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Predictions of Titanium Alloy Properties Using Thermodynamic Modeling Tools

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Thermodynamic modeling tools have become essential in understanding the effect of alloy chemistry on the final microstructure of a material. Implementation of such tools to improve titanium processing via parameter optimization has resulted in significant cost savings through the elimination of shop/laboratory trials and tests. In this study, a thermodynamic modeling tool developed at CompuTherm, LLC, is being used to predict β transus, phase proportions, phase chemistries, partitioning coefficients, and phase boundaries of multicomponent titanium alloys. This modeling tool includes *Pandat*, software for multicomponent phase equilibrium calculations, and *PanTitanium*, a thermodynamic database for titanium alloys. Model predictions are compared with experimental results for one α-β alloy (Ti-64) and two near-β alloys (Ti-17 and Ti-10-2-3). The alloying elements, especially the interstitial elements O, N, H, and C, have been shown to have a significant effect on the β transus temperature, and are discussed in more detail herein.

Keywords property prediction, thermodynamic modeling tools, titanium alloys

1. Introduction

Technical multicomponent titanium alloys are classified as α, β, and α-β alloys depending on the relative amount of α- and β-stabilizing components in the alloy. Within the last category are the subclasses near-α and near-β, referring to alloys whose compositions place them near the α/(α+β) or (α+β)/β phase boundaries, respectively. The microstructure and mechanical properties of a titanium alloy, therefore, strongly depend on the alloy's chemistry. To understand their correlations, multicomponent phase equilibrium information is critically needed. In the traditional approach, a series of labor-intensive experiments must be carried out to determine the phase equilibria even for a binary system, and the amount of experimental work required increases dramatically for a multicomponent system. Recently, with the development of the thermodynamic modeling approach, only a few key experiments are necessary to enable the calculation of phase diagrams and thermodynamic properties of multicomponent systems. The calculated phase equilibria, coupled with kinetic models, can be further used to predict solidification paths, microsegregation, freezing ranges, heats of solidification, and other properties. These calculations, therefore, provide valuable information for alloy design, selection of parameters for such fabrication steps as heat treating, prediction of performance, and failure analysis.

Although only recent developments in modeling and computers have made calculations of multicomponent phase equilibria feasible, the fundamental principles have been known for more than a century (Ref 1). The theoretical basis of thermodynamic calculations rests on the fact that the location of a phase boundary is the result of stability competition between two or more phases. Because the stability of a phase can be described by its Gibbs energy, thermodynamic calculation software, therefore, works by minimizing the Gibbs energy of a system to find the equilibrium state of the system, predicting phases that can form, and ruling out those that cannot. In addition to computer software, a thermodynamic database that compiles the Gibbs energies of all the phases in a system is the other part of the thermodynamic modeling tool. Successful thermodynamic calculations, therefore, depend on the availability of reliable thermodynamic databases and robust computer software.

In this paper, the authors will demonstrate the usefulness of the thermodynamic modeling approach by utilizing it to predict properties of titanium alloys. All the calculations are carried out with *Pandat* (Madison, WI), software for multicomponent phase equilibrium calculations, and *PanTitanium*, a thermodynamic database for titanium alloys developed at CompuTherm.

2. Thermodynamic Database for Titanium Alloys

A reliable thermodynamic database is the prerequisite for all successful thermodynamic calculations. Thermodynamic model parameters used to describe the Gibbs energy of each phase are stored in the database. A thermodynamic database is normally developed using a phenomenological modeling approach (Ref 2). A model type is selected to correspond with the physical and thermodynamic properties of each phase in the alloy system. The most common phase types in metallic alloys are stoichiometric compounds, disordered solutions, and ordered intermetallic phases. The Gibbs energy of a binary stoi-

