Dissolution rates and solubility of some metals in liquid gallium and aluminum

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Abstract. The effect of liquid gallium and aluminum on some hard metals leading to dissolution and formation of intermetallic compounds (IMC) under static conditions and rotation of a specimen is studied. The solubility parameters from the Clapeyron-Clausius equation were considered to estimate the stability of still not studied metals. The presented experimental data on solubility and corrosion in a wide temperature range allow to calculate a number of parameters useful in manufacturing and application of master-alloys.

The breakdown of materials as a result of interaction with liquid metals is determined mainly but not exclusively by solubility. If the decisive stage is diffusion of atoms through a layer of an intermetallic compound (IMC) formed, an increase of the liquid metal flow rate (without cavitation) does not result in an increase of a dissolution rate. For transition metals in liquid aluminum in the laminar flow area, the experimental and theoretical effective widths of the boundary layer differ several tens times [1].

During corrosion a melt interacts with hard metal granules (pieces) without forced mixing. These studies [2] were performed to compare results of industrial melting of master-alloys with available data on solubility and dissolution kinetics.

The dilution in liquid Ga and Al was carried out by isothermal exposure of a fine-disperse hard metal, discharge of the melt from a crucible to a porous plate and filtration in inert atmosphere with subsequent selection of specimens for analysis. Experimental values of solubility up to several atomic percents are shown as straight lines in semilogarithmic coordinates (figure 1). Values of coefficients $A$ and $B$ for some metals in the equation

$$\lg C = A - B/T$$

and their solubility ($C$ in at. %) are given in table 1.

The solubility of IV-group metals in gallium is presented in figure 2 for three temperatures. Manganese displaying much higher solubility than its nearest neighbors chromium and iron falls out from the general series of solubility decrease for IV-group metals in gallium. The solubility formula (1) agrees with the thermodynamic expression for equilibrium between solid and liquid phases deduced from equal activity of dissolved and solid components relative to the same chosen standard state and also from some other simplifications. If a pure solid component B is in equilibrium with a liquid phase, melting is the only phase transition, and the heat capacity of the solid and overcooled liquid components is almost equal, the partial Gibbs energy is

$$\Delta G = RT \ln a_{B,1} = (\Delta S_{\text{melt}} + \Delta S_0)T - (\Delta H_{\text{melt}} + \Delta H_0).$$

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Figure 1. Temperature dependence of solubility of the fourth group metals zirconium and hafnium in gallium.

Table 1. Solubility of some metals in liquid gallium and aluminum.

| Metal      | IMC     | Interval, T, K | $\log C = A - B/T$ | $C$, at.% | 673 K | 773 K |
|------------|---------|----------------|-------------------|-----------|-------|-------|
|            |         |                | $C = A - B/T$     |           |       |       |
| **In gallium** |        |                |                   |           |       |       |
| Copper     | CuGa₂   | 500–700        | 3.52              | 1.61      | 15.0  | 28    |
| Calcium    | CaGa₄   | 500–700        | 3.25              | 2.30      | 0.62  | 1.7   |
| Scandium   | ScGa₃   | 623–973        | 3.99              | 3.65      | 3.5·10⁻² | 0.20 |
| Titanium   | TiGa₃   | 600–800        | 2.60              | 3.12      | 9.5·10⁻³ | 3.9·10⁻² |
| Germanium  | Ge      | 400–600        | 3.60              | 1.78      | 8.9   | 19.8  |
| Vanadium   | VGa₄    | 600–800        | 3.20              | 4.0       | 2.0·10⁻³ | 1.0·10⁻² |
| Chromium   | CrGa₄   | 600–800        | 2.70              | 3.10      | 1.2·10⁻² | 4.9·10⁻² |
| Manganese  | MnGa₆   | 500–700        | 5.40              | 3.90      | 0.40  | 2.3   |
| Iron       | FeGa₃   | 500–700        | 4.00              | 3.85      | 1.9·10⁻² | 0.11 |
| Cobalt     | CoGa₃   | 500–700        | 3.50              | 3.10      | 7.8·10⁻² | 0.31 |
| Nickel     | NiGa₃   | 500–700        | 2.52              | 1.85      | 0.59  | 1.35  |
| Zirconium  | ZrGa₃   | 500–800        | 3.05              | 4.22      | 6.0·10⁻⁴ | 3.9·10⁻³ |
| Hafnium    | HfGa₃   | 500–800        | 6.56              | 7.25      | 6.1·10⁻⁵ | 1.5·10⁻³ |
| **In aluminum** |        |                |                   |           |       |       |
| Scandium   | ScAl₃   | 960–1200       | 7.36              | 7.28      | 1.2   | 19.6  |
| Titanium   | TiAl₃   | 960–1200       | 3.03              | 3.94      | 0.12  | 0.56  |
| Vanadium   | VAl₁₀   | 960–1000       | 4.40              | 4.88      | 0.33  | 2.10  |
| Chromium   | CrAl₇   | 970–1170       | 5.00              | 5.26      | 0.55  | 4.10  |
| Zirconium  | ZrAl₃   | 960–1200       | 6.60              | 7.58      | 0.10  | 1.90  |
| Hafnium    | HfAl₃   | 960–1150       | 6.90              | 7.50      | 0.25  | 4.50  |

