Thermo-Calc Software

TCS Zr-based Alloys Database (TCZR)

Examples Collection

Document created 11/29/2022

Contents

About the Database Examples

There are examples available to demonstrate both the *validity* of the database itself as well as to demonstrate some of its *calculation* capabilities when combined with Thermo-Calc software and its Add-on Modules and features.

For each database, the type and number of available examples varies. In some cases an example can belong to both a validation and calculation type.

- *Validation* examples generally include experimental data in the plot or diagram to show how close to the predicted data sets the Thermo-Calc calculations are. It uses the most recent version of the software and relevant database(s) unless otherwise specified.
- *Calculation* examples are intended to demonstrate a use case of the database. This might be showing a binary or ternary system calculated in a phase diagram, or demonstrate how the database and relevant software features would be applied to a heat treatment application, process metallurgy, soldering process, and so forth. In the case of heat treatment, it might include the result of calculating solidification segregation, determining homogenization temperature and then predicting the time needed to homogenize. There are many other examples specifically related to each database.

Where relevant, most references related to each example set are included at the end of the individual section. You can also find additional references specific to the database itself when using the database within Thermo-Calc. You can also contact us directly should you have any questions.

If you are interested in sharing your own examples using Thermo-Calc products in unique or surprising ways, or if you want to share your results from a peer reviewed paper, send an email to info@thermocalc.com.

TCS Zr-based Alloys Database (TCZR) Resources

Information about the database is available on our website and in the Thermo-Calc software online Help.

- **Website**: On our website the information is both searchable and the database specific PDFs are available to download.
- **Online Help**: Technical database information is included with the Thermo-Calc software online Help. When in Thermo-Calc, press F1 to search for the same information as is contained in the PDF documents described. Depending on the database, there are additional examples available on the website.

Database Specific Documentation

- The *TCS Zr-based Alloys Database (TCZR) Technical Information* PDF document contains version specific information such as the binary and ternary assessed systems, and the phases and models. It also includes a list of the included elements and general information about the included thermophysical properties data.
- The *TCS Zr-based Alloys Database (TCZR) Examples Collection* PDF document contains a series of validation examples using experimental data, and a set of calculation examples showing some of the ways the database can be used.

Go to the Zirconium-based Alloys Database page on our website where you can access an examples collection and the technical information.

Learn more on our website about the CALPHAD Method and how it is applied to the Thermo-Calc databases.

TCZR Validation Examples

In this section:

Prediction of Secondary Phases

The TCS Zr-based Alloys Database (TCZR) can be used to calculate phase equilibria, including phase fractions and compositions, where it reliably accounts for phase transformations with light impurities (O, H, etc.).

All the stable solution phases and intermetallic compounds included with the database are assessed along with the extrapolated systems. The database is able to predict the formation of secondary phases for a given composition within the recommended composition range of the database.

Harte et al. [2018Har] reviewed the secondary phases formed in the Zr-Nb-Fe-Sn-O materials. In the plot below, the results are summarized and applied to an isothermal section of the Zr-Nb-Fe at 973 K. It reveals the type and compositional distributions of the secondary phases, although in some cases the experimental data are quite scattered.

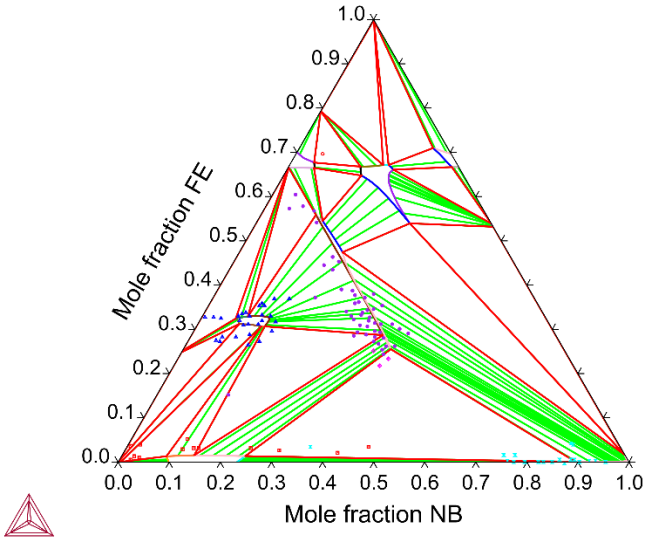

Figure 1: Calculated Zr-Nb-Fe isothermal section at 973 K with second-phase compositions in the Zr-Nb-Fe-Sn-O alloys reviewed by Harte et al. [2018Har].

