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Mg- alloy Database Construction: Investigation of Al-Ca Phase Equilibria

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1 Introduction

Information about possible precipitation of Al-Ca intermetallic phases is important for Mg-alloys with these alloying elements. During the experimental investigation of the ternary Mg-Al-Ca phase diagram we observed some inconsistencies, indicating the existence of additional binary Al-Ca compounds. To solve them, we carried out an investigation of the binary Al-Ca phase diagram.

The Al-rich corner is well investigated and described in the literature. Two binary phases Al_4Ca and Al_2Ca were reported. Only very limited experimental investigations of Ca-rich part were reported.

2 Experimental investigation

2.1 Experimental techniques

The alloys were prepared by levitation melting under argon atmosphere. They were investigated as-cast as well as after annealing at 250°C for up to one month.

The experimental investigation of the Al-Ca phase diagram was carried out with the help of X-ray powder analysis (Siemens 5000, CoK□-radiation), microstructural analysis, SEM/EDX (Scanning electron microscope with EDX) and DTA (Netzsch DTA 404).

2.2 Phase analysis

With EDX analysis of the Ca-rich alloys two new binary phases with the compositions AlCa and Al_3Ca_8 were determined. The alloys with these compositions were prepared and investigated as-cast, after annealing at 250°C and after DTA.

The AlCa phase forms peritectically and its microstructure is presented on the Fig.1. Because of the slow formation it was difficult to prepare sample with a high content of this phase and obtain good X-ray powder pattern.

The Al_3Ca_8 phase forms congruently. The microstructure of this phase is presented on the Fig.2. Its crystal structure is solved using powder methods as described below.

Existence of two other binary compounds, Al_4Ca and Al_2Ca, reported in literature was confirmed.

2.2 Polythermal investigation

The liquidus surface, phase transformations and melting points of the compounds were determined by DTA investigation. The samples were sealed in Ta-containers. Heating and coolig was carried out with a rate 1K/minute. Difference between cooling and heating signals was lower as 4K.

2.3 Crystal structure determination

A single phase sample with a composition Al_3Ca_8 was prepared by levitation melting. The X-ray powder pattern was checked using the PDF-2 database [1]. It was determined, that this compound belongs to the Tl_3Yb_8 structure type. The X-ray powder pattern and crystal structure of Al_3Ca_8 are presented on Fig. 3.

The crystal structure was refined using the Rietveld program WinRietveld 3.01 [2]. The crystallographic parameters are presented in Tab. 1.

2 Thermodynamic modeling

A thermodynamic model of the Al-Ca system was constructed. The calculated Al-Ca phase diagram is presented in Fig.4. The binary phases were modeled

stoichiometric since no homogeneity ranges were found experimentally. The Gibbs energy functions were fitted to the experimental subsolidus phase relations and the measured liquidus temperatures. Using the fitted values of Gibbs energy for new binary compounds and literature data sets, the binary Al-Ca system was calculated. The opmization was carried out with the help of WinPhaD 2.0a program [3].

3 Conclusions

The Al-Ca phase diagram was investigated using the X-ray powder diffraction, microstructure investigation, EDX and DTA.

Two new binary compounds were detected. Two other compounds reported in literature were confirmed.

All ternary phases have negligible homogeneity ranges.

Good agreement between the experimental data and calculated model is

observed and a consistent picture of the ternary system is presented.

Acknowledgment

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References

1. PDF-2 Powder Diffraction File Database. ICDD.
2. Win-Rietveld, Version 3.0.1, SIGMA-C GmbH (1991-98), Bruker Analytical X-ray Systems.
3. CompuTherm, LLC, 437 S. Yellowstone Dr., Suite 217, Madison, WI 53719, USA

Tab. 1.: Crystallographic parameters of Al_3Ca_8 compound.

Composition	Al_3Ca_8
Structure type	Tl_3Yb_8
Space group	P1
Pearson symbol	aP22
Cell parameters	a=0.95121(7) nm α=69.606(7)° b=0.96187(7) nm β=78.851(6)° c=0.96899(6) nm γ=60.321(7)°
R / R_w	6.30 / 7.94
Fitness Quality	1.61
Scan conditions	$CoK\alpha$ - radiation, $\Theta/2\Theta$ - scan, Step size: 0.02°/2Θ, Scan time: 6 s/step

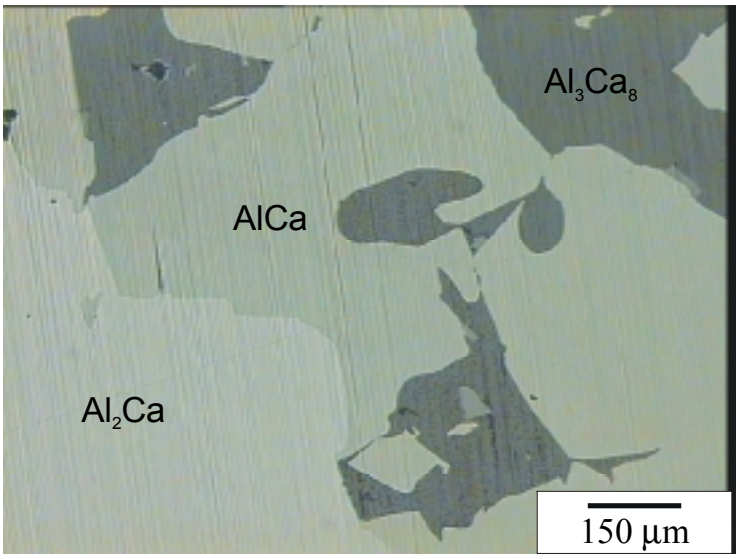

Fig. 1: Microstructure of the three phase sample with a composition AlCa after the DTA measurement.

