ELSEVIER

Materials Science and Engineering A271 (1999) 366–370

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Decomposition process in a Zn-22wt.%Al-2wt.%Cu alloy

Hector J. Dorantes-Rosales [a,*], Víctor M. López-Hirata [a], Yao Hua Zhu [b]

[a] *Instituto Politécnico Nacional, Apartado Postal 75-556, Mexico D.F. 07300, Mexico*
[b] *Instituto de Investigaciones de Materiales, Apartado Postal 70-360, Mexico, D.F. 04510, Mexico*

Received 24 March 1999; received in revised form 24 May 1999

Abstract

The decomposition process in a Zn-22wt.%Al-2wt.%Cu alloy was investigated during aging at 373, 423 and 473 K, using XRD, SEM and TEM techniques. The results of X-ray diffraction of aged samples showed that two kinds of phase transformation occurred. One was the decomposition of metastable η_{FC} phase, as revealed by progressive shifting of the (0002) X-ray diffraction peak. The activation energy for the thermally activated process was determined to be ~ 71.5 kJ mol^{-1}. The other transformation was detected by the disappearance of the ε phase diffraction peaks, accompanied by the appearance of the (110) and $(1\bar{1}0)$ X-ray diffraction peaks of the τ and τ′ phases, respectively. These two events seem to be related to the four-phase reaction: $\alpha + \varepsilon \rightarrow \eta + \tau'$.

Keywords: Decomposition process; Zn-22wt.%Al-2wt.%Cu alloy

1. Introduction

Zn-Al eutectoid alloys exhibit attractive physical and mechanical properties with good wear resistance, making them the choice for many end-use applications [1]. The addition of small amounts of copper increases tensile strength, creep strength and corrosion resistance. However, it is reported that the addition of copper promotes the formation of intermetallic compound particles, which affect the solid state reactions and the dimensional stability of alloy [2,3]. The addition of 2 wt.% copper to this kind of alloy causes the formation of small volume fractions of an intermetallic compound $CuZn_4$, containing 16%Cu, known as ε phase with an hcp structure, and τ′ phase, containing 56% Cu and 13% Zn, which is stable at room temperature with a complex ordered rhombohedral structure [4]. The τ′ phase is close to Al_4Cu_3Zn and its structure has been described by Murphy [4] as an assemblage of five small CsCl-type bcc cells joined corner to corner. Previous works [5–9] have shown that the ε phase transforms to the τ′ phase by the following four-phase reaction, $\alpha + \varepsilon \rightarrow \eta + \tau'$, after being processed by aging treatment at temperatures lower than 523 K, tension test or mechanical grinding of a Zn-22wt.%Al-2wt.%Cu alloy. All the above results have been mainly determined using X-ray diffraction (XRD) and scanning electron microscope (SEM); however, it seems to be relevant to carry out a study of the aging process in these alloys, using transmission electron microscope (TEM) in order to reveal more details of the mechanism in these phase transformations. The present paper will study the decomposition of various phases in more detail using TEM, XRD and SEM.

2. Experimental procedure

A piece of $10 \times 10 \times 10$ mm of Zn-22wt.%Al-2wt.%Cu alloy was prepared and homogenized at 633 K for 7 days and then furnace cooled. Furnace-cooled samples were aged at 373, 423 and 473 K for different times, from 900 s to 900 ks. Aging treatments were carried out in an oil bath with a temperature control of ± 3°C. The XRD analysis was performed in a Siemens diffractometer using Cu Kα radiation. Aged samples were prepared metallographically with 0.05 μm alumina and subsequently observed in JEOL JSF-35F scanning electron microscope, using backscattered electrons.

* Corresponding author. Tel.: +52-5-7396000; fax: +52-5-7520343.

