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# The Al-Ca System, Part 1: Experimental Investigation of Phase Equilibria and Crystal Structures

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The binary aluminum-calcium phase equilibria were investigated using X-ray diffraction methods, metallographic, SEM/EDX analysis, DTA and the diffusion couple technique. The complete phase diagram has been determined. Two new binary compounds AlCa and $Al_3Ca_8$ were found in addition to the established $Al_4Ca$ and $Al_2Ca$ phases. The crystal structure of $Al_3Ca_8$ compound was determined by X-ray powder diffraction methods.

# 1. Introduction

In the framework of the generation of a multicomponent database for magnesium alloys the ternary Al-Ca-Mg systems is investigated as an important subsystem for Mg-Al-Ca-Li-Si-X alloys. Controlling the precipitation of phases from the Al-Ca edge system in the (Mg) matrix requires a precise knowledge of the stability and structure of these phases.

During the experimental investigation of the Al-Ca-Mg ternary 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 system.

Most experimental investigations of the Al-Ca system deal mainly with the Al-rich corner, technically interesting for aluminum alloys. Two Al-rich binary phases were reported in the literature.

The results of experimental phase analysis and crystallographic investigation are presented in this paper. This experimental work was supported and complemented by calorimetric investigations and thermodynamic analysis of the phase equilibria, presented in Part 2 of this paper [01Kev].

### 1.1 Phase diagram

The first extensive investigation of the Al-Ca system was published by Matsuyama et al. [28Mat]. It is a comprehensive study made by thermal and thermoresistometric analysis and by microscopic examination. The liquidus line was determined and two binary phases were found: $Al_2Ca$ melts congruently at 1079°C; "$Al_3Ca$" forms peritectically at 700°C. [28Mat] also confirmed the existence of eutectic reactions at 5.2 at.% Ca and 616° C and at 64.5 at.% Ca and 545°C, which were reported earlier by [08Don] (at ~5.5 at.% Ca and 610°C and at 66.9 at.% Ca and 550°C) and [28Boz] (at 5.5 at.% Ca and 613°). Later, [40Now] proved that the real composition of the $Al_3Ca$ is $Al_4Ca$. Anglezio et al. [94Ang] refer the work of [73Vak], who found eutectic reactions at 4.6 at.% Ca and 616°C and at 68.0 at.% Ca and 545°C.

The information about the solubility of Ca in (Al) is very contradictory. According to the various studies the solubility range is between 0.03 and 1.9 at.% Ca. A detailed discussion of this problem is presented by [88Itk]. Extensive reviews of the experimental literature data are given by [88Itk] and [94Ang].

### 1.2 Crystal structures

The crystal structure of $Al_2Ca$ was reported first by [39Now] as *fcc* with a lattice parameter of a = 0.8022 nm. Three more references given in [91Vil] confirm that the $Al_2Ca$ compound crystallizes in the $Cu_2Mg$ structure type,

The crystal structure of $Al_4Ca$ was determined by [40Now] as tetragonal, which belongs to the $Al_4Ba$ structure type, space group I4/mmm, with the lattice parameters a = 0.4353, c = 1.107 nm. Later, [79Zog] reported that $Al_4Ca$ phase undergoes a martensitic transformation at 130°C. The low temperature structure is monoclinic, a = 0.6158, b = 0.6175, c = 1.118 nm, $\beta$ = 88.9°.

Miller and Nesper [92Mil] reported a Li stabilized $Al_3Ca_{8-x}Li_x$ (x = 0.16) phase, which is isotypic to $Ca_8In_3$ (space group $P\bar{1}$; a=0.9470 nm, b=0.9602 nm, c=0.9646 nm, $\alpha$=99.17°, $\beta$=101.08°, $\gamma$=119.51°). The crystal structure was determined by single-crystal diffractomery. The authors [92Mil] report that attempts to prepare pure binary $Al_3Ca_8$ phase were unsuccessful.

# 2 Experimental investigation

### 2.1 Phase equilibrium study

For the present determination of phase relations in the Al-Ca system 15 alloys were prepared.

Starting materials were aluminum powder (99.8 mass%, Alfa) or aluminum bulk (>99.9999 mass %, Pechiney) and Ca granules (99.5 mass%, Alfa). The elements were weighed and mixed in glove-box under Ar

atmosphere to avoid the oxidation of Ca and pressed under a pressure of 100 MPa into small pellets of around 0.5 g. The pellets were melted by levitation melting under purified argon atmosphere at 1 bar and quenched in a water cooled Cu-crucible. The heating power was controlled carefully to avoid evaporation. The weight losses were less than 1 mass %. For the subsequent annealing the samples were packed in Ta foil and sealed in evacuated silica ampoules. Samples were investigated as-cast, after annealing at 250°C for up to one month and after differential thermal analysis (DTA).

The experimental investigation of the Al-Ca phase equilibria was carried out with X-ray powder analysis (Siemens D-5000, CoKα-radiation), metallographic analysis, SEM/EDX (Scanning electron microscope with energy dispersive X-ray microanalysis (EDX)) and differential thermal analysis (Netzsch DTA 404).

For the X-ray powder diffraction analysis (XRD) the alloys were powdered in a hand mill and mixed with indifferent oil to avoid oxidation of samples. The routine measurements were performed with a step 0.02° of 2 Θ and 3 seconds exposition time in the point. The diffraction patterns were analyzed quantitatively using the program PowderCell 2.1 [99PC]. Further refinement of the X-ray pattern to identify the crystal structure of the compounds was performed using the Rietveld program WinRietveld 3.01 [98WR].

The microstructural analysis was performed using optical microscopy with digital image analysis as well as scanning electron microscopy with EDX to determine the compositions of the phases.

Samples for the DTA investigation were sealed in Ta containers under Ar atmosphere. The measurements were carried out under vacuum with heating/cooling rates of 5 and 1 K/min in the range from room temperature up to about 50 K above liquidus. Each sample was heated and cooled several times for the precise determination of peak positions. The error of measurements is estimated at ±4 K. After the DTA measurements the samples were investigated by XRD, microstructural analysis and EDX for the determination of phase assembly and phase compositions.

Additionally a diffusion couple investigation was carried out for the determination of the overall phase sequence in this system. The preparation is not trivial since an intimate contact at the Al/Ca interface in the bulk couple must be prepared without oxide interlayers.
Pure bulk Al (99.9999 mass%) was freshly ground into an approximate cylinder shape of about 5 mm diameter. Pure Ca (99.5 mass%) granules were melted in a levitation furnace under purified argon to form a sphere of about 5 mm diameter. This Ca-sphere was cut in half, one half was immediately placed on the Al-cylinder and cold pressed together under a uniaxial pressure of 100 MPa to deform into a flat plate of about 10 mm diameter. This severe deformation step disrupted the unavoidable but very thin freshly formed oxide layers on the Al-cylinder and the Ca-half-sphere and generated the necessary clean Al/Ca interface inside the bulk couple. This sample was cut in pieces, packed in Ta foil, sealed in a silica ampoule and annealed at 500°C for 2 weeks. After annealing the sample was cross-sectioned and investigated using metallographic analysis and EDX.

