume % of the material is expected to be in crystallites of diameters 2 nm or less. MA of immiscible elements can then proceed by the dissolution of these fragments corresponding to the tail of the size distribution which have the highest $\Delta G_{\text{interface}}$ values. The MA process will then continue until full dissolution as further deformation reestablishes the original particle size distribution. The schematic free energy construction together with the particle size distribution of Fig. 5 demonstrates this mechanism⁽⁵⁾. For the Fe-Cu system, detailed calculations of the critical Fe particle radius that would dissolve in this manner was found to be close to $r=1$ nm⁽⁴⁴⁾. More work is nevertheless needed in this area. For example, MA of some other immiscible pairs such as Fe and Ag⁽⁴⁵⁾ or Mn and Ag⁽⁴⁶⁾ has not yet been achieved even after cryo-milling. Although $\Delta H_{\text{mix}}(\text{FeAg}) > \Delta H_{\text{mix}}(\text{FeCu}) \gg 0$, the mechanism for the dissolution of the smallest particles might have been expected to drive the dissolution. The explanation may come from a balance between fragmentation and small particle growth and be thus diffusion-controlled. Indeed the interfacial free energy $\Delta G_{\text{int}}(\text{AB})$ can be reduced either by dissolution thus favoring MA, or by coarsening that would remove the driving force for MA. Finally, MA solid-solutions of immiscible elements are unstable and the decomposition process for mechanically alloyed solutions containing low-melting Ag and having very high $\Delta H_{\text{mix}} \gg 0$ may already intervene during milling. The resulting nanostructure scale would thus correspond to a steady-state dynamic phase distribution reflecting the

Fig. 5 Schematic free energy construction for the immiscible A-B system together with B-particle size distribution in G-space

balance between mechanically driven alloying and phase decomposition.

IV. Nanocrystalline Solid-Solutions as Nanocomposite Precursors

The decomposition of nanocrystalline supersaturated phases is likely to generate even finer two- or multi-phased nanostructures with various interesting or novel properties. Such nanostructures are likely to be preserved during thermomechanical shaping processes because grain coarsening is hindered by their two-phased nature. In the following paragraphs we will consider several interesting examples of such nanocomposites.

1. Decomposition of solid-solutions of immiscible Cu and Fe

As mentioned earlier, of all reported mechanically alloyed solid-solutions of immiscible elements, CuFe is the most pertinent one from a thermodynamic view point because effects of impurity atoms from the milling equipment and contamination by atmospheric constituents may be neglected. Upon annealing, a nanostructure of ferromagnetic bcc-Fe zones mixed with paramagnetic fcc-Cu is expected. However decomposition is detected by calorimetry and magnetic measurements long before it can be traced by X-ray diffraction indicating that it is occurring coherently within the nanocrystalline fcc structure. The onset of the decomposition is also nearly impossible to observe by TEM or even HRTEM⁽⁴⁷⁾ because of Fe and Cu atom's equal Gold-Schmid radii and nearly equal electron densities. In this context precision magnetic measurements are the most pertinent experimental tool. Figure 6 shows the magnetization versus composition of supersaturated CuFe solid-solutions as reported by Sumiyama *et al.*⁽⁴⁸⁾⁽⁴⁹⁾ for vapor-deposited samples and some MA samples⁽⁵⁰⁾⁽⁵¹⁾. It is seen that the unstable supersaturated alloys have bcc structure from 0 to 30–40%Cu and are then fcc up to pure Cu. We have therefore followed the magnetization M_s versus annealing time of a

Fig. 6 Magnetic moment μ_b/at at 295 K versus Cu concentration c for $\text{Fe}_{1-c}\text{Cu}_c$ alloys prepared by vapor quenching⁽⁴⁸⁾⁽⁴⁹⁾ and some additional points as indicated.

Fig. 7 Saturation magnetization M_s of fcc-CuFe measured at 300 K after different annealing times at 600 K.

Fig. 8 Coherent domain size D of the fcc and bcc phases after different annealing times at 600 K.

