Digest Journal of Nanomaterials and Biostructures Vol. 10, No. 2, April - June 2015, p. 721 - 728

SYNTHESIS OF A NANOSTRUCTURED Al ALLOY MODIFIED WITH Fe BY HIGH ENERGY BALL MILLING

R. A. RODRÍGUEZ-DÍAZ[a,b*], A. MOLINA-OCAMPO[b], J. PORCAYO-CALDERÓN[b], J. JUAREZ-ISLAS[c]
[a]*Universidad Politécnica del Estado de Morelos, Boulevard Cuauhnahuac 566, Col. Lomas del Texcal, 62574 Jiutepec, Morelos México*
[b]*Centro de Investigación en Ingeniería y Ciencias Aplicadas, UAEM, Av. Universidad 1001, Col, Chamilpa, Cuernavaca Mor., México.*
[c]*Instituto de Investigaciones en Materiales-UNAM, circuito exterior S/N, Ciudad Universitaria, C. P. 04510, México DF, México.*

In this work, mainly a solid solution of Fe dissolved in Al matrix was prepared by the high energy ball milling technique from a stoichiometric mixture of high purity powders of Fe and Al. The ball milling process was performed by using a fixed ball weight/sample weight ratio of 10:1. The particle size increased significantly from 4 to 6 h of milling, but after that time, decreased to the end of milling time (10h). According to X-ray diffraction analysis, a solid solution of Fe in Al (α-Al) begun to form at the fourth hour of milling. The crystallite size corresponding to the solid solution (α-Al) was decreased as the milling time advanced. Also the calculated lattice parameter displayed a tendency to decrease as the milling time elapsed. The transmission electron microscopy (TEM) analysis revealed the precipitation of the Al_5Fe_2 and $Al_{13}Fe_4$ phases in the Al matrix.

(Received April 4, 2015; Accepted June 30, 2015)

Keywords: Al alloy, ball milling, microstructural characterization, solid solution, nanostructured alloy.

1. Introduction

Mechanical alloying MA is one of the most promising methods that have been rapidly developed and has been employed to produce nano-crystalline materials in an industrial scale.[1] In previous studies, a remarkable improvement was observed in some of the mechanical properties as a result of a nano-crystalline structure obtained by the process of mechanical alloying.[2,3]

Mechanical alloying is a powder processing technique which enables production of homogeneous materials, from a mixture of elemental powders.[4,5] In mechanical alloying, the powder particles are trapped between the balls that collide with one another during the mechanical milling, where they undergo deformation, welding or fracture, depending on the mechanical behavior of the basic components of powder.[6,7] Compared to the conventional route of solidification, mechanical alloying is an inexpensive and simpler technique to produce the material in a nano-crystalline or amorphous state. Furthermore, because the mechanical alloying process is performed in the solid state, the restrictions imposed by the phase diagrams do not seem to apply to the phases obtained by this technique.[8]

The process of mechanical alloying (AM) can produce alloys with nanoscale grain size and a disordered crystal structure, these are microstructural characteristics that are desired to improve the mechanical properties, particularly the ductility of the binary Fe-Al alloys. The mechanical alloying process has successfully synthesized Fe-Al alloy systems with different compositions and it has been shown that different phases are formed depending on the milling

---

[*] Corresponding autor: rdiaz.unam@gmail.com

conditions. [9-10] Extension of solid solubility has been achieved in many alloy systems by methods of non-equilibrium processing such as rapid solidification (RS) [11] and vapour deposition.[12]

Similarly, the mechanically alloyed powders also have exhibited extensions of the solid solubility limits in equilibrium. In addition to synthesizing stable solid solutions (in equilibrium), it has also been possible to synthesize metastable solid solutions supersaturated by mechanical alloying or mechanical milling from a mixture of elemental powders in various alloying systems.[1] The extension of the limits of solid solubility can be determined and quantified using the technique of X-ray diffraction (XRD), generally from changes in the lattice parameter values calculated from the displacement of the positions of the diffraction peaks, or even the absence of peaks corresponding to second phases.

