



THE TRICLINIC HIGH TEMPERATURE MODIFICATION OF THE α PHASE OF THE Zn–Al SYSTEM

A. Sandoval-Jiménez¹, J. Negrete², and G. Torres-Villaseñor^{3*}

¹Instituto Nacional de Investigaciones Nucleares, Depto. de Física, Apdo. Postal 18-1027, Col Escandón México D.F. 11801, México

²Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, SLP 78210, México

³Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, México D.F. 04510, México

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ABSTRACT

The structure of the β phase of the Zn–Al system was reinvestigated. The X-ray diffraction (XRD) pattern of the Zn–21.8wt%Al after 9 h at 350°C clearly showed the splitting of some Bragg peaks. The triclinic structure permits a description of the spectra with $a = 285.857$, $b = 285.283$, $c = 285.847$ pm, $\alpha = 59.602^\circ$, $\beta = 59.869^\circ$, $\gamma = 59.716^\circ$. This structure corresponds to a small distortion of the primitive R cell of the high temperature fcc solid solution α -(Al) when the Zn content reaches about 69.5 wt% at 350°C.

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INTRODUCTION

For more than 80 years, the Al–Zn binary system has been investigated. Shepard [1] and Ewen and Turner [2] believed that a high-temperature intermetallic compound (ZnAl) existed between 49.77 at% (70.6 wt% Zn) and 63.16 at% (80.6 wt% Zn) at 340°C, with an eutectoid at 59 at% Zn (78 wt% Zn) ($T = 277^\circ\text{C}$) and a peritectic at 51.48 at% Zn (72 wt% Zn) ($T = 443^\circ\text{C}$). Owen and Pickup [3], with high-temperature X-rays, were unable to confirm the

*To whom correspondence should be addressed.

existence of a peritectic reaction. In 1938, the high-temperature phase disappeared from the phase diagrams, leaving a monotectoid reaction. Observations by Presnyakov *et al.* [4] and Goldak and Parr [5] of anomalies in high-temperature lattice parameters led to the reinstatement of a very narrow two-phase region ($\alpha + \beta$) at 51.48 at% Zn (72 wt% Zn). Controversies still exist, however, regarding the peritectic transformation, the presence of a high-temperature intermetallic phase, the presence of the two-phase region, and the maximum percentage of zinc up to which the eutectic halt is extended.

The present work is an attempt to resolve the high-temperature intermetallic phase question, using high-temperature electron diffraction and high-temperature X-ray techniques applied to flat-surfaced block specimens.

EXPERIMENTAL

Alloy Preparation. The alloy was prepared from 99.995% Zn and 99.98% Al. Melts were cast and homogenized at 380°C for 24 h, and then furnace-cooled to room temperature to obtain stable pearlite structure. Analysis of the final product showed the composition to be Zn–40.32at%Al (21.8 wt% Al).

Electron Microscopy and Diffraction. Thin foils were prepared by ion beam thinning. They were examined in the heating holder of a JEOL 1200 electron microscope working at 120 kV. It was found that the initial microstructure of the alloy was composed of bands (pearlite structure) of α phase (aluminum rich) and η phase (zinc rich). When the transformation temperature (277°C) was reached, the banded structure transformed into a one-phase structure, indicating that the high-temperature phase had been obtained. The working temperature was about 350°C. A typical transmission electron micrograph of the structure, taken after a stabilization of 2 h, is shown in Figure 1. The observed average grain size of the transformed structure was 2 μm .

Zones of the β phase were selected at random and the electron diffraction patterns recorded. A frequently observed pattern is shown in the inset of Figure 1. Careful measurements of the angle between reflections, made on this scanned pattern, show that this zone axis cannot be the [110] zone of aluminum. The measurements were done using the Adobe PhotoShop application program [6] for measuring angles and distances, with an accuracy of 0.1 mm in distance and 0.2° in angular measurements. The angle between reflections 1 and 2 is 54.8° and between 3 and 4 is 54.2°, which is not in accord with cubic symmetry.

X-ray Diffraction. High-temperature X-ray experiments were performed using Cu $K\alpha$ radiation in a Rigaku Dmax 2200 diffractometer equipped with a high-temperature chamber and calibrated with a certified standard of silicon at the working temperature (370°C). The Zn–Al specimen was heated up to 370°C, at a heating rate of 5°C/min. The specimen was maintained at 370°C for 9 h to assure complete transformation before the diffraction experiments were begun.