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chiometric compound A_pB_q is described only as a function of temperature:

$$G_{\mathrm{m}}^{\varphi} = \sum_{i} x_i \cdot G_i^{\varphi,\mathrm{o}} + \Delta_{\mathrm{f}} G(A_pB_q) \qquad \text{(Eq 1)}$$

where x_i is the mole fraction of component i, and $G_i^{\phi,\mathrm{o}}$ represents the Gibbs energy of component i with φ structure; $\Delta_{\mathrm{f}}G(A_pB_q)$, which is normally a function of temperature, represents the Gibbs energy of formation of the stoichiometric compound. If $\Delta_{\mathrm{f}}G(A_pB_q)$ is a linear function of temperature:

$$\Delta_{\mathrm{f}}G(A_pB_q) = \Delta_{\mathrm{f}}H(A_pB_q) - T \cdot \Delta_{\mathrm{f}}S(A_pB_q) \qquad \text{(Eq 2)}$$

then $\Delta_{\mathrm{f}}H(A_pB_q)$ and $\Delta_{\mathrm{f}}S(A_pB_q)$ are the enthalpy and entropy of formation of the stoichiometric compound. Equation 1 is readily extended to a multicomponent stoichiometric compound phase.

A disordered solution phase is described by a substitutional type of model (Ref 3). The Gibbs energy of such a phase in a binary system can be written as:

$$\begin{aligned} G_{\mathrm{m}}^{\varphi} = {} & \sum_{i=A,B} x_i \cdot G_i^{\varphi,\mathrm{o}} + RT \sum_{i=A,B} x_i \ln x_i \\ & + x_A \cdot x_B \sum_{v} L_v \cdot (x_A - x_B)^v \qquad \text{(Eq 3)} \end{aligned}$$

where the first term on the right hand of the equation represents the reference state with x_i, the mole fraction of component i, and $G_i^{\phi,\mathrm{o}}$ the Gibbs energy of pure component i with φ structure; the second term is the ideal mixing term with R the gas constant, and T the temperature; the last term is the excess Gibbs energy of mixing with L_v, the interaction coefficient, and v the power of the polynomial series. When $v = 0$, it is a regular solution model, and when $v = 0$ and 1, it is a subregular solution model, and so on. Equation 3 can be extrapolated into a multicomponent system using geometric models, such as the Muggianu et al. model (Ref 4). Ternary and higher order interaction parameters may be necessary to describe a multicomponent solution phase.

An ordered intermetallic phase is described by a variety of sublattice models, such as the compound energy model (Ref 3, 5) and the bond energy model (Ref 6, 7). In these models, the Gibbs energy is a function of the sublattice species concentrations and temperature. The Gibbs energy of a binary intermetallic phase described by a two-sublattice compound energy model, $(A, B)_p{:}(A, B)_q$, can be written as:

$$\begin{aligned} G_{\mathrm{m}}^{\varphi} = {} & \sum_{i=A,B} \sum_{j=A,B} y_i^{\mathrm{I}} y_j^{\mathrm{II}} G_{i:j}^{\varphi} + RT \left[\frac{p}{p+q} \sum_{i=A,B} y_i^{\mathrm{I}} \ln y_i^{\mathrm{I}} \right. \\ & \left. + \frac{q}{p+q} \sum_{i=A,B} y_i^{\mathrm{II}} \ln y_i^{\mathrm{II}} \right] + \sum_{j=A,B} y_A^{\mathrm{I}} y_B^{\mathrm{I}} y_j^{\mathrm{II}} \sum_{v} (y_A^{\mathrm{I}} - y_B^{\mathrm{I}})^v L_{A,B:j}^{v} \\ & + \sum_{i=A,B} y_i^{\mathrm{I}} y_A^{\mathrm{II}} y_B^{\mathrm{II}} \sum_{v} (y_A^{\mathrm{II}} - y_B^{\mathrm{II}})^v L_{i:A,B}^{v} + y_A^{\mathrm{I}} y_B^{\mathrm{I}} y_A^{\mathrm{II}} y_B^{\mathrm{II}} L_{A,B:A,B} \qquad \text{Eq (4)} \end{aligned}$$