Vegard's law [13, 14] establishes that the crystallographic parameters of a continuous substitutional solid solution vary linearly with the concentration at constant temperature when the nature of the atomic bonding is similar to the phases or constituents. This law has been widely used for calculating densities in solid solutions and to estimate the composition of solid solutions from diffraction data.[15]

Therefore, in this work solid solutions of Fe solute in Al matrix were synthetized by the mechanical alloying technique, in order to study the effect of processing method on the solid solubility, particle size and morphology, and microstructure of the produced alloys.

2. Experimental procedure

Elemental powders of Fe and Al of high purity analytical grade 99.9% were mixed at a ratio of Fe5.5Al (at. %), and placed in a vial with hardened steel balls of the same material. The initial powder mixture was sprayed with a process control agent consisting of analytical grade ethyl alcohol in an amount of 0.002 ml/g of the weight mixture of Fe and Al. Subsequently, the powder mixture was encapsulated within the hardened steel vial under a nitrogen atmosphere. And in this way proceed with the mechanical milling of the initial sample in a high-energy mill (Spex 8000) using a (ball weight/sample weight) ratio of 10:1. The technique of scanning electron microscopy (SEM) was used in order to characterize the evolution of size and morphology as well as the chemical homogeneity of the powders used in the process of mechanical milling as the milling time elapsed. Microstructural characterization was performed in a scanning electron microscope mark Estereoscan 440 connected to a silicon detector with window of berilium (mark Oxford Pentafel) with a resolution of 163 eV which was attached to a software of energy dispersive spectroscopy (EDS), to perform chemical microanalyses. SEM technique was also employed to perform punctual chemical analysis in the un-milled and processed samples. X-Ray diffraction technique was utilized in order to characterize the evolution of the crystal structure of the phases obtained during the mechanical milling process as a function of milling time. To perform this analysis, it was used a Siemens Diffractometer D500, in which a voltage of 30kV was used and a current of 20 mA. The specimens were scanned with a filter of CuKα radiation with a wavelength of $\lambda = 1.5418$ Å and using a step of 0.020°/0.6 sec., in a range of 30° to 120°. The variation of crystallite size and lattice parameter of the phases obtained during the process of MA was also determined from X-ray diffraction patterns.

3. Results and Discussion

3.1 Microstructural characterization by Scanning Electron Microscopy.

Fig. 1a shows the un-milled powder mixture Al-Fe, in which according to chemical analysis, particles of spherical morphology corresponds to the element Al and the larger irregularly shaped particles corresponds to Fe element. The distribution of particle size corresponding to Al element fluctuated within the range of 2 to 14.9 μm with an average size of approximately 5.7 μm, while the distribution of particle size of Fe, varied within the range of 127 to 328μm.

After 4 h of milling, the morphology of particles Fe and Al was changed significantly and the average particle size resulted equal to 11 microns. See Figure 1 b) which displays particles irregularly shaped. This means that the Fe element dramatically decreased in size during the first hours of milling, which is associated to the higher ductility or deformation capacity of Al relative to Fe. Subsequently, the particle size increased up to 15 microns during the 6 h of milling. This behavior can be attributed to the scarce hardening induced by deformation that occurred in the initial stages of milling, which means that at the earlier stages of milling process, the particles are soft (either if being employed combinations of ductile-ductile particles or brittle-ductile in a binary mixture of metal elements), and the trend of particles to weld each other to form particles of a large size is high. The composite particles formed at this stage, adopt a characteristic structure in the form of layers composed of various combinations of the initial constituents.[1]