All experimental work was carried out together with thermodynamic calculations, which are described in details in the 2nd part of this paper [01Kev]. This procedure helped to select the key experiments and to interpret the results.

### 2.2 Crystallographic investigation of the new $Al_3Ca_8$ phase

A single phase sample with a composition $Al_3Ca_8$ was prepared by levitation melting. To avoid an oxidation of the sample the powder was mixed with an indifferent oil. The X-ray pattern for the crystal structure refinement of the $Al_3Ca_8$ phase was collected on the X-ray powder diffractometer Siemens 5000 with $CoK_\alpha$-radiation from 25 to 70 degree of 2Θ in a Θ/2Θ scan and a step size 0.02° of 2Θ and 6 seconds scanning time in the point.

The X-ray powder pattern was checked using the PDF-2 database [PDF]. The X-ray pattern of $Al_3Ca_8$ compound is similar to one of $Tl_3Yb_8$ compound as well as to simulated X-ray pattern of the $Al_3Ca_{8-x}Li_x$ phase [92Mil]. Using both, the crystal structures of $Tl_3Yb_8$ and $Al_3Ca_{8-x}Li_x$ ($Ca_8In_3$ structure type) compounds as possible models the crystal structure of the $Al_3Ca_8$ compound was refined using the Rietveld program WinRietveld 3.01 [98WR]. The temperature factors were refined as isotropic. They were also constrained to be identical for the same types of atoms. The better fitting parameters were obtained by the $Ca_8In_3$ model. Because of this and taking into account the related single-crystal investigation of the $Al_3Ca_{8-x}Li_x$ compound, the $Ca_8In_3$ structure type was assumed as the most probable.

## 3 Results of the phase equilibrium study

The Al-Ca phase diagram including the two newly discovered binary phases AlCa and $Al_3Ca_8$ is presented in Fig.1. The diagram is calculated according to the thermodynamic assessment in part 2 of this study [01Kev]. The experimental data of this work and literature data from thermal analysis are also given in Fig.1.

The results of phase analysis by XRD, metallography and SEM/EDX are presented in Table 1.

Twelve samples were investigated by DTA for the determination of liquidus temperatures and nonvariant reactions (Table 2). In some cases only the cooling signals were used for the reaction temperature determination, because of unsharpness and low intensity of the heating peaks. The determined nonvariant reactions and a comparison to literature data are presented in Table 3.

Two new binary phases, AlCa and $Al_3Ca_8$, were found and the existence of two phases reported in literature, $Al_4Ca$ and $Al_2Ca$, was confirmed. The microstructures of these phases are presented in the Figs. 2 to 5.

Three eutectic reactions were found in the Al-Ca system. The liquid compositions and temperatures are at 5.1 at.% Ca and 613°C, at 66.3 at.% Ca and 556°C and at 80.0 at.% Ca and 560°C. The compositions of eutectic liquids were measured by EDX area scans of the corresponding eutectic regions in the microstructures. These results are given by DTA and EDX and confirmed by the microstructures in Figs. 7 to 9. The metallographic evidence clearly demonstrates the existence of the two newly discovered Ca-rich eutectics in Figs. 8 and 9.

The diffusion couple investigation also confirmed existence of all four binary phases. The micrograph of the Al-Ca diffusion couple after annealing 2 weeks at 500°C is presented in Fig. 6. It should be noted that under these conditions the $Al_4Ca$ and the $Al_3Ca_8$ phases grow fastest.

The X-ray powder pattern of the $Al_4Ca$ phase in as-cast alloys is very similar to the pattern of monoclinic phase described by [79Zog]. It confirms the martensitic transformation of the tetragonal $Al_4Ca$ phase into the monoclinic one.

The composition of the new phase AlCa was determined by EDX. The slow kinetics of formation of this phase during the peritectic reaction from the very stable $Al_2Ca$ phase prevented the preparation of a single-phase sample for the crystallographic investigation. The incomplete formation of the AlCa phase is also seen in Fig. 4.

The composition of the new $Al_3Ca_8$ phase was determined by EDX as well as crystallographically. This compound forms congruently, has a triclinic structure and belongs to the $Ca_8In_3$ structure type. The X-ray powder pattern and crystal structure of $Al_3Ca_8$ are presented in Fig. 10. The crystallographic parameters are presented in Table 4.

During the XRD investigation of Al-rich and Ca-rich alloys no deviations from the theoretical powder patterns were detected for (Al) and (Ca). Therefore the solubility regions of Ca in (Al) and of Al in (Ca) are supposed to be negligible.

## 4 Discussion

The binary Al-Ca phase diagram

presented in this study agrees with literature data only in the Al-rich region. We have confirmed the eutectic and peritectic temperatures on the Al-rich side reported in literature and the corresponding compositions (Table 3). The crystal structures of $Al_4Ca$ and $Al_2Ca$ are confirmed, as well as the martensitic transformation of tetragonal $Al_4Ca$ into monoclinic one. The melting point of $Al_2Ca$ is determined at 1086°C, which is 7 K higher than reported by [28Mat].

In the region between 33 and 100 at.% Ca our results differ substantially from literature data. Two new binary phases AlCa and $Al_3Ca_8$ were found in this region by phase analysis. These two new phases together with the two previously known phases were found also by a diffusion couple investigation (Fig.6). The EDX investigation confirmed that the composition of the phases are $Al_4Ca$, $Al_2Ca$, AlCa and $Al_3Ca_8$.

According our data, the liquidus line of $Al_2Ca$-phase is symmetrical, which is thermodynamically more probable than the one presented by [28Mat]. Also the liquidus line of the L + (Ca) equilibrium is much steeper compared to [28Mat], see Fig 1, which is also thermodynamically more probable since the initial slope of that liquidus line is determined just by the melting enthalpy of pure calcium. This is quantitatively worked out in part 2 of this paper [01Kev].

The crystal structure of the $Al_3Ca_8$ phase is isostructural to the $Al_3Ca_{8-x}Li_x$ (x=0.16) compound. This phase was reported by [92Mil], who's attempts to prepare pure binary $Al_3Ca_8$ phase failed. The authors [92Mil] heated a mixture of Al (99.9 at.%, Merck) and Ca (99.5 at.%, Merck) in a molybdenum crucible under Ar atmosphere to 1180 K and after 2 hours slowly cooled the melt to room temperature over 2 day period. In our work, formation of the $Al_3Ca_8$ compound was observed both after quenching of samples in levitation melting furnace and after slow cooling to room temperature by 1 K/min in Ta crucibles during the DTA investigation. The $Al_3Ca_8$ phase forms very easily and could be found in all samples between 33 and 100 at.% Ca. Annealing of samples at 300°C did not show any indication of an $Al_3Ca_8$ decomposition. This decomposition had been suspected by our preliminary thermodynamic calculation but can be excluded.

The phase AlCa forms very slowly. As a result, three phases were found in all samples in the region between the $Al_2Ca$ and $Al_3Ca_8$ compounds. Because of the slow formation of AlCa some metastable reactions appear in this region, which render the interpretation of DTA signals difficult. The metastable eutectic L = $Al_2Ca$ + $Al_3Ca_8$, obtained by excluding the AlCa phase from the thermodynamic calculation, occurs at 537°C [01Kev].

