Quantitative phase analysis of Mg-Al-Zn and Mg-Zn-Zr alloys

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Abstract. A quantitative method has been developed for the phase analysis of magnesium alloys of the Mg-Zn-Al (MA2-1 and MA5) and Mg-Zn-Zr (MA14) systems based on the measurement of the lattice parameters of a solid solution, the use of Vegard's law, and balance equations of chemical and phase composition. Examples of the application of the technique for assessing changes in the content of alloying elements in a solid solution and the number of intermetallic phases as a result of heat treatment of MA2-1 alloy are presented.

1. Introduction
Quantitative phase analysis makes it possible to objectively assess the structural-phase state of structural materials after various technological operations for the preparation of semi-finished products and welding. In our works, as applied to alloys of the Al-Mg-Li and Al-Cu-Li systems, a method for quantitative phase analysis based on measuring the lattice parameters of a solid solution, Vegard's law, and balance equations of chemical and phase composition is developed [1, 2]. This technique was used to assess the ratio of intermetallic phases during deformation, heat treatment and welding of industrial aluminum and lithium alloys [3-5], magnesium-based alloys [6-8]. In the present work, a similar technique is developed for the most widely used industrial alloys of the Mg-Al-Zn (MA2-1 and MA5) and Mg-Zn-Zr (MA14) systems.

2. Materials and research methods
The method of quantitative phase analysis was developed in relation to the most common magnesium alloys, the compositions of which are given in table. 1.

| Table 1. The compositions of the alloys in weight% |
|---|---|---|---|
| Alloy grade | Al | Zn | Zr |
| MA2-1 | 4.9 | 1.1 | - |
| MA5 | 8.5 | 0.9 | - |
| MA14 | - | 6 | 0.9 |

The lattice parameters of MA2-1 alloy after quenching from 200 and 300°C were determined on a DRON-3 diffractometer by recording the reflection (220) in CuKα radiation with a diffraction angle of ~75°.

3. Results and discussion
Alloys Mg-Al-Zn Al alloys are characterized by the dominance of Al in comparison of Zn, therefore, it can be reasonably assumed that zinc is in solid solution. Therefore, it can be assumed that the alloy is two-phase and consists of a solid solution based on magnesium (α-phase) and β-phase (Mg17Al12). Moreover, in the solid solution contains a constant amount of zinc, equal to its concentration in the alloy and a variable aluminum content, which is determined from the lattice parameter of the solid solution. The mass percentages of both phases in the two-phase region of the double alloy can be determined from the balance equations of the chemical and phase compositions of the alloy:
The accuracy of the determination depends on the accuracy of the determination of the lattice parameters and the slope of the “Vegard” dependences. In our case, with an error in determining the lattice parameter of 0.0001 nm, it amounts to 3-5% of the measured values, namely, the composition of the solid solution and the amount of the β phase. This is a good indicator, especially considering the fact that other methods for determining these quantities simply do not exist. Figure 1a shows the dependence of the α phase (\(a_\alpha\)) on the content of the solid solution in the aluminum and zinc in magnesium (figure 1), given in the Pearson monograph [9]. Thus, the Al content in the α phase is determined directly from (4) in (5), and then, knowing the chemical composition of the alloy, it is possible to calculate the amount of intermetallic phase from (1) in (2).

\[
X^\alpha_{Al(Zn)} W_\alpha + X^\beta_{Al(Zn)} W_\beta = 100 X^0_{Al(Zn)}
\]

From here:

\[
W_\beta = \frac{X^0_{Al(Zn)} - X^\alpha_{Al(Zn)}}{X^\beta_{Al(Zn)} - X^\alpha_{Al(Zn)}}
\]

The composition of the solid solution (\(X^\text{Al}_\alpha\)) is related to the lattice parameters by Vegard's law, then:

\[
a_\alpha = a_{m0} + \frac{\Delta a}{\Delta X} X^\text{Al}_\alpha + \frac{\Delta a}{\Delta X} X^Zn
\]

\[
c_\alpha = c_{m0} + \frac{\Delta c}{\Delta X} X^\text{Al}_\alpha + \frac{\Delta c}{\Delta X} X^Zn
\]

- a change in the lattice parameters “\(\alpha\)” and “\(c\)” by 1 weight percent Al and Zn.

These values were calculated by the least squares method from the experimental values of the “\(\alpha\)” and “\(c\)” parameters of the HCP lattice of a solid solution of aluminum and zinc in magnesium (figure 1), given in the Pearson monograph [9]. Thus, the Al content in the α phase is determined directly from (4) in (5), and then, knowing the chemical composition of the alloy, it is possible to calculate the amount of intermetallic phase from (1) in (2).

Figure 1. The dependence of the aluminum content in the solid solution (\(X^\text{Al}_\alpha\)) (a) and the amount of β-phase (\(W_\beta\)) (b) in the MA2-1 alloy (Mg-4.9Al-1.1Zn) on the value of the lattice parameter of the solid solution (\(a_\alpha\)).

