Thermodynamic calculations in the AlMnSi system

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ABSTRACT

Thermodynamic calculations using the CALPHAD approach were performed for selection of an AlMnSi alloy. The resulting chemical composition of 93%Al, 4%Si, 3%Mn (mass) was experimentally evaluated with an alloy in the as cast condition, as well as, after heated up to 1100 K, in the liquid state, and cooled down to room temperature at 10 K/min. The characterization of the alloy included the techniques of nano hardness, differential scanning calorimetry, X-ray diffraction, scanning electron microscopy and atomic force microscopy. The thermodynamic calculations using the database for light metal alloys COST2000 showed good agreement with the experimental data.

Key-words: AlMnSi alloys, thermodynamic calculations, CALPHAD.

INTRODUCTION

In recent years the use of thermodynamic modeling via the CALPHAD method has been extensively applied to many types of industrial alloys. Although related to equilibrium conditions, valuable information can be obtained for a variety of practical conditions where equilibrium is not reached, as for example in solidification processes.

Thermodynamic calculations were performed for Al based multi component industrial alloys (1). In the study of recycling of the AISI 380 alloy, the goal was to make it plastically conformable by the spray-forming process (1). The great concern as to the use of Al alloys is the presence of intermetallic compounds. The equilibrium intermetallic phases which can appear in Al-Fe-Si alloys are: θ-$Al_{13}Fe_4$ (monoclinic), Al_8Fe_2Si (hexagonal), and β-Al_5FeSi (monoclinic). Depending on chemical composition and alloy solidification conditions, intermetallic compounds in Al-Si based cast alloys may have a morphology harmful to mechanical properties(2).

In this sense, the use of recyclable alloys in a range of composition in which impurities do not affect their mechanical properties could influence the Al alloy market, allowing their use in applications where only high purity alloys with high formability are. A direct consequence would be a decrease of the use of primary Al, an element well known for its high energy fabrication consumption.

In the rapid solidification process of spray-forming, an increasing in the solubility fields were expected and, consequently, a change in the morphology of the intermetallics. However, the result of processing the 380 alloy showed a refined microstructure (1), but formation of the most detrimental phase occurred, the monoclinic β-Al_5FeSi, thus reducing alloy ductility and lowering mechanical formability.

The usual alternatives are heat treatment for precipitate dissolution and/or chemical composition fitting. In the first one, the dissolved phases in the Al matrix during homogenization in thermal treatment may precipitate again during artificial or natural aging. Thermodynamically stable phases are not affected by thermal treatment (2, 3). In the second alternative, the conventional metallurgical processes to eliminate iron harmful effects in aluminum alloys has been largely focused on chemical solutions, either limiting maximum content of iron to avoid formation of the primary compound Al-Fe-Si, or modifying the crystalline structure of this compound to another one with a higher-symmetry lattice.

A possible solution is microstructure control through co-injecting inoculated intermetallic particles (1,3). These particles, pulverized during spray-forming, would act as a substrate for heterogeneous nucleation favoring nucleation and grow into the cubic or α-Al(Fe,Mn)Si phase, at expenses of the β-AlFeSi, allowing a more refined microstructure with the elimination of brittle phases. In this case it was necessary an alloy selection serving as inoculants with the above described function.

In this work thermodynamic calculations are presented, using the COST2000 (4) database and the ThermoCalc software for system selection and inoculate chemical compound definition. The resulting alloy was characterized in terms of structure and morphology of the phases present.

MATERIALS AND METHODS

Material

Several compositions were calculated in different systems and the selection of the alloy occurred in the Al-Mn-Si system. The criteria for that analysis were:

i) a system containing α phase, that would be stable close to the melting temperature of the alloy 380;
ii) field composition without the β-AlMnSi phase.
iii) no iron element in its composition and
iv) low silicon content.

The analysis of solidification was made using the Scheil formalism, i.e. no diffusion in solid state or gradients of concentration in the liquid phase, and an isopleth section was calculated with constant silicon content.

