Supporting Information for

**Thermodynamics Calculation of Reaction Synthesis Pathways for Ag-Al2O3 Powder By First-Principles Calculations**

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#### 1 Introduction

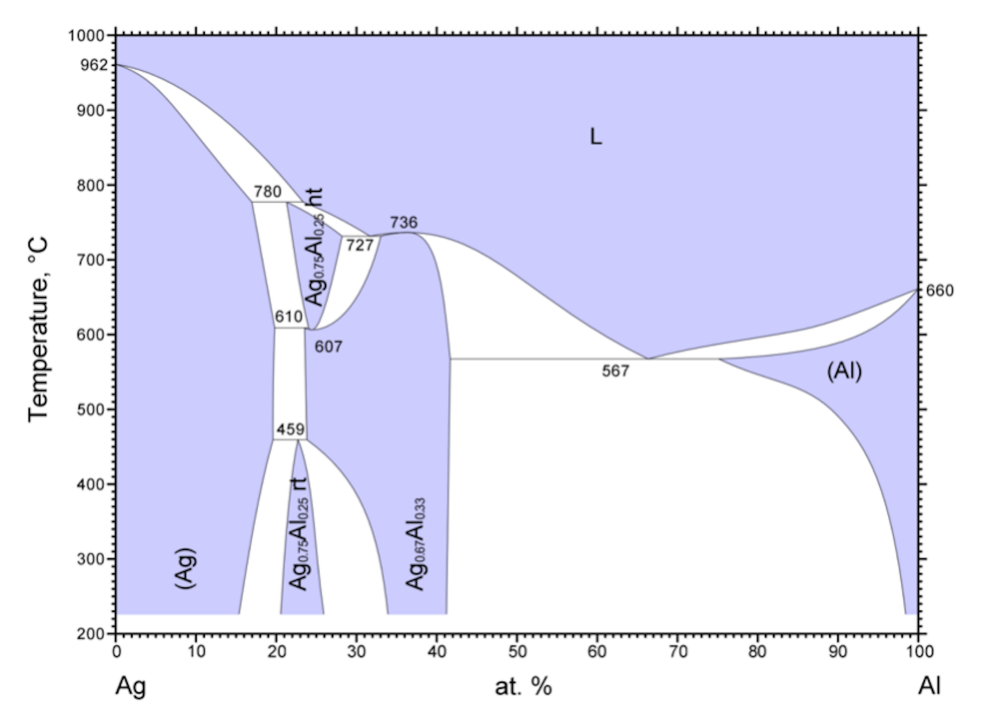


Fig. S1 Binary phase diagrams of Ag-Al

#### 3.2 Calculation of Enthalpy of Formation of Each Phase and the Change of Enthalpy with Temperature

|  |  |
| --- | --- |
|  |  |
| (a) | (b) |
|  |  |
| (c) | (d) |
|  | |
| (e) | |

Fig. S2 The change of enthalpy of different phases with temperature (a)Al2O3, (b)Ag2Al, (c)O2, (d) Ag, (e)Al

#### 3.3 The Results of the Calculation of the Function of the Free Energy of Each Phase with Respect to Temperature

|  |  |
| --- | --- |
| a | b |
| (a) | (b) |
| c | d |
| (c) | (d) |
|  | |
| (e) | |

Fig. S3 The change of Gibbs and Helmholtz free energy with temperature(a)Al2O3,(b)Ag2O,(c)AgAlO2, (d)Ag2Al ,(e)Ag soluted in Al

#### 3.4 Calculation and Analysis of Free Energy of Reaction Formation

The calculated results of the relative free energies of the phases are listed in the form of curves. However, the calculated data for different phases cannot be directly added or subtracted using Equation S1, as the temperature values obtained in the calculation process are not consistent. Therefore, only polynomial function fitting is performed on the obtained data (Figure S2) and the possible phases in the reaction process. The form of the fitted function is shown in Equation S1. The mean square deviation between each fitted function and the original data points is less than 0.001, indicating a good fit. Based on this, to calculate ΔGr or ΔAr for any reaction mentioned in this paper, one only needs to add or subtract the coefficients of the fitted curves for each phase in Figure S3. Due to the large number of reactions and the extensive data, the coefficients of the fitted curves for Figure S3 and related phases, as well as the fitting conditions for each reaction, are shown in Table S1. The calculation of ΔGr or ΔAr in the later stages is carried out using this method, and the detailed data processing procedures are not repeated here.