0921-5093/99/$ - see front matter
PII: S0921-5093(99)00255-5

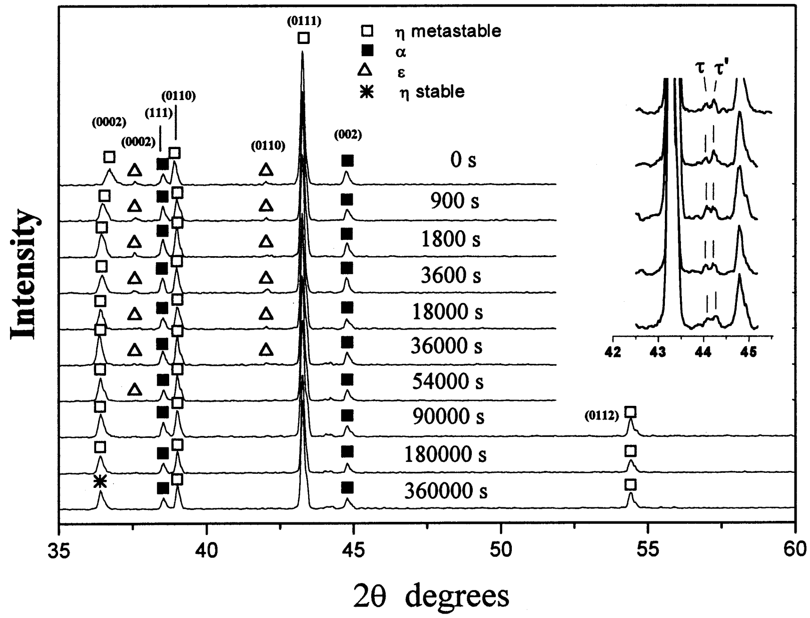

Fig. 1. X-ray diffractograms of Zn-22wt.%Al-2wt.%Cu alloy solution treated, furnace cooled and then aged at 473 K for different times.

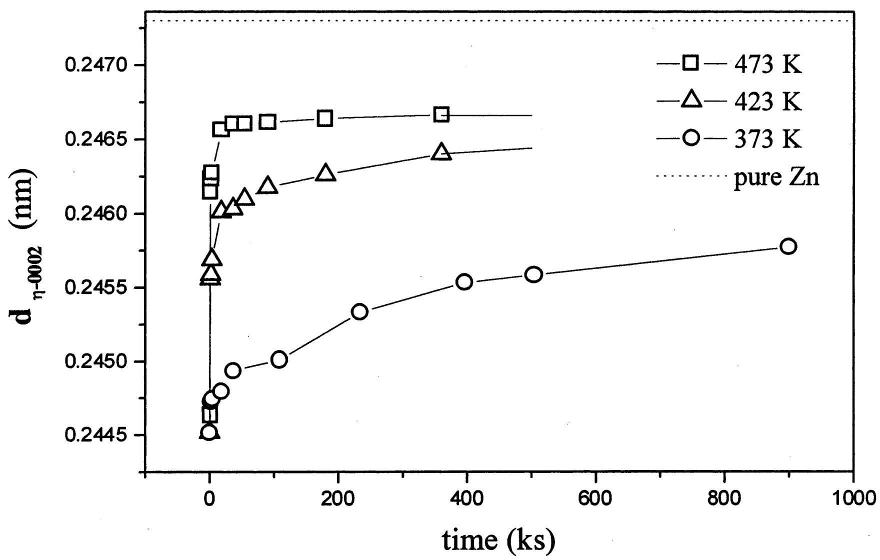

Fig. 2. Change in (0002) interplanar spacing of η phase with aging time at 373, 423 and 473 K.

Samples for TEM analysis of 3-mm diameter and 150-μm thickness were cut with a diamond disk and electroerosion equipment. TEM samples were prepared using a two-jets FISHIONE electropolishing equipment in an electrolyte of 10 vol.% phosphoric acid and 20% glycerol in methanol at −50°C with 50 V and 60 mA.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of Zn-22wt.%Al-2wt.%Cu alloy aged at 473 K for different times. This figure shows that the solution treated and furnace-cooled sample is composed of three phases, η_{FC}, α and ε, where the η_{FC} phase is a Zn-rich hcp metastable phase. Two kinds of phase transformation were observed. The first one was decomposition of the η_{FC} phase. This is suggested by the progressive shifting of (0002) X-ray diffraction peak of η phase, from 2θ angles of 36.7–36.4°, with aging time. The maximum shift of this peak was observed in samples aged for 360 ks at 473 K. In addition, the variation of (0002) plane d-spacing of η phase with aging time is shown for three aging temperatures in Fig. 2. It is found that this plane d-spacing increases with aging time. That is, the (0002) interplanar spacing of η phase approaches the spacing value of pure zinc (0.2473 nm). This means that the aging treatment produced a decrease of aluminum and

