Study of the nanocrystalline bulk Al alloys synthesized by high energy mechanical milling followed by room temperature high pressing consolidation

T. Makhlouf\textsuperscript{a}, M. Azabou\textsuperscript{a}, M. Ghrib\textsuperscript{b}, T. Ghrib\textsuperscript{b}, N. Yacoubi\textsuperscript{b}, M. Khitouni\textsuperscript{a*}

\textsuperscript{a}Laboratoire de Chimie Inorganique(99/UR/12-22), FSS, B. P. 1171 – 3018, Sfax – Tunisia.
\textsuperscript{b}Laboratoire de Photo-thermique Elmrezgua 8000-IPEIN- Nabeul-Tunisia.

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Abstract

In the present study high energy mechanical milling followed by high-pressing consolidation has been used to obtain bulk nanocrystalline Al-Fe-Si alloy. Quantitative XRD analysis and scanning electron microscopy were used to characterize the material evolution during thermal treatments in the temperature range 25 - 500 °C. The cold-worked structure have been synthesized with microstructure showing a mixture of a significant low size of crystallite (70 nm) and a high level of lattice strains (0.85%). Starting from the nanocrystalline specimens, isochronal experiments were carried out to monitor the reserve microstructure and transformations. The high temperature annealing is required for ameliorating the quality of room temperature consolidated materials by removing all porosity and obtaining good interparticle bonding. The thermal conductivity and the thermal diffusivity are investigated with the Photothermal deflection technique. These thermal parameters increase with the annealing temperatures. This behavior is attributed to the increase in the rate of diffusion coefficient of added elements inside the aluminum matrix.

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1. Introduction

It has been well established that high-energy mechanical milling is one of the major techniques for producing powders with nanocrystalline structures [1, 2]. On the other hand, the purpose of high-energy mechanical milling is to produce bulk materials or components with desirable mechanical, physical and chemical properties. In these cases, consolidation of high energy mechanically milled powder is an essential process for achieving the final objectives [3, 4]. The particle shapes in the mechanically milled powders are rather irregular, and often the as-milled powder particles are heavily work hardened. These features might affect the sintering behaviour of the powders, but

\textsuperscript{*} Corresponding author. Tel.: +216-98-656-430; fax: +216-74-274-437.
E-mail address: khitouni@yahoo.fr.

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to date, few study has been carried out to compare the sintering behaviour of high energy mechanically milled powders with that of the powders produced using other methods [2-6].

Nanostructure formation and powder consolidation of Al alloys and Al matrix composites are interesting examples of the new microstructures which are possible with the severe plastic deformation (SPD) technique. But, consolidation of milled powders into bulk, full-density compacts preserving nanometric grain size, which is crucial for possible application of nanophase materials, is not easy to achieve. In fact, full consolidation of nanocrystalline or amorphous aluminium alloy powder during conventional extrusion was achieved only at a higher temperature of 450°C [7, 8].

The thermally-activated mechanisms that operate during sintering have been investigated since the 1950s [9, 10]. Roughly speaking, the transformation induces the welding of the interparticle contacts and the growing of these contacts by solid diffusion, the driving force being the reduction of high-energy solid-pore interphases. Many models have been proposed to describe sintering mechanisms [11-13]. Most of them are restricted to the sintering of regularly or randomly packed, spherical, monocrystalline powder particles. Obtaining bulk nanocrystalline Al alloys by consolidation technique is of the interest not only due to the improved hardness and strength but also because of expectations of better ductility and thermal properties comparing with their coarse-grained counterparts.

The aim of this work is to study the microstructure produced by SPD under room temperature pressure consolidation using nanocrystalline Al-based alloy powders prepared by high-energy mechanical milling and to investigate their mechanical and thermal behaviours. The thermal properties are determined by applying the Photothermal Deflection (PTD) technique which is a nondestructive technique applied for determining the optical and thermal properties of several materials [14-16].

