Complex Metallic Alloy Phases in the Al-Mg-Zn System

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Complex metallic alloys (CMA's) are a fascinating class of materials. They comprise intermetallic compounds with giant unit cells, incommensurate modulated structures and quasicrystalline phases. A famous example is the Al-Mg-Zn system [1–3], which contains four ternary complex intermetallic phases, called τ_1 [4], τ_2 [5–12], q [7] and Φ [13, 14]. The τ_1 and τ_2 phases are crystalline approximants of the quasicrystalline q phase. Their crystal structures can be described as packings of Bergman Clusters, which decorate nodes of canonical cell tilings [15]. The τ_2 phase (*cP*676, $Pa\bar{3}$) has been investigated several times in the past 20 years, however, the results concerning composition and disorder are inconsistent with one another. The crystal structures of the q and the Φ phase are still unknown. *Bourgeois* et al. [14] have determined the unit cell parameters and the space group symmetry (*oP*152, *Pbcm*) of the Φ phase by electron diffraction and they proposed a structural model based on HRTEM images. The main objective of this work is a redetermination of the Al-Mg-Zn system by coupling Calphad modelling with new experimental data and to resolve the ambiguities. Due to the complexity of the ternary phase diagram, we extensively used equilibrated alloy methods like metallography, X-ray diffraction and thermal analysis, with special focus on the simulation of the DTA response [16].

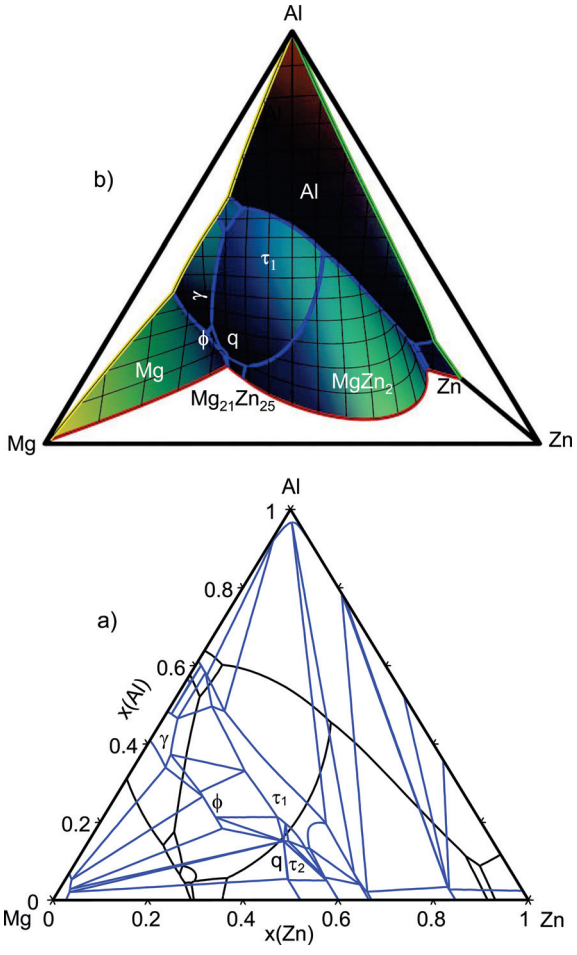

Fig. 1: Isothermal section of the Al-Mg-Zn system at 330 °C with liquidus curve projection (a); 3D view of the liquidus surface (b).

The Al-Mg-Zn Phase Diagram

An isothermal section at 330 °C with liquidus curve projection and a 3D view of the liquidus surface of the Al-Mg-Zn system is shown in Figure 1. Both were calculated based on data from the thermodynamic assessment of *Petrov* et al. [3] by means of the Pandat 8.1 engine [17]. Here, the compositions $Al_{15}Mg_{43}Zn_{42}$ for the τ_2 phase and $Al_{15}Mg_{44}Zn_{41}$ for the q phase were chosen as reported by *Takeuchi* [7]. The Φ phase crystallizes according to this assessment at 55 at.% Mg with a homogeneity range from $Al_{18}Mg_{55}Zn_{26}$ to $Al_{28}Mg_{55}Zn_{17}$. The Φ phase forms in a peritectic ($L + \gamma + \tau_1 = \Phi$) and the τ_2 phase in a quasi-peritectoide reaction ($q + \tau_1 = Mg_4Zn_7 + \tau_2$).