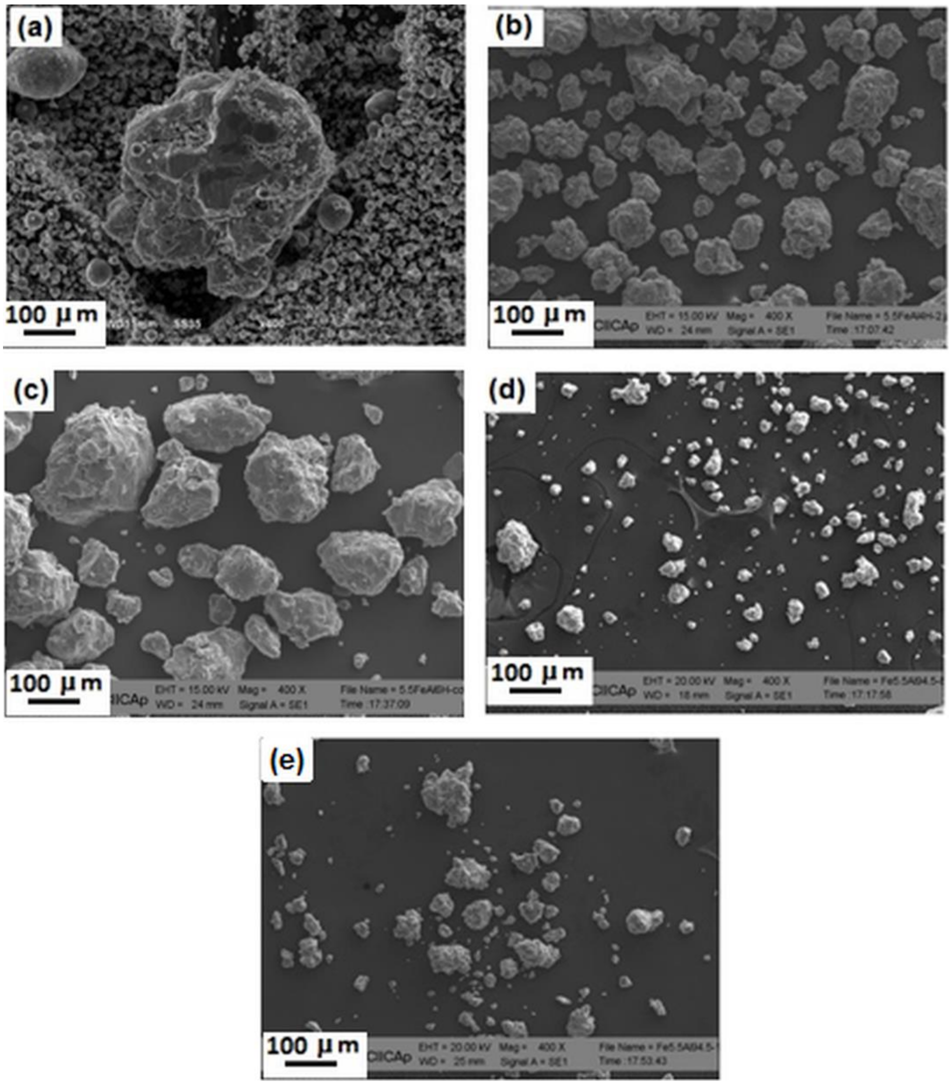

Fig. 1. Microstructural evolution of the mixture of powders of Al-5.5Fe composition (at. %) in function of the milling time. (a) Mixture of Al-Fe powders without milling, (b), (c) and (d) powder mixture subjected to 4, 8 and 10 h respectively of milling.

However; after 6 h of milling, the particles experienced a decrease in particle size up to 10 micro-meters for the milling time of 8 h. This behavior is due to hardening of the particles by mechanical working and fracture by a fatigue failure mechanism and / or by the fragmentation of fragile flakes as milling time advanced. Particle fragments generated by this mechanism can be further reduced in size, only if the strong agglomeration forces are absent. At this stage, the tendency to fracture of the particles predominates over the cold welding.

Figure 2 shows that the particle size decreased slightly from 8 to 10 hours of milling, this is because after a certain process time, an equilibrium of stable state is reached when a balance is achieved by the welding speed, which tends to increase the average particle size with the speed of fracture, which tends to decrease the average size of the composite particle. The smallest particles are able to undergo deformation without fracturing and tend to weld to each other to form larger particles, with an overall tendency to lead fine particles and large particles to an intermediate size.[16]

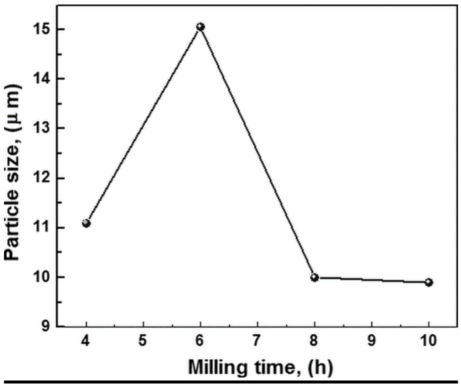

Fig. 2. Dependence of the mean particle size of the powder mixture of Al-5.5Fe composition (at. %) with the milling time.

