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Invited Lecture

Soft magnetic nanocrystalline powders produced by mechanical alloying routes

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This paper presents an overview on the soft magnetic nanocrystalline powders obtained by mechanical alloying routes. First, the different mechanical routes (mechanical alloying, combined mechanical alloying and annealing and mechano-chemical techniques) used for the elaboration of nanocrystalline magnetic powders are discussed. The structural and magnetic properties as a function of experimental conditions are reviewed on the base of following categories of soft magnetic nanocrystalline/nanosized powders: ferrites, Ni-Fe alloys and other iron-based systems. Finally, design of new magnetic materials using nanocrystalline powders produced by mechanical alloying routes is also considered.

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1. Introduction

Materials whose crystallites/particle sizes are smaller than 100 nm are commonly named nanocrystalline /nanostructured/nanosized materials. Nanocrystalline materials behave indeed differently from their macroscopic counterparts if their characteristic sizes are smaller than the characteristic length scales of the physical phenomena occurring in bulk 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]. Thus, the volume fraction of the atoms which are associated with grain boundaries or interfacial boundaries is more than 50 vol. % when the grain size is around 5 nm and decrease at 3 vol.% for grain size of 100 nm [1]. As a consequence, the interface structure plays an important role in determining the physical and mechanical properties of nanocrystalline materials.

The research of nanocrystalline magnetic materials has known a huge development in the last years. This is due to the properties common to both amorphous and crystalline materials and the ability of these alloys to compete with their crystalline counterparts. 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]. According with the random anisotropy model, the crystallite refinement reduces the magnetocrystalline anisotropy due to the averaging effect of magnetisation over randomly oriented nanocrystallites. This leads also to a reduction of H_c and to a D^6 dependence of H_c in the nanometric region with $D < L_{ex}$, where L_{ex} is exchange interaction length. The magnetic permeability shows an analogous behaviour, being essentially proportional to $1/D^6$. The decrease of coercivity in nanocrystalline materials has to be well distinguished from superparamagnetic behaviour, where the vanish of the coercivity is accompanied by a low permeability. Due to the fact that in the soft magnetic nanostructures small ferromagnetic crystallites are parallel coupled by exchange interactions, these materials have simultaneously low coercivity and high permeability [5].

Metastable nanostructures and ultra fine grained materials are produced by a large variety of methods. Besides the incipient crystallisation of amorphous solids [1-3,7], 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 [8–10]. High-energy ball-milling offers indeed supplementary degrees of freedom in the choice of possible routes for synthesizing new materials and appears further as an attractive method of synthesis in view of its potential for large scale production. These techniques allow producing non-equilibrium structures /microstructures including amorphous alloys, extended solid solutions, metastable crystalline phases, nanocrystalline materials and quasi crystals [10-15].

In last two decades, the various mechanical routes used in producing soft magnetic powders (ferrites and alloys) were reported. The present paper reviews these contributions with an emphasis on the soft magnetic ferrites and on the Ni-Fe and Ni-Fe-X nanocrystalline powders obtained by mechanical alloying techniques

2. Mechanical routes

For a period of about 30 years, milling has indeed been a method of synthesis of advanced materials. In last two decades, a large variety of mechanical routes has been developed in order to produce nanocrystalline/amorphous alloys/intermetallic compounds. All these techniques use mechanical energy to achieve chemical reactions and structural changes and involve the milling of the elemental blends or pure metals/compounds in different equipments and conditions.

Mechanical alloying (MA) refers especially to the formation of alloys/compounds from elemental precursors during mechanical milling. Mechanical alloying involves the synthesis of materials by 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 $\Omega \ll \omega$ [16-18].

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. Except for the starting materials, mechanical milling is similar to the mechanical alloying. 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: $mA + nB \rightarrow A_mB_n\,(crystalline) \rightarrow A_mB_n\,(amorphous)$ [10, 19].

Mechanical alloying and mechanical milling of materials are complex stochastic processes which depend on many factors, for instance on physical and chemical parameters such as the precise dynamical conditions, temperature, nature of the milling atmosphere, chemical composition of the powder mixtures, chemical nature of the milling tools, etc. This may partly explain why the theoretical problem of predicting non-equilibrium phase transitions under milling is still in debate. A number of overview papers is dedicated to analyze the mechanical alloying/milling processes [9, 10] and the modeling process of mechanical alloying [20-24]. Also the studies of parameter and process variables are currently in progress [17, 25-28]. An exhaustive selection and classification of the parameters that influence the mechanical milling/mechanical alloying processes was performed and will be published elsewhere [29].

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 [30, 31]. 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. In order to discuss the correlation between milling time and annealing time to obtain the Ni_3Fe phase in the whole sample volume, a milling–annealing–transformation (MAT) diagram has been proposed [31]. The MACA methods present the advantage of reduced contamination by diminishing the milling time.

A new method of mechanical alloying consists in **MACA synthesis with inserting nanocrystalline germs** of the reaction product was proposed in [32]. 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 $(1-x)\cdot(mA + nB) + x\cdot A_mB_n = A_mB_n$. By this method it is possible to reduce the milling time necessary for obtaining A_mB_n intermetallic compounds in the whole volume of the powders mixture [32].

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].

The chemical precursors in reactive milling are typically mixtures of oxides, chlorides and/or metals that react either during milling or during subsequent heat treatment to form a new product or composite powder consisting of the dispersion of ultra fine particles within a soluble salt matrix. These reactions are characterized by a large negative free energy change and are thermodynamically feasible at room temperature. The new phase is obtained at the interfaces of the reactants. By the generation of clean and fresh surfaces, an increased defect density and reduction of particle sizes (as a result of repeated fracturing), reactive milling can increase the reaction kinetics [33]. 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. Some review papers are dedicated to the reactive milling [34,35].

