SOFT MAGNETIC NANOCRYSTALLINE/NANOSTRUCTURED MATERIALS PRODUCED BY MECHANICAL ALLOYING ROUTES

I. Chicinaş

Materials Sciences and Technology Dept., Technical University of Cluj-Napoca, 103-105 Muncii ave., 400641 Cluj-Napoca, Romania, Ionel.Chicinas@stm.utcluj.ro

Materials whose crystallites/particle sizes are smaller than 100 nm are commonly named nanocrystalline/nanostructured/nanosized materials. The unique properties of nanocrystalline materials are derived from their large number of atoms residing in defect environments (grain boundaries, interfaces, interphases, triple junctions) compared to coarse-grained polycrystalline counterparts [1-3]. The benefits found in the nanocrystalline alloys stem from their chemical and structural variations on a nanoscale, which are important for developing optimal magnetic properties [1,2,4]. It is well known that the microstructure, especially the crystallite size, essentially determines the hysteresis loop of the soft ferromagnetic materials. The reduction of crystallite size to the dimensions of the domain wall width increases the coercivity towards an extreme value controlled by the anisotropy [5]. However, the lowest coercivity is found again for crystallite smaller than the correlation lengths like in amorphous and nanocrystalline alloys. Such behaviour has been explained by the random anisotropy model [6].

Besides the incipient crystallisation of amorphous solids [1-3], mechanical alloying is nowadays one of the widely used preparation techniques to obtain nanocrystalline structures. Mechanical alloying techniques involve the synthesis of materials by high-energy ball milling, in which elemental blends (or pre-alloyed powders, oxides, nitrides, etc) are milled to achieve alloys or composite materials [7–9]. These techniques allow producing non-equilibrium structures/microstructures including amorphous alloys, extended solid solutions, metastable crystalline phases, nanocrystalline materials and quasi crystals [9-15]. The disadvantage of ball-milling processes for making nanocrystalline powders is the contamination of products from the milling media (balls and vial) and atmosphere. In last two decades, a large variety of mechanical routes has been developed in order to produce nanocrystalline/amorphous alloys/intermetallic compounds.

Mechanical alloying (MA) refers especially to the formation of alloys/compounds from elemental precursors during high-energy ball milling in planetary mills, vibratory mills, attritors and tumbling ball mills. The repeated collision between balls and powders with very high impact velocity deform and work-harden the powder. In this repetitive cold welding and fracturing mechanism, cold welding of overlapping particles occurs between clean surfaces formed by prior fractures. The competing process of deformation, fracture and welding during milling produces a microstructural refinement and finally some composition changes. In the case of the milling in planetary ball mil, depending of rotation speed of the disk on which the vial holders are fixed (Ω) and the rotation speed of the vial (ω), it has introduced the concept of the shock frequency, the kinetic shock energy and the shock power. According to Ω/ω ratio, it can have the shock mode process (SMP) when $\Omega \gg \omega$, and the friction mode processes (FMP), when $\Omega \ll \omega$ [16, 17].

Mechanical milling (MM) refers to the process of milling pure metals or compounds which are in thermodynamically equilibrium before milling. This process can produce disorder, amorphous materials and composition changes. For MA and MM, the weight rate powder/balls is usually from 1/7 to 1/10, but can be found also rates from 1/5 up to 1/50. The materials obtained by mechanical alloying or mechanical milling present a high number of crystalline defects and it is possible to obtain amorphous alloys by mechanical alloying even for a negative energy for amorphous phase formation, by the way: $mA + nB \rightarrow A_mB_n\ (crystalline) \rightarrow A_mB_n\ (amorphous)$ [9].

Mechanical alloying combined with annealing (MACA) is a new mechanical alloying technique which consists of mechanical alloying/milling and subsequent annealing. If the milling process is stopped before the MA finishing and then the milled powders mixture is subjected to an annealing it is possible to improve (finishing) the solid state reaction of compound/alloy forming [18, 19]. It is important to note the double effect of the annealing on the samples: (i) improvement of the solid-state reaction between elements and (ii) diminution of the internal stresses.