We propose, that the eutectic reaction "L = $Al_2Ca$ + Ca" assumed by [28Mat] at 64.5 at.% Ca and 545°C and by [73Vak] at 68.0 at.% Ca and 545°C correspond to the stable eutectic reaction L = AlCa + $Al_3Ca_8$ at 66.0 at.% Ca and 556°C.

## 5 Conclusion

Two new binary phases AlCa and $Al_3Ca_8$ were found in this system and two phases reported in literature, $Al_4Ca$ and $Al_2Ca$, were confirmed. The complete phase diagram has been determined. It is similar to the literature data below 33 at.% Ca but substantially different in the range of 33 to 100 at.% Ca.

The crystal structure of $Al_3Ca_8$ compound was determined by X-ray powder diffraction methods. It crystallizes in the $Ca_8In_3$ structure type with a space group $P\bar{1}$ and Pearson symbol aP22. All binary phases have negligible homogeneity ranges, the same applies to the terminal solutions of the pure elements. The present results are consistent with a thermodynamic assessment of Al-Ca system.

**Note added in proof**

After submission of this paper the report of Huang and Corbett [98Hua] came to our knowledge, who determined the crystal structures of $Al_{14}Ca_{13}$ and $Al_3Ca_8$ phases by single-crystal X-ray methods.

The $Al_{14}Ca_{13}$ crystallizes with

monoclinic symmetry (space group *C*2/*m*, Z = 2, a = 1.5551(4), b = 0.9873(2), c = 0.9726(2) nm, β = 108.09(2)°), and $Al_3Ca_8$ has the triclinic $Ca_8In_3$-type structure ($P\bar{1}$, Z = 2, a = 0.9484(3), b = 0.9592(3), c = 0.9671(3) nm, α = 99.02(3)°, β = 101.13(3)°, γ = 119.55(3)°).

These results of single-crystal X-ray investigations are in excellent agreement with the results of this study, assuming that $Al_{14}Ca_{13}$ corresponds to AlCa.

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**Table 1: Results of phase analysis by XRD, metallography and SEM/EDX**

| **Sample composition at.% Al - at.% Ca** | **Annealing conditions** | **Phases** *) |
|---|---|---|
| Al90-Ca10 | as cast | $Al_4Ca$ + (Al) + *$Al_2Ca$* |
| Al85-Ca15 | as cast<br>after DTA | $Al_4Ca$ + (Al) + *$Al_2Ca$*<br>$Al_4Ca$ + (Al) |
| Al80-Ca20 | as cast | $Al_4Ca$ + *(Al)* + *$Al_2Ca$* |
| Al73-Ca27 | as cast<br>after DTA | $Al_2Ca$ + $Al_4Ca$<br>$Al_2Ca$ + $Al_4Ca$ |
| Al66.67-Ca33.33 | as cast<br>after DTA | $Al_2Ca$<br>$Al_2Ca$ |
| Al60-Ca40 | as cast<br>after DTA | $Al_2Ca$ + *$Al_3Ca_8$* + AlCa<br>$Al_2Ca$ + AlCa + *$Al_3Ca_8$* |
| Al50-Ca50 | as cast<br>after DTA | *$Al_2Ca$* + *$Al_3Ca_8$* + AlCa<br>*$Al_2Ca$* + AlCa + *$Al_3Ca_8$* |
| Al43-Ca57 | as cast<br>after DTA | $Al_3Ca_8$ + *$Al_2Ca$* + AlCa<br>AlCa + $Al_3Ca_8$ + *$Al_2Ca$* |
| Al34.5-Ca65.5 | as cast<br>after DTA<br>300°C, 1 month | $Al_3Ca_8$ + *$Al_2Ca$* + AlCa<br>$Al_3Ca_8$ + AlCa<br>$Al_3Ca_8$ + AlCa |
| Al28-Ca72 | as cast<br>after DTA<br>300°C, 3 weeks | $Al_3Ca_8$ + AlCa + *$Al_2Ca$*<br>$Al_3Ca_8$ + AlCa<br>$Al_3Ca_8$ + AlCa |
| Al27.27-Ca72.73<br>sample for calorimetry | as cast | $Al_3Ca_8$ |
| Al27-Ca73 | as cast<br>after DTA | $Al_3Ca_8$ + (Ca)<br>$Al_3Ca_8$ + (Ca) |
| Al25-Ca75 | as cast<br>after DTA | $Al_3Ca_8$ + (Ca)<br>$Al_3Ca_8$ + (Ca) |
| Al20-Ca80 | as cast<br>after DTA | $Al_3Ca_8$ + (Ca)<br>$Al_3Ca_8$ + (Ca) |
| Al10-Ca90 | as cast<br>after DTA | (Ca) + $Al_3Ca_8$<br>(Ca) + $Al_3Ca_8$ |

***) Phase sequence corresponds qualitatively to phase amounts. Non-equilibrium phases are printed in italic.**

**Table 2: Results of DTA analysis**

| Sample composition at.% Al – at.% Ca | Heating /cooling rate K/min | DTA signals*) | Assessed experimental temp. °C | Phase boundary or invariant reaction |
|---|---|---|---|---|
| Al85-Ca15 | 5 | 883 c | 873 | L / L + $Al_2Ca$ |
| | 1 | 873 h | | |
| | 5 | 702 h / 697 c | 700 | L + $Al_2Ca$ = $Al_4Ca$ |
| | 1 | 700 h | | |
| | 5 | 613 h / 617 c | 613 | L = (Al) + $Al_4Ca$ |
| | 1 | 613 h | | |
| Al73-Ca27 | 5 | 1063 h / 1054 c | 1063 | L / L + $Al_2Ca$ |
| | 5 | 689 h / 690 c | 691 | L + $Al_2Ca$ = $Al_4Ca$ |
| | 1 | 691 h | | |
| Al66.67-Ca33.33 | 1 | 1086 h / 1086 c | 1086 | L = $Al_2Ca$ |
| Al60-Ca40 | 5 | 1068 h | 1067 | L / L + $Al_2Ca$ |
| | 5 | 1066 h / 1044 c | | |
| | 1 | 1062 h / 1057 c<br>1064 h / 1059 c | | |
| | 1 | 1067 h / 1061 c<br>1065 h / 1060 c<br>1063 h / 1060 c | | |
| | 1 | 634 h / 597 c<br>632 h / 601 c | 633 | L + $Al_2Ca$ = AlCa |
| | 1 | 635 h / 609 c<br>630 h / 608 c<br>627 h / 606 c | | |
| | 1 | 551 h / 553 c<br>550 c | 551 | Metastable<br>(?) L = AlCa + $Al_3Ca_8$ |
| Al50-Ca50 | 5 | 941 h / 919 c | 938 | L / L + $Al_2Ca$ |
| | 1 | 938 h / 936 c<br>931 c | | |
| | 5 | 632 h / 599 c | 632 | L + $Al_2Ca$ = AlCa |
| | 1 | 632 h / 595 c<br>632 h / 584 c | | |
| | 1 | 567 h / 560 c<br>563 h / 561 c | 567 | Metastable<br>(?) L = AlCa + $Al_3Ca_8$ |
| Al43-Ca57 | 1 | 791 c<br>794 c<br>796 c | 791 | L / L + $Al_2Ca$ |
| | 1 | 634 h / 614 c<br>634 h / 616 c<br>634 h / 619 c | 634 | L + $Al_2Ca$ = AlCa |
| | 1 | 570 h / 566 c<br>569 h / 567 c<br>569 h / 568 c | 568 | L = AlCa + $Al_3Ca_8$ |