|  |  |  |
| --- | --- | --- |
|  | *ΔGT=a*0*+a*1*T+a*2*T*2*+a*3*T*3*+a*4*T*4*+a*5*T*5*+a*6*T*6 | (S1) |

Table S1 The fitting result of each phase relative free energy functions with the changes of temperature.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Phase | The coefficient of the polynomial | | | | Mean Square | The highest applicable temperature/K |
| a0 | a1 | a2 | a3 |
| a4 | a5 | a6 |  |
| Ag | −4.42E+00 | −9.18E−03 | −7.69E−05 | 5.53E−08 | 2.00E−06 | 1234 |
| −2.62E−11 | 5.32E−15 | 0.00E+00 |  |
| Al | −4.60E+00 | 6.72E−03 | −8.26E−05 | 6.64E−08 | 1.62E−07 | 933 |
| −3.64E−11 | 8.50E−15 | 0.00E+00 |  |
| O2 | −4.06E+00 | −1.74E−01 | −6.57E−05 | 3.31E−08 | 1.45E−04 | 3000 |
| −1.19E−11 | 2.38E−15 | −2.00E−19 |  |
| Ag2O | −4.22E+01 | −4.27E−02 | −1.55E−04 | 5.14E−08 | 0.00E+00 | 500 |
| 0.00E+00 | 0.00E+00 | 0.00E+00 |  |
| Al2O3 | −1.69E+03 | 4.93E−02 | −2.05E−04 | 9.57E−08 | 1.32E−05 | 2327 |
| −3.49E−11 | 7.58E−15 | −7.21E−19 |  |
| AgAlO2 | −8.74E+02 | 2.01E−02 | −1.91E−04 | 8.79E−08 | 7.39E−06 | 1000 |
| −2.08E−11 | 0.00E+00 | 0.00E+00 |  |
| Ag2Al | −4.37E+01 | 1.37E−02 | −3.33E−04 | 3.78E−07 | 6.14E−04 | 1000 |
| −2.66E−10 | 7.86E−14 | 0.00E+00 |  |
| 7Al7Ag | −3.14E+01 | 6.33E−02 | −8.68E−04 | 1.07E−06 | 1.99E−05 | 1000 |
| −9.89E−10 | 5.34E−13 | −1.24E−16 |  |
| 15Al1Ag | −6.85E+01 | 1.40E−01 | −1.60E−03 | 1.82E−06 | 1.50E−04 | 1000 |
| −1.55E−09 | 7.77E−13 | −1.69E−16 |  |
| 31Al1Ag | −1.39E+02 | 2.97E−01 | −3.24E−03 | 3.71E−06 | 6.43E−04 | 1000 |
| −3.17E−09 | 1.60E−12 | −3.48E−16 |  |
| 47Al1Ag | −1.92E+02 | 4.74E−01 | −4.94E−03 | 5.80E−06 | 1.86E−04 | 1000 |
| −5.15E−09 | 2.70E−12 | −6.14E−16 |  |

#### 3.4.2 Formation Conditions of Ternary Phase AgAlO2 Thermodynamic Reaction

By employing the data processing method described above, the phases of each reaction were added or subtracted according to the coefficients in Table S1 (taking into account the stoichiometric coefficients in the reaction equations), yielding the coefficients of the sextic polynomial functions representing the reaction Gibbs free energies as functions of temperature for the aforementioned five reactions, as shown in Table S2. The sextic polynomial was plotted as shown in Figure 9.

Table S2 The coefficient of the polynomials which describe the change of Gibbs free energy (ΔrG) with temperature in reaction equation (12) to (17).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Reaction equation | The coefficient of the polynomial | | | | | | |
| a0 | a1 | a2 | a3 | a4 | a5 | a6 |
| (12) | −31.33 | 0.06266 | 3.502 E−04 | −7.575 E−08 | 5.835 E−11 | −11.83 E−15 | 0 |
| (13) | −837.168 | 0.14873 | 2.931E−05 | −4.34E−08 | 2.788E−11 | −6.5E−15 | −2.1E−19 |
| (14) | −861.035 | 0.197 | 3.47E−05 | −6.7E−08 | 5.37E−11 | −1.6E−14 | 2E−19 |
| (15) | −806.921 | 0.12335 | 0.000126 | −2.4E−07 | 2.05E−10 | −6.6E−14 | −2.1E−19 |
| *(16)* | −830.789 | 0.17162 | 0.000131 | −2.7E−07 | 2.31E−10 | −7.6E−14 | 2E−19 |
| *(17)* | −23.8674 | 0.04827 | 5.41E−06 | −2.4E−08 | 2.59E−11 | −9.7E−15 | 4.11E−19 |