A new method of mechanical alloying consists in **MACA synthesis with inserting nanocrystalline germs** of the reaction product was proposed in [20]. Basically, the idea of the method consists in changing the solid state reaction of A_mB_n intermetallic compound synthesis from the classical form $mA + nB = A_mB_n$ to the form $(1\text{-}x)\cdot(mA + nB) + x\cdot A_mB_n = A_mB_n$. The effect is the reducing the milling time.

Reactive milling (RM) or mechanochemical synthesis (mechanochemistry) involves mechanical activation of solid state displacement reactions in a ball mill. Thus, mechanical energy is used to induce chemical reactions. Mechanochemical synthesis is generally based on the following displacement reaction $A_xC + yB \rightarrow xA + B_yC$, where A_xC and B are precursors, A is the desired new phase (reaction product) and B_yC is a by-product of the reaction [3, 21].The applications of mechanochemistry include exchange reactions, reduction/oxidation reactions, decomposition of compounds, and phase transformations. This process has been used successfully to prepare nanoparticles of a number of materials, including transition metals, alloys, oxide ceramics, ferrites, etc.

The nanocrystalline/nanosized ferrites were prepared especially by two basically mechanical routes: (i) directly, by reactive milling of oxides or others precursor's mixture and (ii) by dry or wet milling of the polycrystalline ferrites obtained by classical methods. As type of ferrites, by mechanical routes were obtained the follows: Fe_3O_4, $NiFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$, $MgFe_2O_4$, $CoFe_2O_4$, $CdFe_2O_4$, $NiAlFeO_4$, $Mn_{(1-x)}Zn_xFe_2O_4$. In the case of the soft magnetic ferrites produced by mechanical routes, a partial reversibility during milling of the reaction $\alpha\text{-}Fe_2O_3 + MeO \leftrightarrow MeFe_2O_4$ was evidenced and the particles contain several related Fe–Me–O phases [22-25]. As a consequence of the partial reversibility of the reaction, the complete formation of $ZnFe_2O_4$ spinel phase was attained after 1320 hrs of milling, while the $CuFe_2O_4$ spinel phase cannot be obtained by RM even for milling times as long as 1600 hrs [23]. Generally, the soft magnetic ferrites produced by mechanical routes exhibit a reduced particle size under 10 nm. As a consequence, the soft magnetic nanocrystalline/nanosized ferrites produced by mechanical routes present also particle size with a superparamagnetic (SPM) behaviour [26-28] and a spin canted effect [22, 27, 29, 30]. As a consequence of the spin canted magnetic structures, a nonsaturated magnetisation (even at a field of 9 T) and a ΔH_C shift to the left, depending on the milling time, were reported [22, 23]. The properties of the nanocrystalline/nanosized ferrites prepared by different mechanical routes were reviewed in ref. [31].

In last decades, many works were dedicated to obtain, by different mechanical routes, the nanocrystalline soft magnetic powders from some alloys systems based on Fe or Ni. The most studied systems are Fe-Ni and Fe-Cu. The Fe-Cu immiscible system is a representative system to illustrate the possibility of the MA to form the metastable phases, mechanically alloyed Fe_xCu_{100-x} solid solutions, which are never obtained by classical metallurgy or quenching method in immiscible binary systems.