During the calculations a list of existing phases in the system Al-Mn-Si and thermodynamically properties were adopted from the thermochemical database of light alloys COST2000. Calculations were carried out using the ThermoCalc software. The resulting alloy composition was: 93 % Al, 3% Mn and 4% Si (mass).

Al, Si and Mn elements, with a minimum purity of 99,7%, were used to prepare the chosen alloy by arc-melting in argon atmosphere.

Alloy characterization

The phases present in the material were identified and characterized by X-rays diffraction (DRX) using KαCu radiation, nano hardness using instrumented penetration tests were performed on the different phases with a Berkovich tip and a load of 500 μN, scanning electron microscopy (SEM) equipped with an energy dispersive system (EDS) and atomic force microscopy (AFM).

The samples were submitted to conventional metallographic preparation consisting of grinding, mechanical polishing and etching with 10% NaOH in distilled water.

Differential scanning calorimetry (DSC) was carried out in the as cast alloy. Both the sample holder and the reference material were made of Al_20_3. A solid sample weighting 23 mg was taken from the as cast alloy. The measurements were carried out in argon atmosphere, from room temperature up to 1100 K, with heating and cooling rates of 10 K/min. The procedure to determine the beginning of the reactions was the extrapolated “onset”, as recommended in the book of Höhne (5). The choice of the heating cycle for the measures owing to the undercooling in the reverse cycle.

RESULTS AND DISCUSSION

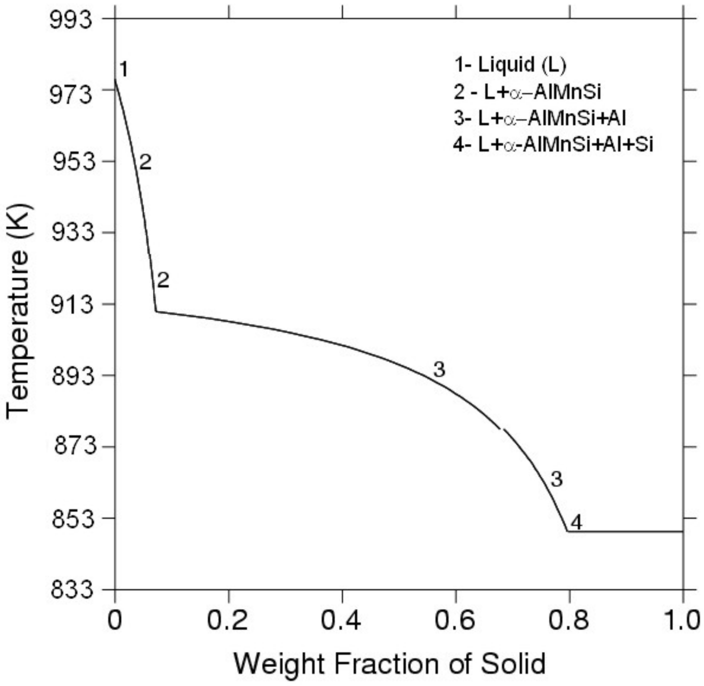
The alloy chosen after simulations had the chemical composition: 93%Al, 4% Si and 3% Mn (in weight percent). The analysis of solidification using the Scheil formalism and an isopleth section, calculated with constant silicon content of 4% mass, are shown in figure 1 (a) and (b), respectively.

The thermal analysis curves obtained by DSC are shown in Figure 2, with the numbers 1, 2, 3 and 4 representing the same phases as in Figure 1. Both samples, in the as cast condition and after solidification in the DSC at 10 K/min, indicated the presence of three phases. The Δ (delta) symbols in Figure 1 (b) indicate the experimental transformations temperatures measured from the DSC essay, in quite good agreement with the calculations.

