Comment on "Stable phase domains of the TiO_2–Ti_3O_5–Ti_2O_3–TiO–$Ti(C_xO_y)$–TiC system examined experimentally and *via* first principles calculations" by J. Kim and S. Kang, *J. Mater. Chem. A*, 2014, 2, 2641

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COMMUNICATION

Comment on "Stable phase domains of the TiO_2–Ti_3O_5–Ti_2O_3–TiO–$Ti(C_xO_y)$–TiC system examined experimentally and via first principles calculations" by J. Kim and S. Kang, *J. Mater. Chem. A*, 2014, **2**, 2641

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The free energy of mixing in the Ti(O,C) shows negative deviation from ideality. A recent paper in *Journal of Materials Chemistry A* erroneously shows a large positive deviation from ideality.

A recent paper by Kim and Kang[1] used activity data fitted to the experimental data of Ouensanga[2] to predict stable phases in the Ti-O-C system. The activities of TiC and TiO in Ti(O,C) (shown in Fig.2 in the Kim and Kang paper[1]), and the free energy of mixing (calculated from the values in Table 2 in that paper†) correspond to formation of a simple regular solution $Ti(O_yC_{1-y})$ from y mol pure TiO and (1-y) mol pure TiC; for such a regular solution the excess free energy of mixing is given by

$$\Delta G^{ex} = a_o y(1-y), \quad (1)$$

where a_o is a constant.

While not explicitly reported in the paper, the fit by Kim and Kang corresponds to a_o=22.5 kJ/mol (see Fig. 1), a large positive deviation from ideality.

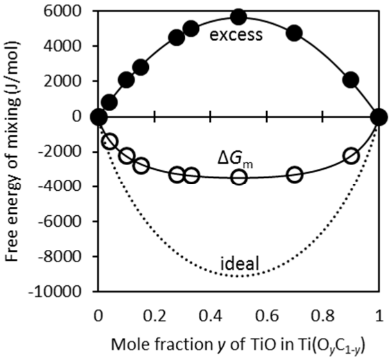

Fig. 1 Ideal free energy of mixing, compared with the free energy of mixing (ΔG_m) and excess free energy of mixing as calculated from Table 2 in Kim & Kang[1] (circles), for a temperature of 1580K. The full lines give the expected behaviour for a regular solution with a_o=22.5 kJ/mol.

A positive deviation from ideality is clearly wrong. It disagrees with results of calculations previously reported by the same group,[3] and also does not agree with the experimental evidence: As examples, the positive deviation would cause immiscibility in the TiC-TiO system at lower temperatures (below approximately 1350K), but there is no evidence of such low-temperature immiscibility: a Ti(O,C) solid solution formed by reaction between TiO_2 and C at 1273K.[4] The activities also disagree with the result reported by Ouensanga,[2] of equilibrium between CO (partial pressure 0.9 atm), Ti_3O_5 and Ti(O,C) solid solution with the composition $TiO_{0.33}C_{0.67}$. This equilibrium can be described by the reaction TiO + ¼CO = ¼TiC + ¼Ti_3O_5, with K=7.95 at 1580K (equilibrium constant calculated with FactSage[5]). The partial pressure of CO can hence be calculated from

$$p_{CO} = \frac{a_{TiC} a_{Ti_3O_5}}{K^4 a_{TiO}^4} \quad (2)$$

The positive deviation from ideality fitted by Kim and Kang predict a_{TiO}=0.71 and a_{TiC}=0.81 in $TiO_{0.33}C_{0.67}$, giving (from equation [2]) a predicted partial pressure of CO of 0.0008 atm (taking the activity of Ti_3O_5 to be 1), three orders of magnitude smaller than the experimental partial pressure. In fact, the experimental result corresponds to a **negative** deviation from ideality, with a_o=-32.3 kJ/mol, yielding a_{TiO}=0.11 (similar to a_{TiO}=0.12 reported later by Ouensanga[6]), and a_{TiC}=0.51. More recent results indicate an even larger negative deviation from ideality, with a_o=-98.8 kJ/mol.[7] The DFT results presented by Kim and Kang themselves (Figure 5a of the paper[1]‡) contradict their fitted positive deviation from ideality. For example, the reported free energy of mixing (from DFT calculations) of approximately -52 kJ/mol at 1500K for y=0.5 implies a large negative excess free energy of mixing of -43 kJ/mol.

Conclusions

Formation of titanium oxycarbide solid solution from TiO and TiC involves a negative excess free energy of mixing, not a large positive value as fitted by Kim and Kang[1]. One implication is that the stability diagrams reported in the Kim and Kang paper (calculated with the erroneous titanium oxycarbide solution model) would not be accurate and should not be used.

Notes and references

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† Table 2 in the paper is mislabeled: the first column gives y, not x=(1-y) (otherwise the table would indicate that the activity of pure TiO is zero, as one example); the last column does not give the Gibbs free energy of mixing as stated, but rather the calculated Gibbs free energy of formation of the solid solution from the pure elements (Ti, C and O_2) in their standard states.

‡ Figure 5a in the Kim & Kang paper[1] contains an error, in that the ideal free energy of mixing is shown as zero for all mixtures, without stating the temperature; the ideal free energy of mixing would be zero at a temperature of zero kelvin only.

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