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978-1-605-11219-0 - Materials Research Society Symposium Proceedings Volume 1242:

Materials Characterization

Editors: Ramiro Pérez Campos, Antonio Contreras Cuevas and Rodrigo A. Esparza Muñoz

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**Materials Characterization by X-Ray Diffraction, Infrared
Spectroscopy, Scanning Electron Microscopy and
Transmission Electron Microscopy**

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Electron Microscopy Characterization of Humidity Ball-Milling AlCuFe Intermetallic Powders

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ABSTRACT

An Al₅₈Cu₂₅Fe₁₇ alloy composition was produced by conventional casting technique. In order to take advantage from the hydrogen-environmental embrittlement reaction, which affects these alloys, this research was carried out subjecting prealloyed powders to wet-ball milling. Through these experiments it has been possible to evaluate the particle size reduction as consequence of hydrogen fracture and milling energy. The morphological and structural characteristics of the samples were performed using x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). The experimental results indicate that the samples with higher contents of humidity have a good particle size reduction. With the increment of milling time, the particle size was diminished even more reaching nanometer size scale.

INTRODUCTION

The AlFe intermetallic compound are closely related to the Al₅(Cu,Fe)₅ intermetallic phase [1,2]. Both phases share similar crystalline structure. However, in Al₅(Cu,Fe)₅ alloy the copper is now part of atomic lattice that has given rise to a substitutional solid solution. AlFe intermetallic has important properties for its applications as structural materials at high temperatures [3-5]. However, the main drawback of these materials is its brittle nature at room temperature and its strong vulnerability to the hydrogen environmental embrittlement (HEE) [6]. The HEE mechanism in intermetallic compounds has been studied in the past [7,8]. The mechanism indicates that the water vapor in the air react with the aluminum of the alloy to produce alumina and hydrogen. Hydrogen diffuses inside of the intermetallic alloy and induces bond instability and causes cleavage fracture of the material. Recently, has been demonstrated that the ball milling under humidity conditions can be used to produce nanoparticles [9]. These experiments were carried out using high aluminum at% alloys. Therefore, in this work we used the high-energy ball milling to increase the rate of HEE reaction and evaluate the particle size reduction of Al₅(Cu,Fe)₅ β-phase.

EXPERIMENTAL DETAILS

Ingots of Al-Cu-Fe were prepared by conventional casting using an induction furnace and high purity elements (99.9%). The nominal composition of the alloy was $\text{Al}_{58}\text{Cu}_{25}\text{Fe}_{17}$. High-energy ball milling in air of prealloyed ingots were subsequently carried out using SPEX 8000 mixer/mill equipment. The samples were milled for 1 and 8 h. Hardened steel vials and balls and ball to powder ratio of 8:1 were using. The relationship between the sample-weight to deionizer-water used was 1:0 and 1:6 (g/ml). The samples were characterized by x-ray diffraction (Siemens D5000, $\text{CuK}\alpha$ radiation), scanning electron microscopy equipped with an energy dispersive x-ray spectroscope (JEOL-6400), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEM-2200 FS) and high resolution transmission electron microscopy (HRTEM).

DISCUSSION

Figure 1a show the XRD pattern of as-cast specimen. As can be seen all the diffraction peaks correspond to the β - $\text{Al}_5(\text{Cu,Fe})_5$ cubic structure of B2 type. After dry-mechanical milling for 8 h (figure. 1b) the XRD patterns show weak and broadened peaks due to the crystal size diminution and internal strain. Figure 1c corresponds to the milled sample with 1:6 humidity and 1 h of milling time.

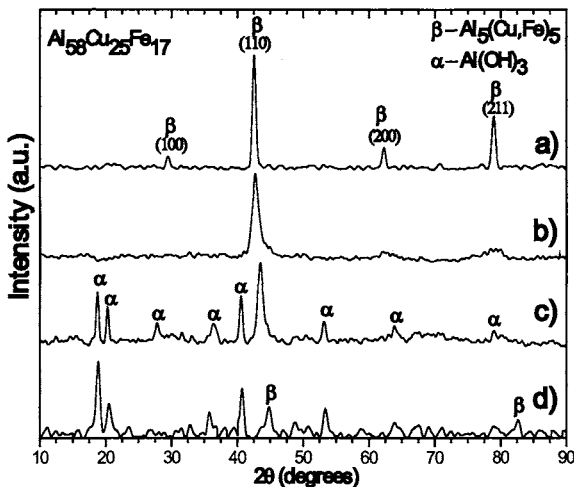


Figure 1. XRD patterns of mechanical milling of the β -phase; a) as cast sample, b) dry-milling for 8 h, c) wet-milling (1:6 g/ml, 1 h) and d) wet-milling (1:6 g/ml, 8h).

