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STRUCTURE DETERMINATIONS OF THE PHASE TRANSFORMATIONS OF THE BETA PHASE OF THE Zn-Al-Cu SYSTEM

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RESUMEN

La posibilidad de la existencia de un compuesto inter-metálico que origine una reacción peritéctica en el diagrama de fases Zn-Al, ha estado en discusión por más de 90 años. En 1961 Presnyakov [4], observó anomalías en los parámetros de la red a alta temperatura, concluyendo que existía una delgada región de dos fases al 50 at %. que separaba una solución sólida de aluminio, de una fase inter-metálica (ß) con la misma estructura que el aluminio. Esta región de dos fases que separa dos estructuras cúbicas centradas en las caras (c.F), con casi la misma composición no ha sido aceptada en forma unánime, de tal manera que existen dos diagramas de fase, actualmente en uso.

En la presente investigación encontramos que un enfriamiento rápido de la aleación eutectóide desde 300° C, (fase ß)no retiene la fase triclínica de alta temperatura, sino que provoca una serie de transformaciones antes de llegar a las fases estables Al(α) y Zn(η). se analizan estas transformaciones.

Palabras Clave: Fase beta ZnAlCu, Difracción de rayos-x, Transformaciones de fase

ABSTRACT

The possibility of the existence of an inter-metallic compound that originate a peritectic reaction in the Zn-Al phase diagram has been in discussion for over 90 years. In 1961 Presnyakov, noted anomalies in the network at high temperature settings, concluding that there was a thin region of two phases at 50% at. It separated a solid solution of aluminium, of an inter-metalic phase (ß) with the same structure as the aluminum. This two-phase region that separates two cubic structures focusing on the faces (c.F), with almost the same composition has not been accepted unanimously, in such a way there are two phase diagrams, currently in use. In this work we found that rapid cooling of the eutectoid alloy from 300˚C (ß phase) does not retain the high temperature triclinic phase, but it causes a series of transformations before reaching the stable phases (α) and Zn (η).

KEYWORDS: Beta phase ZnAlCu, X-ray diffraction, Phase transformations

Structure determination of the phase transformations of the Beta phase of the Zn-Al-Cu system

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1 INTRODUCTION

The crystalline structure of the high temperature ß phase of the binary Zn-Al system has been proposed to be triclinic with a = 285.857 pm, b = 285.283 pm, c = 285.847 pm, α = 59.602º, ß = 59.869º and γ = 59.716º, [1, 2]. This structure corresponds to a small distortion of the primitive R cell of the high temperature f.c.c. solid solution α-(Al) when the Zn content reaches about 48 at.% at 350˚C. A fine lamellar morphology is produced after rapid cooling of this alloy, and there is a transition to a granular structure on aging below ≈150˚C for composition near the eutectoid.

In low zinc alloys (up to 15 % at. zinc) when the solid solution α is quenched from 350˚C, the super saturated solid solution gives rise to the formation [3]:

Spherical G.P. zones → ellipsoidal G.P. zones → R phase
→ cubic α´ (cF) → zinc

where the R phase is a metastable rhombohedral phase with a = 284.6 pm, and α = 60˚.

The R phase subsequently loses some coherency to form the cF. α´ phase, and then zinc. There is some evidence that the R phase transforms directly into zinc in alloys with ≈ 30 at. % zinc [4]. Near the binary eutectoid composition the reaction occurs so fast that details of any homogeneous precipitation is not observable [5, 6, 7].The result of the transformation of the triclinic β phase in ribbons of a Zn-Al eutectoid alloy obtained by the melt spinning rapid solidification method, after being quenched into liquid nitrogen from 350 ºC were both η and R (R3m, a=b=283.5 pm; c=695.5 pm) phases. Reflections of the α phase were not observed at the initial x-ray stage. Having been annealed for 500 hours at room temperature, the R phase was transformed entirely in both α and η stable phases [8]. According to Smith et. al. [9], the addition of copper to the Zn-Al binary alloys increases the time of the transformation of the β-phase from 1 minute to several days at room temperature; Cu additions reduce the rate of transformation because of the stabilizing effect of the Cu on the high temperature ß phase.
The present paper describes the results of an x-ray study of the transformation of the high temperature ß phase of an alloy with nominal composition Zn-20Al-2Cu mass % (zinalco) which was prepared from 99.95 % pure materials.