**Table 2 (continued): Results of DTA analysis**

| Sample composition at.% Al – at.% Ca | Heating /cooling rate K/min | DTA signals | Assessed experimental temp. °C | Phase boundary or invariant reaction |
|---|---|---|---|---|
| Al34.5-Ca65.5 | 1 | 562 h / 567 c<br>568 h / 570 c<br>568 h / 568 c | 568 | L / L + AlCa |
| | 1 | 550 h / 550 c<br>560 h / 556 c<br>557 h / 554 c | 556 | L = AlCa + $Al_3Ca_8$ |
| Al28-Ca72 | 2 | 584 h / 567 c | 578 | L / L + $Al_3Ca_8$ |
| | 1 | 578 h / 578 c | | |
| | 1 | 578 h / 569 c<br>577 h / 568 c<br>578 h / 568 c | | |
| | 2 | 556 h / 555 c | 556 | L = AlCa + $Al_3Ca_8$ |
| | 1 | 556 h / 556 c | | |
| | 2 | 547 c | | ? |
| | 1 | 553 c | | |
| Al27-Ca73 | 1 | 580 h / 575 c<br>579 h / 574 c<br>579 h / 575 c | 579 | L / L + $Al_3Ca_8$ |
| | 1 | 558 h / 564 c<br>560 h / 563 c<br>559 h / 563 c | 560 | L = $Al_3Ca_8$ + (Ca) |
| Al25-Ca75 | 1 | 569 h / 569 c<br>569 h / 569 c<br>568 h / 569 c | 569 | L / L + $Al_3Ca_8$ |
| | 1 | 557 h / 557 c<br>558 h / 558 c<br>559 h / 557 c | 558 | L = $Al_3Ca_8$ + (Ca) |
| Al20-Ca80 | 1 | 560 h / 560 c<br>561 h / 561 c<br>560 h / 561 c | 560 | L = $Al_3Ca_8$ + (Ca) |
| Al10-Ca90 | 1 | 726 c<br>726 h / 726 c | 726 | L / L + Ca |
| | | 566 h / 560 c<br>566 h / 564 c | 566 | L = $Al_3Ca_8$ + (Ca) |

***) h: heating signal, onset for invariant reactions, peak maximum otherwise**
**c: cooling signal, onset**

**Table 3: Experimental nonvariant reactions in the Al-Ca system.**

| Reaction | Reaction type | Temperature, °C | Reference |
|---|---|---|---|
| L = (Al) + $Al_4Ca$ | Eutectic | **613** | This work |
| | | 610 | [08Don] |
| | | 613 | [28Boz] |
| | | 616 | [28Mat] |
| | | 616 | [73Vak] |
| L + $Al_2Ca$ = $Al_4Ca$ | Peritectic | **700** | This work |
| | | 700 | [28Mat] |
| L = $Al_2Ca$ | Melting point | **1086** | This work |
| | | 1079 | [28Mat] |
| $Al_2Ca$ + L = AlCa | Peritectic | **633** | This work |
| L = AlCa + $Al_3Ca_8$ | Eutectic | **556** | This work |
| L = $Al_3Ca_8$ | Melting point | **579** | This work |
| L = $Al_3Ca_8$+ (βCa) | Eutectic | **560** | This work |

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**Table 4: Crystallographic parameters of the $Al_3Ca_8$ compound.**

| | | | | | |
|---|---|---|---|---|---|
| ***Composition*** | | | $Al_3Ca_8$ | | |
| ***Structure type*** | | | $Ca_8In_3$ | | |
| ***Space group*** | | | $P\bar{1}$ | | |
| ***Pearson symbol*** | | | aP22 | | |
| ***Cell parameters*** | | | a=0.94950(8) nm α=99.057(6)°<br>b=0.95922(8) nm β=101.152(7)°<br>c=0.96704(7) nm γ=119.613(8)° | | |
| ***R/R$_w$*** | | | 6.08 / 7.79 | | |
| ***Fitness Quality*** | | | 1.59 | | |
| ***Atom*** | ***Wyckoff position*** | ***x*** | ***y*** | ***z*** | ***B$_{iso}$*** |
| Al1 | 1a | 0 | 0 | 0 | 1.3(4) |
| Al2 | 1h | 1/2 | 1/2 | 1/2 | 1.3(4) |
| Al3 | 2i | 0.679(5) | 0.348(5) | 0.037(4) | 1.3(4) |
| Al4 | 2i | 0.828(5) | 0.163(5) | 0.490(4) | 1.3(4) |
| Ca1 | 2i | 0.027(3) | 0.434(4) | 0.315(3) | 3.4(3) |
| Ca2 | 2i | 0.058(3) | 0.701(4) | 0.108(4) | 3.4(3) |
| Ca3 | 2i | 0.120(3) | 0.108(4) | 0.341(3) | 3.4(3) |
| Ca4 | 2i | 0.262(3) | 0.342(3) | 0.695(3) | 3.4(3) |
| Ca5 | 2i | 0.688(4) | -0.003(4) | 0.121(3) | 3.4(3) |
| Ca6 | 2i | 0.342(3) | 0.369(5) | 0.116(3) | 3.4(3) |
| Ca7 | 2i | 0.532(3) | 0.211(4) | 0.654(3) | 3.4(3) |
| Ca8 | 2i | 0.557(3) | 0.211(3) | 0.344(3) | 3.4(3) |