The disadvantage of ball-milling processes for making nanocrystalline powders is the contamination of products from the milling media (balls and vial) and atmosphere. An analysis of the parameters that influence the powder contamination during mechanical alloying/milling was performed by an exhaustive selection of the factors that influence contamination, followed by their classification [36]. An original method which can be used for minimising the contamination of a powder material during the ball-milling process was reported [37].

3. Soft magnetic ferrites

In last two decades, several mechanical routes were used in order to produce a large variety of soft magnetic nanocrystalline/nanosized ferrites. The properties of the nanocrystalline/nanosized ferrites prepared by mechanical activation and mechanosynthesis were reviewed [38]. As it can see from Fig. 1, two basically mechanical way are used for producing nanocrystalline/nanosized soft ferrites: (i) the nano-ferrite is obtained directly by reactive milling of an oxides or other precursor’s mixture and (ii) the ferrite is obtained by a classical method and then is subjected to a dry or wet milling in order to achieve a nanocrystalline/nanosized state.

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 [39-42]. Thus, in Fe-Cu-O system after 420 hours of milling in a planetary ball mill the starting composition evolved towards the equilibrium composition of α-Fe_2O_3, CuO and spinel phases. The spinel phase formed by RM method was assigned to $Cu_xFe_{3-x}O_4$ ($0 < x < 1$) having cubic structure [39]. On the other hand, the milling of $CuFe_2O_4$ ferrite in closed vial up to 98 hours produces a decomposition of ferrite into α-Fe_2O_3 and CuO phases and subsequent the Fe^{3+} to Fe^{2+} reduction to form Fe_3O_4 and $Cu_xFe_{3-x}O_4$ spinel [40]. By using an open vial neither reduction of Fe^{3+} or Cu^{2+} was detected [41]. In the Mn-Fe-O system the nanocrystalline $MnFeO_4$ spinel appear after 10 hours of milling and reaches a maximum content (≈ 80 mol%) after 35 hours – Fig. 2 [42]. After 50 hours, the spinel phase decreases down to 50 mol%. On the other hand, a wüstite type (Fe, Mn)O phase and metallic iron begin to increase after 35 hours of milling [42]. Also, the multiphase nature of the milled samples was reported on the Ni-ferrites [43].

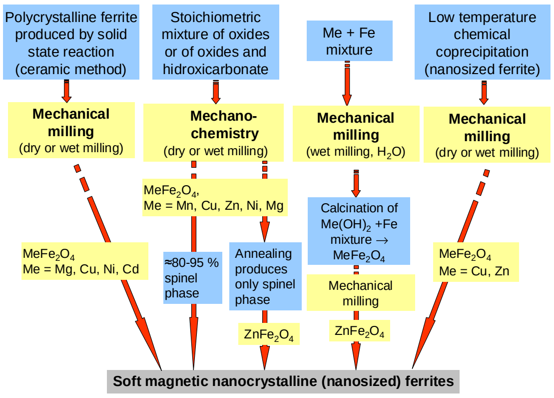

Fig. 1. Mechanical routes used for producing the nanocrystalline/nanosized soft magnetic ferrites.

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 [44]. If the reactive milling is followed by an annealing it is possible to obtain the spinel phase in all volume of the sample. Thus, $ZnFe_2O_4$ phase was obtained by RM of 1:1 molar mixture of α-Fe_2O_3 and ZnO after 623 hrs of milling and 1 h of annealing at 500 K temperature [45]. A complete formation of the Mg-ferrite was also obtained after 23 h of reactive milling of an iron and magnesium oxide mixture, followed by sintering at 1300 °C for 2 hours [46].

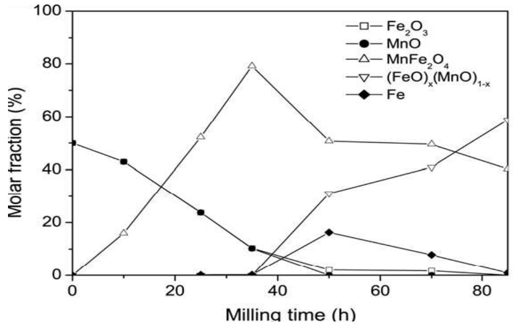

Fig. 2. Phase content of mixtures in Mn-Fe-O system versus milling time [42].

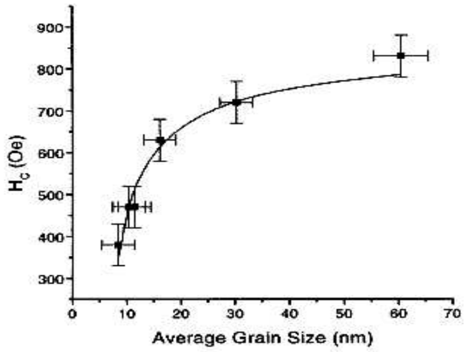

Fig. 3. Room temperature coercive field versus average grain size in $CuFe_2O_4$ [41].

