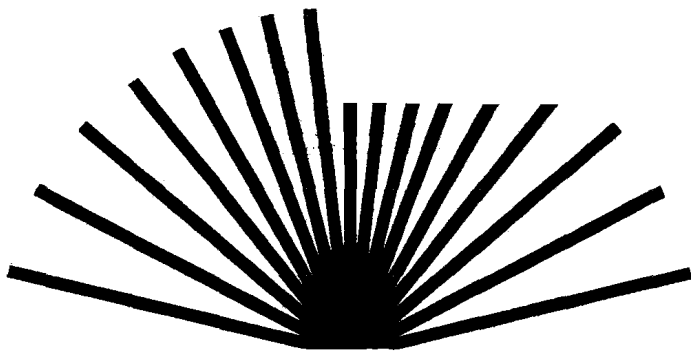


**NOVEL TECHNIQUES
IN SYNTHESIS
AND PROCESSING
OF ADVANCED
MATERIALS**

Edited by
Jogender Singh
and
Stephen M. Copley



NOVEL TECHNIQUES IN SYNTHESIS AND PROCESSING OF ADVANCED MATERIALS

Proceedings of a Symposium
held at Materials Week '94
in Rosemont, Illinois, October 2-6, 1994
by The Minerals, Metals, & Materials Society (TMS)
and the Materials Information Society (TMS International)

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PREFACE

International Conference on Novel Techniques in Synthesis and Processing of Advanced Materials was held at the Fall TMS/ASM Materials Week at Rosemont, Illinois, October 2-6, 1994. This conference was focused into four areas including novel techniques and advancement in processing of materials such as nano-materials (metals, ceramics and composites); electronic, photonic, & magnetic materials; bio materials and super-hard materials. The symposium will emphasize various methods in synthesis of materials including mechanical milling, combustion process, sol-gel process, microwave, laser chemical vapor deposition (CVD) process, metalorganic CVD, combustion synthesis, etc. In addition, the symposium will cover structural characterization at small dimensions thermodynamics, kinetics and properties (including mechanical, electronic, magnetic, optical and thermal) of nano materials. In view of future need for advancement in the electronic industries, a special emphasis is given to the synthesis of nano crystalline electronic materials. This allows to have a better understanding of the chemical and physical phenomena that occurred during synthesis and processing of advanced materials that will have many technological applications. The combination of a wide variety of technological applications and scientific approaches made this years meeting especially interesting. This symposium once again demonstrated the ability of scientific and application research efforts to stimulate each other.

Next challenge is processing large quantity of nano-crystalline materials and fabrication of large components or parts without loosing the critical size of the nano-scale particles. In the past few years, many exciting and superior properties have been discovered with particles or grain size in the nano-meter range.

The principal objective of this symposium was to bring the current state-of-the-art in processing of advanced materials. This proceeding will be beneficial to materials scientists and engineers who are not working directly in this area. Papers in this book have been contributed by recognized experts in their field who have discussed everything from fundamental aspects to synthesis, processing and industrial applications.

This book is intended to be used, for example, by researchers interested in obtaining a broad overview of a new field, as a general reference for individual already working in this field, or as a text book for a graduate-level materials science course.

We wish to gratefully acknowledge all the authors, presenters and participants who took part in the conference, who by their contributions, ideas and enthusiasm made the conference an overwhelming success. We thank also session chairs including Drs. Bruce MacDonald (NSF), Henry Watson (ARL), John Prator (ARO), George and Yorder (ONR) for their assistance in coordinating and conducting the symposium. This conference was primarily sponsored by the Materials Synthesis and Processing Committee of the Materials Information Society (ASM), and co-sponsored by the Electronic, Magnetic and Photonic Materials Division (EMPMD) of the Minerals, Metals & Materials Society (TMS). TMS is

to be thanked for its role in enabling this symposium to flourish. We hope that TMS will continue to serve for organizing such an international conference to this topic.

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FAR FROM EQUILIBRIUM PROCESSING OF LIGHT METALS

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Abstract

Far from equilibrium synthesis allows development of novel crystal structures and microstructures, leading to achievement of enhanced physical and mechanical properties. A number of "far from equilibrium" techniques are reviewed with emphasis on the amount of departure from equilibrium. The ability of two such techniques, mechanical alloying (MA), and physical vapor deposition (PVD) to develop novel structures are discussed in detail. For the MA process emphasis is placed on intermetallic compound compositions. Solubility extension, beyond rapid solidification (RS) levels, is found in terminal compositions but not for the intermetallics. Nanostructure-sized grains ($\leq 100\text{nm}$) form which can be retained after "low temperature" compaction. On continued milling in many cases the nanometer-sized grains transform to an amorphous structure. Ordering is destroyed by MA, except in those intermetallics with large negative enthalpies of formation. For the PVD process, a review of application to terminal light alloy compositions is presented. This includes a new high-temperature aluminum alloy, layered materials with nanometer spacing, corrosion-resistant magnesium alloys and low-density titanium compositions.