The researches concerning alloys from Fe-Cu system produced by mechanical routes cover entire Fe-Cu diagram. The problems involved in mechanical alloying in Fe-Cu system are reviewed in ref. [32]. Generally, the solubility limit can be easily extended at 20 at% Cu in bcc phase and 6o% Fe in fcc phase [33]. A milling map of the Fe-Cu system shows that it is possible to extend to solubility limit both for bcc and fcc phases by increasing the milling time. The Fe-Cu alloys obtained by mechanical alloying present very interesting magnetic properties. Despite both Cu and Fe metals with fcc structures are nonmagnetic, the substitution of Cu atoms by Fe in fcc-Cu lattice leads to the formation of a random solid solution with the appearance of the ferromagnetic order. It was shown that the ferromagnetism (Fe-Fe positive exchange interactions) in the mechanically alloyed Fe–Cu originates when the atomic volume is expanded by a certain value (5.3% of γ-Fe, regardless of copper content), and when a certain number of neighboring iron atoms exist to percolate the ferromagnetic interaction and possibly to induce the magnetic moment on iron [34]. The mixture of Cu and bcc Fe (α-Fe) is magnetically soft with low coercivity. In the case of the fcc $Fe_{50}Cu_{50}$ solid solution an improvement of the coercive field, remanence induction and saturation induction, comparatively with as-milled powders has been found by isothermally annealing at 450 °C.

This behaviour was explained in terms of the precipitation of nanocrystalline/ultrafine Fe in Cu matrix by a spinodal decomposition [35]. A rich synthesis on the coercivity in nanocrystalline alloy powder prepared by MA is given in the reference [36]. Magnetoresistivity measurements performed at 77 K have shown giant magnetoresistance (GMR) behaviour in samples with Fe concentration between 10 and 45 at%. The highest values of GMR ratio were reached at 20 Fe at % ($\Delta\rho/\rho$ = 1% for as-prepared samples milled for 75 hours and 2.75% for as-prepared samples milled for 20 hours [37]. The Invar effect was observed in Fe-Cu solid solutions by means of lattice thermal expansion and magnetisation measurements [38].

The most studied alloys by mechanical routes belong to the Fe-Ni system. Different mechanical routes and very different milling conditions have been used to produce nanocrystalline Fe-Ni powders [15]. Very rich analysis of the phase transformation in $Fe_{1-x}Ni_x$ ($10 \leq x \geq 90$ at%) alloys by mechanical alloying and subsequent annealing was reported [39]. It was shown that single phase solid solution of MA samples is significantly wider than that of thermodynamically stable alloys. A synthesis concerning the phases which could be obtained by mechanical alloying is presented by comparison with the equilibrium phase diagram in the Fe-Ni alloys, figure 1 [40]. It can be seen a considerable extension of the solubility limit and also the obtaining a bct phase by MA. The nanocrystalline Ni_3Fe intermetallic compound was produced by mechanical alloying of elemental Ni and Fe powders and annealing [18, 19, 41-44]. The mean crystallite sizes of about 22 or 12 nm were obtained after 12 and respectively 52 hours of milling and 3 hours of annealing at 330 °C [18, 19].

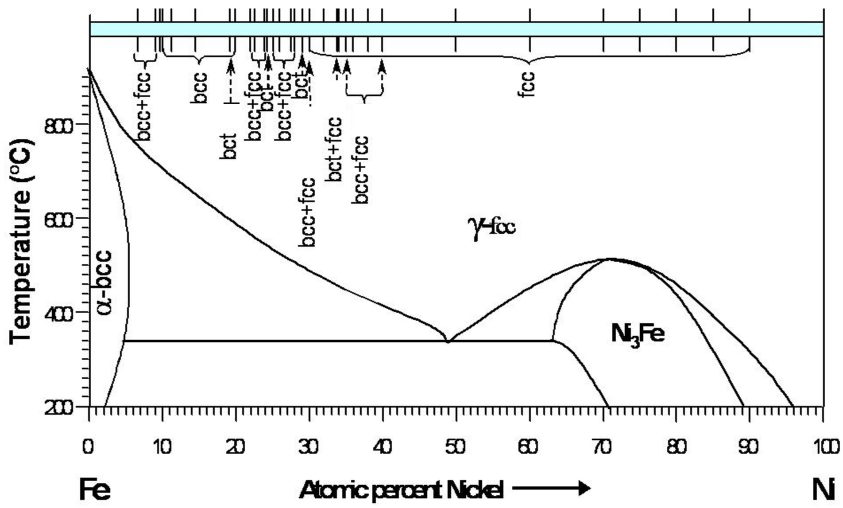

Figure 1. A synthesis concerning the phases which could be obtained by mechanical alloying by comparison with the equilibrium phase diagram in the Fe-Ni alloys. The dotted lines indicate other phases than usually reported [after Ref. 40].