MA CuFe alloy in order to compare the evolution of M_s during decomposition with the M_s curve of Fig. 6. The measurements were made at room temperature using the superconducting coil magnetometer of the Louis Neel laboratory in Grenoble on samples annealed for different times at selected annealing temperature.

Figure 7 shows the room temperature saturation magnetization M_s of the fcc-CuFe solid-solution as a function of annealing time t at 600 K under N_2 gas. M_s is obtained as usual, by extrapolation back to zero field ($H=0$) of the magnetization versus H at high fields that in our setup could go up to 60 kOe. The observed behavior of M_s was also obtained after annealing at other temperatures and under argon⁽⁵⁰⁾. Interestingly, fcc X-ray line breadth (Fig. 8) and dark field TEM images indicated that very little fcc grain growth occurs during the indicated annealing time. While this behaviour is fairly complex, it can in fact be simulated by progressive phase-separation of the 50/50 fcc-solid solution grains into fcc-Cu-rich and fcc-Fe-rich zones that lose coherence and

become bcc only after attaining a size $2r > 10$ nm after which they are X-ray detectable as in Fig. 8. We considered the change in magnetization of the 50/50 CuFe solid-solution as expected from the M_s versus c_{Cu} of Fig. 6 during progressive decomposition into zones with $M_s(c_{\text{Cu}} \pm \Delta c_{\text{Cu}})$ corresponding to values $\pm \Delta c_{\text{Cu}}$ to the right or to the left of the initial $M(c_{\text{Cu}}=0.5)$. The concentration variation during decomposition was approximated as $c = c_0 + A \sin(kx)$ with $c_0=0.5$ the concentration at the beginning of decomposition ($t=0$), k the wave vector ($k=2\pi/\lambda$), x the distance in real space and A the time dependent amplitude that determines the decomposition rate. The experimental magnetization values of $M_s(c_{\text{Cu}})$ of Fig. 6 are fitted with a second order polynomic function and the average value of magnetization M_{av} can be directly calculated as

$$M_{\text{av}} = \frac{\int_{-\lambda/2}^{\lambda/2} M(c(x)) dx}{\int_{-\lambda/2}^{\lambda/2} dx} \quad (3)$$

We note that M_{av} depends only on $M(c(x))$ and is independent of λ .

The results are shown in Fig. 9. It can be seen that the first minimum in the isothermal magnetization $M_s(t)$ measured as a function of annealing time of Fig. 7 is expected simply due to the shape of the $M_s(c_{\text{Cu}})$ curve of Fig. 6. However, in following the curve of Fig. 6 for as-prepared solutions, we have not considered the lag between magnetic and calorimetric detection of the onset of decomposition and the subsequent X-ray detection of α -Fe particles which suggests that some Fe-rich zones will remain coherent (and therefore fcc) beyond the ≈ 35 at% Cu limit. The magnetization of Fe-rich fcc compositions with $c_{\text{Cu}} < 35\%$ have not been measured for the good reason that they have not been synthesized other than for a point at near zero Cu content corresponding to γ -Fe⁽⁵²⁾⁽⁵³⁾, but since the magnetic moment of Fe atoms in γ -Fe is zero at room temperature and nearly equal to that of pure Fe in the supersaturated bcc-Fe(Cu) solid-solutions (Fig. 6), it can only hold intermediate values in su-

persaturated fcc-Fe(Cu) solid-solutions. A range for such intermediate M_s values of the Fe-rich fcc phase are very approximately proposed in the dashed line of Fig. 6. Figure 10 shows a new simulation of magnetic properties during phase separation of fcc-FeCu, now assuming that at least part of the Fe-rich zones remain fcc. In contrast to Fig. 9 such a decomposition mechanism is also capable of generating the second minimum of the magnetization M_s observed for the isothermal annealing of Fig. 7. Our supersaturated fcc FeCu solid solution thus appears to first chemically decompose into coherent fcc Fe- and Cu-rich zones near 500 K. While some of the Fe-rich zones (about 40 volume% of them) seem to quickly loose coherence and transform to bcc during the exothermic chemical unmixing process, the remaining 60% remain fcc and only become bcc after longer annealing times and at higher temperatures as first suggested by Hernando *et al.*⁽⁵⁴⁾. It should also be noted that Drbohlav has excluded⁽⁵⁰⁾ nucleation and growth mechanisms because bcc or α -Fe nucleation and growth was not detected by X-ray diffraction even after most of the positive heat of mixing ΔH_{mix} was released in the calorimeter and in fact the first trace of α -Fe appears with fairly sharp peaks indicating grain-size of about 14 nm compared to the 20 nm of the mother fcc grains. Nucleation of γ -Fe was also excluded because only phase-separation with no sharp concentration profiles can reproduce the shape of Fig. 7 using the shape of the $M_s(c)$ curve of Fig. 6.

