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# Thermodynamic calculations in ternary titanium–aluminium–manganese system

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*Abstract*: Thermodynamic calculations in the ternary Ti–Al–Mn system are shown in this paper. The thermodynamic calculations were performed using the FactSage thermochemical software and database, with the aim of determining thermodynamic properties, such as activities, coefficient of activities, partial and integral values of the enthalpies and Gibbs energies of mixing and excess energies at two different temperatures: 2000 and 2100 K. Bearing in mind that no experimental data for the Ti–Al–Mn ternary system have been obtained or reported. The obtained results represent a good base for further thermodynamic analysis and may be useful as a comparison with some future critical experimental results and thermodynamic optimization of this system.

*Keywords*: thermodynamic calculations; Ti–Al–Mn ternary system; FactSage thermochemical software and database.

## INTRODUCTION

Due to the combination of lightweight and high strength, titanium-based alloys are of practical interest for the aerospace and automotive industries, as well as for various high temperature applications. Alloys with lower contents of aluminium are brittle and provide moderate resistance to oxidation, however alloying with manganese enhance their ductility and strength, as well as their oxidation and corrosion resistance. Nevertheless, a thermodynamic study of the Ti–Al–Mn system has not been completely reported in the literature.

Ti-based alloys were one of the first types of materials to which thermodynamic phase diagram calculation were applied. However, the early limitations in modelling, particularly with respect to the uptake of elements such as oxygen and nitrogen, restricted their use.[1] It is almost 30 years since a detailed presentation of thermodynamic phase diagram calculations for titanium alloys was made

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by Kaufman and Nesor[2] at the 2nd World Conference on titanium. They presented a series of computer calculated phase diagrams for Ti-based alloys and even included an early calculation for the Ti–Al system. Since then substantial advances have been made in terms of theoretical models, computer software and hardware and it is now possible to deal with extremely complex materials on a routine basis.[1]

Kaufman and Nesor[2] showed that some binary and ternary phase diagrams of Ti alloys, in particular the beta isomorphous systems, such as Ti–V and Ti–Nb, could be reasonably represented by simple regular and sub-regular models. However, the combination of the chemical affinity of Ti for light elements, such as O, C and N, and their powerful influence on phase equilibria means that even a simple alloy such as Ti–6Al–4V should be considered as a six-component system. Although Kaufman and Clougherty[3] produced a calculated diagram for Ti–O, this work was not generally extended to produce a database which could handle multi-component alloys with the requisite of O, C and N additions.

In studies by Gros, Ansara and Allibert[4] and Lee,[5] CALPHAD methods were employed for predicting phase equilibria in Ti alloys. Gros[4] published a thermodynamic assessment of the phase equilibria between liquid, $\beta$-Ti, $\alpha$-Ti and $\alpha 2$-Ti3Al phases in the Ti-rich region of the diagram. The Gibbs energies of both the ordered $\alpha 2$-Ti3Al and disordered $\alpha$-Ti phases were described by a unified two-sublattice model. However, the models used in both papers lack the necessary uptake of light elements, which could easily lead to differences between the experimental and observed $T^{\beta}$ of up to 60–80 °C. Murray[6] also applied the same unified formalism to the Gibbs energy of the three ordered phases, while Ohnuma[7] experimentally studied the phase equilibria between the Ti-rich solid phases, which were determined on specimens with carefully controlled low levels of oxygen contamination.

The roots of the CALPHAD approach lie in the mathematical description of the thermodynamic properties of the phases of interest. If they are stoichiometric compounds, the composition is defined and a mathematical formula is then used to describe fundamental properties, such as enthalpy and entropy. Where phases exist over a wide range of stoichiometries, which is usually the case for metallic materials, other mathematical models were used which take into account the effect of compositional changes on the free energy. Details of the modelling procedures can be found in a review of Ansara.[8] All types of models require the input of coefficients that uniquely describe the properties of the various phases and these coefficients are held in databases, which either are in the open literature or are proprietary.

Kattner and Boettinger[9] attempted one of the first extensions of ternaries to the Ti–Al–Nb system. However, although the form of their diagram is reasonable, they did not take into consideration the effect of the ordering of the $\beta$ phase on the structure of B2 CsCl, which has been observed in almost all Ti–Al–X systems, where X is one of the refractory metals, such as Nb and V. Work by Saunders[10] on a series of Ti–Al–X ternaries, where X = Cr, Mn, Mo, Nb or V, showed the importance of including this ordering for an accurate representation of the phase equilibria and it is of particular interest to be able to differentiate between the ordered and disordered form when considering mechanical properties. At the end of this survey, we mention the work of Jingqi,[11] concerning a thermodynamic analysis of the Gd–Mn–Ti system by X-ray powder diffraction and differential thermal analysis in the isothermal section at 773 K should be mentioned.