The magnetic properties of the Ni-Fe powders obtained by MA depend on the milling conditions and of the structure. It was been proved that the milling performed in the "friction mode processes" leads to the formation of alloys exhibiting a soft magnetic behaviour [17, 45]. A strong decrease of the coercive field versus crystallite size appears especially for crystallite size smaller than 20 nm and a limit value of the H_C = 110 A/m was obtained for Fe-Ni 20 at% after 96 hours of milling [46]. An interesting result was obtained for $Fe_{65}Ni_{35}$ alloys, which had not Invar anomaly as suggested by the equilibrium diagram [47]. A higher Curie temperature than that for the equilibrium alloys has been observed for Fe-Ni 35 at% and Fe-Ni 50 at% [47]. Many authors report an increasing of the magnetisation with increasing the milling time [18,19, 41, 45, 47]. In the case of Ni_3Fe, it was found that M_s decreases at milling time longer than 20 hours due to presence of anti-site defects in structure, induced by milling [18,19,41]. A fall in the M_s value was observed for a mean grain size of 8 nm and it was explained by the presence of SPM particles [43].

The progressive synthesis of Ni_3Fe phase by MA and subsequent annealing was checked by XRD and magnetic measurements [18, 19]. It was found that the spontaneous magnetisation tend to a saturation value by Ni_3Fe compound formation. Assuming the M_S as a control parameter of the alloying process by milling and subsequent annealing, a *Milling – Annealing – Transformation* (MAT) diagram was proposed [19]. In this diagram the line M_S = constant corresponds to the milling time – annealing time pairs for which the Ni_3Fe phase is formed in the whole volume of the sample and divide the diagram in to two side.

Because of their attractive soft magnetic properties the Fe-Co powders have been produced in the nanocrystalline state by MA. It was found that in the case of $Fe_{50}Co_{50}$ and $Fe_{rich}Co$ alloys the milling implies diffusion of hcp-Co into α-Fe and finally a disordered bcc-FeCo solid solution is obtained [48-50]. A coexistence of the hcp and fcc phase and an evolution of the hcp/fcc ratio with milling time have been observed for Co-10 at% Fe [51]. It was shown that the coercivity is directly affected by the crystallite size, but not by hcp/fcc phase's ratio [51].

Many works on the ternary and policomponents alloys based on Fe and Ni obtained by mechanical routes have been reported. The nanocrystalline Supermalloy powders (Ni-Fe-Mo) have been obtained from a mixture of pre-alloyed Ni_3Fe and Mo [52, 53] and from 79Ni-16Fe-5Mo (wt%) elemental powders mixture [54, 55]. A minimum in the spontaneous magnetisation vs. milling time shows the presence of different processes in the Supermalloy formation by milling [55]. The coercivity was found to be dependent on the grain size and the domain wall width was estimated at 15 nm [52]. New data about obtaining Ni-Fe-Cu-Mo powders by mechanical alloying and subsequent annealing are recently published [56]. Finemet alloys obtained by mechanical alloying, having soft magnetic properties inferior to those of melt-spun ribbons, have been reported also [57].

The coercivity in the nanocrystalline soft magnetic mechanically alloyed powders is explained in the "random anisotropy model", which was modified in order to take into account the residual stress induced by MM [58].

The nanocrystalline soft magnetic powders produced by mechanical routes are used like powders or like starting materials to design new magnetic materials by powder consolidation. The powder consolidation with preserving the nanocrystalline structure can be made by field activated pressure assisted sintering (FAPAS) and spark plasma sintering (SPS) methods [14] or by producing of the soft magnetic composites. Some applications of these nanocrystalline powders like microwave absorbing or soft composite magnetic materials have been reported [59-61].