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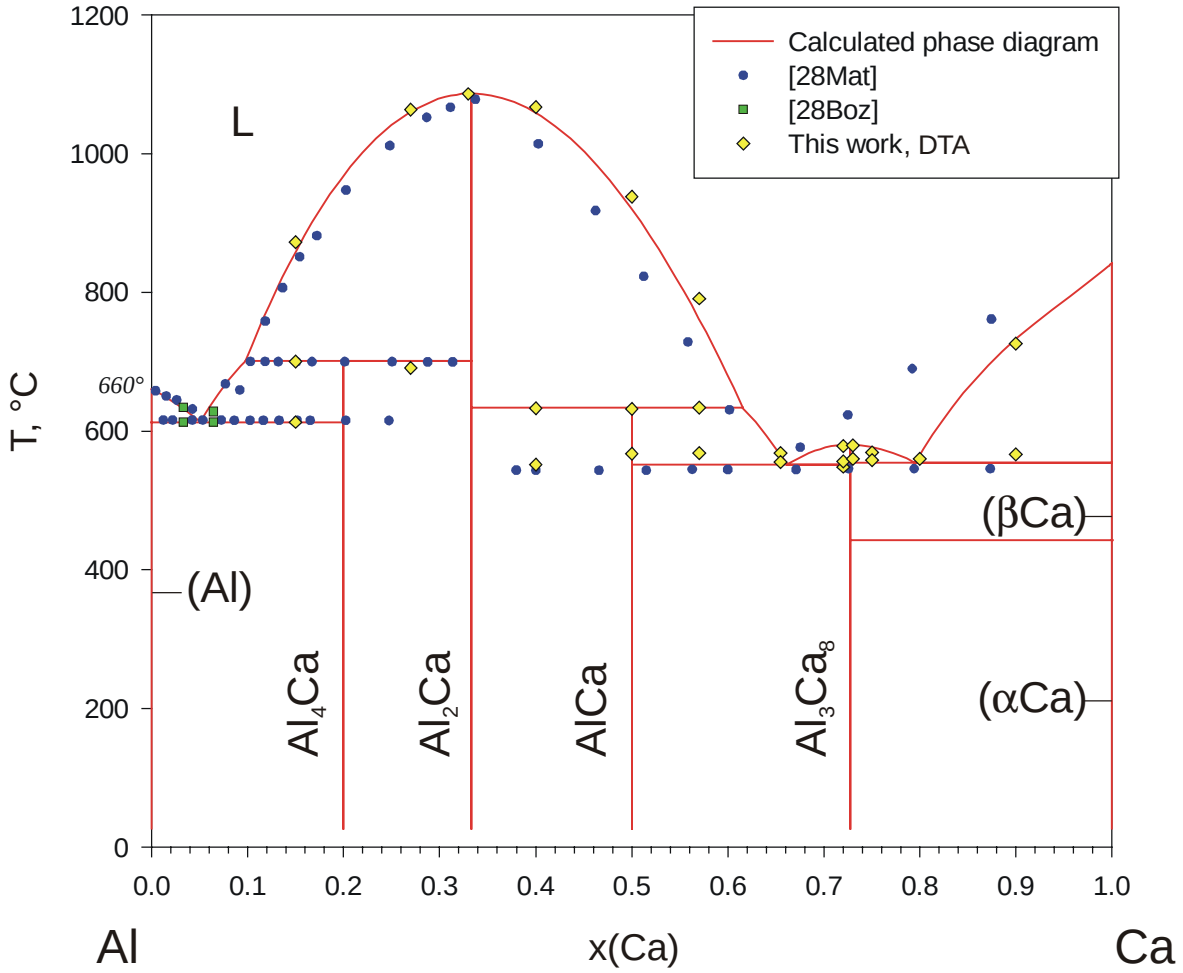


Fig.1.: Calculated Al-Ca phase diagram [01Kev] and experimental DTA data.

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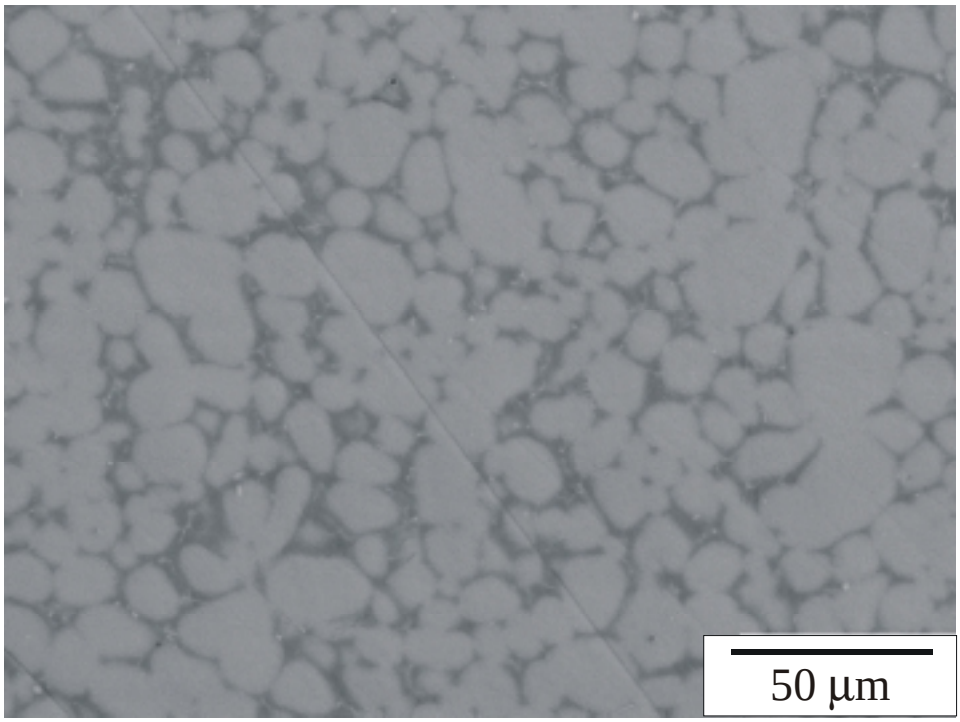


Fig.2.: Secondary electron image of sample $Al_{80}Ca_{20}$ (as cast) showing essentially the $Al_4Ca$ phase.

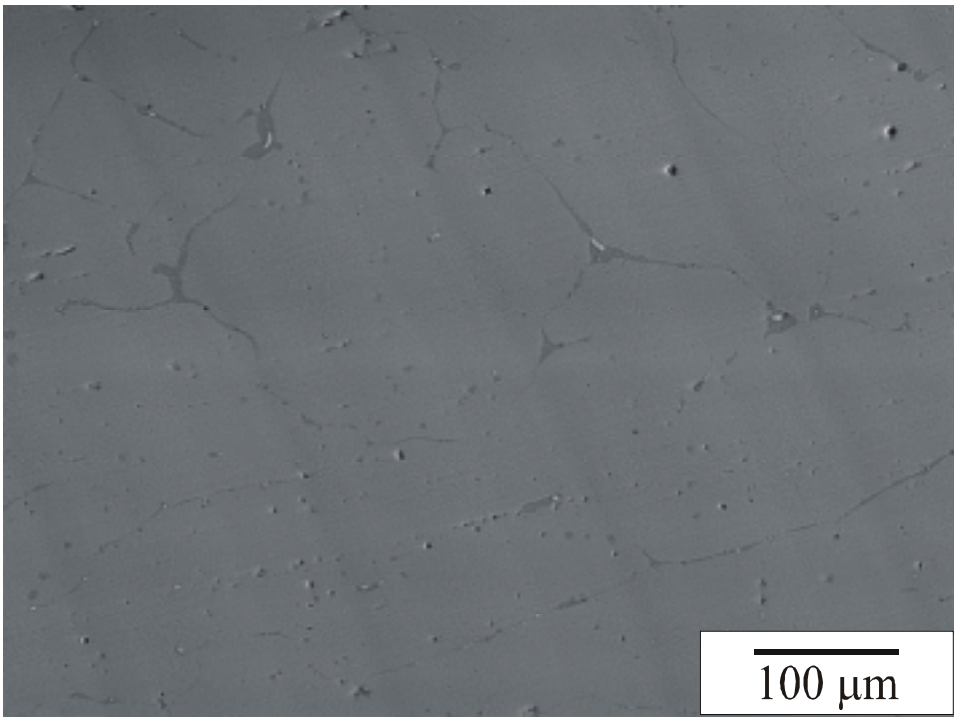


Fig.3.: Secondary electron image of sample $Al_{66}Ca_{33}$ (as cast) showing the virtually pure $Al_2Ca$ phase.

