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Crystal structure and phase stability of the Φ phase in the Al–Mg–Zn system☆

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ABSTRACT

We report on the phase equilibria, the homogeneity range, the crystal and electronic structure of the Φ phase in the Al–Mg–Zn system. The homogeneity range is similar at 360 °C and 330 °C and has a wedge-like shape. Al and Zn vary about 13 at.% and Mg maximal 2.5 at.%. The crystal structure has been characterized by X-ray single crystal structure refinement at two compositions $Al_{23.2}Mg_{54.6}Zn_{22.2}$ ($(Al_{1.856}Mg_{0.368}Zn_{1.776})Mg_4$, $Z = 19$, *oP*152, *Pbcm*, $a = 8.9374(7)$ Å, $b = 16.812(2)$ Å, $c = 19.586(4)$ Å) and $Al_{17.1}Mg_{53.4}Zn_{29.5}$ ($(Al_{1.368}Mg_{0.272}Zn_{2.360})Mg_4$, $a = 8.8822(3)$ Å, $b = 16.7741(7)$ Å, $c = 19.4789(8)$ Å). The structure contains four different types of layers stacked along the *c* axis which can be classified as pentagon–boat, boat, pentagon–triangle and square–triangle tilings. These tilings are decorated by Al and Zn centred icosahedra. The valence band structure can be described by a nearly free electron model except the 3*d* Zn contributions at lower energy. The large solubility for Al and Zn is caused by substitutional disorder at the icosahedral sites. Total energy calculations indicate, that the homogeneity range at higher temperatures splits up at 0 K into two ordered structures with compositions $Al_{16}Mg_{50}Zn_{34}$ and $Al_{10}Mg_{50}Zn_{40}$.

1. Introduction

The Al–Mg–Zn system has been investigated many times for the development of light and high strength alloys. Since the early work of Eger in 1913 [1], several assessments have been reported [2–6], the most recent by Petrov et al. Isothermal sections at 360 °C and 330 °C for the Mg-rich part of the phase diagram are shown in Fig. 1.

In the Al–Mg–Zn system, four ternary intermetallic compounds are known, called τ_1 [7], τ_2 [8], q [8], and Φ [9–13]. τ_1 and τ_2 are Bergman cluster approximant phases with large unit cells and the q phase is the corresponding quasicrystalline phase. The crystal structures of τ_1 and have been solved and refined with X-ray single crystal data, whereas structure investigations of the Φ phase were based only on electron diffraction patterns [11–13]. The Φ phase was first described by Clark and Rhines [9]. Donnadieu et al. found an orthorhombic primitive unit cell, which was then indexed based on X-ray powder data with lattice parameters $a = 8.979$ Å, $b = 16.988$ Å and $c = 19.34$ Å [11]. According to Clark [10] and Donnadieu, the Φ phase has an approximate homogeneity range from 53 to 55 at.% Mg, 18 to 29 at.% Al and 17 to 28 at.% Zn and forms peritectically from L + $\tau_1\gamma$ at 388 °C. In the Calphad assessment (Figs. 1–3), the Φ phase has been modelled with the Mg content fixed at 55 at.%.

Bourgeois et al. derived from Convergent Beam Electron Diffraction (CBED) patterns the spac*cI*58, $I\bar{4}3m$, $a = 10.544$e group *Pbcm* [12]. In addition, they proposed a structure model with 152 atoms per unit cell. The model was derived by packing a cluster in the orthorhombic unit cell, which occurs in the γ phase $Al_{12}Mg_{17}$ (*cI*58, $I\bar{4}3m$, $a = 10.544$ Å [14]).

However, the agreement between calculated and experimental X-ray powder data was insufficient and an attempt to improve the model by refinement was not successful. Recently, Singh et al. [13] have shown that the crystal structure of the Φ phase has similarities with that of the icosahedral quasicrystalline phase q by means of an electron diffraction study.

The objective of this work was to obtain reliable data for the homogeneity range of the Φ phase to allow a better assessment of the Al–Mg–Zn system with solubility of Al, Zn and Mg for the Φ phase. Two temperatures were chosen for investigation, 360 °C and 330 °C. At 360 °C (Fig. 1a), the Φ phase has a two phase field with liquid phase, while at 330 °C (Fig. 1b) all phases are solid. In addition, the crystal structure was investigated using X-ray single

☆ In Memoriam Prof. Dr. Welf Bronger.

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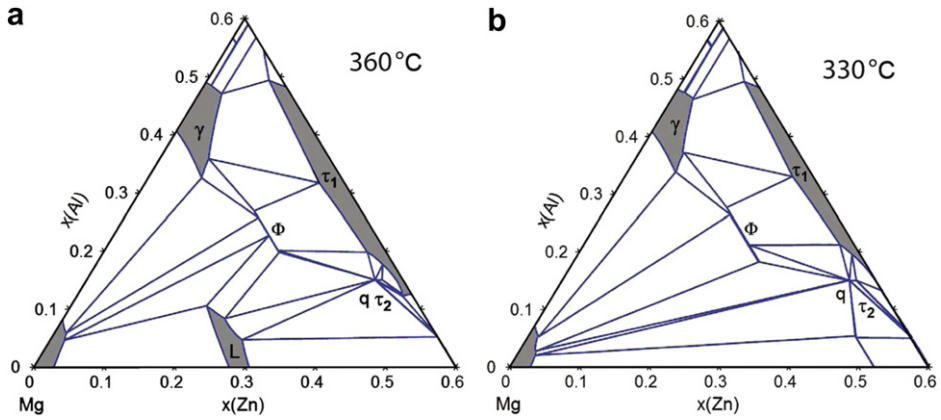

Fig. 1. The Mg-rich part of the isothermal section of the Al–Mg–Zn system at a) 360 °C and b) 330 °C according to Petrov et al. [6]. The Φ phase is modelled here with a fixed Mg content of 55 at.%. These sections were calculated with the Pandat 8.1 software [17], and are based on Petrov's assessment.