3.2 Microstructural characterization by X-ray diffraction technique

In order to characterize the structural evolution of the mixture of Al-Fe powders, Figure 3 displays the X-ray diffraction patterns of the powder mixture Al-5.5Fe which was subjected to different mechanical milling times.

The X-ray diffractograms of the mixture of powders composed of Al-5Fe (at. %) in the un-milled condition are displayed in Figure 3 (a), where the peaks corresponding to the elemental powders Al and Fe are displayed. According to this figure, the diffraction peaks corresponding to pure Fe disappeared at 4 h of milling process, this finding is attributed to the beginning of the formation of a solid solution of Fe in Al at this time of milling. Only the diffraction peaks belonging to the solid solution labeled as α-Al can be observed during the interval of time from 4 to 10 h of milling process. As the time elapsed during 4 to 10 h, the solubilization process occurred which is related to the continuous augment of solubility of Fe in Al as the milling time elapsed. According to the binary alloy Fe-Al phase diagram,[17] the equilibrium solid solubility of Fe in Al at room temperature is only 0.0025 at. %; however an extension of the solid solubility from 0.0025 to 5 at. % of Fe in Al has been achieved by using the mechanical alloying technique in previous investigations.[18-21]

The extension of the limits of solid solubility is determined and quantified by means of the X-ray diffraction technique, and is associated with the absence of peaks corresponding to second phases and also with the displacement of the positions of the diffraction peaks which in turn are related with changes in the lattice parameter values. However; there are some difficulties associated with the determination of solid solubility limits determined in this way in mechanically alloyed powders. One of the principal complications is that the solid solubility limits cannot be exactly calculated only by noting the absence of solute peaks in the X-ray diffraction profiles. For example, Kim et al. [22] mechanically alloyed Al-20 wt% Ti powder mixtures and reported that the Ti diffraction peaks were absent in the X-ray diffraction profiles recorded from the powder mechanically alloyed for 15 h. However, TEM analyses of the same powder evidently displayed the presence of nanometer-sized Ti particles in the aluminum matrix. Thus, it is recommended to use more than one characterization technique to precisely determine the true solid solubility limits.

Fig. 3 displays a broadening at the half height of the diffraction peaks simultaneously with the passing of milling time as shown in profiles of XRD displayed in Figures 3 b), c), d) e). This behavior obviously is associated with a reduction of the crystallite size (nano-metric grains), because the peak width is inversely proportional to the size of crystallite, according to the Scherrer equation.[23,24]

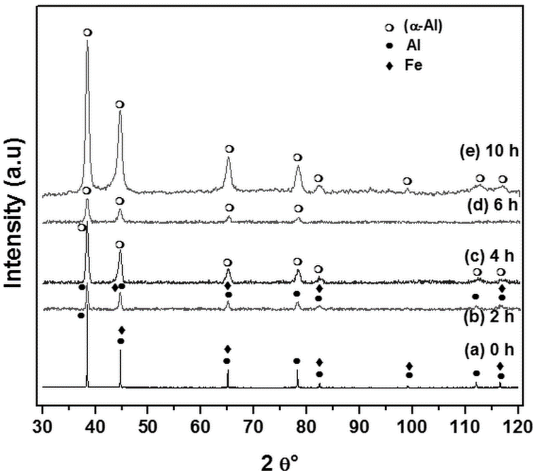

Fig. 3. X-ray diffraction profiles of the powder mixture of Al-5.5Fe (at. %) milled at various times: a) 0 h, b) 2 h, c) 4 h, d) 6 h and e) 10 h.

In Fig. 4 the variation of the crystallite size depending on the milling time is shown, where can be clearly seen a tendency to decrease the nano-scaled grain size simultaneously with the course of the milling process.