Bearing in mind such problems, it could be anticipated that most of the thermodynamic data of ternary and multi-component systems would come from theoretical calculations rather than from direct experimentation. The main reasons are the experimental difficulties, especially the high investigation temperatures required. It is clear that mostly solid alloys and their thermodynamic behaviour have been researched. For this reason, this paper presents the results of thermodynamic calculations of liquid Ti–Al–Mn alloys using FactSage thermochemical software and database.[12]

## CALCULATION PROCEDURE

Thermodynamic calculations and predicting of the ternary Ti–Al–Mn system have been done using FactSage thermochemical software and database.[12]

FactSage was introduced in 2001 and is a fusion of the FACT-Win/F*A*C*T and ChemSage/SOLGASMIX thermochemical packages, which were developed over 25 years ago. The FactSage package consists of a series of information, database, calculation and manipulation modules, which enable access to and manipulation of pure substances and solution databases. With the various modules, a wide variety of thermochemical calculations can be performed and tables, graphs and figures of interest to chemical and physical metallurgists, chemical engineers, inorganic chemists, geochemists, ceramists, electrochemists, environmentalists, *etc*., to be generated.

The FactSage package offers access to the modules of the package, which are grouped into four categories:

1. Info – this includes detailed slide shows of most of the program modules and general information with frequently asked questions on FactSage and its databases.

2. Databases – these program modules enable the user to view, manipulate and edit the pure substances and solution databases, which may be private (read/write) or public (read only).

Calculate – these modules are the central programs of FactSage. They permit the calculation of phase diagrams and thermochemical equilibria in various forms with direct access to the databases.

3. Manipulate – this group offers various graphical and tabular program modules for post-processing the results and manipulating the calculated phase diagrams and other figures.

In this study, the Calculate modules performed all the calculations.

The Calculate modules are the heart of FactSage. One can interact with the software and databases in a variety of ways and calculate thermochemical equilibria in various forms. They consist of a Reaction module, Predom and EpH modules, an Equilib module, Phase diagram and Figure modules.

The Reaction module calculates changes in extensive thermochemical properties (enthalpy, Gibbs energy, entropy, *etc.*) for a single species, a mixture of species or for a chemical reaction. The species may be pure elements, stoichiometric compounds or ions (both plasma and aqueous ions).

With the Predom module, isothermal predominance area diagrams for one-, two- or three--metal systems can be calculated and plotted using data retrieved from the compound databases.

The EpH module is similar to the Predom module and permits the generation of $E_h$ *vs.* pH (Pourbaix) diagrams for one-, two- or three-metal systems using data retrieved from the compound databases, which also include infinitely dilute aqueous data.

The Equilib module is the Gibbs energy minimization workhorse of FactSage. It calculates the concentrations of chemical species when specified elements or compounds react or partially react to reach a state of chemical equilibrium.

The Phase diagram and Figure modules is a generalized module which permits the calculation, plotting and editing of unary, binary, ternary and multi-component phase diagram sections, whereby the axes can be various combinations of temperature, pressure, volume, composition, activity, chemical potential, *etc.* The resulting phase diagram is automatically plotted by the Figure module.

In this study, calculations within the Reaction, Equilib, Phase diagram and Figure modules were performed.

The thermodynamic calculations of the Ti–Al–Mn ternary system were carried out from each corner using 15 cross-sections in total. The compositions of all investigated cross-sections are given in Table I.

TABLE I. Composition of the ternary alloys in the investigated sections

| Cross-section | A | B | C | D | E |
|---|---|---|---|---|---|
| $x_{Al}:x_{Mn}$ | 9:1 | 7:3 | 5:5 | 3:7 | 1:9 |
| $x_{Ti}:x_{Mn}$ | 9:1 | 7:3 | 5:5 | 3:7 | 1:9 |
| $x_{Ti}:x_{Al}$ | 9:1 | 7:3 | 5:5 | 3:7 | 1:9 |

## RESULTS AND DISCUSSION

The thermodynamic properties of the ternary system Ti–Al–Mn were calculated using FactSage at 2000 and 2100 K. The phase diagrams of Al–Mn and Ti–Mn binary systems, as constitutive binaries of the ternary systems Ti–Al–Mn, were calculated by FactSage and are shown in Figs. 1 and 2, respectively.