2 EXPERIMENTAL

The ternary alloy was extruded from the cast ingot into 10 mm diameter bars. The extruded bars were annealed at 350˚C for 2 hours and furnace-cooled. From fractions of an annealed bar, ribbons with a thickness varying from 30 to 80 μm and a width of 2 mm were obtained using single copper roller melt-spinning in a protective argon atmosphere. The temperature of the melt was selected at 500°C, and the melts were ejected with an argon jet applying an overpressure of 100 kPa. The peripheral velocity of the wheel was 35 m/s. X-ray experiments were carried out on both a zinalco alloy at 320 ºC and on ribbons quenched in liquid nitrogen from 350 ºC. Small pieces of ribbon were heated up to 350°C for 30 minutes and then dropped into liquid nitrogen. After 10 minutes the samples were removed from the liquid nitrogen. The quenched specimens were immediately exposed to x-rays. The experiments were performed using Cu K_{α} radiation in a Rigaku Dmax 2200 diffractometer equipped with a high-temperature chamber.

3 RESULTS AND DISCUTION

The analysis of the X-ray diffraction patterns after stabilization at the high temperature ß phase with and without copper additions shows that the high temperature structure corresponds to the same triclinic structure reported in [8]. Figure 1 shows the diffractogram of the zinalco alloy taken at 320 ºC stabilized for 2 hours; only reflections of the β (001) at 2θ=38.7º, β (110) at 2θ=44.94º and η (101) at 2θ=42.88º phases were observed.

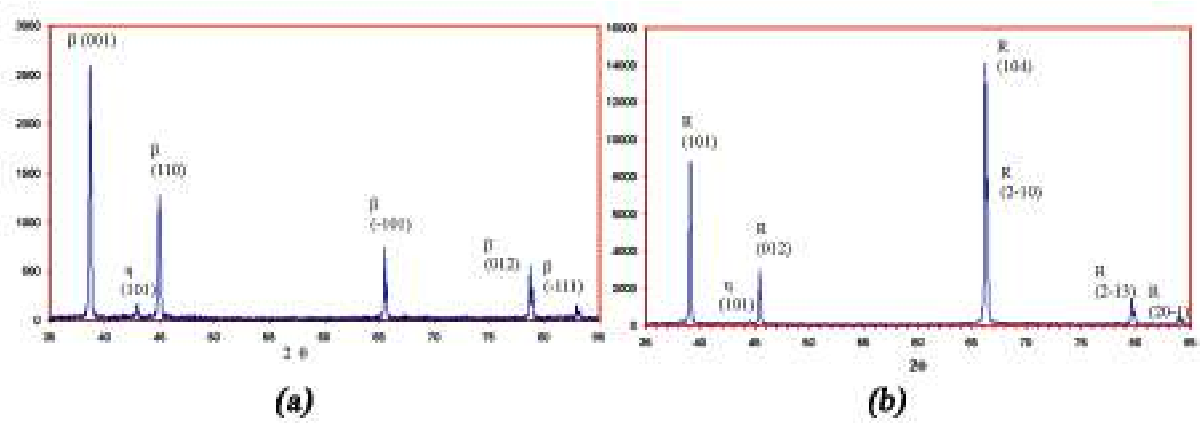

Figure1. X-ray diffraction patterns (a) Zinalco alloy at 320˚C, triclinic phase. (b) Diffraction pattern of the alloy quenched from 320˚C to room temperature and aged 5 minutes