2. EXPERIMENTAL

2.1. Material

The experiments were carried out using a recycled aluminium (94.1%) material received in the form of cast ingots. It was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The chemical composition is given in Table 1. The powder with particle size of 80-120μm was prepared by filing and subsequently annealed at 773 for 6h under a low pressure of argon to ensure homogeneous structure before milling. The obtained powder was milled for 4 h in a Vibrator mixer-Mill. Typical mass of material is 50g. Milling proceeds with a stationary speed of rotation automatically fixed. The duration of milling process is also fixed by an electronic regulator and is fixed on 15 min in order to avoid the heating by milling. The obtained powders were consolidated at room temperature into disks 4 mm thick and 10 mm diameter by high-pressures under stress of 7 GPa.

Table 1. Chemical composition of the investigated material (ppm weight).

|   | Al   | Fe   | Mg   | Cu   | Mn   | Zn   | Si   | Ti   | Cr   | Ni   | Ca   | Co   | Pb   |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Bal. | 2500±25 | 2190 ± 22 | 558 ± 10 | 600 ± 12 | 1660 ± 9 | 1071 ± 11 | 60 ± 0.8 | 56 ± 1 | 36 ± 0.7 | 14 ± 7 | 2.6 ± 0.1 | < 1 |

2.2. Photothermal deflection technique

2.2.1. Principle

The PTD technique consists in heating the sample using a modulated light pump beam (Fig. 1). The optical absorption of the sample will generates a thermal wave that will propagate into the sample and in the surrounding fluid medium, inducing a temperature gradient then a refractive index gradient in the fluid. A Laser probe beam skimming the sample surface and crossing the region with inhomogeneous refractive index gradient is deflected. Its deflection may be related to the thermal properties of the sample.
2. 2. 2. Theoretical model

The used samples are common metallic material which have a great reflection coefficient and should be covered with a thin graphite layer that will absorb the incident light and therefore playing the role of a heat source. In the case of a uniform heating of the samples, a one-dimensional treatment of the thermal wave is sufficient.

The theoretical model which is described in detail in ref. [17] is built on the resolution of the heat equation in the different media, fluid, sample and backing and by applying the continuity of temperature and heat flow at the different interfaces \( x=a \), \( x=-l_1 \), and \( x=-l_1-l_2 \) (Fig. 2). In this model only the thin graphite layer is assumed to absorb the incident uniform light beam.

In these conditions the sample surface’s elevation temperature \( T_0 \) and the deflection \( \psi \) of the probe laser beam are given respectively by equations (1) and (2) as shown in the reference [17]:

\[
T_0 = E[(1 - b)e^{-s b}[(1 - r)(1 - c)e^{-s c} + (1 + r)(1 + c)e^{-s c} - 2(1 + r c)e^{-s c}] \\
- (1 + b)e^{-s b}[(1 - r)(1 + c)e^{s c} + (1 + r)(1 - c)e^{s c} - 2(1 - r c)e^{s c}]]/\\
[[1 + b)e^{s b}[(1 + g)(1 + c)e^{s c} + (1 - g)(1 - c)e^{s c}]] \\
- (1 - b)e^{-s b}[(1 + g)(1 - c)e^{s c} + (1 - g)(1 + c)e^{-s c}]]
\]

(1)

Where \( b=(k_i/k_f)\sqrt{D_f/D_i} \), \( c=(k_i/k_b)\sqrt{D_b/D_i} \), \( g=(k_i/k_f)\sqrt{D_f/D_b} \), \( r=(l_1-\alpha l_2)/2\mu_i \), \( \sigma=(l_1+j\pi f)/\pi f \).

Ki and Di, \( \mu_i \) are respectively the thermal conductivity, the thermal diffusivity and the thermal diffusion length of the i medium.

As \( T_0 \) and \( \psi \) are complex numbers, they may be written as: \( T_0 = T_0 e^{i \theta} \) and

\[
\psi = |\psi| \exp( j(\omega t + \theta)) \\
= -\sqrt{2} \left( \frac{1}{\mu_i} \right) \left( \frac{dn}{dT} \right) [T_0] \exp( -x/\mu_i ) \exp( j(\omega t + \theta + \frac{5\pi}{4} - \frac{x}{\mu_i}))
\]

(2)

\[
|\psi| = \sqrt{2} \left( \frac{1}{\mu_i} \right) \left( \frac{dn}{dT} \right) [T_0] \exp( -x/\mu_i ) \quad (3 a)
\quad \psi = -\frac{x}{\mu_i} + \theta + \frac{5\pi}{4}
\]

(3 b)