where y_i^{I} and y_i^{II} are the species concentrations of component i in the first and second sublattices, respectively. The first term on the right hand of the equation represents the reference state with the mechanical mixture of the pure compounds: A, A_pB_q, B_pA_q, and B. $G_{i:j}^{\phi}$ is the Gibbs energy of the stoichiometric compound i_pj_q with φ structure. The value of $G_{i:j}^{\phi}$ can be obtained experimentally if i_pj_q is a stable compound, or it can be a model parameter obtained by optimization using experimental data related to this phase. Recently, ab initio calculations have also been used to obtain such a value for an unstable i_pj_q compound. The second term is the ideal mixing Gibbs energy, which corresponds to the random mixing of species on the first and second sublattices. The last three terms are the excess Gibbs energies of mixing. The "L" parameters in these terms are model parameters whose values are obtained using the experimental phase equilibrium data and thermodynamic property data. These parameters can be temperature dependent. In this equation, a comma is used to separate species in the same sublattice, while a colon is used to separate species belonging to different sublattices. The compound energy model can be applied to phases in a multicomponent system by considering the interactions from all the constituent binaries. Additional ternary and higher order interaction terms may also be added to the excess Gibbs energy term.

The strategy of building a thermodynamic database for alloys with n components starts with deriving thermodynamic descriptions for all the constituent binary systems using the models described above. The model parameters for each type of model are optimized so that the model gives the best fit to the available experimental data. There are C_n^2 constituent binaries in an n-component alloy system, where $C_n^i \equiv n!/i!(n-i)!$ After thermodynamic descriptions for all the constituent binaries are established, preliminary descriptions for the ternaries are obtained by the extrapolation use of the binary model parameters using geometric models, such as the Muggianu model (Ref 4). Ternary interaction parameters may be necessary to better describe the ternary system. Three binary systems form a ternary system, and there are a total of C_n^3 ternary systems in an n-component system. If a new phase appears in the ternary system that is not in any of the constituent binary systems, a thermodynamic model is selected for this ternary phase and its model parameters are optimized using experimental information for this ternary phase. In this manner, one can develop thermodynamic descriptions of the ternaries. After thermodynamic descriptions of all C_n^3 ternaries for an n-component system are established, the model parameters are simply used to describe quaternary and higher order systems using an extrapolation approach. High-order interaction parameters are usually not necessary because, although interactions between binary components are strong, in ternary systems they are weaker, and in higher ordered systems they become insignificantly weak (Ref 8, 9). However, quaternary phases do appear in rare cases. When this happens, the quaternary phase is modeled using the same techniques that are used for ternary phases.

PanTitanium (Ref 10), a 17-component database for titanium alloys, was developed at CompuTherm using the procedures described above. This database contains most of the alloying elements used in titanium alloys, such as Al, B, Cr, Fe, Mo, Nb, Ni, Si, Sn, Ta, V, and Zr. Interstitial elements, such as C, H, O, and N, are also included in the database. More than 90 phases are considered in the database, such as liquid, hcp (α), bcc (β), fcc (TiC), and Laves. This database has been designed for use with conventional types of titanium alloys. The application scope of this database are suggested as follows: Al ≤ 8%, B ≤ 0.005%, C ≤ 0.3%, Cr ≤ 6%, Fe ≤ 5%, H ≤ 0.03%, Mo ≤ 8%, N ≤ 0.2%, Nb ≤ 3%, Ni ≤ 1%, O ≤ 0.5%, Si ≤ 2%, Sn ≤ 5%, Ta ≤ 1%, V ≤ 15%, Zr ≤ 4%, all in wt.%. Titanium is the major component; its amount should not be less than 75%. It should be pointed out that these composition ranges refer to nominal alloy chemistry only; the equilibrium phase chemistry can be out of this range. This database has been validated by a large number of α-β titanium alloys, including α and near-β alloys. This database, therefore, can be applied to a range of titanium alloys whose nominal compositions fall in the composition range mentioned above. Application of this database to other titanium alloys is still under validation.