Wherein the crystallite size in nm was determined by the Scherrer equation [23] from the width of XRD diffraction peak at half its height. Once the crystallite sizes obtained from all X-ray diffraction peaks were computed, then a mean value of crystallite size was determined. In the same illustration can be seen a drastic decrease from about 21 to 14.4 nm when the powder mixture was milled from 2 to 4 h, respectively. However, during the next two hours of milling (from 4 to 6 h of process) the crystallite size decreased in a more moderate way. But, after 6 h, the nano-metric grain size decreased from 14 nm to 10.8 nm when the process time increased from 6 to 10 h respectively.

It is worth noting that there has not been many investigations developed in order to explain why and how the materials that have been produced by MA or mechanical milling (MM) have obtained grain sizes with a nano-metric scale.

Hellstern et al., [25] have described the mechanism of formation of nanostructures by mechanical milling and mechanical alloying by using high resolution transmission electron microscopy (HRTEM), these authors reported that in the early stages of the MA process, shear bands were observed due to the high deformation speeds experienced during the MA process.

These shear bands, which contain a high density of dislocations, have a typical thickness of approximately 0.5 - 1.0 microns. Subsequently, during milling, the average deformation at the atomic level, increases due to the increase of dislocation density. Then, when there has produced a certain dislocation density within these highly strained regions, then the crystal is disintegrated into sub-grains which are separated by grain boundaries of low angle. Subsequently, the boundaries of low angle are replaced by grain boundaries of large angle, which implies rotation of grains, as observed by Hellstern et al. [25] in the absence of texture in the diffraction patterns of electrons and the random orientation of the grains observed in electron micrographs of high resolution.

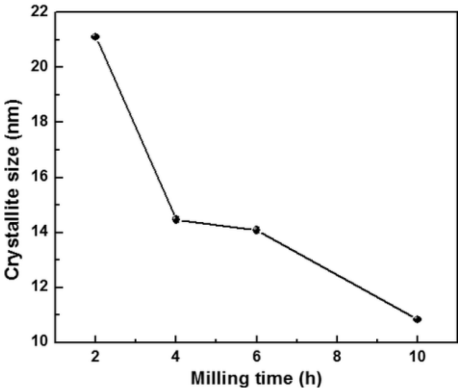

Fig. 4. Crystallite size dependence (nanoscale grain) of the powder mixture of Al-5.5Fe composition (at. %) with the milling time.

In the mixture of powders subjected to mechanical alloying, an inter-diffusion between components can occur, and if conditions permit, a solid solution can be formed. The solubility limit is expected to increase with the milling time and as the diffusion process proceeds to reach a level of (super) saturation, where beyond it, no further extension of the solid solubility occurs. In order to determine "qualitatively or quantitatively" the solid solubility levels of the solute Fe in the solvent Al, the lattice constants were determined from the peak positions of the X-ray diffraction profiles, which are shown in Figure 3. Similarly, the variation of the lattice parameter was determined from the displacement of the peak positions in the X-ray diffraction patterns.

In Fig. 5, the variation of the lattice parameters as a function of milling time is displayed. These lattice parameter values were determined from the diffraction peak of Al located approximately at the value of 38.4 ° of 2Θ,

In most peaks where both elements Fe and Al overlapped, the lattice parameter not was calculated, this in order to determine the variation of solid solubility of Fe in Al, which is linked to the shift of the diffraction peak generated by the family of crystallographic planes {111} belonging to Al.[26]

In Figure 5, it can be seen that the lattice parameter decreased during the time interval of 2 to 6 h of milling, but later the lattice constant increased until 10 h of mechanical milling process. In this case, the decrease of the lattice parameter of Al, is congruent because the aluminum has a lattice parameter of 4.0495 Å,[26] which is higher than that of Fe with a value of 2.8664 Å. This is because the components of the Al-Fe system, tend to form an isomorphic system during the milling process. However, it cannot be completely formed because the Al is present in much larger amount acting as the solvent. In this case, the lattice parameter of one of metals decreases and the other increases with milling time. Subsequently, when stable conditions are established, the two lattice parameters converge and then it gives rise to the formation of a homogeneous solid solution with the expected lattice parameter.[1]

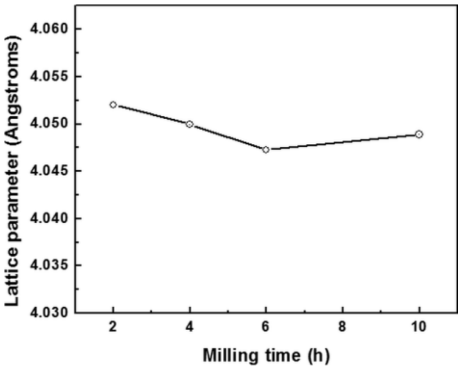

Fig. 5. Variation of the size of the lattice parameter of the powder mixture of composition Al-5.5Fe (at. %) based on the milling time.