Table 1. Soft magnetic nanocrystalline ferrites produced by mechanical routes.*

Ferrite type	Method of preparation	Some magnetic properties	General Ref.
Fe_3O_4	wet MM	superparamagnetic behaviour at room temperature	48, 49
$CuFe_2O_4$	PF + MM [39-41] RM [39]	• the hysteresis loop is not symmetrical about the origin and is shifted to the left - ΔH_C [39]; • cation redistribution between A and B sites, the spin canting effect, superparamagnetic relaxation were evidenced [40].	39-41
$NiFe_2O_4$	RM [46, 54] PF + MM [43, 53] CP + MM [52]	• superparamagnetic behaviour [51-53]; • annealing strong reduces coercive field [53]; • canted spin configuration [53, 54].	43, 46, 51-54
$ZnFe_2O_4$	RM [43, 57] RM + AN [44] PF + MM [55, 56] CP + MM [58] wRM + CN + MM [59]	• spin canting effect [43, 44, 55]; • superparamagnetic behaviour [58, 59].	43, 44 55-59
$MgFe_2O_4$	RM [45] PF + MM [61-63]	• spin canting effect [62]; • the hysteresis loop is not symmetrical about the origin and is shifted to the left - ΔH_C [62]; • T_C decreases with increasing milling time [63].	45, 60-63
$MnFe_2O_4$	RM [42] RM + AN [64]		42, 64
$CoFe_2O_4$	RM [65] CP+MA+AN [66]	• anisotropic nanoparticles obtained after magnetic annealing [66].	65, 66
$CdFe_2O_4$	PF + MM [67, 68]	• spin canting effect [67, 68].	67, 68
$NiAlFeO_4$	RM + AN {69]		69

*PF – polycrystalline ferrite; CP – co-precipitation; AN – annealing; CN – calcination.

The influence of the milling method on the Mg-ferrite and Ni-ferrite was reported in [47]. The Mg-ferrite formation begin after 25 hrs of milling in the case of centrifugal mill, while using a vibratory mill it was not detected the presence of the ferrite after 160 hours. The formation of the Ni-ferrite begins after 3 hours of milling and the difference between the milling in vibratory and centrifugal mill was negligible.

A general picture of the soft magnetic ferrites obtained by different mechanical routes and their general magnetic properties are shown in Table 1.

The elaboration and properties of the nanocomposite materials based on ferrites were reported [70,71]. XRD show that the Ni/Fe_2O_3 mixtures are transformed in a wüstite phase after 32 hrs of MA. After subsequently annealed at 500-900 °C, the decomposition of the wüstite phase resulted in the formation of a Ni-rich intermetallic phase and a ferrite [70]. The magnetic properties of $NiFe_2O_4$-SnO_2 nanocomposite produced by MA show a large variation of hysteresis loops for the different milling times. Specimens with smaller particles displayed strong superparamagnetism (SPM) [71].

Generally, the soft magnetic ferrites produced by mechanical routes exhibit a reduced particle size under 10 nm. As a consequence, almost all nanocrystalline/ nanosized ferrites exhibit a superparamagnetic behaviour, without magnetic hysteresis, see Table 1. The magnetic properties of the nanocrystalline/nanosized soft magnetic ferrites are generally associated with a canted spin configuration in small particles (an surface effect) and with the non-equilibrium cation redistribution resulting in a decrease of the number of magnetic Fe^{3+}(A)-O^{2-}-Fe^{3+}(B) linkages and leading to the weakening of the primary (A)-O-(B) superexchange interactions [39,40,54]. The hysteresis loops measured at 4.2 K show that the loops of milled samples are not symmetrical about the origin but is shifted to the left [41, 62]. As a consequence, a ΔH_C shift appears and its value and behaviour depend on milling time. Thus, in the case of $CuFe_2O_4$ ferrite the ΔH_C shift increases rapidly from 3 Oe for sample milled 1h to 130 Oe for sample milled 7 h and then slowly rises to 145 Oe for sample milled 29 hrs [41]. The coercive field decreases from its maximum value to zero with decreasing particle size due to the superparamagnetic relaxation effect – Fig. 3 [41]. In Fig. 3 the solid curve is the best fit using the relation $H_C = H_{C0}(1 - (D_P/d)^{3/2})$, where H_{C0} is the coercivity for bulk material at this temperature, from which the critical size for SPM effect D_P = 6(1) nm and H_{C0} = 0.8(1) kOe.

The magnetisation of the $CuFe_2O_4$ particles dos not saturate even at a field of 9 T [40]. The nonsaturated magnetisation and shift of the hysteresis loops are typical features of the canted magnetic structures [40,62].

Annealing the milled $NiFe_3O_4$ has turn it to a structural state similar to the bulk one, and its magnetic properties are gradually restored. Thus, the increase of the annealing temperature leads to a continuous decrease of the μ_0H_C from 0.245 T (as milled sample) to about 0.011 T for the sample annealed at 1198 K [53].

4. Nanocrystalline Ni-Fe soft magnetic powders

The Ni-Fe and Ni-Fe-X alloys present interesting magnetic properties, consequently these materials are widely studied for both basic properties and applications. For Ni-Fe (Fe-Ni) and Ni-Fe-X nanocrystalline soft magnetic powders the following mechanical routes were used:

- mechanical alloying (MA), using dry high-energy milling process; an exception is reported in ref. [72], where was used an horizontal low energy ball mill and in ref. [73, 74] was reported a comparative study between low- and high-energy ball milling;
- mechanical alloying combined with annealing (MACA) [30,31,75,76];
- mechano-chemical processes (MC), which consist in mechanical milling of oxides blend, reduction of oxides and then alloying by heat treatment [77];
- two-step mechanical alloying, which consist in obtaining nanocrystalline alloy by mechanical alloying, followed by a second step which modifies particle size by mechanical milling [78];
- mechanical alloying and annealing by inserting nanocrystalline germs of the reaction product [32].