3. Computer Software

Computer software plays a critical role in thermodynamic calculations. As mentioned previously, the theoretical basis of thermodynamic calculations rests on the fact that the phase boundary is the result of stability competition between two or more phases. Thermodynamic calculation software, therefore, works by finding the most stable state of a system, predicting phases that can form, and ruling out those that cannot. Due to the complexity of commercial alloy materials, the software should be able to handle multicomponent, multiphase systems. All calculations should be carried out in an automatic, consistent manner without requiring initial values from the user. A user-friendly interface is also a necessity. *Pandat* (Ref 11), a software package for multicomponent phase equilibrium calculations, was developed at CompuTherm. The global minimization algorithm adopted in *Pandat* ensures that it always finds the stable phase equilibrium. However, metastable phase diagrams can be calculated by suspending the stable phases if the user wishes to do so. This feature is important in understanding the phenomena observed in practice. Although some phases are thermodynamically stable, they may not form or form only a tiny amount for kinetic reasons. When this is the case, it is more reasonable to calculate a metastable equilibrium instead of a stable one. The unique combination of *Pandat* software and the thermodynamic database for titanium alloys, *PanTitanium*, allows the prediction of thermodynamic properties of multicomponent commercial titanium alloys with a few mouse clicks. Examples of such calculations are presented in the next section.

4. Application of the Thermodynamic Modeling Tool to Titanium Alloys

The thermodynamic modeling tool developed in this study was primarily focused on α-β type titanium alloys, such as Ti-6Al-4V (Ti-64) and Ti-6Al-2Sn-4Zr-6Mo (Ti-6246). Subsequently, its application was later extended to near-β alloys, such as Ti-5Al-2Sn-2Zr-4Mo-4Cr (Ti-17) and Ti-10V-2Fe-3Al (Ti-10-2-3). It is noteworthy to point out that the chemistries given above are the nominal compositions (wt.%). For commercial alloys, the actual composition in each alloy varies. In addition, it is inevitable that commercial alloys always contain minute amounts of other alloying elements, such as Fe, Si, C, O, N, and H. A number of applications are targeted for use of this thermodynamic modeling tool. One example is to use it for the prediction of the β transus, the temperature at which α starts to form from β during solidification. To achieve desired microstructure and mechanical properties for a given alloy, a proper heat-treatment process needs to be used. The β transus temperature is an important reference parameter used by metallurgical engineers in the selection of specific heat treatment conditions for titanium alloys. Current aerospace industrial practice calls for measurement of the β transus on every heat of titanium material, which is costly and time consuming. The use of the thermodynamic modeling tool could reduce these operations and their associated costs. Detailed information on phase fraction as a function of temperature is also important, and can be used to dial-in on specific volume fraction of primary α during the final heat treatment of components. Examples for the prediction of β transus and phase fraction as a function of temperature are presented below.

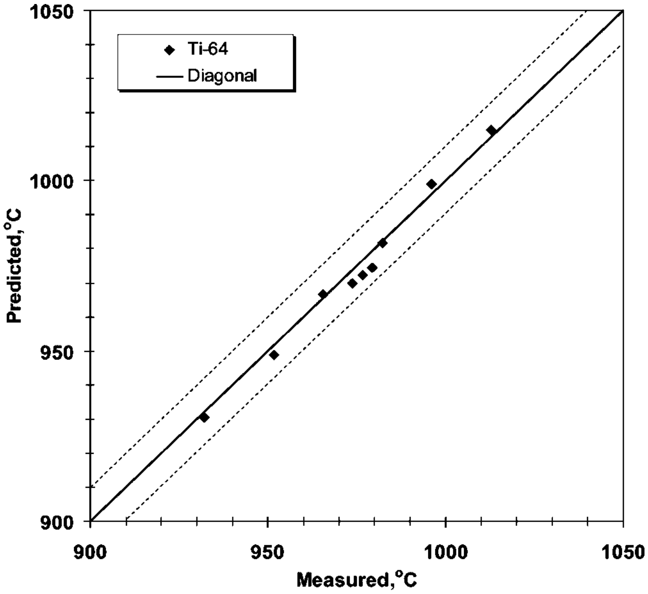

Fig. 1 Comparison between the calculated and measured β transus temperatures for Ti-64 alloy; experimental data are from Venkatesh (Ref 12)