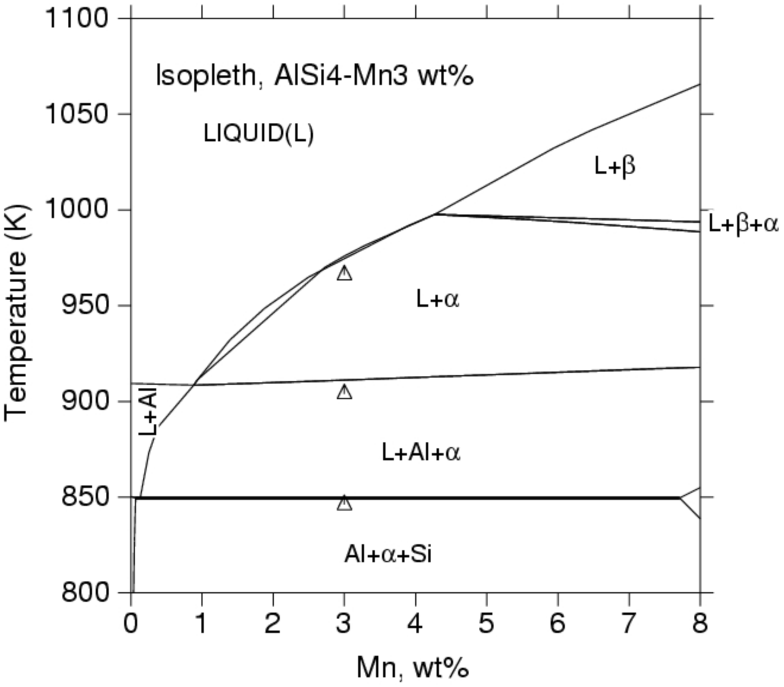
The x-ray diffraction patterns are presented in Figure 3. The three phases obtained from the calculations are present: Al, Si and α-AlMnSi.

Scanning electron and atomic force microscopy showed different morphologies and phase distribution for the as cast and the heat treated samples. Figure 4 is an atomic force microscopy image, in the height mode, of the as cast sample. Four distinct regions can be identified:

1. the aluminum matrix;
2. the α-AlMnSi phase, which appears white;
3. silicon, close to the α-AlMnSi precipitate;
4. and the darker region, named in this paper as Al solid solution more rich in silicon.



(a)



(b)

Figure 1 – Thermodynamic calculations and experimental results. (a) Solidification diagram using the Scheil formalism and (b) isopleth calculated with Si 4 wt%. The measured transition temperatures on cooling, after DSC essay, are superimposed.

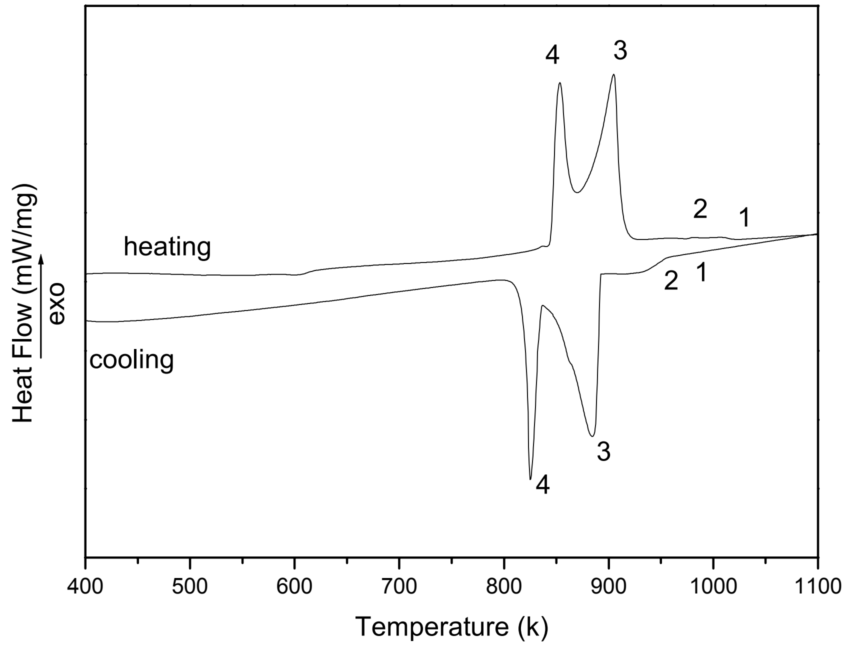


Figure 2 - DSC curves showing the phase transformations on heating and cooling, with10 K/min.