Activity values in the investigated Ti–Al–Mn ternary system from titanium, aluminium and manganese at 2000 and 2100 K are shown in Figs. 3–8, respectively.

The binaries Ti–Al and Al–Mn have negative values for the integral excess Gibbs energy, while the Ti–Mn system has positive values, considering that Al was selected as the symmetrical component by some others and different models for thermodynamic prediction.

The enthalpies of mixing values indicate that the strongest chemical interaction between the components in the investigated Ti–Al–Mn ternary system exist between aluminium and manganese and the weakest between titanium and manganese.

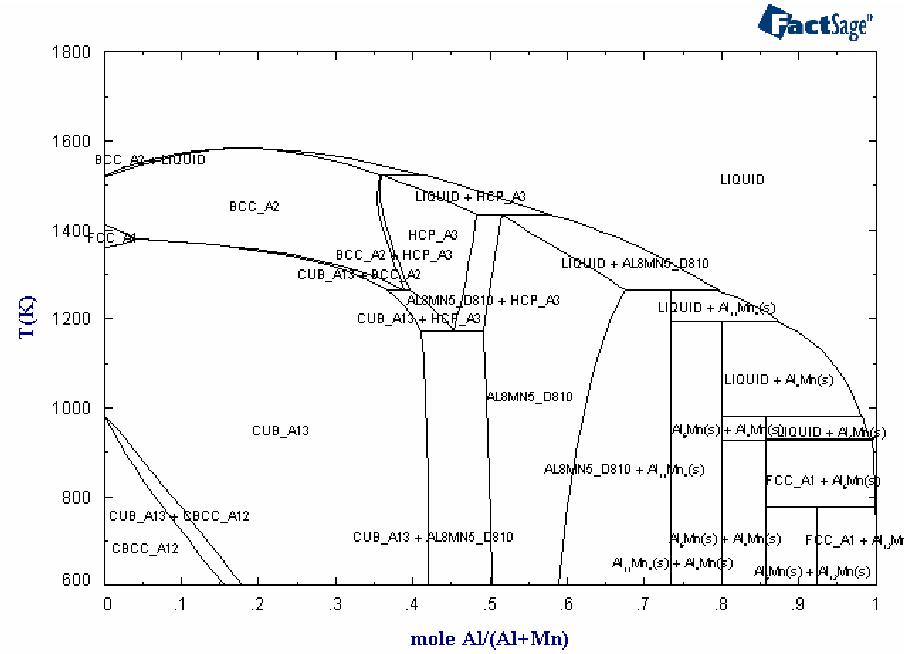

Fig. 1.Al–Mn phase diagram.

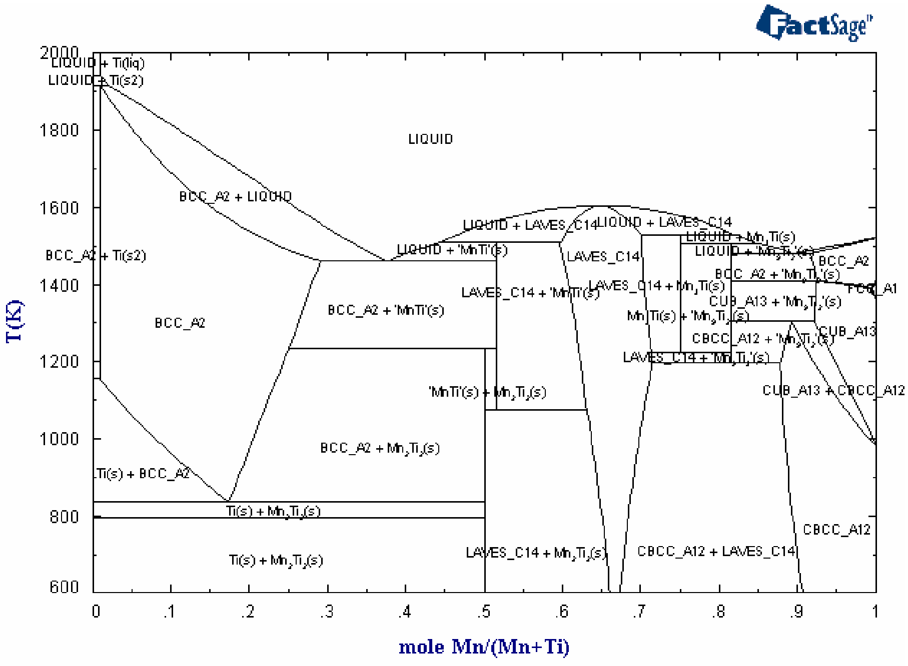

Fig. 2. Mn–Ti phase diagram.