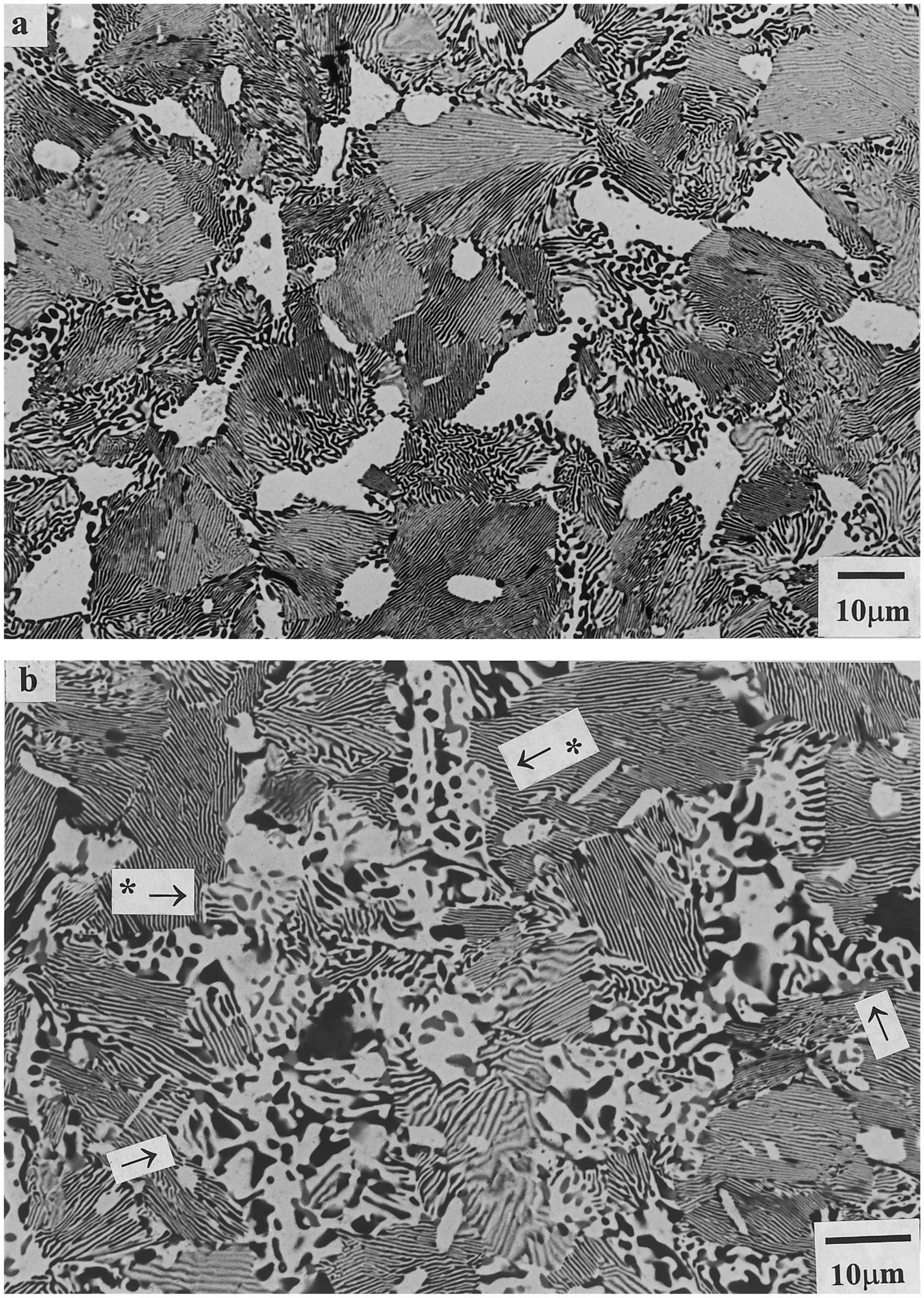

Fig. 3. SEM micrographs of Zn-22wt.%Al-2wt.%Cu alloy (a) solution treated and furnace cooled and (b) then aged at 473 K for 900 ks.

copper contents in the η phase. It is also found that the decomposition of η phase is faster for the aging treatment at 473 K than that at 373 and 423 K (Fig. 2). By analysis of these curves the fraction transformation as function of time was obtained. An activation energy of 71.5 kJ mol^{-1} was determined for the thermally activated process, using the Arrhenius relationship of ln t versus $1/T$ for a fraction transformation of 0.8. This value of activation energy is similar to those reported for the interdiffusion process in Zn-Al-Cu alloys [10]. The other phase transformation was the four-phase reaction, $\alpha + \varepsilon \rightarrow \eta + \tau'$, which occurred for aging times longer than 900, 54 and 3.6 ks at 373, 423 and 473 K, respectively. It was calculated that (110) d-spacing of the τ phase was 0.2065 nm, and $(1\bar{1}0)$ d-spacing of the τ′ phase was 0.2055 nm. The co-existence of τ phase and the τ′ phase was observed for the first time.