Introduction

To enhance the mechanical property combinations of advanced structural materials innovations in process/synthesis are required [1-6]. In this paper the capability of various "far from equilibrium" synthesis techniques [7,8] to produce novel constitutional and microstructural effects, and hence potentially enhanced physical and mechanical properties, in advanced materials is presented. The application of two such methods, mechanical alloying (MA) and physical vapor deposition (PVD) is discussed in detail. For the MA process emphasis is on intermetallic compositions with consideration given to solid solubility extension, microstructural refinement, amorphization, and formation of intermetallic compounds. For the PVD process application to terminal light alloy compositions is discussed.

Far From Equilibrium Processing

More than ten years ago, Turnbull attempted to quantify departure from equilibrium in terms of an "energize and quench" parameter [9]. However, while this approach was a step forward, it excluded other processes in which "quenching" does not play a part. Over the past few years, the present authors have investigated various "far from equilibrium" processes, from both theoretical and experimental standpoints, and attempted to quantify the magnitude of the departure from equilibrium [7,8]. Recently Shingu [10] has published calculated values of the departure for various processes.

In this section we will consider how far from equilibrium various phenomena take us [7,8]. We will consider the free energy change on forming Avogadro's number of atoms(N_a)* of product phase from an unstable (metastable) phase. Elements are considered in equations 1 through 7, and alloys in equations 8 through 10. T is the actual temperature, T_0 is the temperature at which the phases are in equilibrium, R is the gas constant and ΔG is the departure from equilibrium.

Elements

1. Supercooled Vapor. Here P_e is the equilibrium pressure, P is the actual pressure, T_b is the boiling temperature and ΔH_b is the enthalpy of boiling.

$$\Delta G = -RT \ln P/P_e$$

$$\text{Take } P_e = A \exp (-\Delta H_b/RT)$$

$$\text{Assume } P = 1 \text{ atmosphere}$$

$$\Delta G = \Delta H_b(1-T/T_b)$$

$$\Delta H_b \approx 10RT_b$$

$$\text{If } T_b = 2000K, T \rightarrow 0$$

* We originally considered "one mole" of product phase. However, this strictly does not apply to compounds which may contain more than N_a atoms, so we have chosen to use N_a number of atoms.

$$\Delta G = 160 \text{ kJ, maximum} \quad (1)$$

2. Undercooled Liquid or Amorphous Phase. T_m and ΔH_m are the melting temperature and melting enthalpy, respectively.

$$\Delta G = \Delta H_m (1 - T/T_m)$$

$$\Delta H_m \approx RT_m$$

$$\text{If } T_m = 1000\text{K, and } T \rightarrow 0$$

$$\Delta G = RT_m \approx 8 \text{ kJ, maximum} \quad (2)$$

3. Allotropic Transformation. Here α and β are two phases, and ΔH is the enthalpy of the transformation.

$$\alpha \rightarrow \beta$$

$$\Delta G = \Delta H(1 - T/T_0)$$

ΔH for an allotropic transformation is typically of the order of 10% of ΔH_m for melting, so for $T_0 = 1000\text{K}$, and $T \rightarrow 0$

$$\Delta G \sim 1\text{kJ, maximum} \quad (3)$$

4. Excess Vacancies.

$$\Delta G = X_v RT \ln X_v/X_v^\circ, \text{ where}$$

X_v , X_v° are actual and equilibrium concentrations of vacancies and ΔH_v is the molar enthalpy of vacancy formation.

$$X_v^\circ = \exp(-\Delta H_v/RT)$$

$$\Delta G = X_v(\Delta H_v + RT \ln X_v)$$

$$\Delta H_v \sim 100 \text{ kJ/mole of vacancies.}$$

$$\text{At the most, } X_v = 0.1$$

$$\text{If } T \rightarrow 0$$

$$\Delta G = 10 \text{ kJ, maximum} \quad (4)$$

5. High Dislocation Density. Here W/L is the dislocation line energy per unit length of the dislocation line, L/V is the dislocation line length per unit volume, μ is the shear modulus and b is the Burger's vector.

