JPEDAV (2009) 30:617–619
DOI: 10.1007/s11669-009-9587-x
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Al-Ca-Sr (Aluminum-Calcium-Strontium)

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The combined effect of the chemically similar additives Ca and Sr to Al- and Mg-based alloys cannot be described adequately by clubbing them together as (Ca + Sr) [2009Jan]. A thermodynamic treatment of this system using the modified quasi-chemical model was carried out by [2008Alj], without considering the ternary solubilities in the binary phases. Supported by new results from a limited number of key experiments and taking into account the solubility data of [2001Zha] along the Al_2Ca-Al_2Sr join, [2009Jan] presented a revised thermodynamic assessment of this system.

Binary Systems

The Al-Ca system was experimentally reinvestigated by [2001Kev1] and assessed thermodynamically by [2001Kev2]. There are four intermediate phases in this system: Al_4Ca ($D1_3$, Al_4Ba-type tetragonal), Al_2Ca ($C15$, $MgCu_2$-type cubic), AlCa (or $Al_{14}Ca_{13}$; monoclinic, space group $C2/m$) and Al_3Ca_8 (Ca_8In_3-type triclinic). The Al-Sr phase diagram [2004Zho] depicts the following intermediate phases: Al_4Sr ($D1_3$, Al_4Ba-type tetragonal), Al_2Sr ($CeCu_2$-type orthorhombic), Al_7Sr_8 (Al_7Sr_8-type cubic) and Al_3Sr_8 (Ca_8In_3-type triclinic). The Ca-Sr system [2003Zho] shows complete liquid and solid solubility. The isomorphous pairs βCa-βSr (bcc) and αCa-αSr (fcc) form continuous solid solutions.

Ternary Phase Equilibria

To identify key experiments, [2009Jan] used preliminary calculations based on binary extrapolations. With starting metals of 99.998% Al, 99.99% Ca and 99.99% Sr, three alloy samples with Al contents ranging between 50 and 79 mass% were prepared and sealed in Ta capsules. Differential thermal analysis was performed at heating/cooling rates of 1 and 5 °C per min. The phases were identified with scanning electron microscopy and electron probe micro-analysis. The sample containing 60 mass% Al had not attained equilibrium.

In their thermodynamic calculations, [2009Jan] used the binary descriptions of [2001Kev2] (Al-Ca), [2004Zho]