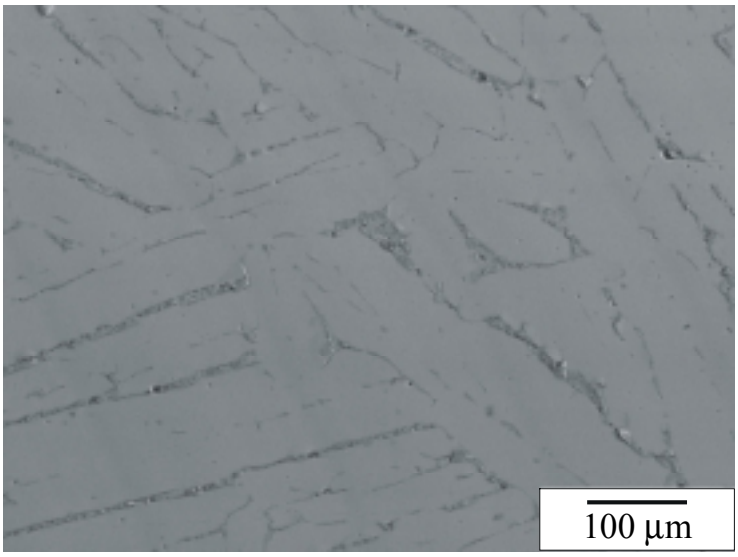

Fig. 2: Microstructure of the Al_3Ca_8 phase.

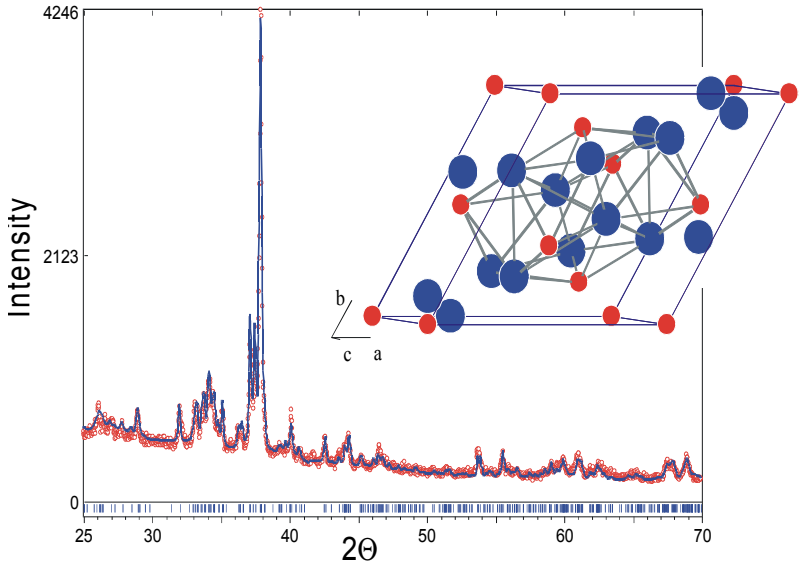

Fig. 3: X-ray powder pattern and crystal structure of Al_3Ca_8 compound.

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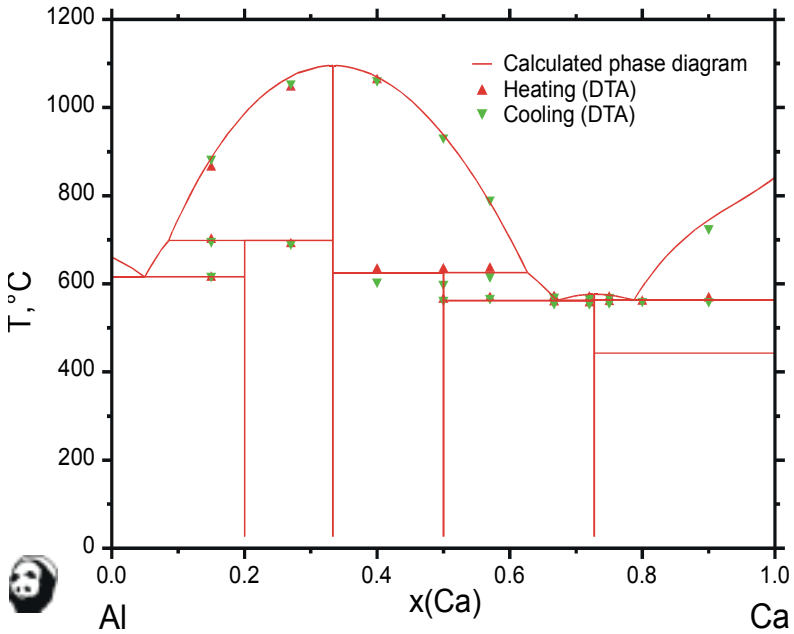

Fig. 4: The calculated Al_3Ca_8 phase diagram with results of DTA investigation.