One can notice that these expressions are function of the sample thermal properties and the modulation frequency.
2.2.3. Experimental set-up of the PTD technique

The experimental set-up is described in Figure 2. The used samples which have a great optical reflection coefficient should be covered with a thin graphite layer that will absorb the incident light and therefore serve as a heat source. The samples are heated by a halogen lamp light of Power 100W modulated by a mechanical chopper at a variable frequency. An He-Ne laser probe beam of diameter \( d = 100 \mu m \), skimming the sample surface at a distance \( z \), is deflected. This deflection can be detected by a four quadrant photo-detector and converted to an electrical signal which is measured by a lock-in amplifier (EG & G5210). Through the intermediary of the interfaces of the mechanical chopper and the Look-in amplifier a microcomputer will set the desired modulation frequency and read the values of the amplitude and phase of the photo-thermal signal and then draw their variations according to the square root modulation frequency.

![Fig. 2. 1-Table of horizontal and vertical micrometric displacement, 2-Sample, 3-Photodetector position, 4-Fixed laser source, 5-Halogen lamp, 6-Look-in amplifier, 7-Mechanical chopper, 8-Computer](image)

2. RESULTS AND DISCUSSIONS

3.1. X-Ray diffraction analysis

Fig. 3a shows the typical X-ray diffraction patterns of Al alloy after room temperature consolidation and as a function of annealing temperature. It contains the (111), (200), (311) and (222) fundamental reflections. In addition to the reflections relative to f.c.c solid solution, other peaks of very low intensities were recorded (Fig. 3b). From the XRD data and X-ray emission spectrometry in the SEM, these peaks were found to be relative to Fe-rich phases. In addition, from SEM measurement one can see the presence of the Cr-rich phase.

![Fig. 3. (a) XRD patterns of Al alloy obtained after room temperature consolidation and as a function of annealing temperatures. (b) Precipitates XRD peaks as a function of annealing temperature.](image)
In order to obtain information on the crystallite sizes and on the lattice distortions evolutions as a function of annealing temperature, an inspection of the shape of the diffraction peaks was performed. The peak broadening of the most intense reflection is shown in figure 3a, for three selected annealing temperatures i.e. 25, 200 and 500°C. It is clear that the FWHM of this peak decreases with the annealing temperatures. This behaviour is related to the changes of microstructure, i.e. the increase of crystallite size and the important reduction of the lattice strains by annealing. In addition, from a direct examination of diffraction patterns, one can note that peaks are shifted towards lower or higher values of θ angles as a function of annealing temperatures (Fig. 3b). Many features should operate simultaneously: the annihilation of stacking faults initially introduced by plastic deformation is probably one of the reasons of this shift. Another feature is the change of the lattice parameter during annealing. The line profile analysis, using Halder-Wagner plot [18], allows us to ascertain the evolution of the apparent size, <D>, and the equivalent lattice strain, (ε²)½. The obtained microstructure parameter evolutions are represented in figure 4. As shown for the dependence of crystallite size on the annealing temperature, a linear increase in temperature below 250°C, leading to a steady state value in the elevated temperatures (Fig. 4a). The average crystallite sizes are increased from about 70 nm for the consolidated sample to 107 nm after annealing at 250°C. For temperature above, the steady state achieved is characterized by a value of an average crystallite size about 107-115 nm. On the other hand, the lattice strain decreases rapidly to a value about 0.25 % in 100°C, then one can note a slowly decrease to a value of about 0.05% (Fig. 4b). Moreover, a significant increase in the lattice parameter was observed after annealing at 300°C, leading to a steady state value in the elevated temperatures. The maximum relative variations was Δa/a₀= 0.039% Å. The increase of the lattice parameter is probably caused by the grain expansion due to the increase in the diffusivity reaction of alloying elements.