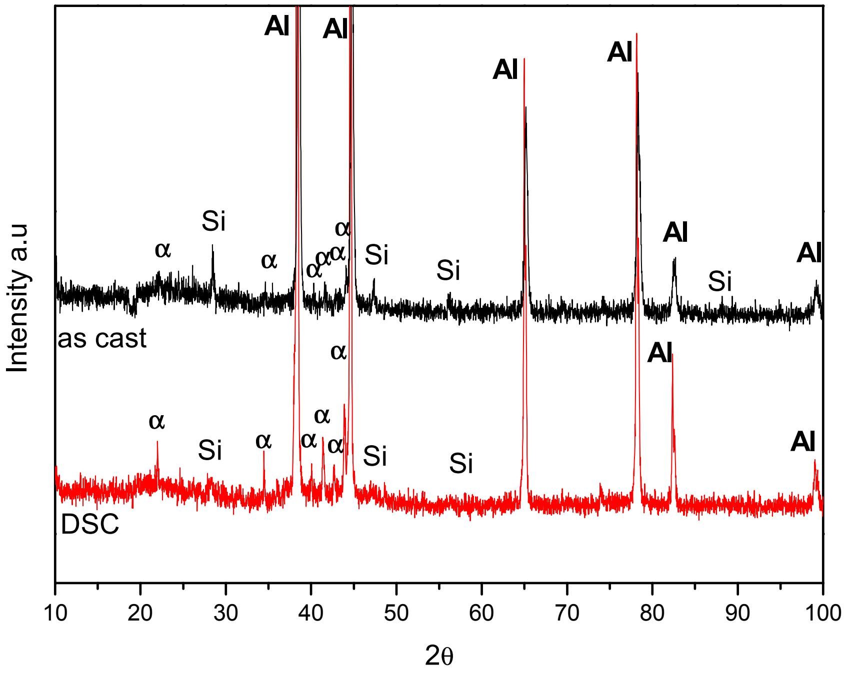


Figure 3 - X-ray diffraction patterns of the Al alloy in the as cast condition and after heating and cooling at 10 K/min

The microstructure of the alloy after the heat treatment in the DSC is shown in figure 5. In the Al matrix, the primary α-AlMnSi appears with large compact polyhedron and

Chinese script morphologies. Two distinct Al solid solution regions are not present anymore. Silicon is now an interdendritic eutectic. The sequence o solidification observed in the sample at the rate a 10 K/min is good agreement with these observations.