4.1 Ti-64 Alloy

Ti-6Al-4V (Ti-64) is the most widely used titanium alloy in the world, with 80% of its usage going toward aerospace industry. β transus temperatures of Ti-64 range from 900 to 1000 °C, depending on the amounts of alloying components and interstitial elements, such as oxygen, carbon, nitrogen, and hydrogen. This temperature can be calculated very accurately using the thermodynamic modeling approach. Figure 1 compares the calculated and experimentally measured (Ref 12) β transus temperatures for nine heats with slightly different chemistries. Excellent agreement between the calculation and measurement is obtained, with an average difference of 3 °C. As an α-β alloy, Ti-64 has different volume fractions of α and β phases, depending on alloy chemistry and heat treatment conditions. Figure 2 shows the calculated α approach curve and the experimentally measured (Ref 12) fraction of α phase as a function of temperature for one Ti-64 chemistry heat. The calculation agrees with the measurements very well.

4.2 Ti-17 Alloy

Ti-5Al-2Sn-2Zr-4Mo-4Cr (Ti-17), a high-strength, deep hardenable, forging alloy developed primarily for gas turbine engine components, has strength properties superior to those of Ti-64 and is classified as a near-β alloy, with a β transus of 890 ± 10 °C. A comparison between the calculated and measured

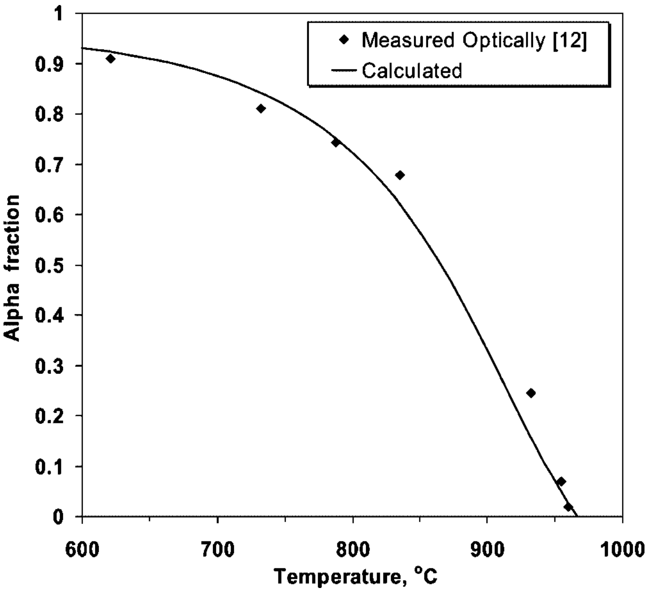

Fig. 2 Calculated and experimental measured fraction of α phase as a function of temperature for one Ti-64 heat; experimental data are from Venkatesh (Ref 12)

(Ref 13) β transus temperatures for Ti-17 alloy shows excellent agreement with an average difference of 3.9 °C (Fig. 3).

4.3 Ti-10-2-3 Alloy

Ti-10V-2Fe-3Al (Ti-10-2-3), a high-strength, near-β titanium alloy, can attain a wide variety of strength levels depending on the selection of heat treatment. The β transus of Ti-10-2-3 is reported in the range of 790-805 °C. A comparison between the calculated and measured (Ref 13) β transus temperatures for Ti-10-2-3 alloy is shown in Fig. 4. The calculated fraction of α phase as a function of temperature is shown in Fig. 5, with experimental data (Ref 14) plotted on it for comparison. Again, excellent agreement is obtained.