3.3 Microstructural characterization by Transmission Electron Microscopy

Fig. 6 (a) displays a transmission electron micrograph of the Al-5Fe alloy which was mechanically milled for 10 h together with its respective electron diffraction pattern exhibited in figure 6 (b). Grains with a mean nano-meter size of 11.06 nm are shown in the first illustration. Figure 6 (b) shows electron diffraction patterns in form of circles belonging to the whole region exhibited in figure 6 (a). This electron diffraction pattern is viewed from [0-22] zone axis. The following phases were identified after indexing the electron diffraction pattern: Al, $Al_{13}Fe_4$ and Al_5Fe_2. The later phase exist in the Fe-Al phase diagram at the right of the zone where exist the (Al) solid solution. However, the $Al_{13}Fe_4$ phase probably is metastable because is not present in the mentioned binary alloy phase diagram.

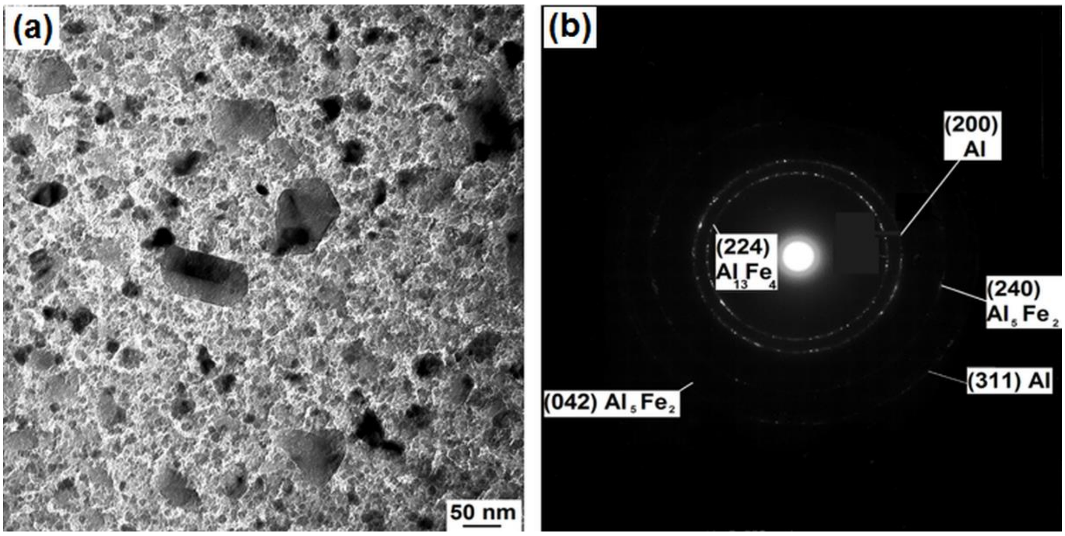

Fig. 6. (a) Transmission electron micrograph of Al-5Fe (at. %) alloy milled during 10 h, (b) electron diffraction pattern viewed from the zone axis [0-22] with respect to Al of the sample zone shown in (a).

4. Conclusions

The particle size was increased significantly from 4 to 6 h of milling, but after that time, diminished to the end of milling time (10h). Where the initial increment of particle size is due to the predominance of the welding process among particles, and the lack of hardening by deformation that occurs in the initial stage of milling. From 8 to 10 h of milling, a balance between fracture and welding processes among particles was achieved, because the size of particles remained stable during this interval of milling process. According to the DRX and TEM analysis performed in the specimens milled after 4 h, the size of grains resulted nano-metric. The crystallite size corresponding to the solid solution of Fe in Al (α-Al) obtained during the ball milling process, decreased as the milling time advanced from 4 to 10 h. Also the calculated lattice parameter of the formed solid solution (α-Al) displayed a tendency to decrease as the milling time elapsed. This behavior is because when the two component metals form an isomorphous system, the lattice constant of one of the metals diminishes and that of the other increases with milling time. Once steady-state conditions are achieved, the two lattice parameters converge and a homogeneous solid solution with the expected lattice parameter is formed. The TEM analysis performed in specimens which were previously milled during 10 h, revealed the precipitation of the Al_5Fe_2 and $Al_{13}Fe_4$ phases in the nanostructured Al matrix.