Figure 2 shows the diffraction patterns after a stabilization of 9 h. The observed peaks almost match those of an aluminum pattern. A detailed examination of the diffraction peaks revealed the presence of extra reflections. In order to obtain a relative separation of the diffraction peaks, we explored selected Bragg peaks, using a peak identification program [7]. We observe multiplets at each reflection in Figure 2, where the (111) and (200) reflections of the “aluminum” pattern (Fig. 2a) split up into four and three peaks, respectively, and at

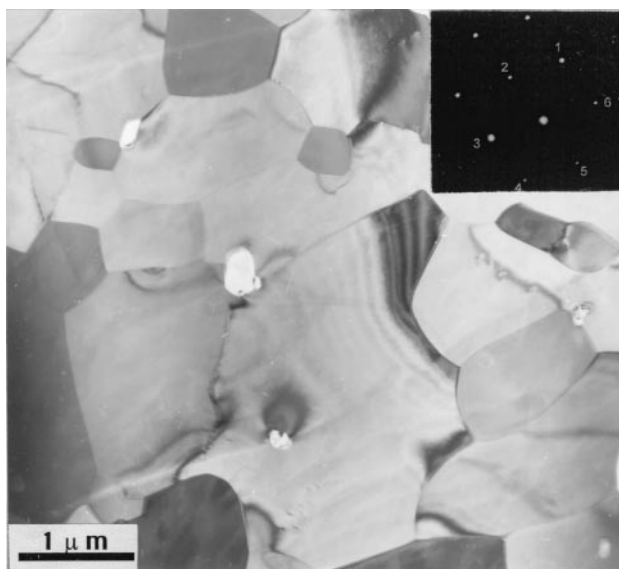


FIG. 1

A representative transmission electron micrograph of the microstructure of the high-temperature phases taken at 350°C. Inset shows a frequently observed pattern.

higher angles, the (220), (331), and (222) reflections split into more than six peaks. The analysis showed that the structure corresponded to a triclinic structure with cell parameters given in Table 1. The observed and calculated d values for the triclinic β phase are reported in Table 2, together with corresponding indices and intensities. Intensity and d calculations were made with CaRine Crystallography version 3.1 software [8].

DISCUSSION

The structure transition from fcc (aluminum solid solution at high temperature) to triclinic could be caused by a weak distortion of the cubic phase when the Zn content reaches 49.77 at% (70.6 wt%). When this occurs, the primitive rhombohedral unit cell ($a = 285.671$ pm, $\alpha = 60^\circ$) of the fcc structure is also distorted, forming a triclinic cell. According to measured triclinic cell parameters (Table 1), the cell parameters of the high-temperature aluminum structure are $a = 405.057$, $b = 403.466$, $c = 403.437$ pm, $\alpha = 90.225^\circ$, $\beta = 89.99^\circ$, $\gamma = 90.23^\circ$, giving a new triclinic unit cell based on the distortion of the rhombohedral primitive cell contained in this distorted fcc structure. Ellwood [9] observed a decrease in the cell parameter a of the high-temperature α phase from 404.09 pm at 49.22 at% Zn (70 wt% Zn) to 403.71 pm at 56.65 at% Zn (76 wt% Zn). The latter value is close to the cell parameter of the distorted cubic α phase described here. The calculated d values are in close agreement with the experimental pattern.

A significant difference was observed between the calculated and measured intensities. The difference was probably due to the development of annealing texture. Diffraction patterns taken after 1 h of annealing at 370°C show a 111 peak intensity (Al notation)