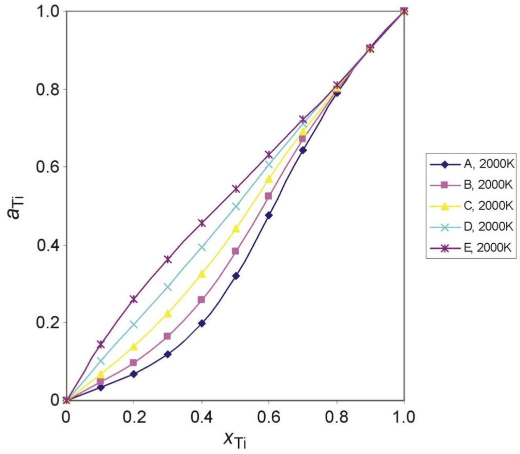

Fig. 3. Activity of titanium in Ti–Al–Mn at 2000 K.

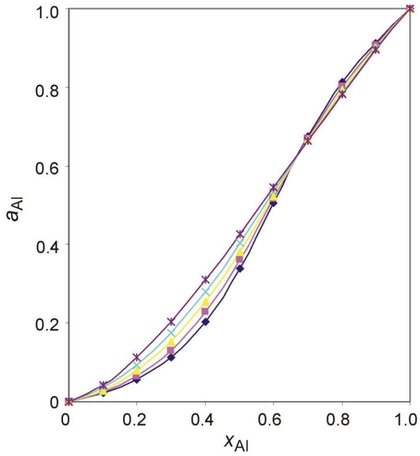

Fig. 4. Activity of aluminium in Ti–Al–Mn at 2000 K.

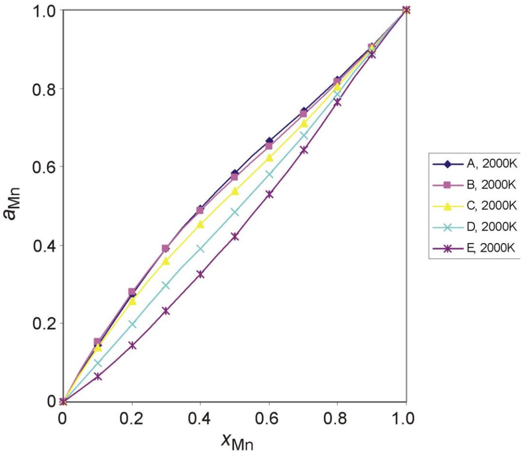

Fig. 5. Activity of manganese in Ti–Al–Mn at 2000 K.

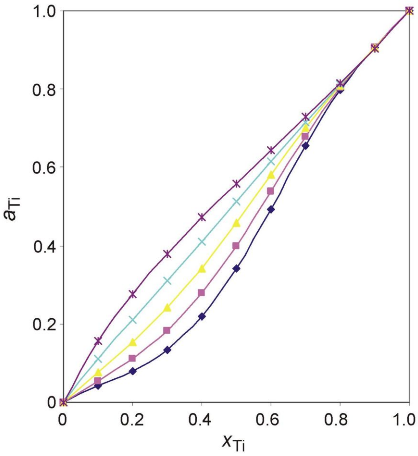

Fig. 6. Activity of titanium in Ti–Al–Mn at 2100 K.

In the case of the investigated sections from the aluminium corner, the enthalpy of mixing values are strongly affected by the Ti–Mn binary system. The activity values of titanium decrease and the activity values of manganese increase proportionally in the Ti–Al and Al–Mn systems, while those of aluminium decrease with increasing titanium content and increase with increasing manganese content, as would be expected for behaviour according to the Raoult law.

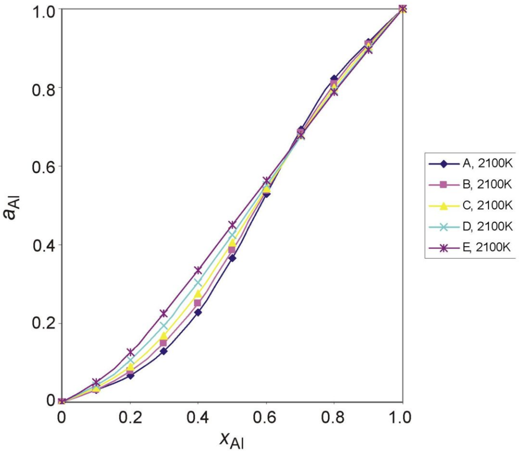

Fig. 7. Activity of aluminium in Ti–Al–Mn at 2100 K.