Acknowledgements

The authors express their gratitude to CONACyT-Méxco for the financial support granted for the development of this research. Also to the technician Adriana Tejeda for the realization of the X-ray diffraction analyses.

References

[1] C. Suryanarayana, Prog. in Mater. Sci. **46**, 1 (2001).
[2] S. X. McFadden, R. S. Mishra, R. Z. Valiev, A. P. Zhilyaev, A. K. Mukherjee, Nat. **398**, 684 (1999).
[3] R. W. Siegel, G. E. Fougere, Nanostructured Mater. **6**, 205 (1995).
[4] J.S. Benjamin, Mater. Sci. Forum **88-90**, 1 (1992).
[5] C. Suryanarayana, E. Ivanov, V.V. Boldyrev, Mater. Sci. and Eng. A **304-306**, 151 (2001).
[6] J. S. Benjamin, T.E. Volin, Metall. Trans. **5**, 1929 (1974).
[7] J. B. Fogagnolo, F. Velasco, M. H. Robert, J. M. Torralba, Mater. Sci. and Eng. **A342**, 131 (2003).
[8] M. Mhadhbi, M. Khitouni, L. Escoda, J. L. Sunol, & M. Dammak, J. of Alloys and Compds. **509**, 3293 (2011).
[9] E. P. Yelsukov & G. A. Dorofeev, J. of Mater. Sci. **39**, 5071 (2004).
[10] M. H. Enayati, M. & Salehi, J. of Mater. Sci. **40**(15), 3933 (2005).
[11] T. R. Anantharaman & C. Suryanarayana, J. of Mater. Sci. **6**(8), 1111 (1971).
[12] C. Suryanarayana, Non-equilibrium processing of materials, 1st Ed. (Pergamon Press, Oxford, 1999).
[13] L. Vegard, Z. Phys. **5(**17), 17(1921).
[14] L. Vegard, Z. Kristall. **6(**72), 239 (1928).
[15] N. Nishiyama, J. Lin, A. Okazaki, M. Iwasaka, K. Hirakawa, Jpn. J. of Appl. Phys. **29**, 369 (1990).
[16] J. S. Benjamin, Scientific Am. **234**(5), 40 (1976).
[17] T. B. Massalski, Binary alloy phase diagrams, American Society of Metals, Metals Park Ohio **2**, 1710 (1986).
[18] B. Huang, K. N. Ishihara & P. H. Shingu, Mater. Sci. and Eng. **A231**, 72 (1997).
[19] V. I. Fadeeva & A. V. Leonov, Mater. Sci. Forum, **88-90**, 481 (1992).

[20] D. K. Mukhopadhyay, C. Suryanarayana & F. H. Froes, Metall. Mater. Trans. **A26**, 1939 (1995).
[21] F. H. Froes, (JOM) J. of the Min., Met and Mater. Soc. **42**(12), 24 (1990).
[22] H. Kim, D. Suhr, G. Kim & D. Kum, Met. and Mater. **2**(1), 15 (1996).
[23] P. Scherrer, Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, mathematisch-physikalische Klasse, **26**, 98 (1918).
[24] J. I. Langford & A. J. Wilson, J. of Appl. Crystallogr. **11(**2), 102 (1978).
[25] E. Hellstern, H. J. Fecht, C. Garland, W. Johnson, L. E. McCandish, D. E. Polk, B. H. Kear: ‘Multicomponent ultrafine microstructures, presented in the Proc. Mater. Res. Soc. December, Boston Massachusetts, EUA, **132**, 137 (1989).
[26] R. W. Wyckoff, Crystal Structures, Interscience Publishers, New York (1963).