$$\Delta G = (W/L) (L/V) (\text{Vol/mole})$$

$$W/L \approx \mu b^2 = (1 \times 10^{11} \text{Pa}) (3 \times 10^{-10} \text{m})^2$$

$$= 1 \times 10^{-8} \text{ J/m}$$

$$L/V = 10^{12}/\text{cm}^2 = 10^{16}/\text{m}^2 = \text{high dislocation density}$$

$$V/\text{mole} \approx 10^{-5} \text{ m}^3/\text{mole}$$

$$\Delta G = (1 \times 10^{-8} \text{ J/m}) (10^{16}/\text{m}^2) (10^{-5} \text{ m}^3/\text{mole})$$

$$= 1 \times 10^3 \text{ J}$$

$$= 1 \text{ kJ, maximum} \quad (5)$$

6. High Surface/Volume Ratio, (1 nm grain size): here γ is the grain boundary energy.

$$\Delta G = (\gamma \text{ J/m}^2) (\text{m}^2 \text{ Surface}/\text{m}^3 \text{ Volume}) (\text{Volume}/\text{mole})$$

$$\gamma = 1 \text{ J/m}^2, \text{ m}^2/\text{m}^3 \sim 1/\text{grain size} = 10^9 \text{ m}^{-1} \text{ (for 1 nm grain size)}$$

$$\Delta G = (1) (10^9) (10^{-5}) = 10^4 \text{ J}$$

$$= 10 \text{ kJ, maximum} \quad (6)$$

7. Electrochemical Over Voltage. Here N is the number of electrons transferred, ϵ is the over voltage and F is Faraday's constant ($F = 96,500$ coulombs/equivalent).

$$\Delta G = NF\epsilon$$

Take ϵ as 5 volts and N as 1

$$\Delta G = (1) (96,500) (5)$$

$$= 500 \text{ kJ, maximum} \quad (7)$$

Alloys

8. Precipitation from Supersaturated Solid Solution. Normally immiscible elements may be forced to form a solid solution. At low temperatures the entropy terms are unimportant and the free energy change is entirely enthalpic. For a 50:50 alloy, for instance:

$$\Delta G = \Delta H = \Omega/4, \text{ where } \Omega \text{ is the regular solution constant.}$$

For sparingly soluble elements, e.g. Fe in Cu, $\Omega = 40 \text{ kJ}$

$$\text{So, } \Delta G = 10 \text{ kJ, maximum} \quad (8)$$

9. Disordering of an Ordered Alloy (in the solid state). Here we define the "disordering energy" as the difference in free energy between the ordered phase and its nearest equivalent crystal structure in the disordered state [11].

Consider an alloy AB

Here ΔH is the ordering energy.

$$\Delta G = \Delta H (1 - T/T_0)$$

$$\Delta H \approx RT_0/2, \Delta G = RT_0/2 \text{ at } T=0$$

If there is a very stable ordered phase with a high T_0 (i.e. in this case the disordering temperature), say 1500K,

$$\Delta G = 6 \text{ kJ, maximum} \quad (9)$$

10. Disordering of an Ordered Alloy (which is ordered at the melting point). This is similar to #9 with a higher ΔG [11].

$$\Delta G = 12 \text{ kJ, maximum} \quad (10)$$

These departures from equilibrium are summarized in Table I. Using these values, we have calculated the maximum departures from equilibrium which are possible with various "far from equilibrium" processes in Table II. While we feel confident that the majority of these values are realistic, we have some concerns with adding together disordering (either in the solid state or at the melting point) and supersaturation of the solid solution. The question here is, is it an either/or situation? However, based on a suggestion from Cahn [12] the disordered alloy,

Table I. Maximum Departure From Equilibrium ΔG

Phenomenon	Equation	Max. ΔG (kJ/N _a)
Supersaturated vapor → solid	1	160
Supersaturated liquid → solid (also for amorphous)	2	8
Allotropic $\alpha \rightarrow \beta$	3	1
10% Vacancies	4	10
10^{16} dislocations/m ²	5	1
1 nm grain size	6	10
5V over voltage	7	500
Precipitation from supersaturated solid solution	8	10
Disordering Alloy (disorders in solid state)	9	6
Disordered Intermetallic (ordered to MP)	10	12

especially when the ordering energy is high, is effectively a distinct phase with its own thermodynamic properties. For example [12] computed free energy versus composition curves for compounds such as Ni_3Al show significantly different curves for the ordered and disordered forms, with minima that do not necessarily occur at the same composition.