This XRD pattern shows the presence of the peaks indexed with an aluminum hydroxide (α - $\text{Al}(\text{OH})_3$, bayerite phase) coexisting with the β -phase. Bayerite phase has a hexagonal

structure with lattice parameters $a=5.047\text{\AA}$ and $c=4.73\text{\AA}$ and appear as a result of the environmental embrittlement reaction widely studied in the past [6]. In this reaction the aluminum of the alloy react with the water vapour to form bayerite and hydrogen. In this work, the wet-mechanical milling is carried out to increase the reaction rate and evaluate the particle size reduction due to the hydrogen fracture. Figure 1d shows that with increasing milling time the bayerite formation is increased. Can be clearly observed that the (110) peak decrease in intensity and the bayerite diffraction peaks are increased. This is an indication that the HEE reaction is accelerated to produce bayerite and hydrogen. As consequence of this the particle size reduction proceeded. From these figures can be concluded that the increment of milling time leads to increment the reaction rate to produce more bayerite phase and reduce the crystal size of the material.

Figures 2a illustrates a SEM image where lengthened fibers morphology can be observed. This typical growth corresponds to the aluminum oxides phases. The elemental chemical mapping of Al, O, Fe and Cu, of grey image are shown in figures 2b-e respectively. The areas with more aluminum contents appear in the same areas of those of oxygen, suggesting that both elements are formed the bayerite phase. Areas integrated with Al, Cu and Fe signals can clearly observe in other image regions. From these results one can deduce that after the wet-mechanical milling, there is clear evidence to assure the coexistence of α and β phase. In addition, as the wet-milling times are increased the aluminum content in the cubic phase decreased. These results are in agreement with those obtained by XRD.

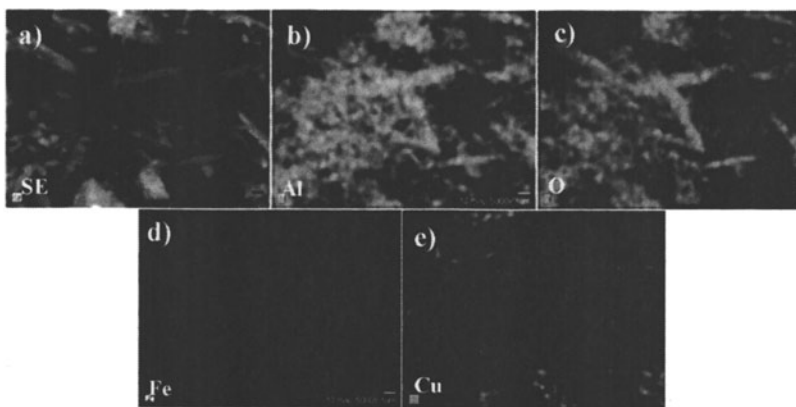


Figure 2. Chemical elemental mapping obtained from SEM, (1 h and 1:6 g/ml).

Figure 3 shows an image obtained using transmission electron microscopy (HAADF-STEM). The specimen corresponds to 1:6 humidity relationship and 1 h of milling time. In this image, as a consequence of the Z-contrast, it is easy to identify the different morphological changes in the material. The small particles have bigger contrast intensity, therefore, have a bigger atomic number. Thus, the small spherical particles (metallic phase) are surrounding by the bayerite phase. These results suggest that the powders under these experimental conditions

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consist of nanometer-sized crystals embedded in the ceramic matrix. Figure 4 show a bright-field TEM image obtained from the previous zone. More details of the homogeneous distribution of the particles absorbed in the previously mentioned matrix can be observed.

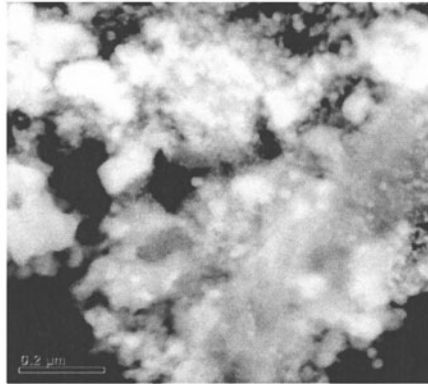


Figure 3. HAADF-STEM image which correspond to the sample milled by 1 h and 1:6 g/ml humidity conditions.