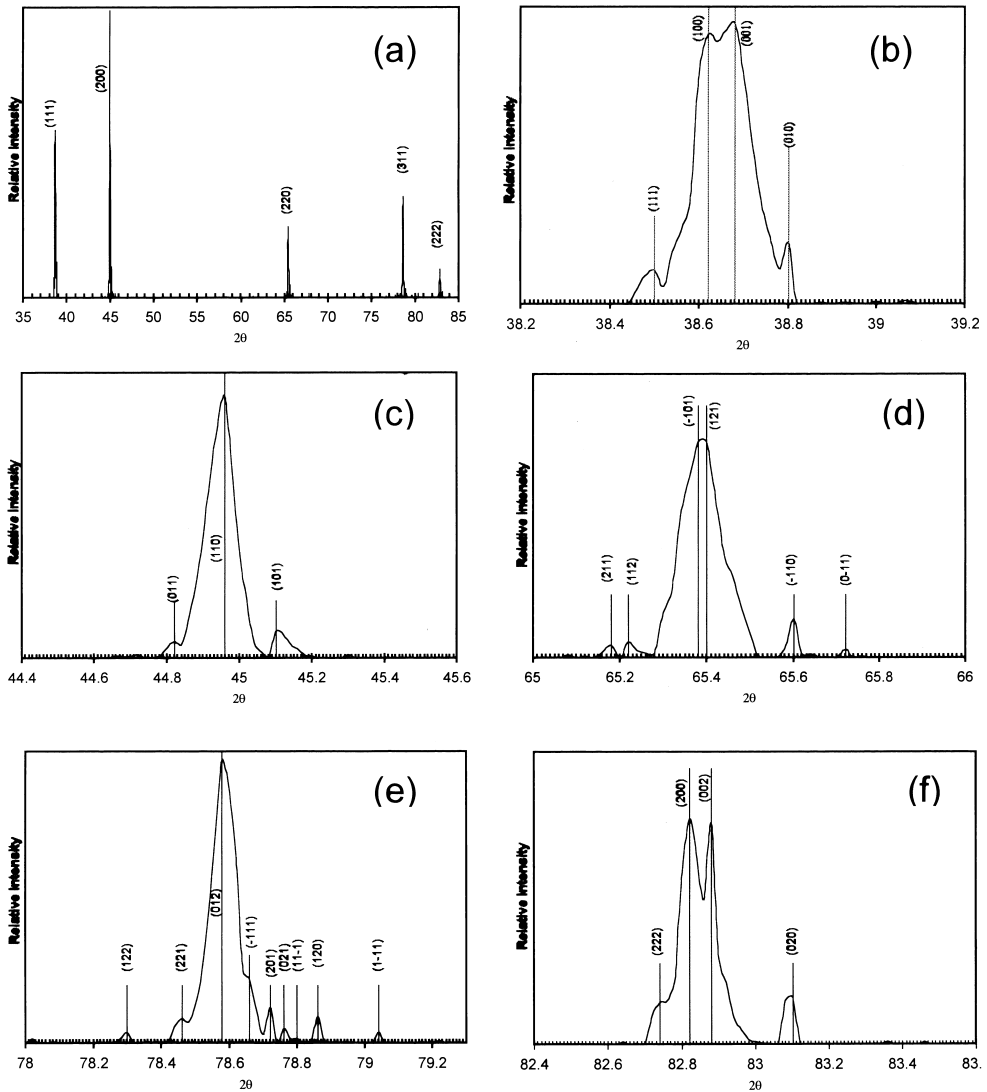


FIG. 2

High-temperature diffractometer traces from Zn-40.32at%Al alloy. The peaks at (a) are indexed according to an aluminum pattern to facilitate reference. The corresponding indices in terms of the triclinic cell are given in (b) to (f).

greater than that of the 200 peak, in accordance with the calculated intensities; then the intensity of the 200 peak starts to increase with time. This fact is interpreted as texture phenomena.

According to the theory of electronic phases, the change from a large unit cell to a smaller one gives a larger first Brillouin zone, with the possibility to store a greater number of electrons with low energy. Thus, this transformation reduces the energy of the system.

TABLE 1
Cell Parameters of the β Phase

Lattice constant (pm)	Probable error	Standard error
$a = 285.857$	0.002	0.003
$b = 285.283$	0.002	0.003
$c = 285.847$	0.002	0.003
$\alpha = 59.602$	0.0052	0.0288
$\beta = 59.869$	0.0060	0.028
$\gamma = 59.716$	0.0050	0.000

TABLE 2
X-ray Data for β Phase

Plane indices (triclinic)	d Calculated (nm)	d Measured (nm)	Relative intensity I/I_{\max}	
			Calculated (%)	Measured (%)
(111)	0.2337	0.23364	34	10.71
(100)	0.2329	0.23294	100	58.17
(001)	0.2326	0.23260	100	69.69
(010)	0.2318	0.23191	99	38.37
(011)	0.2019	0.20206	65	10.17
(110)	0.2015	0.20146	64	100
(101)	0.2013	0.20087	64	46.31
(211)	0.1429	0.14301	20	3.46
(112)	0.1429	0.14293	20	3.77
(-101)	0.1426	0.14262	20	25.32
(121)	0.1426	0.14258	20	26.03
(-110)	0.1422	0.14220	19	15.59
(0-11)	0.1419	0.14197	19	2.85
(122)	0.1219	0.1220	11	6.78
(221)	0.1218	0.1218	11	6.78
(212)	0.1218	Not observed	11	Not observed
(012)	0.1218	0.12164	22	31.53
(210)	0.1217	Not observed	22	Not observed
(-111)	0.1216	0.12154	11	6.78
(201)	0.1215	0.12146	22	6.78
(021)	0.1214	0.12141	22	6.78
(11-1)	0.1214	0.12136	11	6.78
(102)	0.1214	Not observed	22	Not observed
(120)	0.1212	0.12128	22	6.78
(1-11)	0.1210	0.12105	11	6.78
(222)	0.1169	0.11655	3	3.39
(200)	0.1164	0.11643	10	9.82
(002)	0.1163	0.11639	10	9.49
(020)	0.1159	0.11641	9	4.75

CONCLUSION

The phase diagram with the peritectic reaction has commonly been used and accepted for metallurgical research [10,11], without full identification of the high-temperature β phase. The present work, based on high-temperature electron and X-ray diffraction observations, provides some evidence that the high-temperature β phase of the Zn–Al system has a triclinic structure. This structure forms when the fcc high-temperature structure α suffers a small distortion just after the Zn content reaches 48.46 at% (70.6 wt%). This small deformation produces a distortion of the primitive rhombohedral unit cell contained in the fcc structure originating a triclinic cell with cell parameters reported in Table 1.

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