#### 3.4.4 Determination of Ag2Al Generated by Solid Solution Reaction

By employing the data processing method described above, the phases of each reaction were added or subtracted according to the coefficients in Table S1 (taking into account the stoichiometric coefficients in the reaction equations), yielding the coefficients of the sextic polynomial functions representing the reaction Gibbs free energies as functions of temperature, as shown in Table S3.

Table S3 The coefficient of the polynomials which describe the functions of Gibbs free energy (ΔrG) with the changes of temperature in reaction equation 18 to 19

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Reaction equation | The coefficient of the polynomial | | | | | | |
| a0 | a1 | a2 | a3 | a4 | a5 | a6 |
| 18 (a) | −1.68E+03 | 2.94E−01 | 1.09E−04 | −2.26E−07 | 2.46E−10 | −1.48E−13 | 3.78E−17 |
| 19 (a) | −1.68E+03 | 2.90E−01 | 1.19E−04 | −2.44E−07 | 2.58E−10 | −1.47E−13 | 3.51E−17 |
| 18 (b) | −1.68E+03 | 2.93E−01 | 9.11E−05 | −1.78E−07 | 1.78E−10 | −9.77E−14 | 2.29E−17 |
| 19 (b) | −1.67E+03 | 2.91E−01 | 9.65E−05 | −1.89E−07 | 1.86E−10 | −9.89E−14 | 2.21E−17 |
| 18 (c) | −1.68E+03 | 2.92E−01 | 9.49E−05 | −1.85E−07 | 1.82E−10 | −9.82E−14 | 2.24E−17 |
| 19 (c) | −1.67E+03 | 2.92E−01 | 1.07E−04 | −1.97E−07 | 1.89E−10 | −9.94E−14 | 2.20E−17 |
| 18 (d) | −1.68E+03 | 2.91E−01 | 9.87E−05 | −1.95E−07 | 1.99E−10 | −1.10E−13 | 2.60E−17 |
| 19(d) | −1.68E+03 | 2.90E−01 | 1.00E−04 | −1.99E−07 | 2.01E−10 | −1.11E−13 | 2.57E−17 |

Table S4 Cohesive energy and oxygen solution energy of the model of elementai Al with O and Ag2Al with O.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Species | | O  /at% | Model Volume before Geometry Optimization/Å3 | Model Volume after  Geometry Optimization/Å3 | Volume Change  /% | Cohesive energy/（eV∙atom−1） | Oxygen solution energy  /eV |
| Elemental Al with O | 16Al1O−8 | 5.9 | 259.232 | 264.000 | 1.839 | −3.9950 | −2.8218 |
| 16Al1O−4 | 5.9 | 259.232 | 264.395 | 1.992 | −4.0935 | −4.4969 |
| 24Al1O−8 | 4.0 | 388.848 | 395.707 | 1.764 | −3.9307 | −2.8079 |
| 24Al1O−4 | 4.0 | 388.848 | 394.701 | 1.505 | −4.0010 | −4.5654 |
| 32Al1O−8 | 3.0 | 518.464 | 522.879 | 0.852 | −3.9097 | −3.1948 |
| 32Al1O−4 | 3.0 | 518.464 | 522.683 | 0.814 | −3.9673 | −5.0974 |
| Al |  |  |  |  | −3.7958 |  |
| Ag2Al with O | 16Ag8Al1O−8−1 | 4.0 | 393.920 | 409.243 | 3.890 | −3.4904 | −3.4813 |
| 16Ag8Al1O−8−2 | 4.0 | 393.920 | 406.764 | 3.261 | −3.4835 | −3.3086 |
| 16Ag8Al1O−4−1 | 4.0 | 393.920 | 408.992 | 3.826 | −3.4293 | −1.9533 |
| 16Ag8Al1O−4−2 | 4.0 | 393.920 | 406.827 | 3.277 | −3.4861 | −3.3746 |
| Ag2Al |  |  |  |  | −3.3091 |  |