With certain assumptions, the concentration $C$ of a dissolved substance (in at. %) may be used instead of activity $a$. For binary systems having no IMC, estimated values and values determined from calorimetric measurements are in satisfactory agreement if the concentration of a dissolved substance is smaller than 2 at. %. Equation 2 takes the form
\[ \lg C = \left( 2 + \frac{\Delta S_{\text{melt}} + \Delta H_{\text{melt}}}{2.3R} \right) - \frac{\Delta H_{\text{melt}} + \Delta H_{\text{melt}}}{2.3RT} = A - B/T , \]  

where \( \Delta H_B = 2.3R \Delta B - \Delta H_{\text{melt}} \) and \( \Delta S_B = 2.3R \Delta A - \Delta S_{\text{melt}} \) are determined from experimental values of \( A \) and \( B \).

Figure 2. Solubility of the fourth group metals in gallium at:
1 – 573 K; 2 – 673 K; 3 – 773 K

For systems of compounds, the \( \Delta H_B \) value characterizes the enthalpy of displacement of a compound rather than of an initial pure metal.

The reverse problem, i.e. determination of solubility from individual properties of metals, can be solved on the base of melting temperature and heat with the use of the Clapeyron-Clausius equation or solubility parameters [3]. Estimation of solubility from parameters of two nearest neighbors gives better results. Thus, estimated and experimental (in brackets) solubility values for middle elements of the eighth group triads at 773 K are as follows, at.\%: 0.36 (0.35) for cobalt, 1.27 (1.27) for rhodium, 0.11 (0.053) for iridium. Hence, satisfactory results may be obtained even quantitatively.

When there is no interaction, the dissolution consists in breakdown of metallic bonds holding atoms on the surface of metal and their replacement by bonds between atoms of different kinds. Corrosion resistance of a metal in this case is proportional to binding energy of atoms in the solid state. The second stage is the removal of reaction products from surface into the depth of the liquid-metal solution. Diffusion through the solution layer adjacent to a hard metal acts often as a limiting process. Considering the dependence between the dissolution rate and the mixing rate, a motive force here is the diffusion gradient. The dissolution rate in this case is determined by the Fick law, i.e. it is directly proportional to the difference of concentrations \( (C_{\text{H}} - C) \) of a dissolved substance on the boundary with a solid state and in the bulk and is inversely proportional to the width of the diffusion layer. The rate of corrosion decreases with time according to equation:

\[ \frac{C}{C_{\text{H}}} = 1 - \exp(-\alpha S \tau/V), \]  

where \( S \) is the surface area of dissolution, \( V \) is the volume of a liquid metal, \( \alpha \) is the dissolution rate constant, and \( \tau \) is time.

