Thermodynamic Simulations of Multicomponent Phase Diagrams on the Base of Aluminum and Experimental Microstructure Analysis of the Alloys with a Considerable Quantity of Multiphase Eutectics

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Experimental and thermodynamical investigations fragments of phase diagrams of the multicomponent systems Al-Zn-Mg + additions of the eutectic forming elements (Ni, Fe, Mn, Cr) in different combinations were carried out using ThermoCalc software with TTAL5 and COST 507 data bases. Morphological microstructure features of ternary eutectics were studied in the as-cast and heat-treated conditions. The alloys with considerable quantity of eutectics were found, including alloys with very dispersive microstructure after solidification at not high cooling rates. Phase composition and chemical composition of aluminum solid solution were calculated at the temperatures 10 °C below nonequilibrium solidus. Fine eutectic morphology disposes to fragmentation and spheroidization of eutectic intermetallic particles during solution treatment.

Keywords: Aluminum, eutectic alloys, phase diagrams.

1. Introduction

The main part of aluminum alloys could be strengthened by heat treatment. The structure of these alloys consists of dispersed strengthened aluminum solid solution with small amount of surplus phases. The alloys of the Al-Zn-Mg system play the important role between them. The recent studying carried out in National University of Science and Technology “MISiS” showed that the properties of Al-Zn-Mg system alloys can be improved by using additions of transition metals, which increase the casting properties, technological plasticity and form additional strengthening particles of the eutectics origin and particles formed during decomposition of Al-solution during high temperature treatment [1]. It must be noted that mainly binary eutectics were used in these works such are (Al)+Al3Ni and (Al)+Al3FeNi. The aim of the present work is the based on examination of the multicomponent phase diagrams search of the new alloying systems of the Al-Zn-Mg matrix for the formation of the structures with high fraction of the ternary eutectics.

2. Experimental

Following materials were used for alloys preparation: aluminum A99 (99,99 %), zinc (99,9%), magnesium (99,9%) and master alloys: Al–20%Ni, Al–10%Fe, Al–10%Mn, Al-10%Cr.

Alloys with composition corresponding to ternary eutectics (Al)+Al6Mn+Al3Ni, (Al)+Al6Mn+Al3Fe, (Al)+Al3Fe+Al1Cr and alloys with Al-4Zn-4Mg matrix additionally alloyed by eutectic forming elements were examined in the present work.
Alloys were prepared in a laboratory electric resistance furnace in graphitic crucibles. Casting was performed in a steel ingot mould with a cooling rate of \( \sim 5 \) K/sec. Phase-transition temperatures were determined by using differential scanning calorimeter Labsys DSC-1600. Structural analysis was performed using light (LM) and scanning electron microscopy (SEM). The concentration of alloying elements in the matrix aluminum solid solution was determined by electron microprobe analysis (EMPA). Calculation of fragments of phase diagrams, phase composition and the composition of Al-solid solution was carried out using the program ThermoCalc data bases and software (version TCW-4, database TTAL5).

3. Results and discussion

It is well known, that dispersion of eutectics increases with increase of the amount of forming phases. At the first stage the metallographic analysis of the different ternary eutectics structures was carried out. The literature [2] and calculation data about the chemical composition of these eutectics was used. It was found that the most disperse structure have ternary eutectics \((\text{Al})+\text{Al}_6\text{Mn}+\text{Al}_3\text{Ni}, (\text{Al})+\text{Al}_6\text{Mn}+\text{Al}_3\text{Fe}, (\text{Al})+\text{Al}_3\text{Fe}+\text{Al}_7\text{Cr})\) (Fig. 1).

![Microstructure of ternary eutectics alloys in the as-cast state (SEM):](image)

**Fig. 1.** Microstructure of ternary eutectics alloys in the as-cast state (SEM):

- a) Al-1,7%Fe-0,3%Cr;
- b) Al-0,75%Mn-1,25%Fe;
- c) Al-5,3%Ni-1,3%Mn

The composition Al-4Zn-4Mg was chosen as a basic one. This matrix alloy is characterized by considerable effect of strengthening by dispersed particles and as a result has high strength in combination with satisfactory technological properties in comparison with the alloys with concentration ration Zn/Mg>2.
Before carrying out experiments with the aim to determine the influence of selected additions of the eutectic forming elements (Fe, Ni, Mn, Cr) on the structure of the matrix alloy, the analysis of phase diagrams of systems of Al-4Zn-4Mg-Ni-Mn, Al-4Zn-4Mg-Fe-Mn, Al-4Zn-4Mg-Fe-Cr was made: polythermal and isothermal sections of these diagrams were plotted (Fig. 2, Fig. 3).

![Fig. 2. Polythermal section system Al-4Zn-4Mg-1.2%Mn-%Ni](image)

In accordance with plotted sections the compositions of the alloys, which contain the maximal fraction of the ternary eutectics were selected. The phase and aluminum solid solution compositions were calculated. The results of these calculations for some of the examined alloys are represented in Tables 1 and 2.