Simulation of the first minimum of the $M_s(t)$ curve of Fig. 7 using the $M_s(c)$ curve of Fig. 6 depends only on the shape of the latter and not on the wavelength λ of eq. (3). The decomposition probably begins by segregation of the element with the lower interfacial energy (Cu) to the nanograin boundaries assisted by higher diffusivities near the boundaries and accompanied by the formation of a Fe-rich depletion layer inwards. This is equivalent to a concentration wave in the form of concentric outer shells. Thermodynamics indicate that the critical concentration fluctuation wavelength should be about 2 nm

Fig. 9 Modeling of M_s using the results (solid line) of Fig. 6 ($1\mu_b/\text{at}=93.6$ emu/g).

Fig. 10 Modeling of M_s using the modification indicated by dotted line in Fig. 6.

while kinetic factors favor decomposition to first occur near the surface/interfaces. In the later stages, coherency loss will occur with coarsening of the zones within each nanograin. The occurrence of the second minimum of the $M_s(t)$ curve of Fig. 7 depends on continuation of coherency (fcc-lattice) for Fe-rich zones below the limit of ≈ 35 at% Cu of Fig. 6. This is likely to be the case in the smaller nanograins (with for example $2r < 15$ nm where the central Fe-zones remain less than 10 nm thick even after coarsening of the decomposition wavelength. Consistent with the X-ray data, such zones will ultimately turn bcc when they reach larger sizes after grain growth at higher T and t .

2. Nanocrystallization of amorphous alloys

Recently, several important new classes of metal-metal nanocomposites have been obtained by a combination of rapid solidification and thermal treatment. We can cite three categories: a) Fe-based soft-magnetic materials obtained by nanocrystallization of amorphous Fe-Si-B alloys with Nb and Cu addition⁽⁵⁵⁾ as well as amorphous Fe-B based alloys with Zr, Hf or other larger atom species⁽⁵⁶⁾; b) FeNbB- or FeSmB-type intermetallic nanograins interdispersed with α -Fe nanograins for hard-magnetic applications⁽⁵⁷⁾ and c) Al-based nanocrystalline materials with promising mechanical properties obtained from partial crystallization of Al-based amorphous alloys⁽⁵⁸⁾.

While the soft-magnetic category a) is desired in ribbon form and is unlikely to perform as well with powder processing including MA, the hard magnetic category b) and the Al-based or light nanocrystalline category c) for mechanical properties are just as interesting via powder processing and MA or milling.

A behavior common to Fe-based and Al-based amorphous precursors of these nanocrystalline materials (whether obtained from the liquid state or by MA or milling) is the onset of primary crystallization during annealing some hundred degrees below the temperature of formation of intermetallics via crystallization of the remaining amorphous matrix. We will now consider the causal relation between nanocrystallizability and this temperature difference ΔT between for example nucleation of primary α -Fe and of Fe₃B-type intermetallics or that of fcc-Al and Al-based intermetallics. The main criteria for the alloy design of such amorphous precursors are the following: 1) While a significant volume-fraction of primary crystalline phase (α -Fe or fcc-Al) is to be generated by annealing, nucleation and growth conditions are to be such that crystallite size remain small, with radii $r < 15$ nm for the soft-magnetic alloys and only slightly larger for mechanical properties. 2) The intermetallic phases should not nucleate during primary phase nanocrystallization as they have high magnetocrystalline anisotropy and are mechanically brittle. We need to maximize time t for more nucleation events and a slowing of the growth of nucleating embryos can provide this time. In other terms, the crystal growth rate must decrease rapidly with increasing nucleus radius. Such a time depen-