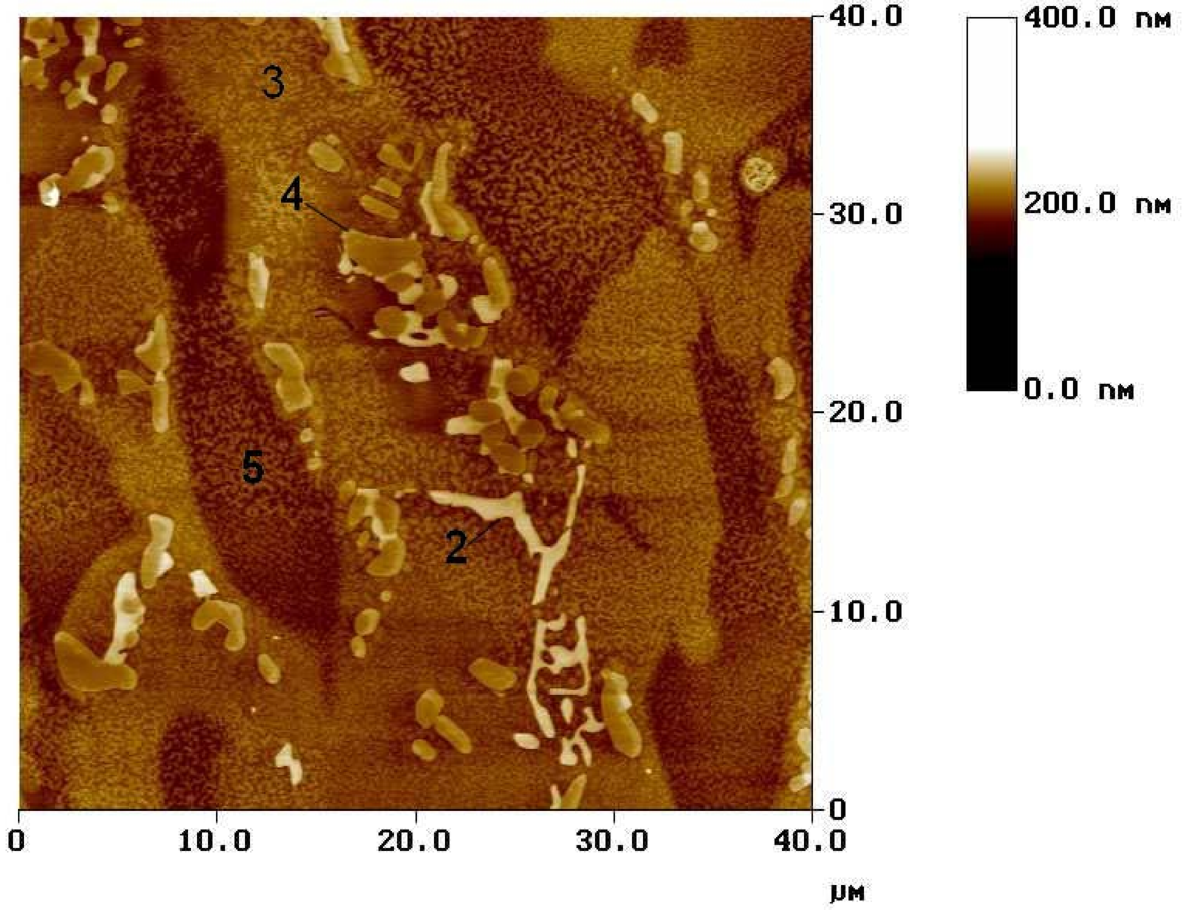
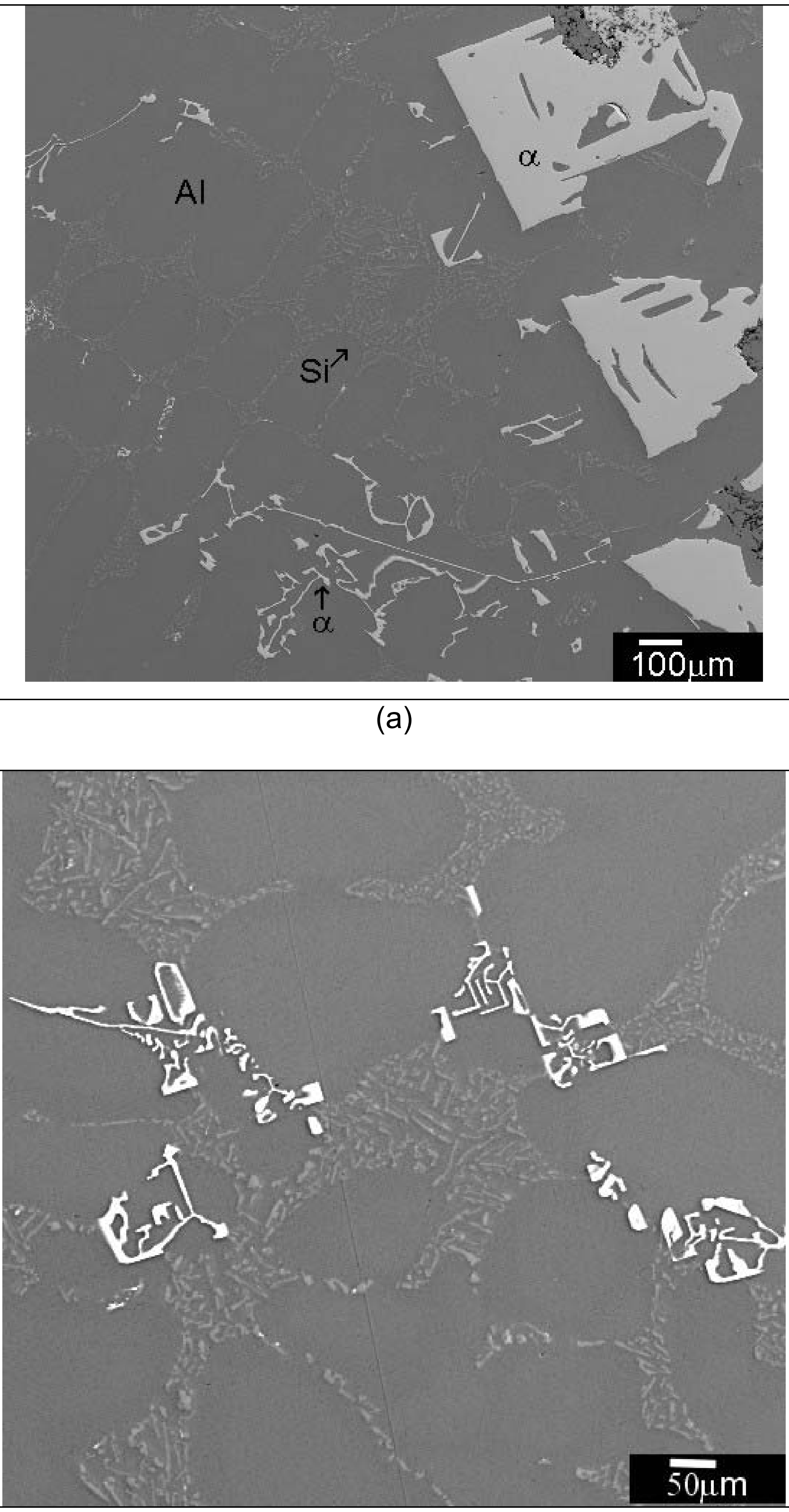