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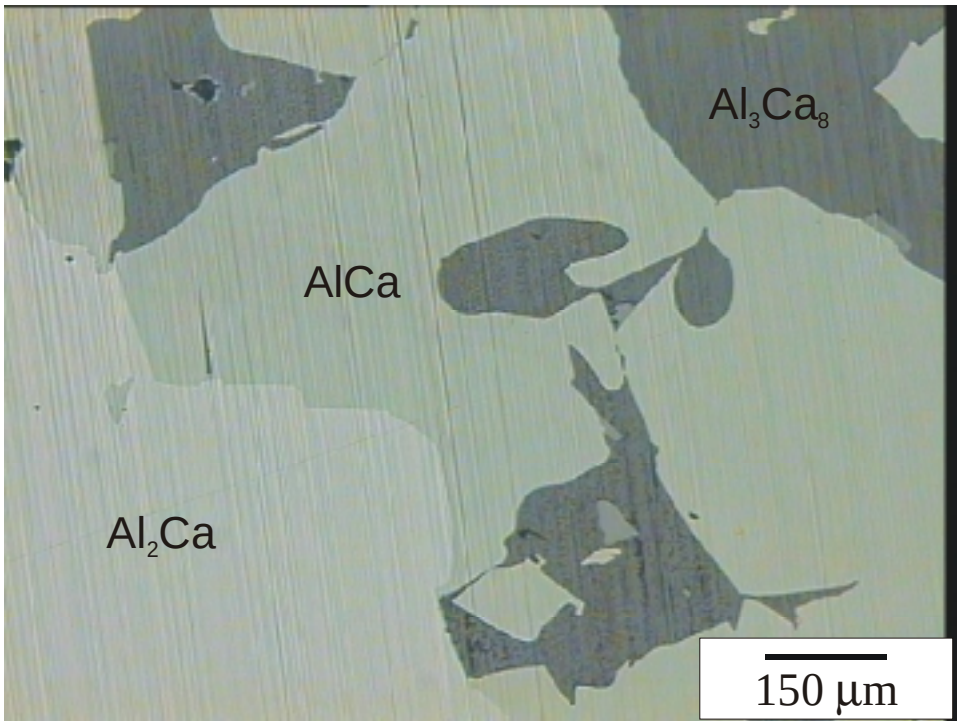


Fig.4.: Optical microscopic image of a three-phase sample with the composition $Al_{50}Ca_{50}$ after the DTA measurement showing still incomplete formation of the AlCa phase.

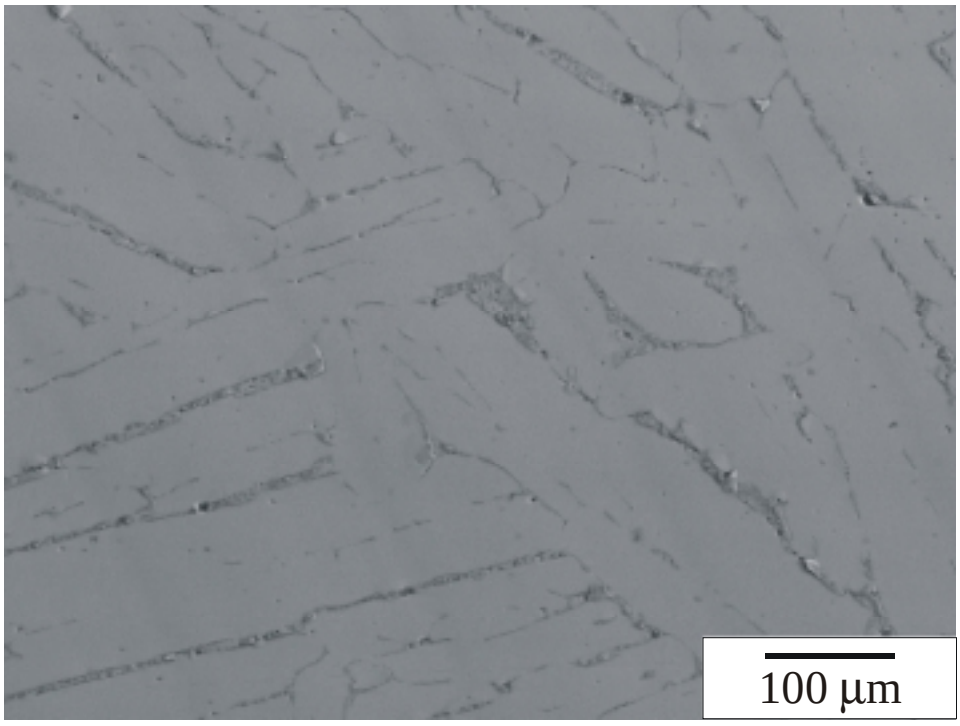


Fig.5.: Secondary electron image of sample $Al_{28}Ca_{72}$ (300°C, 3 weeks) showing the $Al_3Ca_8$ phase and a small amount of eutectic, $Al_3Ca_8$+AlCa.