In all the reported researches elemental powders (Ni, Fe, and other) were used as raw materials for producing Fe-Ni and Fe-Ni-X nanocrystalline powders, except in [77], where a blend of NiO and α-Fe_2O_3 oxides were used. Generally, different planetary ball mills have been used for millings. However, the use of a horizontal low energy ball mill has been reported [72,73]. Very different milling conditions have been used; for example, the ball/powder mass ratio was between 30:1 [79] and 5:1 [80] for high-energy ball milling and 50:1 for low energy ball milling [73].

The mechanical synthesis process has been checked generally by X-ray diffraction and Mössbauer spectroscopy. The particles morphology and thermal stability have been characterised by SEM, TEM, EDX, DTA, DSG, TG or TA measurements. Magnetic measurements have been used also for checking synthesis process and for materials characterisation.

The researches concerning alloys from Ni-Fe system produced by mechanical routes cover entire Ni-Fe diagram: Fe-rich, Ni-Fe50% and Ni-rich region, Table 2. A complete analysis of the phase transformation in $Fe_{1-x}Ni_x$ ($10 \le x \ge 90$ at%) alloys at mechanical alloying and subsequent annealing was reported [81-83]. It was determined the ranges of extended solubility and phase composition of the alloys as a function of the Ni content, Table 2. The concepts of “shock mode processes” ($\Omega \gg \omega$) and “friction mode processes” ($\Omega \ll \omega$) [16] were applied to the magnetic properties obtained by MA [84, 85]. It has been proved that the milling performed in the friction mode leads to the formation of alloys exhibiting a soft magnetic behaviour. However, magnetisation is not affected by the mode used [85]. A strong decrease of the coercive field versus crystallite size appears especially for crystallite size smaller than 20 nm [86]. A comparative study concerning the Fe-Ni alloys’ producing by low- and high-energy ball milling has been reported [73]. In high-energy ball milling process the fcc solid solution γ(Fe,Ni) in alloys $Fe_{65}Ni_{35}$ was formed after 36 hours, while in the low-energy milling process the Fe lines disappeared after 400 hours of milling [73]. However, no influence of the milling intensities on the magnetic properties and of the structure and local atomic order of Ni atoms was observed in both processes [73, 74]. Most interesting results were obtained for $Fe_{65}Ni_{35}$ alloys, which had not invar properties as suggested by the equilibrium diagram [73].

The nanocrystalline structure of $Fe_{85}Ni_{15}$ particles improves the performance of microwave complex permeability in the range 1-10 GHz, remarkably the increase of μ'', and adds an important effect on the influence of particle size on performance for microwave application [78]. It has been found that magnetisation increases with increase milling time [30,31,73,76,84,86-88]. The increase of magnetisation versus milling time is found to be linked to the grain size reduction [80,84-86]. In the case of Ni_3Fe, it was found that M_s decreases at milling time longer than 20 hours – Fig. 4 - due to presence of anti-site disorder in structure, induced by milling [30, 31, 88]. As a result of the reduction of the anti-site defects, the annealing of the samples milled for 52 h induces a small increase of the M_s in comparison with the as milled samples [30,31,88]. For a mean grain size of 8 nm a fall in the M_s value of N_3Fe value was observed and it was explained by the presence of SPM particles [89].

Table 2. Nanocrystalline Fe-Ni powders produced by mechanical alloying techniques.

Alloys Composition	Structure	Some magnetic properties	General Ref.
Fe$_{1-x}$Ni$_x$, x = 7.69, 9.09, 11.11 at%	bcc and fcc phase mixture for x = 7.69 and 9,09 and only bcc phase for x = 11.11 at% [91]	Ni doped decreases the resonance frequency of the Fe-Ni alloys, but Ni doping enhances the frequency stability [91].	91
Fe$_{1-x}$Ni$_x$, x = 10, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 50, 60, 70, 80, 90 at %	bcc phase, x ≤ 20 at% bcc + fcc phase for x = 22, 24, 26, 28 at% fcc phase for x ≥ 30 at% [82]	annealed alloys with 22-28 at% Ni are not ferromagnetic at room temperature [83].	81-83
Fe-10 wt% Ni	bcc solid solution [100]	• H$_C$ = 200 A/m after 96 h milling [86]; • H$_C$ = 1600 A/m for shock power mode milling conditions [84].	74, 84-86, 93, 100
Fe-15 wt% Ni	bcc solid solution [78]	high value of complex permeability in 1-10 GHz [78].	78
Fe-20 wt% Ni	α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) [101] bcc phase [100]	• M$_s$ = 219 Am^2/kg [86]; • H$_C$= 110 A/m after 96 h milling [86]; • H$_C$ = 1420 A/m for shock power mode milling conditions [84].	72-74, 84-86, 93, 100, 101
Fe-25 wt% Ni	α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) [101]		101
Fe-30 wt% Ni	α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) [79, 101]		79, 101
Fe-35 wt% Ni Fe-35 at% Ni	α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) → γ(fcc) [101] final structure α'-Fe(bct) + γ(fcc) [79]	• Invar anomaly for 35 at% was not detected [73]; • larger T$_C$ than that for equilibrium alloys [73].	72-74, 79, 101
Fe-50 at%Ni Fe-50 wt%Ni	γ (fcc) after 22 h [73]	larger T$_C$ than that for equilibrium alloys [73].	72-74, 94, 95
Ni$_3$Fe	cfc, disordering by milling time [73]	• H$_C$=800A/m pt D = 11 nm [80]; • H$_C$ increases with increase milling time [90]; • there is a fall in the M$_s$ for the 70 h milling due to the presence of super paramagnetic particles [89]; • M$_s$ decreases at milling time longer than 20 h, due to presence of anti-site disorder [30, 31, 88].	30, 31, 75, 80, 87, 89, 94, 97, 102