The accuracy of the determination depends on the accuracy of the determination of the lattice parameters and the slope of the “Vegard” dependences. In our case, with an error in determining the lattice parameter of 0.0001 nm, it amounts to 3-5% of the measured values, namely, the composition of the solid solution and the amount of the β phase. This is a good indicator, especially considering the fact that other methods for determining these quantities simply do not exist. Figure 1a shows the dependence of the α phase (\(a_\alpha\)) on the content of the solid solution in the function of the lattice period “\(\alpha\)" and the dependence of the amount of β phase in the MA2-1 (Mg-4.9Al-1.1Zn) alloy on figure 1b. An example of the application of the method for the quantitative phase analysis of MA2-1 alloy in the form of a pressed profile as the initial state and after quenching from 300°C is shown, while the lattice parameter of the solid solution decreased from 0.3192 to 0.3187 nm, which corresponds to an increase in the aluminum content in the solid solution (\(X^\text{Al}_\alpha\)) from 3.3 to 4.8% and a decrease in the amount of intermetallic phase (\(W_\beta\)) from 4.3 to 3%. Similar dependences are given for the MA5 alloy (Mg-8.5Al-0.5Zn), figure 2 and MA14 (Mg-6Zn-0.9Zr), figure 3.
Figure 2. The dependence of the aluminum content in the solid solution ($X_{\alpha}^{Al}$) (a) and the amount of $\beta$-phase ($W_\beta$) in the MA5 alloy (Mg-8.5Al-0.5Zn) on the value of the lattice parameter of the solid solution ($a_\alpha$).

Figure 3. The dependence of the aluminum content in the solid solution ($X_{\alpha}^{Al}$) (a) and the amount of the $\beta$ phase ($W_\beta$) (b) in the MA14 alloy (Mg-6Zn-0.9Zr) on the value of the lattice parameter of the solid solution ($a_\alpha$).

Information on the quantitative ratio of phases in alloys allows reliable control of the state of alloys after deformation and heat treatment. In addition, knowing the phase composition, one can calculate the volumetric and linear dimensional changes accompanying the heat treatment. It must be taken into account that a change in the density and specific volume with a change in the composition of a magnesium-based solid solution is affected not only by a change in the lattice parameter, but also by the substitution of alloying elements with an atomic weight different from magnesium. Thus, when calculating the specific volume, it is necessary to take into account the average atomic weight as well as the lattice distance. The specific volume, $V_\alpha$, of a single-phase magnesium-based solid solution can be calculated as follows [10]:

$$V_\alpha = \frac{N_A a_\alpha^2 c_\alpha \sqrt{3}}{2 A_\alpha n}$$  \hspace{1cm} (6)

Where: $N_A$ is the Avogadro number $6.022 \times 10^{23}$ (mol$^{-1}$); $a_\alpha$ and $c_\alpha$-parameters of the lattice of Mg solid solution at 25ºC (cm) (calculated from (2)); $n$ is the number of atoms per unit cell $= 2$. For pure Mg, we obtain $V_{Mg} = 0.5755 \text{ cm}^3/\text{g}$ ($A_{Mg} = 24.32 \text{ g/mol}$).

The atomic weight ($A_\alpha$) for a solid solution of aluminum in magnesium is calculated from the ratio:
Where: \( Y^\alpha_{Al} \) - atomic percentage of aluminum in the \( \alpha \) phase; \( A_{Al} \) - atomic weight of aluminum = 26.97 g/mol.

In accordance with the rule of mixtures, the specific volume of the Mg-Al alloy is calculated from the ratio:

\[
V_{alloy} = \frac{W_\alpha V_\alpha + W_\beta V_\beta}{100}
\]

Where: \( W_\alpha \) and \( V_\alpha \) are wt. % and specific volume of \( \alpha \)-solid solution, respectively; \( W_\beta \) and \( V_\beta \) are mass% and specific volume of the \( \beta \) phase, respectively. According to PDF # 73-1148, the density of the \( \beta \) phase (\( Al_{12}Mg_{17} \)) is 2.088 g cm\(^3\), which corresponds to a specific volume of \( V_\beta = 0.4789 \) cm\(^3\)/g.

A change in the specific volume of a solid solution with a change in its concentration and a simultaneous change in the amount of the second phase have a major effect on the dissolution / precipitation processes. It's obvious that:

\[
\Delta V = V_2 - V_1
\]

The relative change in volume is:

\[
\frac{\Delta V}{V_1} = \frac{V_2 - V_1}{V_1}
\]

4. **Conclusion**

A method for quantitative phase analysis has been developed as applied to magnesium alloys of the Mg-Al-Zn and Mg-Zn-Zr systems, which include the most well-known industrial alloys MA2-1, MA5 and MA14. The method is based on the measurement of the lattice distances of a solid solution, Vegard's laws, and balance equations of chemical and phase composition. An example of the application of the developed technique for calculating the concentration of alloying elements in a solid solution and the amount of intermetallic phases in the MA2-1 alloy after heat treatment is shown.

5. **References**

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