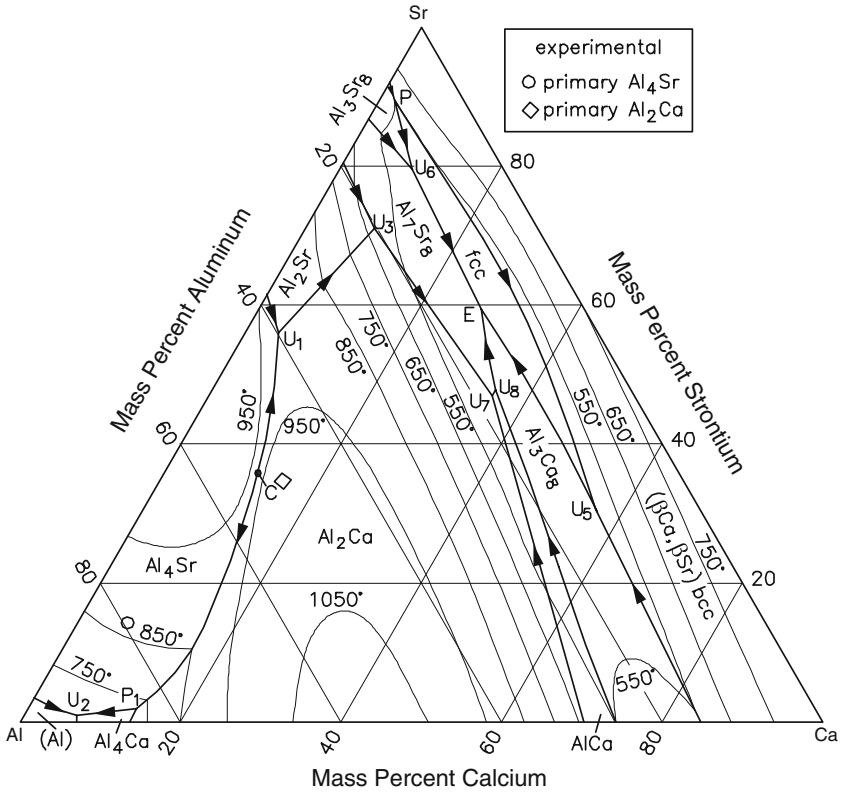

Fig. 1 Al-Ca-Sr computed liquidus projection [2009Jan]

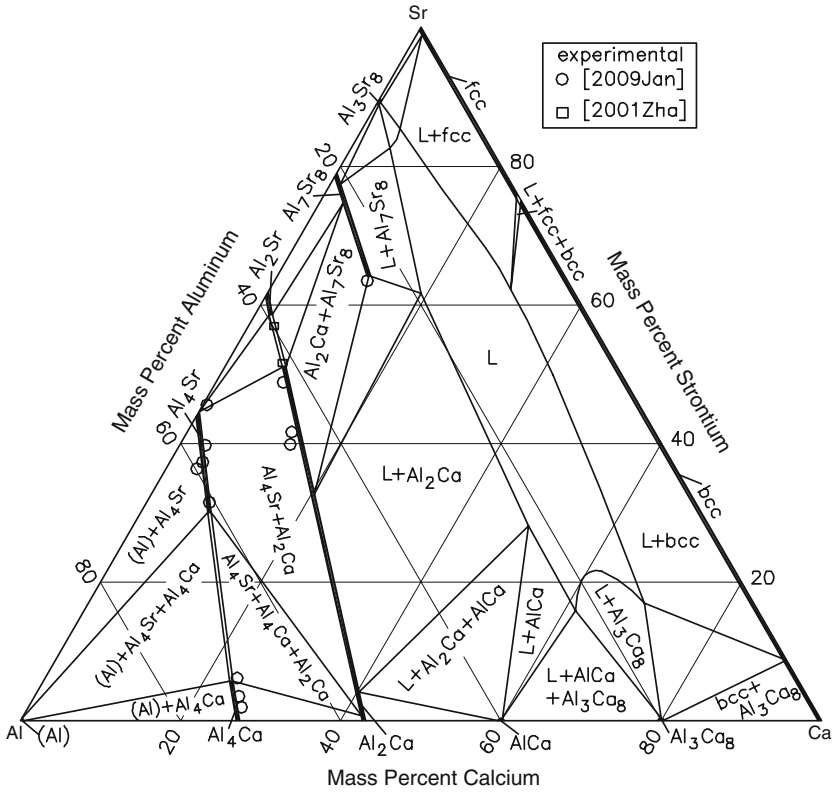

Fig. 2 Al-Ca-Sr computed isothermal section at 500 °C [2009Jan]