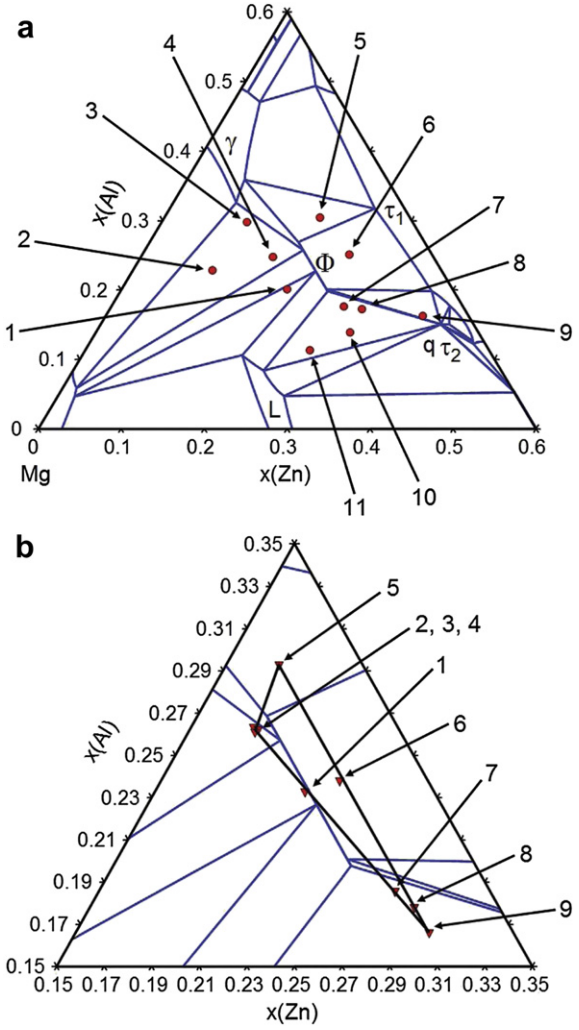

Fig. 2. The Mg-rich part of the isothermal section of the Al–Mg–Zn system at 360 °C according to the data of Petrov et al. [6]. a) The ICP-OES compositions of the samples of Table 1 are shown by red circle marks. b) The WDXS composition of the Φ phase for samples heat treated at 360 °C are shown as red triangles; Magnification of a). The homogeneity range of the Φ phase has a wedge-like shape and is shown as an overlay. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

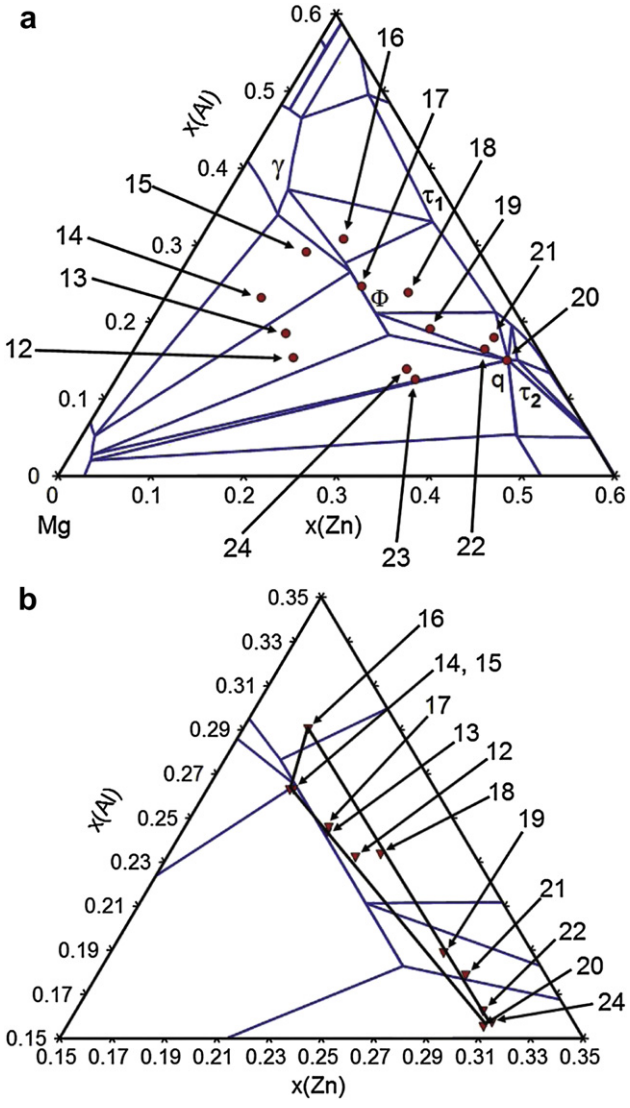

Fig. 3. The Mg-rich part of the isothermal section of the Al–Mg–Zn system at 330 °C according to the data of Petrov et al. [6]. a) The ICP-OES compositions of the samples of Table 2 are shown by red circle marks. b) The WDXS composition of the Φ phase for samples heat treated at 330 °C are shown as red triangles. Sample No. 17 is single phase Φ, Crystal 1 was obtained from Sample No. 12; Magnification of a). The homogeneity range of the Φ phase has a wedge-like shape and is shown as an overlay. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)