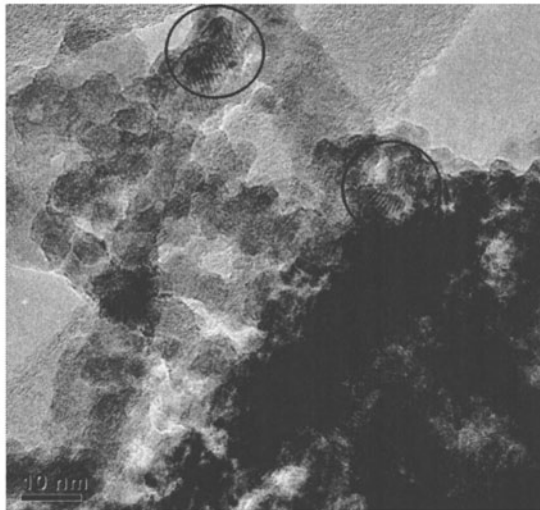


Figure 4. Bright-Field image which correspond to the sample milled by 1 h and 1:6 g/ml of humidity conditions.

Nanocrystals superimposed form Moirés fringes patterns which are indicating in the image by a circle. The average size of smaller crystals is about 10 nm. Nanocrystals

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agglomeration embedded in a ceramic matrix can also be observed. These results are agreement with previous authors [9].

High resolution electron microscopy (HREM) investigation was also carried out to recognize the atomic structure of α -Al(OH)₃ and β -Al₅(Cu,Fe)₅ phases after wet ball-milling. Figure 5 shows HREM micrographs of β -phase nanoparticles coexisting with α -phase nanoparticles. From the contrast transfer function (CTF) the planar distances for β -phase that the electron microscopy can resolve, correspond to the (100) and (110) planes. The planar distances which were directly measurement in the picture which correspond to those planes have 0.283 and 0.206 nm respectively. For the bayerite structure the measurement of the parallel lattice fringes corresponding to 0.217 and 0.219 nm, belong to (-1-11) plane.

These results confirm that the hydrogen fracture process take place and can be used to nanoparticles synthesis. However, metallic nanoparticles are embedded in the ceramic phase which has a smaller density. Therefore, to liberate the metallic particles it is necessary a separation process or the modification of the reaction conditions, for example, the PH [10].

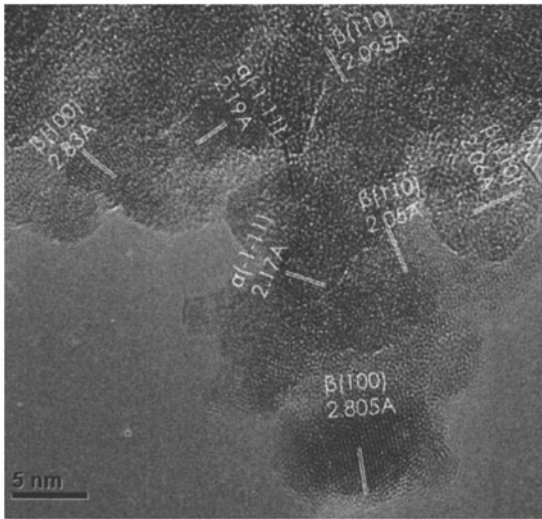


Figure 5. Nanoparticles HREM image of the cubic and ceramic phase.

CONCLUSIONS

In the present work, the Al₅₈Cu₂₅Fe₁₇ alloy produced by conventional casting process was mechanically milled under humidity conditions. After that the milled powders were characterized by XRD and HREM techniques. Both XRD and HREM results indicate the

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coexistence of β - Al₅(Cu,Fe)₅ and α -Al(OH)₃ phases as a result of aluminum corrosion of Al₅(Cu,Fe)₅ alloy expose to water. The evolution of this reaction confirms hydrogen production and progressive crystal size reduction as milling time was increased. The particle size reduction from hydrogen fracture of the material reaches nanometric size and the aluminum content in the Al₅(Cu,Fe)₅ alloy diminishes. However, nanocrystals are trapped in the ceramic phase which has a smaller density than the metallic one.

ACKNOWLEDGMENTS

G. Rosas would like to thank the financial support received from the National Council for Science and Technology of Mexico (CONACYT) under the grant 48716-25535.