References

1. C. Suryanarayana, Int. Mater. Reviews **40,** 41 (1995).
2. K. Lu, Mater. Sci. Eng. **R16**, 161 (1996).
3. S.C. Tjong , H. Chen, Mater. Sci. Eng. **R41**, 1 (2004).
4. M.E. McHenry, M.A. Villard, D.E. Laughlin, Prog. Mater. Sci. **44**, 291 (1999).
5. G. Herzer, Nanocrystalline Soft Magnetic Alloys, in Handbook of Magnetic Materials, Ed. by K.H.J. Buschow, Elsevier Science BV, Amsterdam-Lausanne (1997)
6. G. Herzer, Physica Scripta **T49**, 307 (1993).
7. B.S. Murty, S. Ranganathan, Int. Mater. Rev. **43**, 101 (1998).
8. C. C. Koch, J. D. Whittenberger, Intermetallics **4**, 339 (1996).
9. C. Suryanarayana, Progr. Mater. Sc. **46**, 1 (2001).
10. A. R. Yavari, Mater. Trans. JIM **36**, 228 (1995).
11. P. H. Shingu, K. N. Ishihara, Mater. Trans. JIM **36**, 96 (1995).
12. A. Arrott, Nanostructured Mater. **12**, 1135 (1999).
13. D.L. Zhang, Progr. Mater. Sci. **49**, 537 (2004).
14. E. Gaffet, G. Le Caër, Mechanical Processing for Nanomaterials, in Encyclopaedia of Nanoscience and Nanotechnology, vol.X, Ed. by H.S. Nalwa, American Sci. Publishers (2004).
15. I.Chicinaş, J. Opt. Adv. Mater. **8**, 439 (2006).
16. M. Abdellaoui, E. Gaffet, Acta. Metall. Mater. **44**, 1087 (1995).
17. R. Hamzaoui, O. Elkedim, E. Gaffet, Mater. Sci. Eng. **A 381**, 363 (2004).
18. I. Chicinaş, V. Pop, O.Isnard, J.M. Le Breton, J. Juraszek, J. Alloys Comp. **352**, 34 (2003).
19. V. Pop, O. Isnard, I. Chicinaş, J. Alloys Comp. **361**, 144 (2003).
20. Z. Sparchez, I. Chicinaş, O. Isnard, V. Pop, F. Popa, J. Alloys and Compounds, **434–435**, 435 (2007).
21. L. Takacs, Progr. Mater. Sci. **47**, 355 (2002).
22. G.F. Goya, H.R. Rechenberg, J.Z. Jiang, J. Appl. Phys. **84**, 1101 (1998).