The Φ Phase

The phase diagram in close vicinity to the Φ phase was redetermined using equilibrated alloys by metallographic examination, EDX, WDX, thermal analysis and X-ray diffraction methods. Some results of the phase analysis for alloys, heat-treated at 330 °C, are shown in Figure 2. In addition to the broad homogeneity range in Al and Zn, it has been observed that the Φ phase exhibits a small phase width in Mg ranging from 55 at.% to 57 at.% at high Al content. For most samples we have also compared the DTA curves with calculated DTA

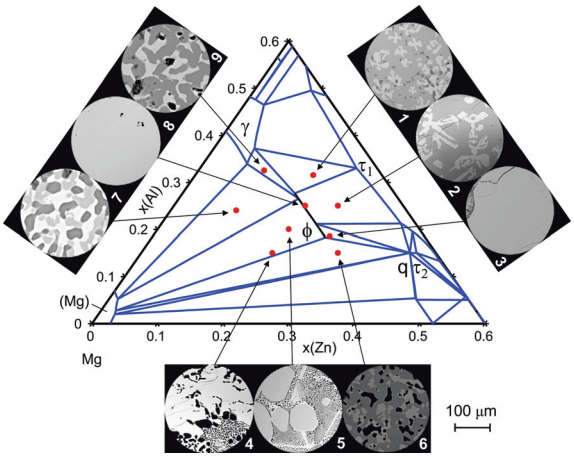

Fig. 2: The Mg-rich part of the isothermal section of the Al-Mg-Zn system at 330 °C and micrographs (BSE) for various alloys are shown; the composition of the Φ phase (EDX) is as follows: 1) $Al_{28}Mg_{55}Zn_{17}$, 2) $Al_{23}Mg_{55}Zn_{22}$, 3) $Al_{18}Mg_{55}Zn_{27}$, 4) $Al_{20}Mg_{55}Zn_{25}$, 5) $Al_{22}Mg_{57}Zn_{21}$, 6) $Al_{16}Mg_{54}Zn_{30}$, 7) $Al_{25}Mg_{57}Zn_{18}$, 8) $Al_{23}Mg_{55}Zn_{22}$, 9) $Al_{25}Mg_{57}Zn_{18}$.

curves. Here, the enthalpy versus temperature for full equilibrium melting and freezing and for Scheil freezing was used as input. In summary, it can be said that the phase diagram in the vicinity of the Φ phase is in good agreement with the experimental results of this work. The crystal structure of the Φ phase was determined by X-ray single crystal structure analysis (*R1* = 6.1%, *wR2(all)* = 14.6%). The Φ phase crystallizes with *a* = 8.937(3) Å, *b* = 16.812(2) Å, *c* = 19.586(4) Å in space group *Pbcm* with 152 atoms per unit cell. 12 crystallographic sites with coordination numbers 14 and 16 and large Voronoi cell volumina are fully occupied by Mg atoms. These sites correspond to 50 at.% Mg. The remaining 11 crystallographic sites have coordination numbers *CN* = 11 and 12 and occupancy factors for Zn from 8% to 87%. Assuming full occupation for each crystallographic site and using information from the chemical analysis these sites must be randomly mixed occupied with Al, Mg and Zn leading to the composition $Al_{21}Mg_{55}Zn_{24}$ and the crystallographic formula $(Al_{0.42}Mg_{0.1}Zn_{0.48})Mg$ with *Z* = 76.

The crystal structure can be described as a sequence of 12 nearly flat atom layers per unit cell along the *c* axis. The four different layer types are shown in Figure 3 as tilings. Similar tilings have been used to describe the layer types of decagonal quasicrystals and their approximants [18], thus the Φ phase can be thought of as an approximant structure. The crystal structure can also be described as a distorted hexagonal close packing of clusters. The cluster has the shape of the red pentagon with one missing vertex as shown in Figure 3.

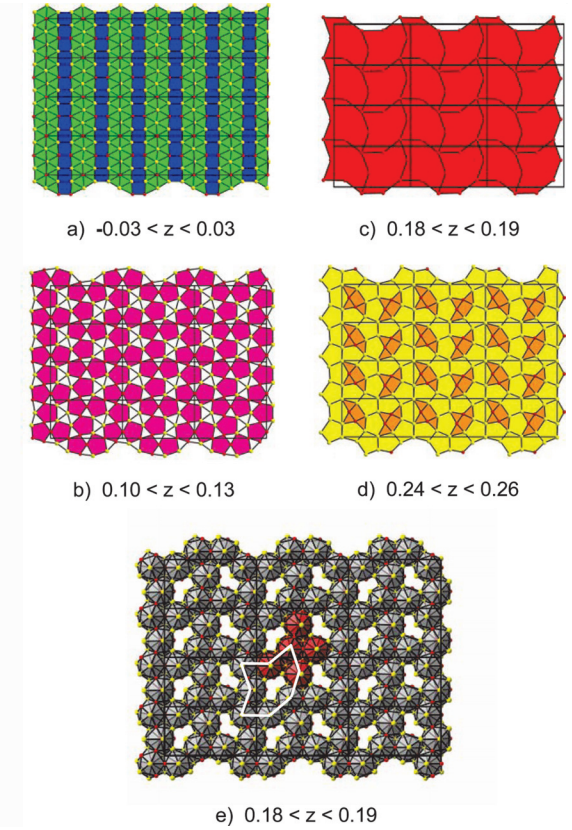

Fig. 3: The four different atom layer types in the crystal structure of the Φ phase are shown as tilings: a) square-triangle tiling, b) pentagon-triangle tiling, c) boat tiling d) pentagon-boat tiling, e) decoration of boat tiling by icosahedra; one cluster is shown in red colour.