Fig. 3 shows the microstructure of Zn-22wt.%Al-2wt.%Cu alloy obtained with backscattered electrons in SEM. The light contrast corresponds to the η and ε

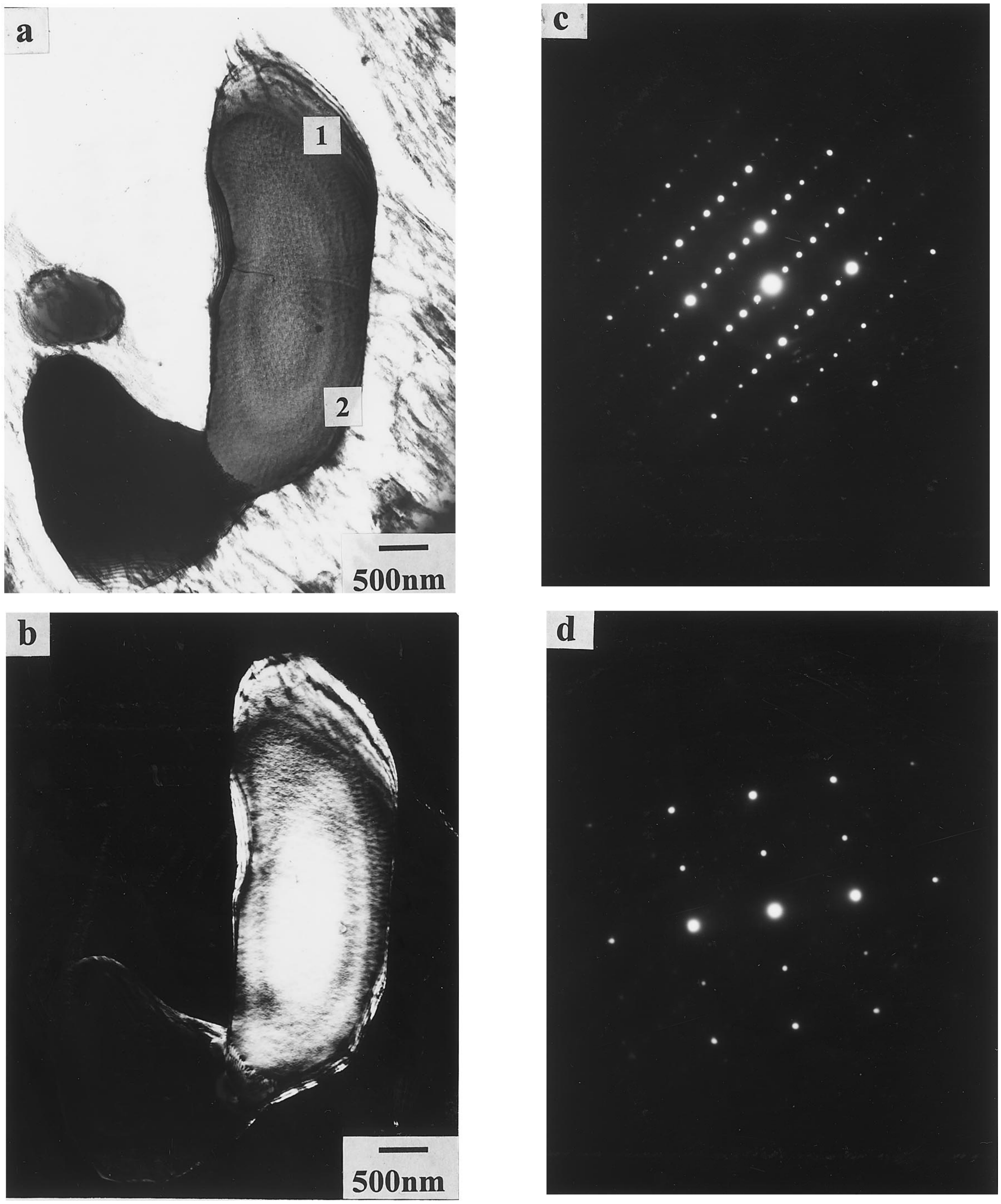

Fig. 4. Morphology of superstructure τ' phase. (a) Bright field, (b) dark field using g = [001], (c) diffraction pattern, $B = [011]_{\tau}$ and $B = [01\bar{1}]_{\tau'}$, and (d) diffraction pattern, B = [011].