23. G.F. Goya, H.R. Rechenberg, J. Metastable and Nanocrystalline Mater. **14**, 127 (2002).
24. J.Z. Jiang, G.F. Goya, H.R. Rechenberg, J. Phys.: Condens. Mater. **11**, 4063 (1999).
25. F. Padella, C. Alvani, A. La Barbera, G. Ennas, R. Liberatore, F. Varsano, Mater. Chem. Phys. **90**, 172 (2005).
26. G.F. Goya, J. Mater. Sci. **39**, 5045 (2004).
27. V. Šepelák, D. Baabe, D. Mienert, D. Schultze et al., J. Magn. Magn. Mater. **257**, 377 (2003).
28. S. Ozcan, B. Kaynar, M.M. Can, T. Firat, Mater. Sci. Eng. B **121,** 278, (2005).
29. M. Menzel, V. Šepelák, K.D. Becker, Solid State Ionics **141-142**, 663 (2001).
30. V. Šepelák, I. Bergmann et al. J. Phys. Chem. *C* **111** (2007), 5026
31. V. Šepelák, I. Bergmann, S. Kips, K.D. Becker, Z. Anorg. Allg. Chem. **631**, 993 (2005).
32. J.Z. Jiang, C. Gente, R. Bormann, Mater. Sci. Eng. **A242**, 268 (1998)
33. P.J. Schilling, J.H. He, R.C. Tittsworth, E. Ma, Acta Mater. **47**, 2525 (1999).
34. H. Ino, K. Hayashi, T. Otsuka, D. Isobe, K. Tokumitsu, K. Oda, Mater. Sci. Eng. **A304-306**, 972 (2001)
35. B.N. Mondal, A. Basumallick, P.P. Chattopadhyay, J. Magn. Magn. Mater. **309**, 290 (2007)
36. R.B. Schwarz, T.D. Shen, U. Harms, T. Lollo, J. Magn. Magn. Mater. **283**, 223 (2004).
37. L.M. Socolovsky, F.H. Sánchez, P.H. Shingu, Hyperfine Inter. **133**, 47 (2001)
38. P. Gorria, D. Martinez-Blanco, J.A. Blanco, Phys. Rev. B **69**, 214421 (2004)
39. S.D. Kaloshin, V.V. Tcherdyntsev, I.A. Tomilin, Yu.V. Baldokhin, E.V. Shelekhov, Physica B **299**, 236 (2001).
40. V. Pop, I. Chicinaş, J. Optoelectron. Adv. Mater. **9,** 1478, (2007).
41. I. Chicinas, V. Pop, O. Isnard, J. Magn. Magn. Mater. **242-245**, 885 (2002).
42. C. N. Chinnasamy, A. Narayanasamy, K. Chattopadhyay, N. Ponpandian, Nanostr. Mater., **12**, 951 (1999).
43. C. N. Chinnasamy, A. Narayanasamy et al. Mater. Sci. Eng. **A304-306**, 408 (2001).
44. B.H. Meeves, G.S. Collins, Hyperfine Interact. **92**, 955 (1994).
45. R. Hamzaoui, O. Elkedim, E. Gaffet, J. Mater. Sci. **39**, 5139 (2004).
46. R. Hamzaoui, O. Elkedim, N. Fenineche, E. Gaffet, J. Craven, Mater. Sci. Eng. **A 360**, 299 (2003).
47. E. Jartych, J.K. Żurawicz, D. Oleszak, M. Pękała, J. Magn. Magn. Mater. **208**, 221 (2000).
48. M. Sorescu, A. Grabias, Intermetallics **10**, 317 (2002).
49. Y. Liu, J. Zhang, L. Yu, G. Jia, C. Jing, S. Cao, J. Alloys Comp. **377**, 202 (2004).
50. H. Moumeni, S. Alleg, J.M. Greneche, J. Alloys Comp. **386**, 12 (2005).
51. N.E. Fenineche, R. Hamzaoui, O. El Kedim, Mater. Lett. **57**, 4165 (2003).
52. Y. Shen, H.H. Hng, J.T. Oh, J. Alloys Comp. **379**, 266 (2003).
53. Y. Shen, H.H. Hng, J.T. Oh, Mater. Lett. **58**, 2824 (2004).
54. I. Chicinas, V. Pop, O. Isnard, J. Mater. Sci. **39**, 5305 (2004).
55. O. Isnard, V. Pop, I. Chicinas, J. Magn. Magn. Mater. **290-291**, 1535 (2005).
56. F. Popa, O. Isnard, I. Chicinaş, V. Pop, J. Magn. Magn. Mater. **316,** e900, (2007).
57. M. Manivel Raja, K. Chattopadhyay, B. Majumdar, A. Narayanasamy, J. Alloys Comp. **297**, 199 (2000).
58. T. D. Shen, R. B. Schwarz, J. D. Thompson, Phys.Rev B **72**, 014431-1 (2005).
59. P.H. Zhou, L.J. Deng, J.L. Xie, D.F. Liang, L. Chen, X.Q. Zhao, J. Magn. Magn. Mater. **292**, 325 (2005).
60. I. Chicinas, O. Geoffroy, O. Isnard, V. Pop, J. Magn. Magn. Mater. **290-291**, 1531 (2005).
61. I. Chicinas, O. Geoffroy, O. Isnard, V. Pop, J. Magn. Magn. Mater. **310**, 2474 (2007).