dence can be obtained if the growing nuclei reject solutes that increase the viscosity and decrease atomic diffusivity of the surrounding amorphous phase and this is the case for both interstitial-type small atoms and substitutional-type larger atoms⁽⁵⁹⁾. For example when primary α -Fe nuclei form in Fe-B based amorphous alloys containing Nb or Zr addition, they reject both B atoms and Nb and Zr atoms into the surroundings. Since $r_B \ll r_{Fe}$ and $r_{Nb} > r_{Fe}$, B-atoms occupy interstitial Bernal-type or trigonal prism-type interstitial holes in the amorphous alloy while Nb and Zr take substitutional sites with less free-volume around them. Diffusivities decrease sharply with such additions as witnessed by increasing stability of the glass and higher crystallization temperatures with increasing B⁽⁶⁰⁾ and Nb⁽⁶¹⁾. While decreased diffusivities in the diffusion layers ahead of the growing α -Fe crystallites slow their growth thus allowing more nuclei to form in the remaining amorphous phase, the increased crystallization temperature of the latter retards incubation and growth of the more complex intermetallic phase nuclei and conditions 1) and 2) for obtaining the nanocrystalline structure are satisfied. The same evolution is expected upon rejection of Nb, Y or other larger atoms by nucleating fcc-Al crystallites within an Al-based amorphous alloy. We have therefore combined the two stated conditions into a single one given by:

$$dT_x(am)/dc_i > 0 \quad (4)$$

for species i rejected by primary crystallization⁽⁶²⁾. This condition was already satisfied by some hypoeutectic FeSiB alloys that were found to nanocrystallize years ago⁽⁶³⁾ but their magnetic properties were not yet discovered at that time.

In the case of hard-magnetic duplex nanostructures of for example intermetallic Fe₁₄Nd₂B and α -Fe, the former insure high coercivity while the latter increase the magnetization⁽⁵⁷⁾. Here also crystallization of a eutectic-type MA amorphous alloy is likely to provide different morphologies than hypo- or hypereutectic amorphous compositions but the metastable phase diagrams are not well known and more data is needed before generalizations can be attempted.

V. Nanocomposites Obtained by Reactive Milling

Reactive ball milling has been used for producing ceramics by reaction between elemental powders or between a metal powder and the milling atmosphere⁽⁶⁴⁾. Thus carbides⁽⁶⁵⁾, silicides⁽⁶⁶⁾ and borides⁽⁶⁷⁾ were produced by milling carbon, silicon or boron with the appropriate element. Many nitrides⁽⁶⁸⁾⁻⁽⁷⁰⁾ were obtained by milling metals under nitrogen or ammonia. A dispersion of aluminium nitrides was obtained by milling aluminium alloys in liquid nitrogen⁽⁷¹⁾. Titanium carbide dispersions were also produced in a copper matrix by ball milling the three elemental powders together⁽⁷²⁾. TiAl-Al₂Ti₄C₂ nanocomposites were obtained by milling of elemental Al and Ti with n-heptane⁽⁷³⁾. Another method consists of milling a metal/oxide couple, chosen so as to obtain an oxygen

Fig. 11 (left) X-ray diffraction patterns of Ti powder first milled 12 h under vacuum (top) then milled 6, 14, 18 and 24 h under N_2 gas showing progressive dominance of TiN peaks $\diamond$ over Ti peaks $\bullet$ together with small Fe contamination peak $+$. (right) TEM dark field image of the 1 square micron area of nitrated Ti powder.

transfer by an exothermic reaction⁽⁷⁴⁾. ISMA-91⁽²⁾ and ISMANAM-94 proceedings⁽³⁾ should be consulted for recent developments in reactive milling.