phases, while dark contrast corresponds the α phase. The furnace-cooled alloy is shown in Fig. 3(a). It has been reported [7] that the coarse lamellar structure in this sample is derived from the decomposition of the α' phase by the following cellular reaction $\alpha' \rightarrow \alpha + \eta + \varepsilon$, and the fine lamellar structure is formed at a lower temperature from the decomposition of the β' phase via the following eutectoid reaction $\beta' \rightarrow \alpha + \eta + \varepsilon$. Nevertheless, it is important to mention that the presence of ε phase is difficult to detect in both lamellar structures due to the similar SEM light contrast of ε and η phases. The aging treatment at 473 K caused an increase of the volume fraction of coarse lamellar with aging time. This coarse lamellar seems to be formed by a discontinuous precipitation in the η phase regions (see arrows in Fig. 3(b)). This has also been associated with the decomposition of η_{FC} phase. Zhu et al. [6] pointed out that the following cellular reaction, $\eta' \rightarrow \eta + \alpha + \varepsilon$ produces the coarse lamellar structure. The τ' phase appears as gray-contrast precipitates in the ε phase regions (see * → in Fig. 3(b)), which supports the existence of a four-phase reaction $\alpha + \varepsilon \rightarrow \eta + \tau'$.

Fig. 4 is a TEM micrograph of a τ' phase rounded particle in the sample aged at 473 K for 900 ks. This particle is divided into τ and τ' phases (zones 1 and 2, respectively, in Fig. 4(a)). The diffraction pattern in Fig. 4(c) shows superlattice reflection along the [111] direction of bcc structure (zone 1). Similar results were observed in the Zn-58wt.%Al-14wt.%Cu alloy aged at 250°C [4]. In zone 2, no superlattice reflections were observed (Fig. 4(d)). This fact supports the XRD results concerning the presence of τ and τ' phases. Analysis of this type of particle aged at 473 K showed that the superstructure of τ' phase of ordered tetragonal structure (equilibrium structure at room temperature) was not completed after 900 ks of aging, and before of this time the predominant phase was the disordered bcc τ phase. Therefore it was reasonable to suggest that the formation of τ' phase was preceded by the formation of the τ phase.

4. Conclusions

The phase transformations that occur during the aging process of the Zn-22 wt.%Al-2wt.%Cu alloy are, first, the decomposition of η phase with an activation energy for the thermally activated process of ~ 71.5 kJ mol^{-1}, and then the four-phase reaction, $\alpha + \varepsilon \rightarrow \eta + \tau'$ takes place. The formation of τ' phase (superstructure) is preceded by that of the τ phase (bcc).

Acknowledgements

The authors wish to acknowledge the financial support from DEPI-IPN and CONACYT. H.J.D.R. also acknowledges the CONACYT and PIFI-IPN scholarships.

References

[1] O. Ruano, Rev. Metal. CENIM 18 (1982) 275.
[2] M.E. Houghton, M.T. Murray, Metal Forum 6 (1984) 211.
[3] E. Gervais, H. Levert, M. Bees, Trans. Am. Foundr. Saoc. 88 (1980) 183.
[4] S. Murphy, Metal Sci. 9 (1975) 163.
[5] R. Ciach, J. Krol, K. Wegrzyn-Tasior, Bull. Acad. Pol. Sci. 17 (4) (1967) 371.
[6] Y.H. Zhu, G. Torres-Villaseñor, C. Piña, J. Mater. Sci. 29 (1994) 1549.
[7] Y.H. Zhu, Chi, J. Met. Sci. Technol. 6 (1990) 125.
[8] Y.H. Zhu, J. Mater. Sci. Lett. 15 (1996) 1888.
[9] Y.H. Zhu, V.M. López, M. Saucedo, J. Mater. Proc. Technol. 63 (1997) 624.
[10] T. Savaskan, S. Murphy, Z. Metallk. 74 (1983) 76.