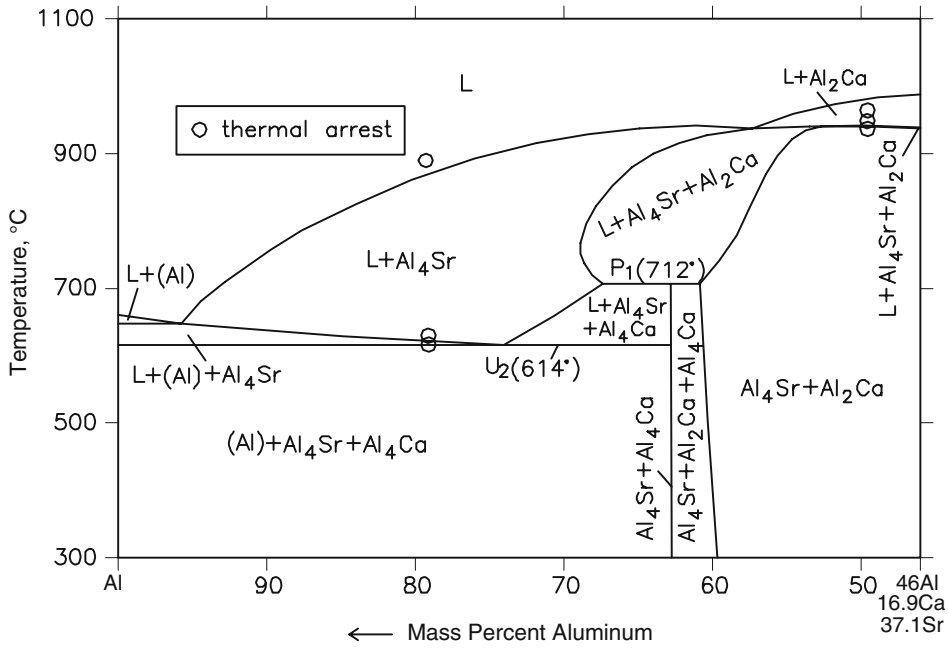

Fig. 3 Al-Ca-Sr computed vertical section along the Al_{100}-$Al_{46}Ca_{16.9}Sr_{37.1}$ join [2009Jan]

(Al-Sr) and [2003Zho] (Ca-Sr). Liquid, fcc (Al, αCa, αSr), and bcc (βCa, βSr) phases were described by the substitutional solution model. No ternary interaction parameters were found necessary to describe these phases. The ternary solubility of Sr or Ca at constant Al content in the binary compounds Al_4Ca, Al_2Ca, Al_4Sr, Al_2Sr and Al_7Sr_8 was

taken into account in the sublattice model. The solubility data along the Al_2Ca-Al_2Sr join from [2001Zha] were included in the optimization. [2001Zha] had shown that, in the formula $Sr_{1-x}Ca_xAl_2$, Al_2Sr dissolves Ca up to $x = 0.108$ and Al_2Ca dissolves Sr in the range of $x = 0.226$-1.0. A two-phase region prevails between $x = 0.108$ and 0.226. Due to lack of experimental data, the ternary solubility in AlCa, Al_3Ca_8 and Al_3Sr_8 compounds was ignored.

The liquidus projection computed by [2009Jan] is shown in Fig. 1. Constant temperature contour lines are shown at 100° intervals between 1050 and 550 °C in Fig. 1. The contour lines between 550 and 250 °C are crowded in the primary crystallization regions of fcc and Al_7Sr_8. To preserve clarity of the figure, these are not shown. A temperature maximum C (939 °C) occurs in the L + Al_2Ca + Al_4Sr univariant line. Eight U-type transition reactions were found: U_1 (907 °C), U_2 (614 °C), U_3 (604 °C), U_4 (554 °C), U_5 (451 °C), U_6 (405 °C), U_7 (360 °C) and U_8 (322 °C). The reaction labeled as U_4 by [2009Jan] is probably a ternary peritectic reaction (relabeled as P in Fig. 1), which yields fcc (αCa,αSr) phase within the ternary region. The binary phase Al_4Ca forms through the ternary peritectic reaction P_1 at 712 °C [2009Jan]. The final solidification is through the ternary eutectic reaction E in the Al-poor region at 235 °C, which is a surprisingly low temperature as compared to the lowest solidification temperatures in the binary systems. More experimental data are needed in this region to validate this prediction.

Figure 2 shows the computed isothermal section at 500 °C [2009Jan]. Al_2Ca dissolves a large amount of Sr replacing more than two-thirds of Ca. Good agreement is seen between the experimental points of [2009Jan] and [2001Zha] and the computed phase boundaries. The liquid in the Al-poor region, where the final solidification occurs at 235 °C, is stable over a large region. As pointed out above, this region needs further experimental investigation including the determination of the ternary solubility in AlCa, Al_3Ca_8 and Al_3Sr_8.

Figure 3 shows a computed vertical section along the Al_{100}-$Al_{46}Ca_{16.9}Sr_{37.1}$ join, on which lies the composition of two experimental alloys of [2009Jan]. The thermal arrests from the two experimental alloys show satisfactory agreement with the computed vertical section.

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