In the framework of a previous research program⁽⁷⁵⁾, we developed a related technique of metal-ceramic nanocomposite fabrication by nitridation-reduction of selected AB alloys with one nitrophilic and one nitrophobic element. The basic idea can be summarized by the equations:

This reaction predominates when the heat of formation of the BN-type ceramic product is much more negative than that of the intermetallic or solid-solution AB-type precursor and provided that the heat of formation of any nitrides of A are positive. A similar reaction may be written for oxidation reduction under O_2 gas. We tested such reactions with alloys such as CuZr, AuTi, FeTi CuTi⁽⁷⁵⁾. Here we will give some results⁽⁷⁶⁾ concerning nitridation of CuTi and FeTi, the latter having also been studied by Ogino *et al.*⁽⁷⁰⁾⁽⁷⁷⁾.

After verification that nitriding of pure Ti indeed occurs in our milling conditions as shown in Fig. 11, we attempted the following reaction

using the following experimental procedure: The meltspun ribbons of composition $Cu_{83}Ti_{17}$ were milled under nitrogen gas for different milling times. Figure 12 presents the evolution of X-ray diffraction patterns during milling and after annealing at 785°C . While copper peak displacements due to titanium nitridation are seen, only a fine scanning shows the emergence of a reflection near $37.5^\circ 2\theta$ degrees, which can be attributed to the (111) plane of titanium nitride. Its low intensity is due to the low structure factor of the ceramic phase compared to that of copper.

At the end of milling, the coherent domain size calcu-

Fig. 12 X-ray diffraction pattern during ball milling and annealing of $Cu_{83}Ti_{17}$ with $\bullet$, $\diamond$, $+$, and $\times$ referring respectively to positions of pure Cu, TiN, Fe contaminant and reference Si added for eccentricity corrections.

lated from the 111 copper reflection was about 10 nm. Grain superpositions prevent good TEM image analysis but in the bright field image of Fig. 13, the dark (diffracting) grains can be seen to have sizes varying from 5 to 20 nm.

Figure 14 shows the evolution of the copper lattice parameter during ball milling and annealing of $Cu_{83}Ti_{17}$ for the 111, 200, 220 and 311 reflections. The milling down of the melt-spun ribbon to powder form was first performed under argon gas in order to separate effects of deformation from those of nitrogen dissolution and nitride formation during milling under N_2 gas. It can be seen in Fig. 14 that initial milling under argon results in a significant drop in the lattice parameter. While alloy powder milled under argon gas has a lattice parameter of $a=0.3463$ nm (deduced from the 111 reflection), it increases to 0.3682 nm after subsequent milling for 12 h under N_2 gas. This strong variation due to interstitial dissolution of nitrogen shows that the presence of titanium drastically increases nitrogen solubility in the alloy from near zero in pure copper. There is then a steady decrease of the lattice parameter with milling time as nitride for-

Fig. 13 TEM transmitted beam image of $\text{Cu}_{83}\text{Ti}_{17}$ milled 146 h under nitrogen atmosphere. Grain size is between 5 and 20 nm.

Fig. 14 Copper lattice parameter during ball milling and annealing of $\text{Cu}_{83}\text{Ti}_{17}$ using the 111, 200, 220 and 311 reflections.

mation removes the titanium from the fcc-lattice and reduces at the same time N-solubility.

We have explained⁽⁷⁶⁾ the behavior of the lattice parameter of the CuTi solid-solution at various stages of the milling process in the following manner: Initial milling generates dislocation jogs whose forced displacements produce large vacancy supersaturation. These vacancies form clusters if they meet each other before reaching grain boundaries or other sinks. A common such cluster-type defect is a vacancy disk on the {111} planes which can collapse upon growth and form a stacking fault. However Ti atoms in solid solution in the milled ribbon will interact with the effective negative charge and the elastic strain field of the vacancies and form impurity—vacancy defects. This is due both to Ti's higher valency compared to the host Cu^+ ions and because of its larger size. Any vacancy defects such as disks are therefore expected to be decorated by Ti atoms. Both vacancy defects and Ti-vacancy associations contribute to the initial reduction of the lattice parameter.