5. Discussion

It should be pointed out that the calculated phase fractions from *Pandat* as shown in Fig. 2 and 5 are mole fractions, while the measured values are volume fractions. However, because the molar volume of the α phase is very close to that of the β phase, the error induced due to the direct comparison between them is small (<0.5%). Predicted β transus temperatures from *Pandat* agree very well with the measured values, as shown in Fig. 1, 3, and 4. The accuracy of the prediction depends on many factors, such as the reliability of the database, the accuracy of the measured β transus, and the alloy chemistry used in the calculation. It is found that the calculated β transus is very sensitive to the amounts of interstitial elements, such as oxygen, carbon, nitrogen, and hydrogen, as shown in Tables 1 and 2.

In Table 1, the nominal chemistry for Ti-64 is given as Ti-6Al-4V-0.12O-0.01C-0.01N-0.005H (wt.%). It is seen that 10 wppm of additional interstitial elements (O, C, N, H) will result in a change of the β transus of Ti-64 alloy by 0.27, 0.49, 1.03, and 1.08 °C, respectively. To change the β transus of Ti-64 by 5 °C, only a small amount of each interstitial element is needed, as listed in the last column of Table 1. Table 2 lists the effect of these interstitial elements on the β transus of Ti-17. It is seen that N has a much greater effect than the other three elements of this alloy.

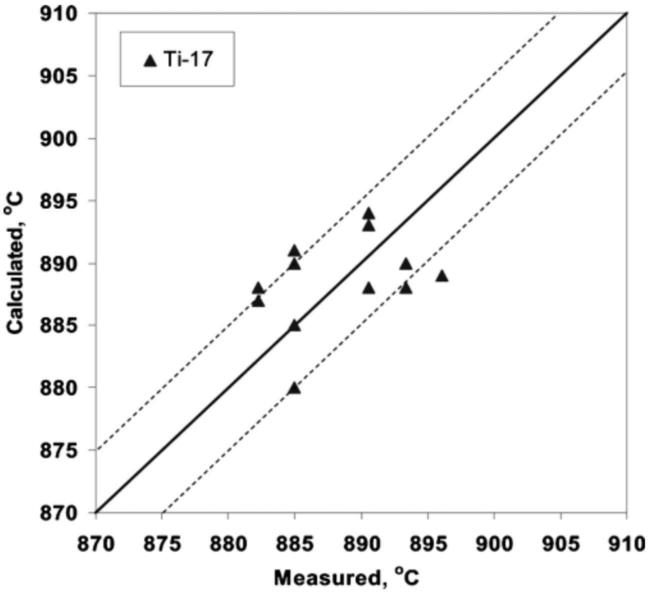

Fig. 3 Comparison between the calculated and measured β transus temperatures for Ti-17 alloy; experimental data are from Furrer (Ref 13)

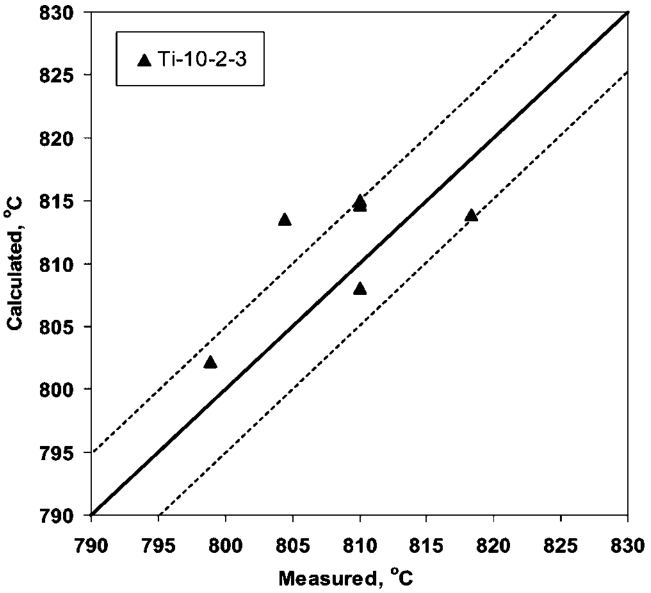

Fig. 4 Comparison between the calculated and measured β transus temperatures for Ti-10-2-3 alloy; experimental data are from Furrer (Ref 13)