The progressive synthesis of the nanocrystalline Ni$_3$Fe intermetallic compound by mechanical alloying and subsequent annealing was evidenced by X-ray diffraction and magnetization measurements [30,31]. A Ni-Fe solid solution is observed after 1 h of milling followed by annealing. Annealing at 330 °C for longer than 3 hours induces the progressive formation of the Ni$_3$Fe phase even for the 2 h-milled sample. The influence of the annealing on the solid-state reaction of the Ni$_3$Fe phase formation is very efficient for the 4 h-milled sample [31]. It was shown from magnetic measurements that the annealing influence on the Ni$_3$Fe phase formation is more effective for lower annealing times. In order to discuss the influence of the synthesis conditions on the Ni$_3$Fe phase formation in the whole sample, a *Milling – Annealing - Transformation* (MAT) diagram was proposed, Fig. 5 [31].

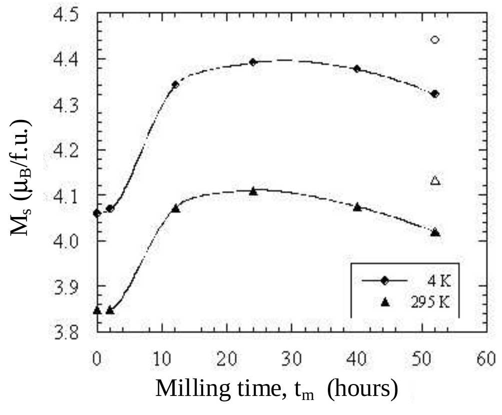

Fig. 4. Spontaneous magnetisation versus milling time (Ni$_3$Fe). The open symbol refers to the annealed sample. The line is a guide for the eyes [30].

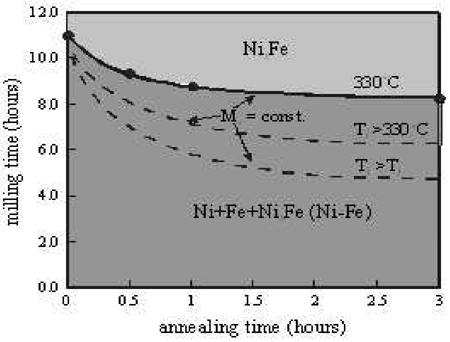

Fig. 5. The Milling – Annealing – Transformation (MAT) diagram for obtaining Ni_3Fe intermetallic compound by mechanical alloying and annealing [31].

Lattice parameters, crystallite sizes and strains induced by milling have been studied versus milling time in almost all references mentioned above. A short review of the Ni-Fe and Ni-Fe-X soft magnetic nanocrystalline powders produced by MA techniques was presented in ref. [103].

5. Nanocrystalline soft magnetic Ni- and Fe-based powders

Nanocrystalline powders $(FeNi_3)_xAg_{1-x}$ [96], $Ni_{50}Al_{50-x}Fe_x$ [98], $Fe_{49}Ni_{46}Mo_5$, $Fe_{42}Ni_{40}B_{18}$ [92], $Fe_{40}Ni_{40}P_{20-x}Si_x$ (x = 6, 10, 14) [104], $Fe_{80}Cu_{20}$ (at.%) and Fe-2%Al-6%Si (wt%) [105], $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{84}Nb_7B_9$, $Fe_{80}Ti_8B_{12}$, $Fe_{80}Ti_7B_{12}Cu_1$, $Fe_{56}Co_7Ni_7Zr_2(Nb/Mo/V)_8B_{20}$, $Fe_{32}Ni_{36}(Nb/Mo/V)_7Si_8B_{17}$ [106] Ni-15%Fe-5%Mo (wt%) [98, 107] and Ni-16%Fe-5%Mo (wt%) [75, 76] were obtained by different mechanical alloying routes. Mechanical alloying of the soft magnetic Fe-based alloys leads to the formation of supersaturated solid solution, solid solution + boride phase or a mixture of amorphous and crystalline phases [107]. The presence of Ag in $(FeNi_3)_xAg_{1-x}$ alloys increases the coercive field as compared to the value of Ni_3Fe, especially in the early stages of the process [94]. Both Mo and B have a dramatic effect on the MA process and magnetic properties of Fe-Ni-based materials, mainly by changing the thermodynamic and kinetics of amorphisation and nanocrystallites formation [92].

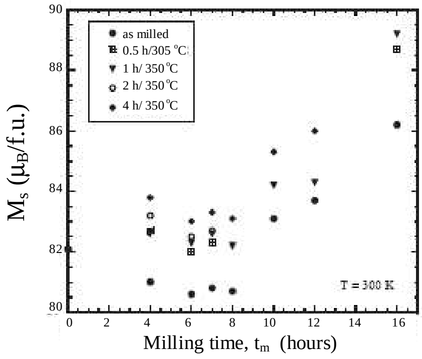

Fig. 6. Spontaneous magnetisation of the Supermalloy vs. milling and annealing conditions [76].

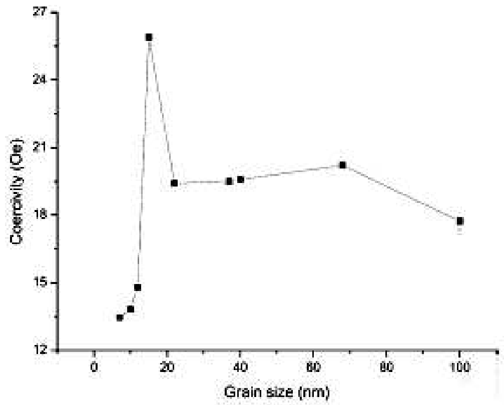

Fig. 7. Coercivity of Ni–15%Fe–5%Mo (wt%) powders as a function of grain size [98].