Table II. Departure From Equilibrium Achieved in Various Processes [8]

PROCESS	MAXIMUM DEPARTURE FROM EQUILIBRIUM (kJ/N _a)
SOLID STATE QUENCH	16 ^a
QUENCH FROM LIQUID (RAPID SOLIDIFICATION)	24 ^b
CONDENSATION FROM VAPOR	160 ^c
IRRADIATION/ION IMPLANTATION	30 ^d
MECHANICAL COLD WORK	11 ^e
MECHANICAL ALLOYING	30 ^d

- ^a Assuming disordering of an ordered intermetallic (not ordered to MP) [6 kJ/N_a], and a supersaturated solid solution [10 kJ/N_a].
- ^b Assuming disordering of an ordered intermetallic (not ordered to MP) [6 kJ/N_a], amorphous phase formation [8 kJ/N_a] and a supersaturated solid solution [10 kJ/N_a].
- ^c Assuming a supercooled vapor transforms to a solid [160 kJ/N_a].
- ^d Assuming a strongly ordered intermetallic (ordered to MP) disorders [12 kJ/N_a] and becomes amorphous [8 kJ/N_a], and is a supersaturated solid solution [10 kJ/N_a].
- ^e Assuming 10¹⁶ dislocations per m² [1kJ/N_a], and 10% vacancies (10kJ/N_a).

A comparison of the values listed in Table II and the calculations of Shingu [10] are generally in agreement but there are also some disagreements. The two calculations of departure from equilibrium for undercooled liquids are generally in agreement. Shingu considered rather smaller undercooling than in the present work, but on the basis of the same undercoolings, the calculations are in agreement. The two separate calculations of the amount of free energy associated with fine particle sizes or grain sizes are also in agreement, differing only in the particle size assumed for the calculation.

Shingu estimates the excess free energy introduced by mechanical alloying from stored energy and activity measurements. The final values, a few tens of kJ/mole are consistent with our estimates made from mechanistic estimates of the energies associated with the added defects, forced solubility increases, and disordering associated with the mechanical alloying process.

Shingu estimates an excess free energy of 20 kJ/mole associated with powder mixing. The most extreme state of solid state departure from equilibrium would correspond to the dissociation of a very stable compound into its elemental constituents. A free energy of formation of 40 kJ/mole of an AB compound corresponds to 20 kJ/mole of atoms, the basis of the calculations in this paper. This appears to be a reasonable value.

Shingu estimates that pressure quenching could produce free energy differences of a few kJ/mole. Pressures of a few GPa and about a 10% change in molar volume would give such free energy differences. Shingu also estimates that pressures of the same magnitude would give some 30 kJ/mole free energy differences in mechanical alloying of Fe and Cu. A pressure is effective in promoting alloying only if the partial molar volume of the element entering into solid solution is significantly ($\approx 10\%$) less than its volume in the elemental state. At ambient temperatures, BCC Fe and FCC Cu have almost the same molar volumes. Perhaps the partial molar volumes are significantly less, but we have no reason to believe so.

The departures from equilibrium characteristic of MA and PVD (condensation from the vapor), in excess of that exhibited by rapid solidification (RS) processing, open up the opportunity for greater flexibility in constitutional and microstructural manipulation than possible using the RS approach.

Mechanical Alloying

The Process

Mechanical alloying is a high energy ball milling operation involving repeated welding, fracturing and rewelding of powder particles (Figure 1) [13-17]. The large departures from equilibrium possible by MA lead to the attributes shown in Table III, including production of stable dispersoids, extension of solubility levels, refinement of the microstructure into the nanometer range, synthesis of novel crystalline and amorphous phases, alloying of elements with significantly different melting points and/or involving complex solidification paths, and initiation of chemical reactions at much lower temperatures than those at which they would normally occur [13-19]. In addition, it is a process which is scaleable to commercial production quantities, unlike some other "far from equilibrium" processes.

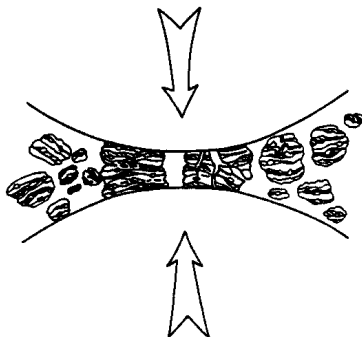


Figure 1 - Schematic of mechanical alloying process.