![Fig. 4. (a) Crystallite size, lattice strains evolution and (b) lattice parameter variations as a function of annealing temperature.](image)

3.2. Microscopic observations

Figure 5 shows the microstructure evolutions of the consolidated sample as a function of annealing temperature: processing of the milled powder by consolidation under stresses of 7 GPa in 25°C resulted in a microstructure characterized by an almost perfect regions and the identified pores are located at the interfaces between particles. By increasing the annealing temperature, one notices a progressive elimination of the pores The fully consolidated disks are observed at a temperature higher than 300°C: all porosity was removed and a good interparticle bonding was obtained. The relative density of the consolidated sample then annealed at 300°C, evaluated by the Archimedes method, was about 95%.
3.3. Determination of the thermal properties

In order to determine the thermal properties evolutions with the annealing temperature we have to study the variation of the photothermal signal with the square root of the modulation frequency for different values of the annealing temperature. The experimental variations of the normalised amplitude and phase of the photothermal signal with the square root modulation frequency for the investigated samples are given in figure 7. The thermal conductivity $K_s$ and the thermal diffusivity $D_s$ of the samples are determined by comparing the experimental amplitude and phase curves to the corresponding theoretical ones. The best theoretical fitting between the experimental and theoretical curves are obtained for fixed values of the couple $(K_s, D_s)$ [17, 19].
Fig. 7. Experimental variation of the amplitude and phase of the photothermal signal versus the square root modulation frequency for the Al alloys for different annealing temperature.

Figure 8 represents the experimental and theoretical curves of amplitude and phase of the photo thermal signal variation versus square root modulation frequency for the sample annealed at a temperature \( \theta = 100^\circ \text{C} \). The coincidence between this two curves is obtained for the unique couple \( K_s = 87 \, \text{W.m}^{-1}.\text{K}^{-1}, D_s = 0.6 \times 10^{-4} \, \text{m}^2.\text{s}^{-1} \).

The representation of the two thermal properties with the quenching temperature gives the curves presented in figure 9. One can remark their increasing with the annealing temperature.

Fig. 8. Experimental and theoretical variation of the amplitude and phase of the photothermal signal versus the square root modulation frequency for the Al alloys at the annealing temperature \( \theta = 100^\circ \text{C} \).

Fig. 9. Experimental thermal conductivity and diffusivity of the Al alloys versus the annealing temperatures.
A kinetic study [11, 12] shows that the thermal diffusivity in a metallic compound obeys the following equation

\[ \lambda = \frac{3D}{v} \]

where \( v \) is the electrons mean speed of values 3600 m\(^{-1}\)s\(^{-1} \) and \( \lambda \) is its mean free path. This mean free path is the contribution of several parameters, which are summarized in:

\[ \frac{1}{\lambda} = \frac{1}{\lambda_i} + \frac{1}{\lambda_d} + \frac{1}{\lambda_g} + \frac{1}{\lambda_c} \]  

where \( \lambda_i \) is the crystal lattice, \( \lambda_d \) is the contribution due to the deficiency rate in the sample, \( \lambda_g \) is the contribution due to the mesoscopic grain size constituting the sample and \( \lambda_c \) is the contribution due to the constraint added in material. On the other hand, we have demonstrate in the paragraph (4.1) that the crystallite size and the crystal lattice increase, while the lattice constraint decreases with the annealing temperature which can influence the conduction of the heat in the sample. Furthermore, the temperature elevation can active the vacancy mobility and the annihilation of defects introduced by mechanical milling followed by high-pressure consolidation which can favourite the increasing of the thermal properties.

For Weidmann-Franz the thermal conductivity \( K_s \) and the electrical conductivity \( \gamma \) are in relationship by:

\[ K_s = \gamma L T \]

where \( L = 2.4 \times 10^{-8} \text{ U.S.J} \) and \( T=300 \text{ K} \) is the sample temperature equal to laboratory one. Using this relationship we can deduce the electrical conductivity evolution with the annealing temperature or its evolution with the thermal conductivity as shown in figure 10.

![Electrical conductivity variations with the thermal conductivity.](image)

**4. CONCLUSION**

In this work we have studied the microstructure and the thermal properties evolution of a nanocrystalline bulk Al alloys synthesized by high energy mechanical milling followed at room temperature and at a high pressing consolidation. We have demonstrated that the crystallite size, the crystal lattice increase and the lattice constraint decreases with the annealing temperature. The determination of the thermal properties is understudied by the PTD technique and we have observed that simultaneously the two thermal properties increase with the annealing temperature and we have linked this evolution changes in the crystallite and the crystal lattice size and the diminution of the pores density in the material matrix. And after this we have obtain an idea about the value of the electrical conductivity knowing that of the thermal conductivity.
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