Al-Ca-Mg-Mn-Sr (Aluminum-Calcium-Magnesium-Manganese-Strontium)

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Addition of Ca and Sr to Al-Mg alloys is done in practice to improve their mechanical properties. The industrial Al-Mg alloys often contain small quantities of Mn. Recently, [2009Jan2] presented a thermodynamic description of this quinary system, supplementing it with a limited number of key experiments.

Ternary and Quaternary Subsystems

There are ten sub-ternaries in a quinary system. Thermodynamic descriptions are available for only five of these in this system. The Al-Ca-Sr and Ca-Mg-Sr ternary systems are updated in this issue on the basis of the results of [2009Jan1]. The Al-Ca-Mg system was updated by [2009Rag], based on the results of [2009Jan3]. The Al-Mg-Sr was updated by [2007Rag] from the results of [2007Jan]. A review of the thermodynamic descriptions of the Al-Mg-Mn system appears in this issue.

A thermodynamic analysis of the Al-Ca-Mg-Sr quaternary system was presented by [2009Jan2]. No data appear to be available for the other four quaternary subsystems.

Quinary Phase Equilibria

The presence of a true quaternary or quinary compound was discounted by [2009Jan2]. Preliminary calculations extrapolated from ternary descriptions were used by [2009Jan2] to identify the invariant reactions in the quinary system. The temperatures of such reactions are among the most decisive data for experimental validation. The centroid composition of an invariant reaction, which *fully* converts the reacting phases to the product phases and thereby yields the maximum heat effect, can also be found by calculation. A total of 45 transition-type reactions and one eutectic reaction were found by computation in the quinary region. Twelve out of these 46 reactions contain both liquid and (Mg) and pertain to Mg-rich alloys. Out of the twelve, six were degenerate reactions that cannot be distinguished experimentally from the corresponding quaternary reactions. From the remaining six, only two reactions were chosen as worthy of experimental validation. The two compositions (in mass percent) identified on the basis of calculations were: Mg_{47.73}Al_{31.21}Ca_{3.37}Sr_{1.85}Mn_{15.83} (Alloy 1) and Mg_{76,57}Al_{2,36}Ca_{11,96}Sr_{8,31}Mn_{0,80} (Alloy 2). Two more samples investigated by [2009Jan2] were commercial alloys of



 $\label{eq:rescaled} Fig. 1 \quad Al-Ca-Mg-Mn-Sr \ computed \ section \ along \ Mg_{89.06}Al_{10}Ca_{0.5}Sr_{0.22}Mn_{0.22}-Mg_{91.56}Al_{6}Ca_{2}Sr_{0.22}Mn_{0.22} \ join \ (mass\%) \ [2009Jan2]$



Fig. 2 Al-Ca-Mg-Mn-Sr computed section along $Mg_{78,11}Al_{0.82}Ca_{12.42}Sr_{8.65}Mn_0-Mg_{39,74}Al_{39,21}Ca_{0.99}Sr_{0.06}Mn_{20}$ (mass%) [2009Jan2]

composition (in mass%): $Mg_{90.53}Al_{8.00}Ca_{1.01}Sr_{0.24}Mn_{0.22}$ (Alloy 3) and $Mg_{91.92}Al_{6.16}Ca_{1.49}Sr_{0.21}Mn_{0.22}$ (Alloy 4). Differential thermal analysis (DTA) was performed on all four samples. The thermal arrests from DTA were compared with calculated phase transitions or invariant reactions and the agreement was found to be satisfactory. Only one invariant reaction at 490 °C U₂₀: L + Al₈Mn₅ \leftrightarrow (Mg) + C15 + Al₄Sr + Al₁₁Mn₄ was found experimentally in Alloy 1.

[2009Jan2] calculated liquidus projections and isothermal sections at 700, 500 and 400 °C for five ternary systems with known thermodynamic descriptions. The phase equilibria in the other five ternary systems were calculated by extrapolation from the corresponding binaries. The quinary equilibria were calculated by extrapolating the ternary (or binary) descriptions, assuming the absence of quaternary and quinary phases.

A vertical section was computed along the Mg_{89.06}Al₁₀-Ca_{0.5}Sr_{0.22}Mn_{0.22}-Mg_{91.56}Al₆Ca₂Sr_{0.22}Mn_{0.22} join and compared with the experimental arrests found in the commercial alloys (3 and 4) with 1.01 and 1.49 mass% Ca. Figure 1 shows this comparison. No experimental arrest was found corresponding to the phase transition at the highest temperature (precipitation of Al₈Mn₅ from the liquid). This was attributed by [2009Jan2] to the very small quantity of the precipitate formed and hence a very weak thermal signal not detected by DTA. The transitions at the next two lower temperatures show good agreement. Alloy 3 was expected to show a third signal at 490 °C at the U₂₀ reaction, but it was not detected. The composition of the alloy was far removed from the centroid composition, which resulted in a weak signal (not detected). The second computed section depicts the phase equilibria that lie between the compositions: $Mg_{78.11}Al_{0.82}$. Ca_{12.42}Sr_{8.65}Mn₀ and $Mg_{39.74}Al_{39.21}Ca_{0.99}Sr_{0.06}Mn_{20}$. This particular choice was made to include along the join the two key compositions identified by calculation. Figure 2 shows this section and is compared with the experimental signals from Alloy 2 with 0.80Mn and Alloy 1 with 15.83Mn (mass%). The agreement is good in both cases. The first alloy with 15.83Mn undergoes the six-phase invariant reaction U_{20} : L + Al₈Mn₅ \leftrightarrow (Mg) + C15 + Al₄Sr + Al₁₁Mn₄ at 490 °C.

In Fig. 1 and 2, many phase boundaries are located so close to each other that it is not possible to apply properly the rules of adjoining phase regions for two-dimensional sections in order to label the phase fields. Only those phase fields marked by [2009Jan2] are shown in the figures.

The approach adopted by [2009Jan2] for selection of key alloy compositions opens up new possibilities for tackling the study of phase equilibria in multi-component systems, without the cost of experimentation getting out of hand. The limitations appear to be: (i) if several phase transitions occur in a very narrow temperature interval, the thermal signals may not differentiate between them; (ii) the problem of degeneracy has to be kept in mind and a lower-order reaction should not be mistaken for a true higher-order reaction; (iii) a missing thermal signal at a phase boundary has to be justified by a small computed fraction of the transforming product forming at the boundary; (iv) the finite cooling rates employed in thermal analysis can introduce deviations from equilibrium in the nature, composition and fraction of phases found in the microstructure; and (v) reliable descriptions of at least the ternary subsystems

Section II: Phase Diagram Evaluations

are a prerequisite for computing higher-order phase equilibria. The paper of [2009Jan2] is an important contribution which has highlighted these questions, providing answers to many of them by elegant calculations.

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