The nanocrystalline Supermalloy powders (Ni-Fe-Mo) have been obtained from pre-alloyed Ni_3Fe + Mo mixture [98,107] and from 79Ni-16Fe-5Mo (wt%) elemental powders mixture [75,76]. A minimum in the spontaneous magnetisation vs. milling time shows the presence of different processes in the Supermalloy formation by milling, Fig. 6 [76]. The coercivity was found to be dependent on the grain size, Fig. 7. The domain wall width is about 15 nm [98]. New data about obtaining Ni-Fe-Cu-Mo powders by mechanical alloying and subsequent annealing are recently published [108].

The "random anisotropy model" was modified in order to take into account the residual stress in the mechanically alloyed nanocrystalline powders [105]. A review of soft magnetic of both in bulk amorphous alloys obtained by flux melting and water quenching and in nanocrystalline alloys obtaining by MA is presented in [109].

The nanocrystalline soft magnetic powders produced by mechanical alloying techniques are used like powders or for design of new magnetic materials by powder consolidation. The powder consolidation with preserving the nanocrystalline state can be made by field activated pressure assisted sintering (FAPAS) and spark plasma sintering (SPS) methods [15] 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 [78, 110, 111].

6. Conclusions

The possibility of producing chemical transformations through mechanical energy has been extensively studied in metallic and in oxide systems. The nanocrystalline/nanosized powders obtained by different mechanical routes exhibit very interesting properties, some from them different from those of their crystalline counterparts.

The Fe-Ni and Fe-Ni-X alloys present interesting magnetic properties, consequently these materials are widely studied for both fundamental and application point of view. In last decade many researches concerning alloys from Ni-Fe system (both Fe-rich and Ni-rich zone of the phase diagram) produced by mechanical routes have been reported. From ternary alloys systems Ni-Fe-Mo system has been studied by MA techniques, especially the alloys like Supermalloy composition.

Other nanocrystalline soft magnetic Ni- and Fe-based powders with interesting properties have been produced also by mechanical alloying routes.

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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] T. Kulik, J. Non-Cryst. Solids **287**, 145 (2001).
[8] B. S. Murty, S. Ranganathan, Int. Mater. Rev. **43**, 101 (1998).
[9] C. C. Koch, J. D. Whittenberger, Intermetallics **4**, 339 (1996).
[10] C. Suryanarayana, Progr. Mater. Sc. **46**, 1 (2001).
[11] A. R. Yavari, Mater. Trans. JIM **36**, 228 (1995).
[12] P. H. Shingu, K. N. Ishihara, Mater. Trans. JIM **36**, 96 (1995).
[13] A. Arrott, Nanostructured Mater. **12**, 1135 (1999).
[14] D. L. Zhang, Progr. Mater. Sci. **49**, 537 (2004).
[15] 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).
[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] R. Hamzaoui, O. Elkedim, E. Gaffet, J. Mater. Sci. **39**, 5139 (2004).
[19] K. Suzuki, K. Sumiyama, Mater. Trans. JIM **36**, 188 (1995).
[20] R. Watanabe, H. Hashimoto, G. G. Lee, Mater. Trans. JIM **36**, 102 (1995).
[21] T. H. Courtney, Mater. Trans. JIM **36**, 110 (1995).
[22] S. K. Pabi, D. Das, T. K. Mahapatra, I. Manna, Acta Mater. **46**, 3501 (1998).
[23] J. R. Harris, J. A. D. Wattis, J. V. Wood, Acta Mater. **49**, 3991 (2001).
[24] P. P. Chattopadhyay, I. Manna, S. Talapatra, S. K. Pabi, Mater. Chem. Phys. **68**, 85 (2001).
[25] D. Choulier, R. Rahouadj, E. Gaffet, Ann. Chim. Sci. Mat. **22**, 351 (1997).
[26] M. Abdellaoui, E. Gaffet, Acta Metall. Mater. **43**, 1087 (1995).
[27] J. F. Valderrouten, G.A. Pérez Alcázar, L. Civale, J. Mater. Sci. **39**, 5445 (2004).
[28] M. H. Enayati, Z. Sadeghian, M. Salehi, A. Saidi, Mater. Sc. Eng. **A375-377**, 809 (2004).
[29] Z. Spârchez, I. Chicinas, in preparation.
[30] I. Chicinas, V. Pop, O. Isnard, J. M. Le Breton, J. Juraszek, J. Alloys Comp. **352**, 34 (2003).
[31] V. Pop, O. Isnard, I. Chicinas, J. Alloys Comp. **361**, 144 (2003).
[32] Z. Spârchez, I. Chicinas, O. Isnard, V. Pop, F. Popa, J. Alloys Comp. (2006) accepted.
[33] C. Suryanarayana, E. Ivanov, V. V. Boldyrev, Mater. Sci. Eng. **A304–306**, 151 (2001).
[34] G. Cocco, G. Mulas, L. Schiffini, Mater. Trans. JIM **36**, 150 (1995).
[35] L. Takacs, Progr. Mater. Sci. **47**, 355 (2002).
[36] Z. Spârchez, I. Chicinas, Proc. World Congress on Powder Metallurgy, PM 2004, Vienna, Austria, **1**, 213 (2004).
[37] Z. Spârchez, I. Chicinas, Proceedings of Euro PM2005 Congress, Prague, **2**, 99 (2005).
[38] V. Šepelák, I. Bergmann, S. Kips, K. D. Becker, Z. Anorg. Allg. Chem. **631**, 993 (2005).
[39] G. F. Goya, H. R. Rechenberg, J. Phys.: Condens. Mater. **10**, 11829 (1998).
[40] G. F. Goya, H. R. Rechenberg, J. Z. Jiang, J. Appl. Phys. **84**, 1101 (1998).
[41] J. Z. Jiang, G. F. Goya, H. R. Rechenberg, J. Phys.: Condens. Mater. **11**, 4063 (1999).
[42] F. Padella, C. Alvani, A. La Barbera, G. Ennas, R. Liberatore, F. Varsano, Mater. Chem. Phys. **90**, 172 (2005).
[43] M. Menzel, V. Šepelák, K. D. Becker, Solid State Ionics **141-142**, 663 (2001).
[44] G. F. Goya, H. R. Rechenberg, Mater. Sci. Forum, **403** and J. Metastable and Nanocrystalline Mater. **14**, 127 (2002).
[45] G. F. Goya, H. R. Rechenberg, J. Magn. Magn. Mater. **203**, 141 (1999).
[46] S. F. Mustafa, M. B. Morsi, Mater. Lett. **34**, 241 (1998).
[47] M. E. Rabanal, A. Várez, B. Levenfeld, J. M. Torralba, Mater. Sci. Forum **426-432**, 4349 (2003).
[48] G. F. Goya, J. Mater. Sci. **39**, 5045 (2004).
[49] G. F. Goya, Solid State Commun. **130**, 783 (2004).
[50] G. F. Goya, J. Mater. Sci. Lett. **16**, 563 (2004).
[51] Y. Shi, J. Ding, X. Liu, J. Wang, J. Magn. Magn. Mater. **205**, 249 (1999).
[52] V. Šepelák, D. Baabe, K. D. Becker, J. Mater. Synth. Proces. **8**, 333 (2000).
[53] V. Šepelák, D. Baabe, D. Mienert, D. Schultze,