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Mater. Res. Soc. Symp. Proc. Vol. 1242 © 2010 Materials Research Society

Spectroscopy Analysis of the Ring Opening Reaction in Functionalized Spiropyran FilmsRaúl J. Delgado-Macuil¹, Marlon Rojas-López¹, Valentín L. Gayou¹, Abdu Orduña-Díaz¹, Joel Díaz-Reyes¹ and Virginia Camacho-Pernas².¹Centro de Investigación en Biotecnología Aplicada del IPN. Tepetitla, Tlaxcala. 90700. México.²Universidad Politécnica de Puebla, Carrera de Electrónica y Telecomunicaciones. Puebla, Pue. México. Author contact: rdelgadom@ipn.mx**ABSTRACT**

In this work we used the Fourier Transform Infrared spectroscopy and UV/Vis spectroscopy to analyze the behaviour of self-ensemble films of spiropyran when the films were irradiated by UV. In UV/Vis spectroscopy is possible observe the generation of the absorption peak, at 575 nm, associated to the merocyanine state when the ring-opening process is induced by UV light. In ATR the kinetics of the ring-opening was determinate too; following the spectra changes in real time.

INTRODUCTION

Actually, the design and generation of organic materials in compact and order arrays, is one of the goals of many researchers groups [1]. The most important of this, it is the development of surfaces generation protocol, which increases their value with all applications that can be conceived. The main applications can be: superficial organic reactions [2-3], studies of electronic transfers' process [4-5], electrochemical or optical sensors for molecular recognition [6-8], nanometric design of electronic devices [9-10], etc.

By the other hand, the increase and demand of information induces to the electronics and information industries to require materials with high optical properties. Since the discovery of the spiropyran photochromic reactions in 1952 by Fisher and Hirshberg [11], the interest in the use of spiropyran dyes, for photoelectric and photoelectrochemical devices, has been increasing. The spiropyran have been the most extensively photochromic material studied over the past decades.



Figure 1. Schematic molecular structure of the sample before the UV illumination and after the isomerization. The process is reversible under visible illumination.

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In general, spiropyran (SP) absorbs in the ultraviolet (UV) region and not in the visible region. Upon UV illumination, the SP colourless isomer undergoes heterolytic cleavage of the NO bond to form the coloured isomer (merocyanine). The coloration change (colourless to blue) in the sample is the physical observation of the molecular transformation. This process can be reversed by visible illumination, see figure 1.

No matter the applications where the spiropyrans have been found, it is necessary a detailed understanding of the transitions kinetics between the spiropyran (SP) to merocyanine (MC) forms. For this, it is necessary to analyze the molecular behaviour of these kinds of structures. In this context, vibrational spectroscopies would seem to be appropriated to study them, since they provide subtle details about molecular structure in liquids, gas or solid state. For example, Infrared [12-15, 8] and Raman [8,15] spectroscopic studies were done to observe the conformational and intermolecular interactions between the polymeric base and the spiropyran. Other works analyzed the solvent polarity effects into spiropyran molecule using only the absorption spectrum of the structure [16-18].

Attempts to detect the main structural changes occurring in the ring-opening/closing process in spiropyrans, using IR vibrational spectroscopy were reported by Schiele and Arnold for a series of indolinonitrosopyrans [19] and later by Guiliano et al. for benzothiazolinonitrosopyrans [20].

For all these, the aim of this work is to analyze the ring opening reaction in functionalized spiropyran films. Fourier Transform Infrared spectroscopy (FTIR) and UV/Vis spectroscopy were used to analyze this behaviour. By FTIR in ATR sampling mode, the kinetics of the ring-opening was determinate following the spectra changes in real time.

EXPERIMENTAL PROCEDURE

Sample preparation

The spiropyran used in this work was 1',3'-Dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro [2H-1-benzopyran-2,2'-(2H) indole, 97%], which was dissolved in 75 ml of acetone. The spiropyran molecular structure used in this work is showed in figure 1. A commercial functionalized substrate was used for self-assembled of spiropyran. The spiropyran was added to the functionalized substrate by substrate immersion. Four samples were deposited 2 and 4 hours and 3 and 7 days of substrate immersed in spiropyran solution.

UV/Visible spectroscopy

The absorption of spiropyran – merocyanine films was performed in a Thermo scientific Evolution 600 UV/Vis spectrometer. First, the spiropyran functionalized films were measured and after that the films were illuminated with a Black-Ray Mercury Spot UV lamp of 100 Watts for 20 min. A functionalized substrate was used as baseline in all the measurements.

Infrared spectroscopy

An Infrared spectrometer FTIR Bruker Vertex 70 in Attenuated Total Reflexion (ATR) sampling mode was employed. A diamond ATR crystal of one reflection was used during the measurements. The silane spectrum was used as baseline and the acquisition time was 30