When the milling is subsequently continued under N_2

Fig. 15 X-ray diffraction patterns of $\text{Cu}_{83}\text{Ti}_{17}$ milled under nitrogen and then densified. • and × designating respectively the positions of the Cu phase and the reference Si added for eccentricity corrections.

Fig. 16 Lattice parameter for Cu-Ti alloys as a function of Ti content⁽⁷⁸⁾. Arrow shows Ti-content of the compact deduced from its lattice parameter.

gas, the lattice parameter first increases sharply. This can be explained by the dilatation of the fcc lattice due to interstitially dissolved nitrogen atoms whose solubility has increased due to the presence of titanium. The lattice parameter then decrease again as TiN formation evacuates both Ti and N from the fcc lattice. TiN nuclei are expected to preferentially form on vacancy-Ti defects and Ti-lined stacking faults that form in the previous deformation stage.

Another batch of $\text{Cu}_{83}\text{Ti}_{17}$ ribbons was milled under nitrogen and densified under dynamic primary vacuum by 3 min of uniaxial die pressing at 900°C with a pressure of 57 MPa. The resulting cylindrical compact's microhardness was determined and it was then spark cut to obtain a rectangular thin rod. Melt-spun ribbons of intermediate composition $\text{Cu}_{93}\text{Ti}_7$ were prepared. Electrical conductivities of the rod and ribbons of a few different compositions were determined using a four-point set-up.

Figure 15 shows X-ray diffraction spectra of milled powder after uniaxial die pressing at $T=900^\circ\text{C}$. Figure 16 presents the evolution of copper lattice parameter as a function of titanium concentration. The initial point at 0.3615 nm is the new value accepted for pure copper⁽⁷⁸⁾⁽⁴⁵⁾. The two other points are the $\text{Cu}_{93}\text{Ti}_7$ and $\text{Cu}_{83}\text{Ti}_{17}$ melt-spun ribbons lattice parameters calculated using a $\cos^2 \theta$ -type plot. The value of 0.3620 nm for the hot-pressed

compact deduced from Fig. 15 corresponds to a residual titanium concentration near 2.5 at%.

Figure 17 presents the measured electrical conductivity of pure copper, of the melt-spun ribbons and of the hot-pressed compact. It is observed that the compact's conductivity corresponds also to a residual titanium concentration of 2.5 at% as expected from the X-ray results of Fig. 16.

2.5 at% of titanium thus remains in solid solution in the densified sample for which the ball to powder weight ratio was 50% less than the first batch in which nitridation goes to completion and the pure Cu lattice parameter is restored after annealing. A more energetic milling under N₂ gas should provide materials having very good conductivity.

The microhardness after hot-pressing was evaluated as the average value of ten tests at 363 Hv.

The copper grain size at the end of milling is about 10 nm and is kept at 30 nm after annealing at 785°C: the nanocrystalline character of the Cu/TiN composite can thus be conserved after densification, a result which is of particular interest for applications.

Figure 18 shows X-ray diffraction results concerning a

similar nitridation process corresponding to the reaction

A particularity that is essential for these materials' potential applications is their nanodispersoid character which results in hardening, blocks crack propagation, slows grain-growth rates and renders them insensitive to radiation damage. However they may exhibit brittle behaviour when the hard-phase volume fraction reaches the percolation limit.

VI. Conclusions

Research in the past few years has demonstrated that mechanical alloying and milling generate new supersaturated solid-solutions (amorphous or nanocrystalline). Their decomposition with annealing or via reactive milling can be used to design new nanocrystalline and nanocomposites with improved properties. Promising mechanical, magnetic and catalytic properties are likely to generate a number of new applications⁽²⁾⁽³⁾. The thermodynamic and kinetic behavior of nanocrystalline hydrides are also under study.

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Fig. 17 Electrical conductivity of Cu-Ti solid solutions as a function of Ti content.

Fig. 18 X-ray diffraction patterns of Fe₆₂Ti₃₈ (a) milled under nitrogen (top) and annealed at 785°C after 192 h of milling and at 770°C after 375 h milling ◇, •, *, + and × designate respectively Fe₂Ti, Fe-α, TiN, FeTi and the reference Si added for excentricity corrections.

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