Figure 2 show the evolution of the structure at room temperature in ribbons of the zinalco alloy, from 5 minutes after being quenched in liquid nitrogen up to 1460 hours of aging, including intermediate registration times such as 3, 5, 8, 48, 360 and 1464 hours. Figure 1a shows the phases that are present after 5 minutes of quenching from the high temperature β phase. The β phase reflections are not observed. The recorded phases are the same η (101) phase observed at high temperature with displacement to a greater angle (2θ=44.1º) and the R phase with reflections (101) at 2θ=39.08º and (012) at 2θ= 45.44º, which in our case, match well with the R structure described by lattice parameters *a*=281.4846 pm, *c*=690.2349. The lattice parameters were found using a peak identification program [10]. The R phase has a triple hexagonal crystalline structure (R3m). Anantharaman [11] has found that the R phase has a range of lattice parameters depending on the Zn concentration.

Having elapsed 3 hours, the (101) η phase reflection increased its intensity -with a displacement to 2θ=43.62º- and the reflections (101) and (012) of the R phase reduced its intensity. The reflections (111) at 2θ=38.5º and (200) at 2θ=44.76º of the α phase started to be observed, (fig. 2a). This transformation indicates that the R phase transforms into α phase.
After five hours, the reflection (111) of the α phase was very manifest at 2θ=38.46º and the reflection (200) of the α phase at 2θ= 44.74º increased its intensity. The reflection (101) of the η phase increased its intensity and the reflection (002) of the same phase started to appear at 2θ=36.54º; the intensity of the reflection (101) of the R phase diminished and the reflection (012) of R disappeared, (fig. 2b). The transformation of the R phase into the α phase was completed after 8 hours; incipient reflections at 2θ= 36.34º and at 2θ=41.7º started to appear; these reflections correspond to the (002) η phase and to the (100) ε phase, respectively (fig.

2c). In this phase transformation step, the lattice parameters of both α and η phases do not correspond to the parameters of the stable phases, but are in the interval of the lattice parameters achieved by other authors [12, 13].

Another peak at 2θ= 37.34º, which fits in with the reflection (100) of the ε phase appeared after 48 hours of aging (fig. 2d). Lattice parameters of both α and η phases continue stabilizing. Having elapsed 100 hours, the peak of the reflection (111) of the α phase at 2θ=38.4º split, thus giving place to a new reflection (100) of the η phase at 2θ=38.74º.