Table 1. The phase composition of alloys in the temperature quenching, % vol. (calculation/experiment)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( T, ^\circ C ) liquidus</th>
<th>( T, ^\circ C ) solidus equilibrium</th>
<th>( T, ^\circ C ) solidus nonequilibrium</th>
<th>( T, ^\circ C ) quench</th>
<th>The phase composition of alloys in the temperature quenching, % vol. (calculation/experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-4Mg-4Zn-1.6Ni-0.8Fe-0.5Mn</td>
<td>638</td>
<td>556</td>
<td>445</td>
<td>500</td>
<td>( \text{Al}_6\text{Mn} ) 1.8/1.7, ( \text{Al}_9\text{FeNi} ) 7.1/6.9</td>
</tr>
<tr>
<td>Al-4Mg-4Zn-4.2Ni-1Mn</td>
<td>628</td>
<td>558</td>
<td>445</td>
<td>500</td>
<td>( \text{Al}_6\text{Mn} ) 3.3/3.0, ( \text{Al}_9\text{FeNi} ) 9.9/9.3</td>
</tr>
<tr>
<td>Al-4Mg-4Zn-0.5Cr-0.9Fe</td>
<td>710</td>
<td>568</td>
<td>445</td>
<td>500</td>
<td>( \text{Al}_6\text{Mn} ) 2.4/2.1, ( \text{Al}_9\text{FeNi} ) 2.4/2.0</td>
</tr>
<tr>
<td>Al-4Mg-4Zn-1Cr-1Fe</td>
<td>750</td>
<td>572</td>
<td>445</td>
<td>500</td>
<td>( \text{Al}_6\text{Mn} ) 2.6/2.0, ( \text{Al}_9\text{FeNi} ) 5.5/5.1</td>
</tr>
</tbody>
</table>

Table 1 shows the calculated results and experimental data obtained by metallographic method (SEM) for the volume fraction of insoluble phases of crystallization origin at the quenching temperature (10-15 °C below the non-equilibrium solidus). These results show that the differences between calculation and experimental data are insignificant.

Table 2 shows the results of calculation and experimental EMPA data for concentrations of alloying elements in the matrix aluminum solid solution at the quenching temperature. It follows from the
Table 2 that the convergence of calculation results and experimental data is quite sufficient here as well.

Table 2. Alloying Al-matrix calculations and the data on EMPA

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Concentration in (Al) solid solution (calculation / experiment), % mass.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>Al-4Mg-4Zn-1,6Ni-0,8Fe-0,5Mn</td>
<td>4,4</td>
</tr>
<tr>
<td>Al-4Mg-4Zn-4,2Ni-1Mn</td>
<td>4,6</td>
</tr>
</tbody>
</table>

Investigation of microstructure of Al-4Zn-4Mg alloys with examined additions of the eutectic forming elements (Fig. 4) showed that the morphological characteristics of eutectics are similar to those obtained on the alloys without zinc and magnesium (Fig. 1). The nature of the microstructure shows the possibility of substantial improvement in the properties of the investigated matrix as a result of the structure of ternary eutectics.

Fig. 4. Typical microstructure of alloys Al-Zn-Mg with additions of the eutectic forming elements in the case cast (a-c) and quenched T4 (d) conditions: a, d) Al-4Zn-4Mg-1,2%Mn-4,2%Ni; b) Al-4Zn-4Mg-0,9%Fe-0,5%Cr; c) Al-4Zn-4Mg-1.2%Fe-0.75Mn
Taking as an example the microstructures of the alloy Al-4Zn-4Mg-1,2%Mn-4,2%Ni in as-cast and as-quenched state (T4) it is possible to make a conclusion that during the heating before quenching the fragmentation and spheroidization of the eutectic phases with relatively even distribution of the particles in the volume takes place. Such morphology of the phases of crystallization origin must positively effect on mechanical properties of the alloys [1].

4. Conclusions

1. The influence additions of the eutectic forming elements nickel, iron, manganese and chromium on the structure of alloys based on the matrix Al-4Zn-4Mg is studied.

2. Using the «Thermo-Calc» software the polythermal and isothermal sections of the Al–Zn–Mg–Ni–Mn, Al–Zn–Mg–Fe–Cr, Al–Zn–Mg–Fe–Mn systems were plotted. The phase composition, volume fractions of the phases and composition of the aluminum solid solution was calculated. Comparison of thermodynamic calculations and experimental data showed good convergence of results.

3. On the base of the obtained in the present work results and structural studies it is possible to make a conclusion about the prospects of further studies of alloys based on a matrix system Al-Zn-Mg with the addition of elements (Ni, Mn, Fe, Cr), which are forming dispersed ternary eutectics.

Present work was made in the frame and under financial support of the program of the foundation and development of National University of Science and technology "MISIS"

References