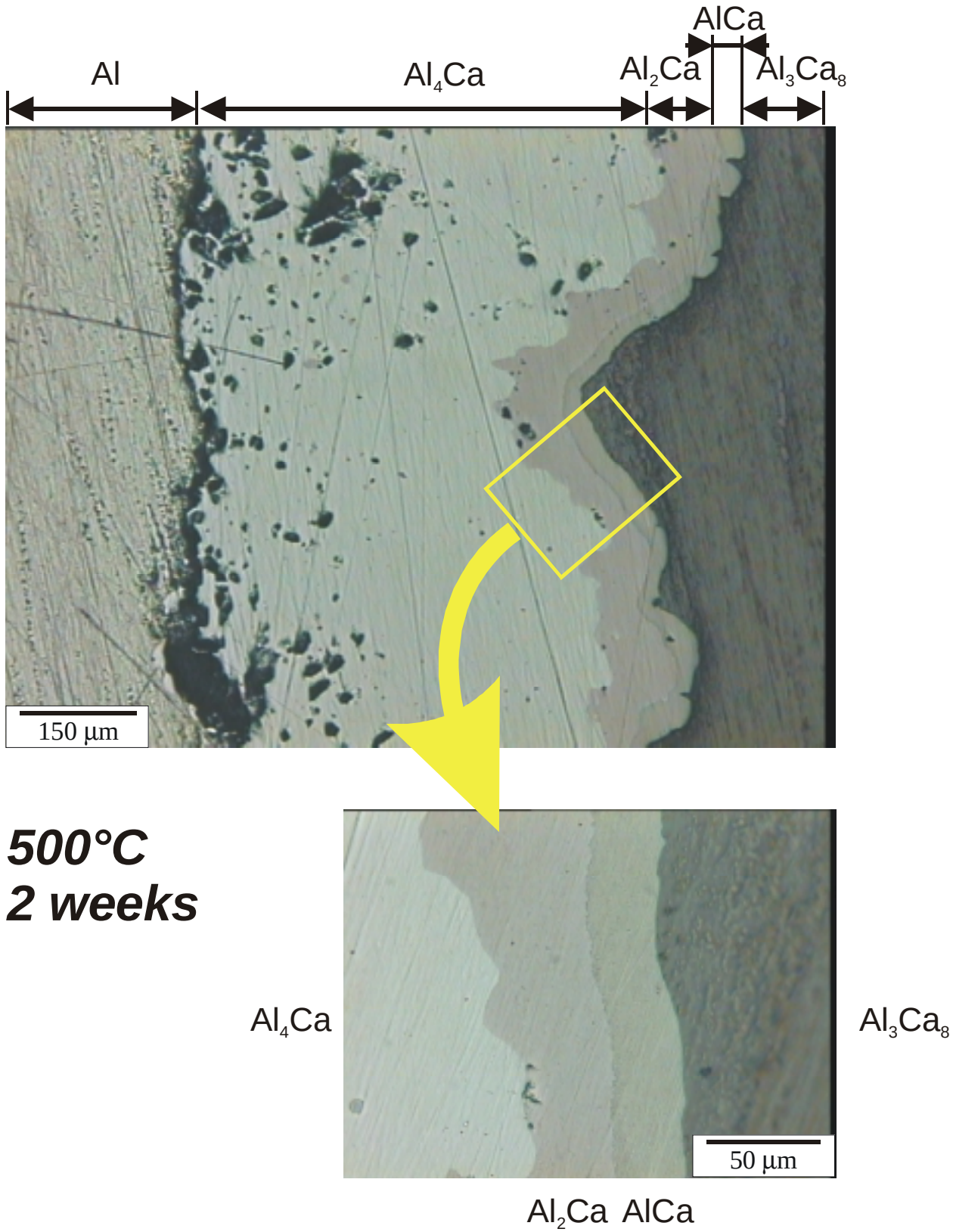


Fig. 6: Cross-section of an Al/Ca diffusion couple annealed 2 weeks at 500°C. The optical image reveals the existence of all the binary phases, including the two new compounds AlCa and $Al_3Ca_8$, also confirmed by EDX.

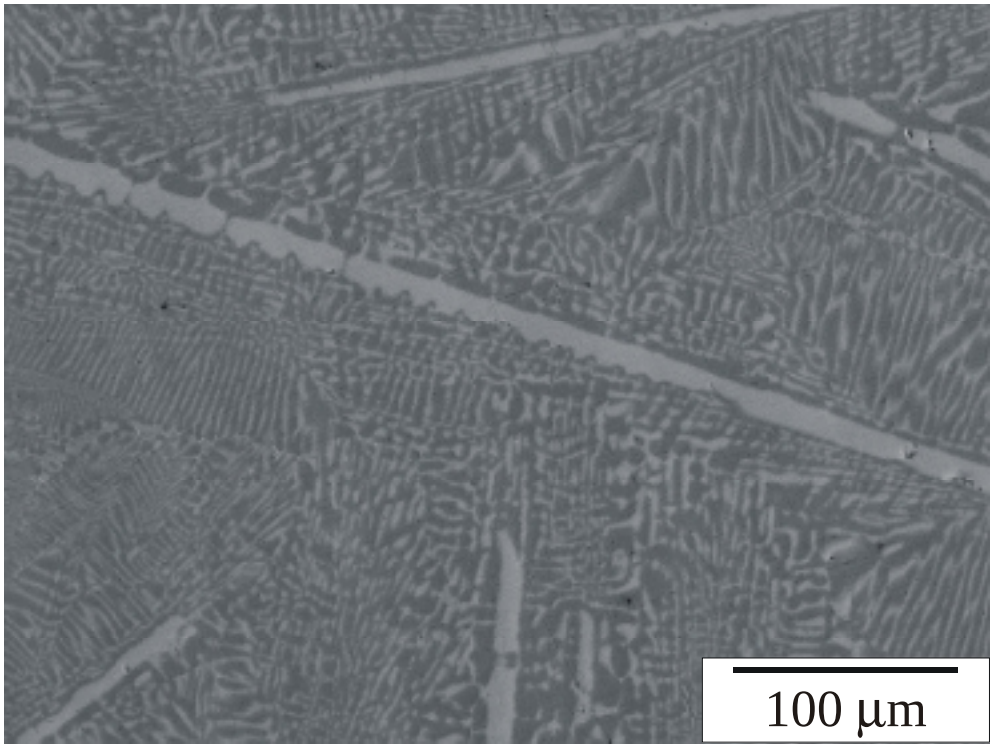


Fig. 7: Secondary electron image of sample $Al_{90}Ca_{10}$ (as cast) showing microstucture of the eutectic reaction L = (Al) + $Al_4Ca$ at 5.1 at.% Ca and some primary dendrites.

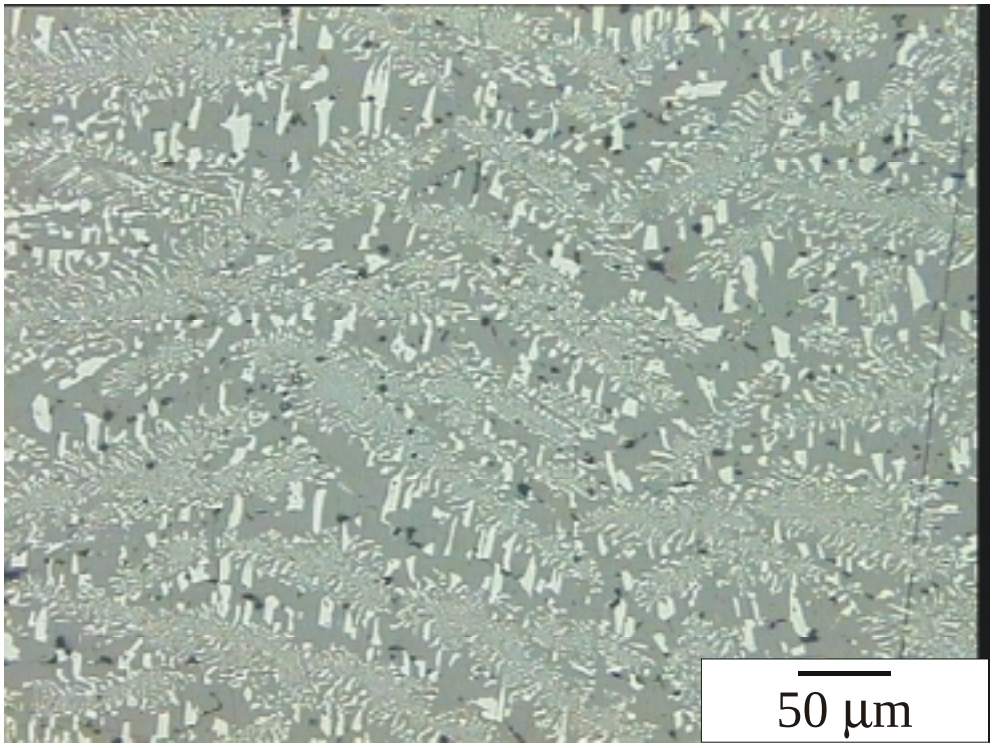


Fig. 8: Secondary electron image of sample $Al_{34.5}Ca_{65.5}$ (as cast) showing microstucture of the eutectic reaction L = AlCa + $Al_3Ca_8$ at 66.3 at.% Ca.