6. Summary

The authors have demonstrated herein the powerful features of a thermodynamic modeling tool by applying it to several commercial titanium alloys. For the successful application of such a tool, reliable computer software and thermodynamic databases are needed. For the present work, the software for

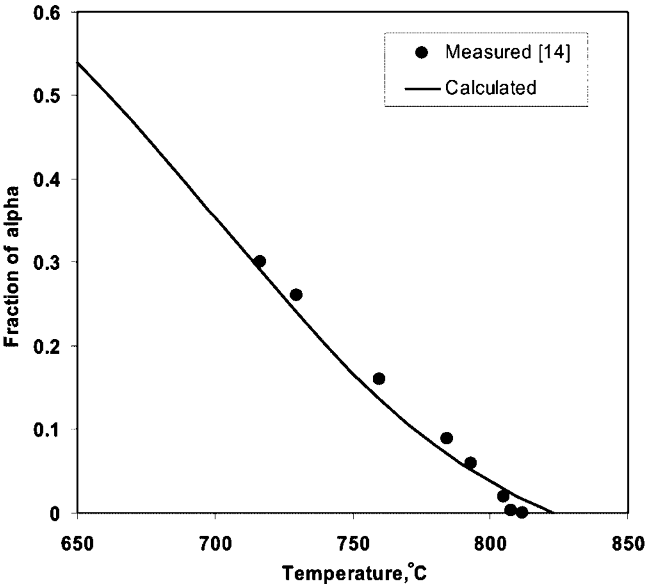

Fig. 5 Calculated and experimental measured fraction of α phase as a function of temperature for one Ti-10-2-3 heat; experimental data are from Duerig et al. (Ref 14)

Table 1 Effects of 10 wppm interstitial elements on the β transus of Ti-64 alloy

Alloy chemistry, wt.%	β transus, °C	ΔT, °C (compare to Ti-64)	ΔX, wppm (needs to change ΔT by 5 °C)
Ti-64: Ti-6Al-4V-0.12O-0.01C-0.01N-0.005H	982.59	…	…
Ti-64 + 10 wppm O	982.86	0.27	185.2
Ti-64 + 10 wppm C	983.08	0.49	102.0
Ti-64 + 10 wppm N	983.62	1.03	48.5
Ti-64 + 10 wppm H	981.51	−1.08	46.3

Table 2 Effects of 10 wppm interstitial elements on the β transus of Ti-17 alloy

Alloy chemistry, wt.%	β transus, °C	ΔT, °C (compare to Ti-17)	ΔX, wppm (needs to change ΔT by 5 °C)
Ti-17: Ti-5Al-2Sn-2Zr-4Mo-4Cr-0.1O-0.01C-0.005N-0.005H	901.84	…	…
Ti-17 + 10 wppm O	901.96	0.12	416.7
Ti-17 + 10 wppm C	902.26	0.42	119.0
Ti-17 + 10 wppm N	906.48	4.64	10.8
Ti-17 + 10 wppm H	900.64	−1.2	41.7

multicomponent phase equilibrium calculation and the thermodynamic database for titanium alloys, developed at CompuTherm, were used in the calculations. Demonstration and validation of these thermodynamic modeling tools allows the potential of many industrial applications. Increased speed and accuracy of phase-transformation temperature determination can lead to decreased end-product manufacturing cycle-time and increased capability. Reductions in direct measurement operations can result in reduced titanium material and component costs. The use of thermodynamic modeling tools in conjunction with solidification models shows great potential in prediction of microscopic and macroscopic segregation. Increased understanding of phase equilibria during casting and heat treating will allow for further advancement in existing alloys. The speed of development of new titanium alloys and processes will also be increased through the use of these analytical tools, eliminating years of trial and error chemistry and processing assessment.

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