F. Krumeich, F. J. Litterstb, K. D. Becker, J. Magn. Magn. Mater. **257**, 377 (2003).
[54] V. Šepelák, M. Menzel, I. Bergmann, M. Wiebcke, F. Krumeich, K. D. Becker, J. Magn. Magn. Mater. **272-276**, 1616 (2004).
[55] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, H. Guerault, J.-M. Greneche, Scripta Mater. **44**, 1407 (2001).
[56] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, Mater. Sci. Eng. **A304-306**, 983 (2001).
[57] J. P. Muňoz Mendoza, O. E Ayala Valenzuela, V. Corral Flores, J. Matutes Aquino, S. D. De la Torre, J. Alloys Comp. **369**, 144 (2994).
[58] S. D. Shenoy, P. A. Joy, M. R. Anantharaman, J. Magn. Magn. Mater. **269**, 217 (2003).
[59] S. Ozcan, B. Kaynar, M. M. Can, T. Firat, Mater. Sci. Eng. **B 121**, 278 (2005).
[60] V. Šepelák, D. Schultze, F. Krumeich, U. Steinike, K. D. Becker, Solid State Ionics **141-142**, 677 (2001).
[61] V. Šepelák, M. Menzel, K. D. Becker, F. Krumeich, J. Phys. Chem. **B106**, 6672 (2002)
[62] V. Šepelák, D. Baabe, D. Mienert. F. J. Litterst, K. D. Becker, Scripta`Mater. **48**, 961 (2003).
[63] M. E. Rabanal, A. Várez, B. Levenfeld, J. M. Torralba, J. Mater. Process. Techn. **143-144**, 470 (2003).
[64] J. Ding, P. G. McCormick, R. Street, J. Magn. Magn. Mater. **171**, 309 (1997).
[65] J. Ding, P. G. McCormick, R. Street, Solid State Commun. **95**, 31 (1995).
[66] Y. Shi, J. Ding, H. Yin, J. Alloys Comp. **308**, 290 (2000).
[67] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, R. Justin Joseyphus, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, K. Nakatsuka, J. M. Greneche, J. Appl. Phys. **90**, 527 (2001).
[68] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, R. J. Joseyphus, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, K. Nakatsuka, H. Guerault, J.-M. Greneche, Scripta Mater. **44**, 1411 (2001).
[69] M. Mozaffary, J. Amighian, J. Magn. Magn. Mater. **260**, 244 (1997).
[70] Y. Shi, J. Ding, L.H. Tan, Z. Hu, J. Magn. Magn. Mater. **256**, 13 (2003).
[71] A. S. Albuquerque, J. D. Ardisson, W. A. A. Macedo, T. S. Plivelic, I. L. Torriani, J. Larrea J., E. B. Saitovitch, J. Magn. Magn. Mater. **272-276**, 2211 (2004).
[72] M. Pękała, D. Oleszak, E. Jartych, J. K. Żurawicz, Nanostr. Mater. **11**, 789 (1999).
[73] E. Jartych, J. K. Żurawicz, D. Oleszak, M. Pękała, J. Magn. Magn. Mater. **208**, 221 (2000).
[74] E. Jartych, J. Magn. Magn. Mater. **265**, 176 (2003).
[75] I. Chicinas, V. Pop, O. Isnard, J. Mater. Sci. **39**, 5305 (2004).
[76] O. Isnard, V. Pop, I. Chicinas, J. Magn. Magn. Mater. **290-291**, 1535 (2005).
[77] X. Y. Qin, S. H. Cheong, J. S. Lee, Mater. Sci. Eng. **A 363**, 62 (2003).
[78] P. H. Zhou, L. J. Deng, J. L. Xie, D. F. Liang, L. Chen, X. Q. Zhao, J. Magn. Magn. Mater. **292**, 325 (2005).
[79] L.-H. Zhu, X.-M. Ma, L. Zhao, J. Mater. Sci., **36**, 5571 (2001).
[80] H. N. Frase, R. D. Shull, L.-B. Hong, T. A. Stephens, Z.-Q. Gao, B. Fultz, Nanostr. Mater. **11**, 987 (1999).
[81] Yu. V. Baldokhin, V. V. Tcherdyntsev, S. D. Kaloshin, G. A. Kochetov, Yu. A. Pustov, J. Magn. Magn. Mater. **203**, 313 [1999].
[82] S. D. Kaloshin, V. V. Tcherdyntsev, I. A. Tomilin, Yu. V. Baldokhin, E. V. Shelekhov, Physica B **299**, 236 (2001).
[83] S. D. Kaloshin, V. V. Tcherdyntsev, Yu. V. Baldokhin, I. A. Tomilin, E. V. Shelekhov, J. Non-Cryst. Solids **287**, 329 (2001).
[84] R. Hamzaoui, O. Elkedim, E. Gaffet, Mater. Sci. Eng.. **A 381**, 363 (2004).
[85] R. Hamzaoui, O. Elkedim, E. Gaffet, J. Mater. Sci. **39**, 5139 (2004).
[86] R. Hamzaoui, O. Elkedim, N. Fenineche, E. Gaffet, J. Craven, Mater. Sci. Eng. **A 360**, 299 (2003).
[87] I. Chicinas, V. Pop, O. Isnard, J. M. Le Breton, Proc. ”Materiaux 2002” Congress, ISBN 2-914279-08-6, Tours, (on CD).
[88] I. Chicinas, V. Pop, O. Isnard, J. Magn. Magn. Mater. **242-245**, 885 (2002).
[89] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, M. Saravanakumar, Mater. Sci. Eng. **A304-306**, 408 (2001).
[90] C. N. Chinnasamy, A. Narayanasamy, K. Chattopadhyay, N. Ponpandian, Nanostr. Mater. **12**, 951 (1999).
[91] Y. Liu, J. Zhang, L. Yu, G. Jia, C. Jing, S. Cao, J. Magn. Magn. Mater. **285**, 138 (2005).
[92] S. W. Du, R. V. Ramanujan, J. Magn. Magn. Mater. **292**, 286 (2005).
[93] R. Hamzaoui, S. Guessasma, O. Elkedim, E. Gaffet, Mater. Sci. Eng. **Bxxx** (2005) in press
[94] L. H. Bennett, L. Takacs, L. J. Swartzendruber, J. Weismuller, L. A. Bendersky, A. J. Shapira, Scripta Metall. Mater. **33**, 1717 (1995).
[95] A. Djekoun, B. Bouzabata, A. Otmany, J. M. Greneche, Catalysis Today **89**, 319 (2004).
[96] Z. G. Liu, J. T. Guo, L. Z. Zhou, Z. Q. Hu, M. Umemoto, J. Mater. Sci. **32**, 4857 (1997).
[97] I. Chicinas, C. Nitray, N. Jumate, Proc. of the 2nd Int. Conf. Powder Metall. RoPM2000, UT Press, Cluj-Napoca, **2**, 637 (2000).
[98] Y. Shen, H. H. Hng, J. T. Oh, J. Alloys Comp. **379**, 266 (2003).
[99] V. Hays, R. Marchand, G. Saindrenan, E. Gaffet, Nanostr. Mater. **7**, 411 (1996).
[100] V. V. Tcherdyntsev, S. D. Kaloshkin, I. A. Tomilin, E. V. Shelekhov, Yu. V. Baldokhin, Nanostr. Mater. **12**, 139 (1999).
[101] L.-H. Zhu, Q.-W. Huang, H.-F. Zhao, Scripta Mater. **51**, 527 (2004).
[102] B. H. Meeves, G. S. Collins, Hyperfine Interact. **92**, 955 (1994).