Figure 4 - Atomic force microscopy height image obtained in contact mode. Micrograph showing the solidification microstructure present in the sample in the as cast condition. (2) White phase: α-AlMnSi (3) Matrix: Al. (4) Si. (5) Aluminum solid solution.



(b)

Figure 5 – Scanning electron microscopy of the alloy after treatment in the DSC, at 10K/min cooling rate.
Matrix: Al. White regions: α-AlMnSi, with two morphologies, massive polyhedron and Chinese script. Interdendritic: Si eutectic.

The results measured in the test of nano hardness in the regions identified in Figure 4 are showed in the Table 1. The values presented of nano hardness (H) and reduced elastic modulus (E_R) are mean values, σ is standard deviation. In the darker region identified by number 5 in the Figure 4, denominate in this article as Al solid solution more rich in silicon showed the nano hardness lightly higher than that of the region 3. The regions 2 and 4 presented approximately the same hardness, but with higher dispersions compared with the matrix.

Table 1 - Results of the instrumented penetration tests of the $Al_{93}Mn_3Si_4$ alloy phases as cast.

Region / Phase	**H** (GPa)	σ	**E_R** (GPa)	σ
2 / α-AlMnSi	5,5	0,7	89,9	5,2
3 / Matrix-fcc	1,4	0,1	92,3	9,5
4 / Silicon	5,3	1,7	91,6	13,5
5 / Matrix-fcc	1,5	0,1	90,7	4,2

CONCLUSIONS

The temperature of transformations measured in thermal analysis and the phases characterization by SEM, DRX and AFM are in good agreement with the isopleth calculation and phases prevision.

The cooling rate may be mentioned as one of the factors which determine morphology and chemical composition of those phases

Thermodynamic calculations presented in this paper are equilibrium calculations and should not be considered for non-equilibrium microstructure effects. However, results presented here show they can be used in alloy selection and may be a great help for interpreting experimental results.

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