The present paper will report on work using MA as a synthesis technique, with emphasis on materials in the compositional range of intermetallic compounds. This will be addressed under the categories of solid solubility extension, nanostructure sized grains, amorphous phase formation, and synthesis of intermetallics. Details of the experimental techniques used can be found elsewhere [8].

Mechanical alloying of either blended elemental (BE) powders or prealloyed (PA) powders (sometimes referred to as mechanical milling) results in an increase in energy in the materials which can lead to the various effects listed in Table III. The general sequence of events for BE material is for solid solution formation (of increasing solute content with time), followed in some cases by intermetallic compound formation. The degree of ordering in the intermetallic is a balance between the disordering resulting from the MA and the tendency for thermally activated reordering. Finally, in some cases, amorphization takes place. Grain refinement occurs during MA of both the solid solution and the intermetallic. The PA material with an intermetallic composition, will generally start with some degree of ordering so that MA will decrease the long range order to a degree depending on the stability of the ordered structure. Then, as in the BE case, grain refinement and possibly amorphization will occur.

Table III. Attributes of Mechanical Alloying (MA)
and Physical Vapor Deposition (PVD)

1.	Production of a Fine Dispersion of Second Phase Particles
2.	Extension of Solubility Limits
3.	Refinement of the Matrix Microstructure down to the Nanometer Range
4.	Synthesis of Novel Crystalline Phases
5.	Development of Amorphous (Glassy) Phases
6.	Possibility of Alloying of Difficult to Alloy Elements
7.	Inducement of Chemical Reactions at Low Temperatures ^a
8.	Scaleable Process

^a MA only.

Solid Solubility Extension

The solubility extensions obtained by MA, and corresponding values developed using RS, where available, are listed in Table IV. These are the solubility levels obtained in terminal solid solutions, rather than in intermetallics. In accordance with Table II, MA should generally allow even greater solid solubility extension (SSE) than RS. Schwarz et al. [20] suggested that this SSE could be rationalized in terms of the metastable equilibrium between the terminal solid solution and an amorphous phase rather than the stable equilibrium between the terminal solid solution and an intermetallic. This explanation appears to hold true for a variety of systems [21-27]. A comparison of Table IV and Table V indicates that an amorphous phase has been detected in four of the six systems investigated; both ends of the Al-Nb phase diagram are included [8]. Data is still being developed on the Al-Mg system; but

interestingly this is the only system where RS gives greater SSE than MA, a result confirmed by others [28]. To date no amorphous phase has been detected in the Ti-Mg system. Thus the data developed in the present work generally agrees with the model proposed by Schwarz et al. [20]. In those cases where an amorphous phase does not form, the reason for the increased solubility after MA is still to be fully rationalized.

Table IV. Solid Solubility Extension By Mechanical Alloying and Rapid Solidification

SOLVENT	SOLUTE	SOLID SOLUBILITY (at.%)		
		EQUIL. AT RT	BY RS	BY MA
Al	Fe	0.025	4.3	4.5
Al	Hf	0.0007	0.3	1.5
Al	Mg	18.9	40	23
Al	Nb	0.065	2.4	> 25, < 30
Al	Zr	0.015	1.3	6.3
Ag	Ni	~0	--	3.8
Mg	Ti	~0	--	4.2
Nb	Al	< 6	25	60
Ni	Ag	~0	--	9.0
Ti	Al	< 11	--	≥33
Ti	Mg	< 0.2	--	3.6

There is little data on SSE by MA in intermetallic compounds. This may result from the fact that amorphization is more likely to occur in the intermetallic than in the terminal solid solution. Substantial extension of solubility for the AlCo phase has been reported, but here Al atoms segregate to the open grain boundary regions, with no change in lattice parameter of the AlCo phase in the grain interiors, implying no SSE in these regions [29].

Nanostructured Grains

The large amount of energy transmitted to the powder results in a dislocation cell structure within shear bands which transforms to random nanostructured grains with increasing MA time [18,30]. A summary of the nanostructured grains obtained in this work is given in Table VI [8]. In the Ti-Al-Nb and Nb-Al systems, the crystal size in the MA'd powder decreased exponentially with milling time and reached nanometer levels in about 5h, Figure 2; decreased milling intensity (lower BPR) resulted in slower decrease in the crystal size, Figure 2d. The rate of decrease is faster in the PA powder than in the BE powder. The size of the nanostructured grains was confirmed by transmission electron microscopy in some cases (Figure 3) [8]. The minimum (saturation) grain size formed, which occurs prior to amorphization in some cases, decreases as the intensity of milling is increased (Figure 2d), confirmed by other work [30].