The τ_2 Phase

The phase formation of the τ_2 phase was first reported by *Takeuchi* [5]. According to his results, the τ_2 phase forms at $Al_{15}Mg_{43}Zn_{42}$ close to the q phase at $Al_{15}Mg_{44}Zn_{41}$. The crystal structure was first described by *Sugiyama* [10,11], later again by *Spiekermann* [8] and then by Lin [12]. The composition reported by *Spiekermann* agrees well with that of *Takeuchi.*

However, for the composition of the τ_2 phase *Sugiyama* reports $Al_{17}Mg_{46}Zn_{37}$ and *Lin* $Al_{13}Mg_{32}Zn_{55}$. The latter two compositions are points in the three phase fields Φ + τ_1 + q and τ_1 + η + Al, respectively. None of the authors has observed a perceptible homogeneity range and they report nearly equal lattice parameters (a = 23.04 Å).

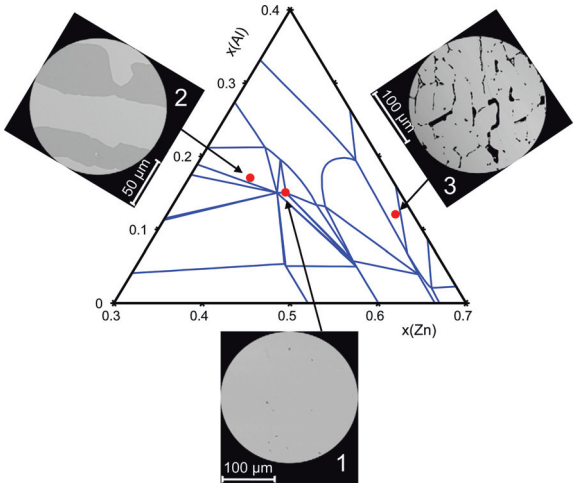

Fig. 4: Part of the isothermal section of the Al-Mg-Zn system at 330 °C in the vicinity of the τ_2 phase and micrographs (BSE) for alloys at various compositions proposed for single-phase τ_2: 1) $Al_{15}Mg_{43}Zn_{42}$, 2) $Al_{17}Mg_{46}Zn_{37}$, 3) $Al_{13}Mg_{32}Zn_{55}$.

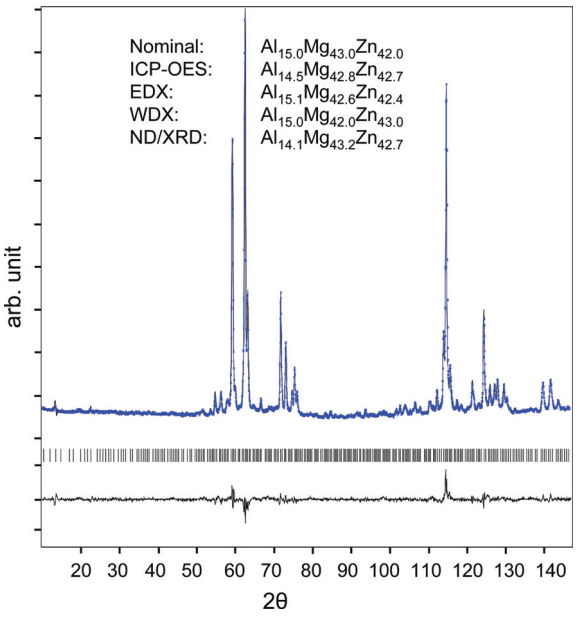

Fig. 5: Intensity versus 2θ-plots of the observed and calculated neutron pattern of τ_2 at $Al_{15}Mg_{43}Zn_{42}$; X-ray and neutron data have been combined in the Rietveld refinement.

The stability range and the crystal structure have been redetermined in the present work.

Single phase material of the τ_2 phase at the target composition $Al_{15}Mg_{43}Zn_{42}$ has been obtained by reaction melting in weld-sealed Ta ampoules followed by annealing at 330 °C for two weeks. The composition determined by ICP-OES, EDX, WDX, XRD and PXRD is in good agreement with the target composition. The sample at the composition $Al_{17}Mg_{46}Zn_{37}$ contains two phases ($\Phi + \tau_2$), as well as the sample at the composition $Al_{13}Mg_{32}Zn_{55}$ (Al + η). At $Al_{15}Mg_{43}Zn_{42}$ there is only the phase τ_2 (Fig. 4 and Fig. 5). This strongly supports that the composition of the τ_2 phase reported by *Sugiyama* and also by *Lin* are wrong. While investigating a large number of samples in the region x(Al) < 18 at.%, we have found that most relationships as proposed by the currently accepted phase diagram are not in agreement with the experimental data because a number of ternary complex metallic alloy phases in the vicinity of the Mg-Zn subsystem have been overlooked.

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