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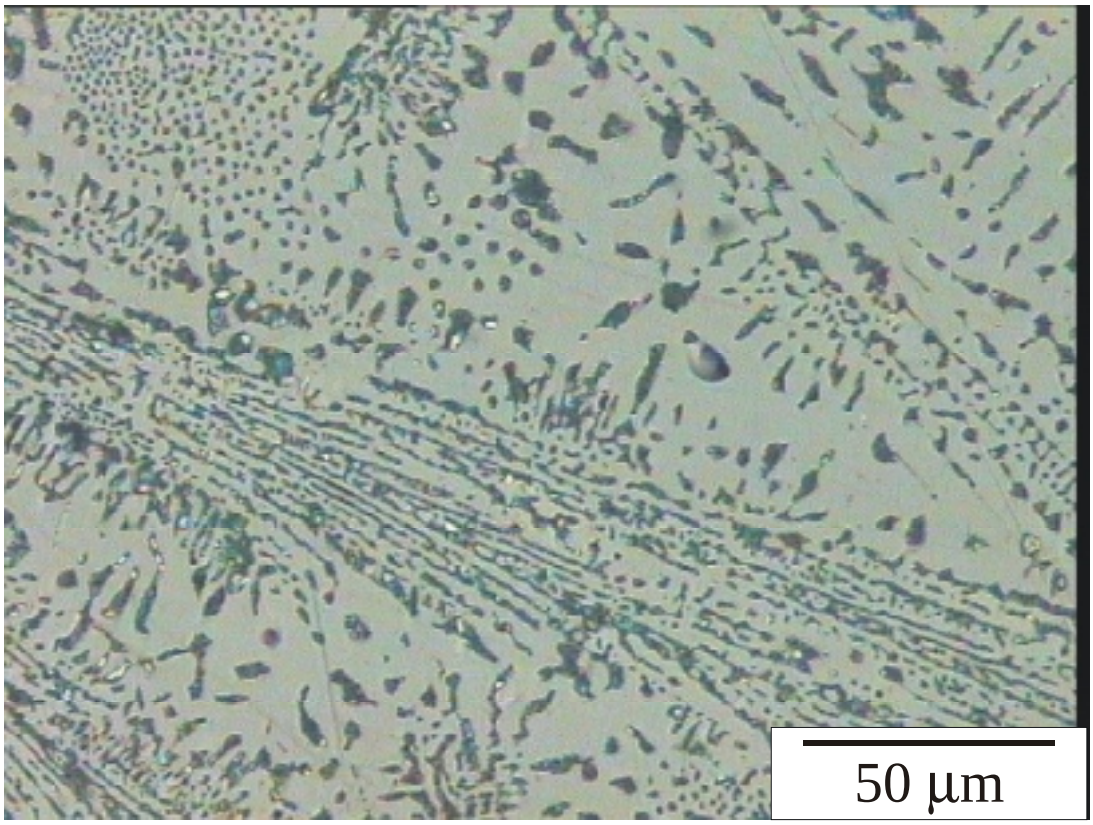


Fig. 9: Secondary electron image of sample $Al_{20}Ca_{80}$ (as cast) showing microstucture of the eutectic reaction L = $Al_3Ca_8$+ (βCa) at 80 at.% Ca.

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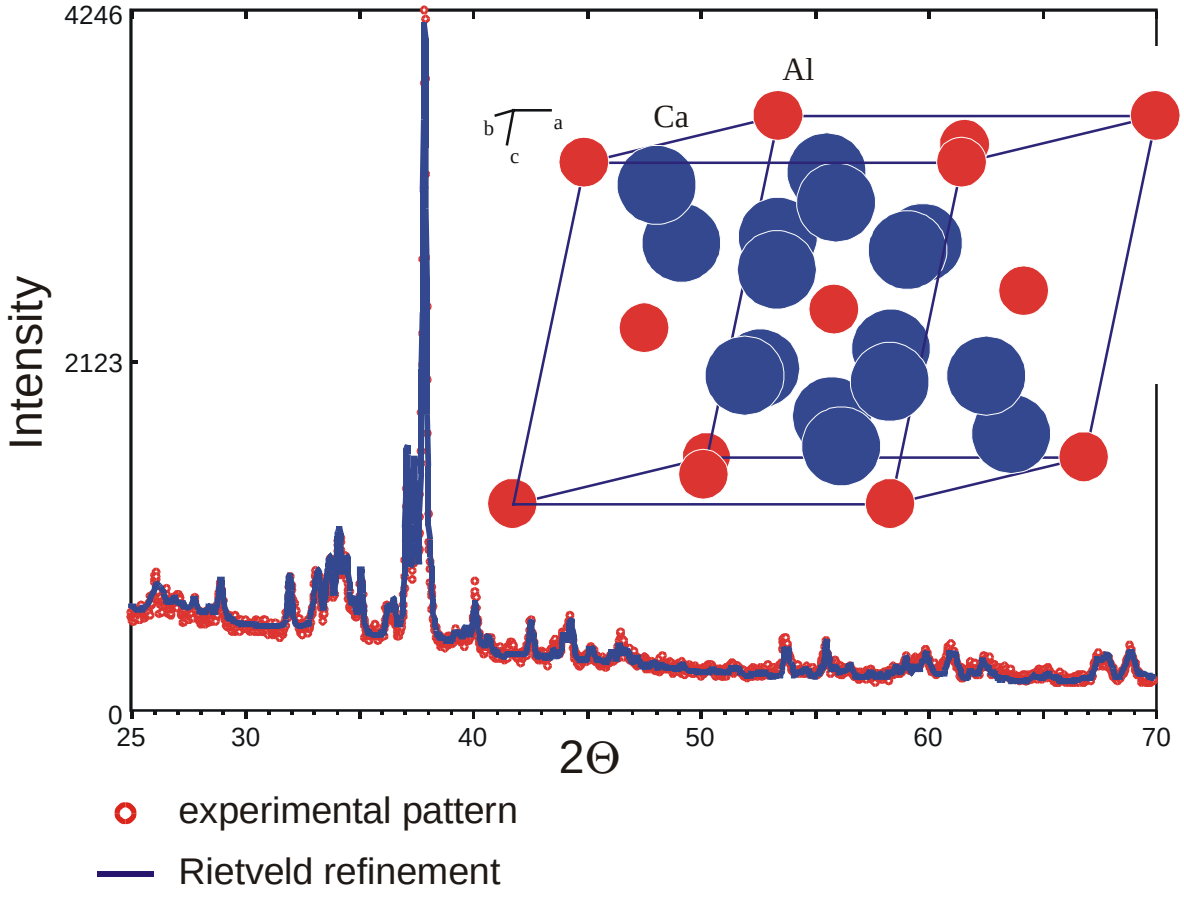


Fig.10: The X-ray powder pattern and crystal structure of $Al_3Ca_8$.