The rates of corrosion of substances are compared at similar \( S/V \) values. Corrosion for a time interval is determined by the equation:

\[ Q = d C_{\text{H}} (V/S) [1 - \exp(-\alpha S \tau/V)], \]  

where \( d \) is a specific mass of a liquid-metal solution.

The mass loss as a result of corrosion depends on the properties of the medium and the specimen and the \( S/V \) ratio.
The duration of exposure of specimens till complete breakdown versus inverse temperature is presented in semilogarithmic coordinates in figure 3. For convenient comparison of corrosion resistance of various metals, the values are calculated for a reference thickness (15 μm). Provided that upon dissolution of a specimen the solubility is still far from saturation, a direct dependence between the exposure time and the specimen thickness was assumed (table 2).

![Figure 3. Temperature dependence of complete corrosion time (lgτ) of hard metal specimens in gallium: left – metals of the first long period; right – other metals.](image)

| Metal     | Specimen thickness (μm) and their ratio | Ratio of specimen exposure times | 673K | 773K |
|-----------|-----------------------------------------|---------------------------------|------|------|
| Scandium  | 30/18; 1.7                               | 2.1                             | 1.8  |
| Iron      | 35/19; 1.8                               | 2.2                             | 1.9  |
| Cobalt    | 40/20; 2.0                               | 2.4                             | 2.05 |
| Nickel    | 30/15; 2.0                               | 2.2                             | 1.9  |

The specimens were treated similarly.
Over a wide temperature range, the values of corrosion exhibit a linear dependence:

\[ \lg \tau = A + B/T, \]  

where \( \tau \) is time, s; \( T \) is temperature, K; \( A \) and \( B \) are constants.

The coefficients from (6) determined from plots in figure 3 are listed in table 3 along with the temperature ranges.

It is seen from the plots in figure 3 that the exposure time till specimen breakdown increases abruptly at a certain temperature different for each metal. Consequently, each metal may be characterized by a temperature, below which the first stage of the corrosion process is limiting. Above this temperature, the process is limited by the second stage, namely diffusion. It also explains almost identical inclination angles of the corresponding lines on the plots for different metals. The values of the coefficient \( B \) do not differ more than twice from the average value for the whole group of metals.
Table 3. Corrosion of pure metals in gallium.

| Metal      | Coefficients from equation (6) | Temperature range, K | Corrosion at 673K, mg/cm²-h |
|------------|---------------------------------|----------------------|-----------------------------|
|            | −Α , 10³ | B, 10³                 |                      |                             |
| Scandium   | 0.50    | 2.97                   | 593–873               | 1.10                        |
| Titanium   | 1.15    | 3.81                   | 773–1073              | 2.0·10⁻²                    |
| Zirconium  | 1.40    | 3.23                   | 573–873               | 7.3                         |
| Hafnium    | 1.45    | 3.30                   | 623–873               | 14.3                        |
| Iron       | 0.75    | 2.85                   | 573–973               | 7.1                         |
| Cobalt     | 1.85    | 3.46                   | 773–973               | 2.3                         |
| Nickel     | 2.00    | 2.77                   | 573–873               | 2.0·10²                     |

Metals can be arranged according to the minimum temperatures, at which their stability in gallium becomes linear. This sequence characterizes the change in the Me–Me bond strength as compared with Me–Ga. If the atomic bond energies differ slightly, their detachment from the surface and “solvation” by a solvent obeys a statistical law. The strength of atomic bonds in a hard metal correlates with melting, sublimation and evaporation heats (see figure 4). Metals with small ΔH values have weaker stability. Elements with covalent bonding (Si, Ge) require greater energies for detachment of atoms comparing with long-range order breakdown in metals. On the lgr – ΔHₘₑₙₐₜ plot (figure 4a), these elements are displaced to the right. However for the ΔH sublimation (figure 4b) the deviations for Si and Ge fit into the general scatter of points. Analysis of corrosion versus the ratio of surface tension of a metal σₘₑ to the surface tension of gallium (figure 5) shows that metals with a face-centered cubic (FCC) lattice are below the curve plotted in the system of coordinates lgr = σₘₑ/σ₈ₐ. Metals with a body-centered cubic (BCC) and hexagonal (hexag.) lattice are in the vicinity of the smooth line, whereas those with a diamond-type (diam.) structure are located much higher. Figure 6 displays the relationship between physical and chemical properties of elements and the periodical character of their corrosion stability. This allows to predict the corrosion stability of metals, for which the experimental data are not available.