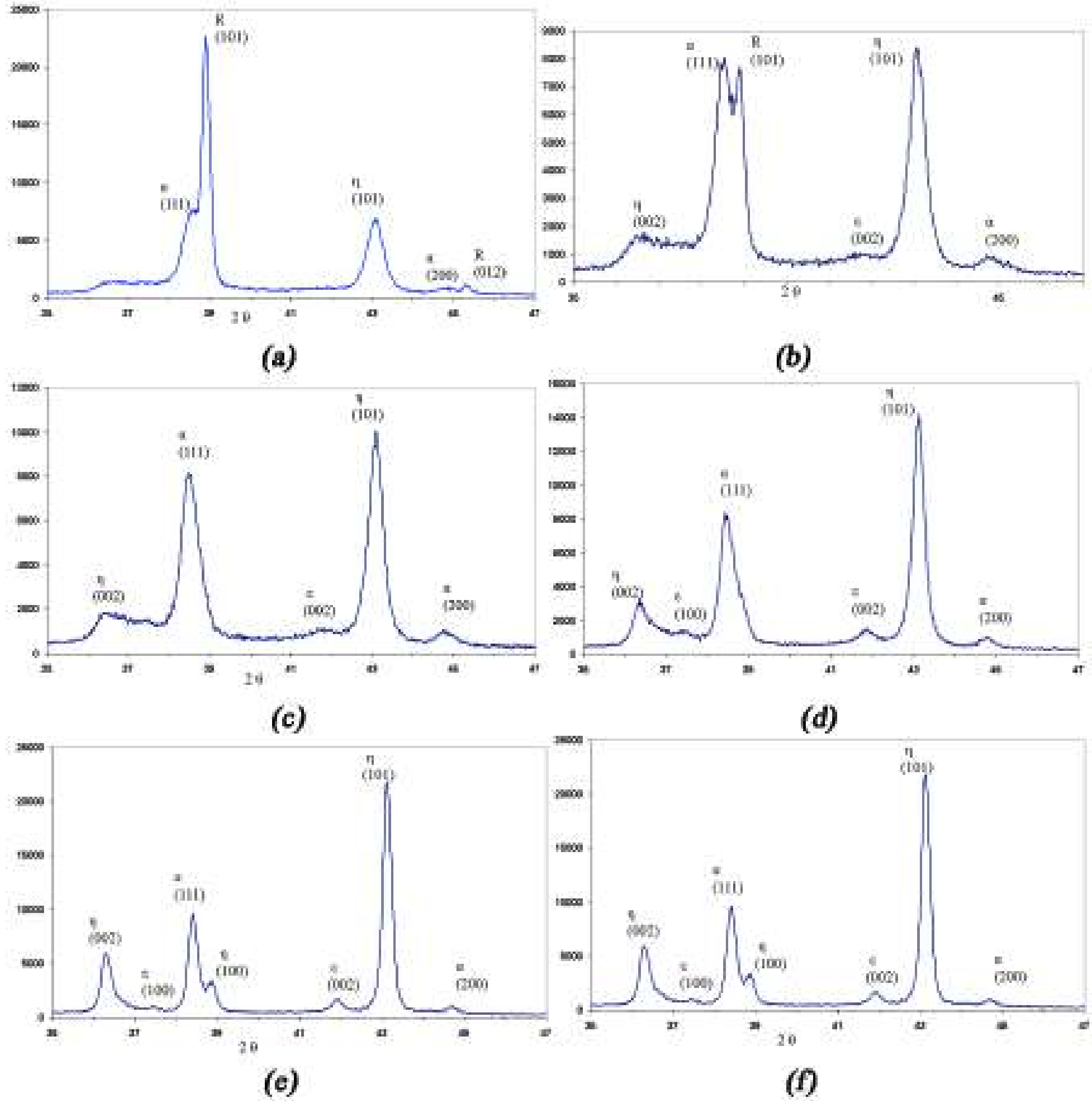

Figure 2. X-ray diffraction pattern of the zinalco alloy, quenched from 320˚C in liquid nitrogen an aged at room temperature (a)3hours, (b) 5 hours, (c) 8 hours, (d) 48hours, (e) 360 hours, (f) 1464 hours

After 360 hours of aging the reflections observed correspond to (111) and (200) of the α phase, (002), (100) and (101) of the η phase and (100) and (002) of the ε phase, (fig. 2e). In the diffractogram recorded up to 1464 hours of aging the reflections of the ε metastable phase no longer appeared; only the α and η stable phases were observed, including a reflection of the τ' stable phase at 2θ=43.1º (fig. 2f).

In this alloy with a composition near the eutectoid composition, the sequence of phase transformations was similar to that observed in the Zn-22Al mass % binary alloy [8]. In agreement with the diffractograms of the alloy quenched in liquid nitrogen, immediately after the quenching treatment, the triclinic structure started its transformation into the R rhombohedral phase; the observed η phase in figure 1b comes from the high temperature β+η phases recorded in figure 1a. In the zinalco alloy, the Cu element did not delay the transformation of the β triclinic phase. In the Zn-Al binary alloys the phase transformation took place in about 2 minutes.

In its turn, the R phase transformed into the α phase and the intensity of the reflections of η phase increased. The lattice parameters of the α, η and R phases were not stable, but were in the range of the lattice parameters published by other authors. The stable phases appeared in the diffractogram recorded after 1464 hours of aging. In accordance with the analyzed diffractograms, the solid-solid reaction sequence of the phase transformations in the Zn-20Al-2Cu mass % alloy was:

$$ß + \eta_m \rightarrow R + \eta_m \rightarrow \alpha_m + \eta_m \rightarrow \alpha + \eta + \varepsilon$$

$$\alpha + \varepsilon \rightarrow \tau' + \eta$$

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