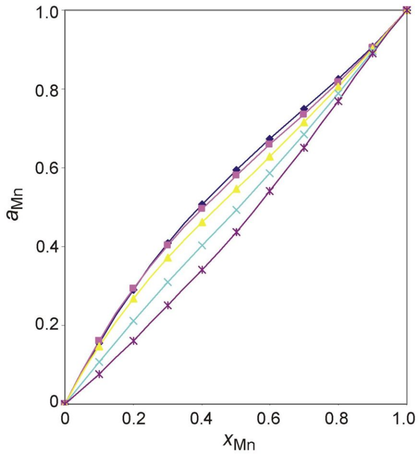

Fig. 8. Activity of manganese in Ti–Al–Mn at 2100 K.

## CONCLUSIONS

The thermodynamic properties of the ternary system Ti–Al–Mn at 2000 and 2100 K were calculated using FactSage thermochemical software and databases.

Bearing in mind that no experimental data for the Ti–Al–Mn ternary system have been obtained or reported, the presented results are a good base for further thermodynamic analysis, which will involve a comparative study of the thermodynamic properties of liquid alloys based on different thermodynamic predicting methods.

The obtained thermodynamic data may be useful as a comparison with some future critical experimental results and for the further thermodynamic optimization of this system, as well as to show the possibility of the application of the employed software for the thermodynamic description of the investigated system.

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## ИЗВОД

## ТЕРМОДИНАМИЧКИ ПРОРАЧУНИ У ТЕРНАРНОМ СИСТЕМУ ТИТАН–АЛУМИНИЈУМ–МАНГАН

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У овом раду приказани су резултати термодинамичких прорачуна у тернарном систему Ti–Al–Mn. FactSage термохемијски софтвер и база података коришћени су за све прорачуне у овом систему у циљу дефинисања термодинамичких величина стања као што су актив-

ности, коефицијенти активности, парцијалне и интегралне вредности за Гибсове енргије мешања и Гибсове енергије у вишку на двема различитим температурама: 2000 и 2100 K. У досадашњој литератури нема публикованих експерименталних података везаних за термодинамичке прорачуне у испитиваном систему, јер се ради о високотемператуном систему. Зато добијени резултати представљају једну добру полазну базу за сваку даљу термодинамичку анализу и могу бити од користи за поређења са неким будућим критичним експерименталним резултатима, као и у термодинамичкој оптимизацији наведеног ситема.

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## REFERENCES

1. N. Saunders, *Titanium '95: Science and Technology*, P. Bleckinsop, W. J. Evans, H. M. Flower, Eds., Institute of Materials, London, 1996, p. 2167
2. L. Kaufman, H. Nesor, *Calphad* **2** (1978) 325
3. L. Kaufman, Clougherty, *Metallurgy at High Pressures and High Temperatures*, in *AIME Met. Soc. Conf.,* Vol. 22, Gordon and Breach, New York, 1964, p. 322
4. J. P. Gros, I. Ansara, M. Allibert, in *Proceeding of 6th World Conference on Titanium,* Vol. III, P. Lacombe, R. Tricot, G. Beranger, Eds., Les Editions de Physique, Paris, 1989, p. 1553
5. H. M. Lee, J.-R. Soh, Z.-H. Lee, Y.-S. Kim, *Scripta Met.* **29** (1993) 497
6. J. L. Murray, *Metall. Trans. A* **9** (1988) 243
7. I. Ohnuma, Y. Fujita, H. Mitsui, K. Ishikawa, R. Kainuma, K. Ishida, *Acta Mater.* **48** (2000) 3113
8. I. Ansara, *Int. Met. Rev.* **22** (1979) 20
9. U. R. Kattner, W. J. Boettinger, *Mater. Sci. Eng.* **A152** (1992) 9
10. N. Saunders, *CALPHAD XXIV,* Kyoto, Japan, 1995, p. 21
11. L. Jingqi, Q. Jiqin, D. Ren, Z. Yinghong, H. Jinli, *J. Alloys Comp.* **414** (2006) 97
12. C. W. Bale, P. Chartrand, S. A. Degterov, G. Eriksson, K. Hack, R. B. Mahfoud, J. Melancon, A. D. Pelton, S. Petersen, *Calphad* **26** (2002) 189.