The corrosion of specimens in a liquid metal as a function of the medium motion rate is also described by equations (4) and (5), where only the dissolution rate constant (α) is changed. The functional dependence on the liquid metal motion rate ν was established as the power function αₘₒᵗ = b·νⁿ. The exponent (n) is 0.5 for a laminar flow and 0.2 for a turbulent flow [5]. However when corrosion decreases substantially (10 times), the constant α is better described by the linear dependence αₘₒᵗ = a₀ + b·ν. If initial sections of the dissolved transition metal dependences are used, the dissolution rate constants are calculated from plots in semilogarithmic coordinates ln(Cₕ/Cₕ₋₀) vs S·ν/V. The corrosion of Sc, Ti, Zr, Hf in liquid aluminum was studied at temperatures 1073 and 1173K and the specimen rotation rate equals to 1 and 2 rps. Their dissolution rates are listed in table 4.

Table 4. Dissolution rates n of Sc, Ti, Zr, Hf in aluminum melt, 10⁻³ g/cm²·s.

| Metal      | Time of experiment, 10⁻³ s | Dissolution temperature and rotation rate |
|------------|-----------------------------|------------------------------------------|
|            | 1073 K                      | 1173 K                                   |
|            | 1 rps 2 rps                 | 1 rps 2 rps                              |
| Scandium   | 3.6–10.8                    | 2.4                                      |
| Titanium   | 3.6–10.8                    | 3.9                                      |
| Zirconium  | 3.6–7.2                     | 4.3                                      |
| Hafnium    | 3.6–7.2                     | 4.1                                      |
Figure 4. Dependence of $\lg \tau$ of hard metals in gallium at 773 K on atomic melting $(a)$ and sublimation $(b)$ heat. Values for Li and Pb are given for their melting temperatures.

Figure 5. Dependence of $\lg \tau$ of metals in gallium at 773 K on relative surface tension of metals.

The leading stage of the process is established from the character of breakdown. When the dissolution surface is uniform, diffusion plays a main role. Intermetallic compounds $\text{MeAl}_3$ are formed in the considered systems and therefore the values refer to the phases in equilibrium with the melts. The rates of formation of these phases under chosen conditions are higher than the rates of their dissolution. For zirconium, this was earlier established by Eremenko et al. [6]. Diffusion mobility of these complexes is small. Therefore the process of dissolution will involve the following stages: diffusion of refractory metal atoms in the intermetallic layer and their transition to the melt and only after that refractory metal atoms will diffuse in the diffusion boundary layer. The assumed specimen rotation rates (1 and 2 rps) are comparable with free convection.

These results show that saturation of melts with alloying components may be accelerated by using of an alloying metal in a disperse form and also by intensive mixing. The dissolution rate increases appreciably when the temperature is raised from 800 to 900°C. However even at 1000–1100°C large pieces of metals are dissolved for several hours if mixing is weak. The results obtained can be used to
calculate diffusion coefficients, effective radii of diffusing particles and their dependences on temperature and activation energy in liquid aluminum. Inaccurate values of kinematic viscosity only slightly affect the calculations, whereas solubility data give the main error.

![Graph](image)

**Figure 6.** Characteristic of corrosion stability of elements (in points and mg/cm²·h) in gallium at 673 K as a function of atomic number.

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