[103] I. Chicinas, O. Isnard, V. Pop, Proc. Euro PM2005 Congress, Prague **1**, 445 (2005).

[104] J. J. Sunol, T. Pradell, N. Clavaguera, M. T. Clavaguera-Mora, Phylosofical Magazine **83**, 2323 (2003).

[105] T. D. Shen, R. B. Schwarz, J. D. Thompson, Phys. Rev B **72**, 014431-1 (2005).

[106] P. Krakhmalev, D. Yi, L. Nyborg, Proc. 22nd Riso Int. Symp. Mater. Sci. Denmark 2001, p. 301.

[107] Y. Shen, H. H. Hng, J. T. Oh, Mater. Lett. **58**, 2824 (2004).

[108] F. Popa, O. Isnard, I. Chicinas, V. Pop, Proc. Int. Conf. Powder Metall., Sinaia, Romania **2**, 887 (2005).

[109] R. B. Schwarz, T. D. Shen, U. Harms, T. Lilo, J. Magn. Magn. Mater. **283**, 223 (2004).

[110] I. Chicinas, O. Isnard, O. Geoffroy, V. Pop, Proc. World Congress Powder Metall., Vienna, Austria, **4**, 623 (2004).

[111] I. Chicinas, O. Geoffroy, O. Isnard, V. Pop, J. Magn. Magn. Mater. **290-291**, 1531 (2005).

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