Reference

[2018Har] A. Harte, M. Griffiths, M. Preuss, The characterisation of second phases in the Zr-Nb and Zr-Nb-Sn-Fe alloys: A critical review. J. Nucl. Mater. 505, 227–239 (2018).

Prediction of Phase Transition Temperatures

The TCS Zr-based Alloys Database (TCZR) enables extrapolations from binaries and ternaries to higher order systems. Thus, it can be used to predict the α/β phase transformation temperatures as a function of the chemical composition of typical industrial alloys. These transformations are of technological interest since it occurs during fabrication routes, welding operations, and/or accidental thermal transients i.e. in *loss of coolant accidents*.

Chung [1979Chu] and Forgeron et al. [1998For] investigated the zirconium-rich portion of the pseudobinary Zircaloy 2/4-oxygen phase diagram by resistometric measurements and metallographic analysis. The BCC and HCP transition temperatures were determined and compared with calculation results where, in general, the agreement is good.

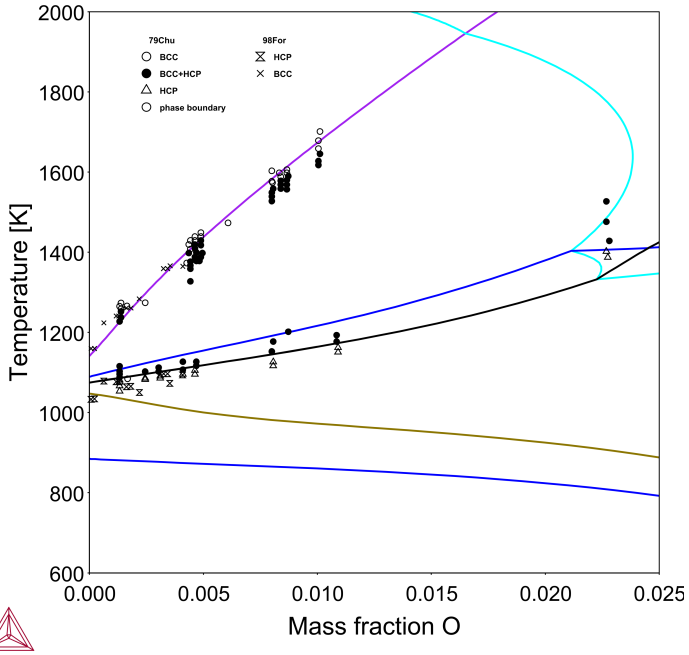

Figure 2: Calculated α/β phase boundaries of the pseudobinary Zircaloy 2/4-oxygen system with experimental data from [1979Chu] and [1998For].

The α+β → β transformation temperature is very sensitive to oxygen levels—with a 0.1 wt.% (1000 ppm) oxygen difference the temperature difference could be over 50 °C.

However, the α → α+β transformation temperature is not as sensitive. Therefore, if the oxygen level in the experimental study is unknown, the calculation results could be different as the measured transition temperatures, especially for α+β → β.

For more results about oxygen and hydrogen impact on phase equilibria and transition temperatures see these examples: Oxygen Impact on Phase Equilibria and Transition Temperatures and Hydrogen Impact on Phase Equilibria and Transition Temperatures

References

[1979Chu] H. M. Chung, T. F. Kassner, Pseudobinary zircaloy-oxygen phase diagram. J. Nucl. Mater. 84, 327–339 (1979).

[1998For] T. Forgeron, J. Brachet, F. Barcelo, A. Castaing, J. Hivroz, J. Mardon, C. Bernaudat, Experiment and Modeling of Advanced Fuel Rod Cladding Behavior Under LOCA Conditions: Alpha-Beta Phase Transformation Kinetics and EDGAR Methodology, in Zirconium in the Nuclear Industry: Twelfth International Symposium (ASTM International, PA), 1998; pp. 256-278.

Oxygen Impact on Phase Equilibria and Transition Temperatures

Oxygen is one of the major impurities in Zr-based alloys. The oxygen level in Zr alloys inevitably accounts for various features such as α/β transus temperatures, phase compositions, and for fractions vs. temperature. In the TCS Zr-based Alloys Database (TCZR) the oxygen solubility and oxide phases in binary and ternary Zr systems are carefully assessed.

Zr-Ni-O

The plot below shows the calculated Zr-rich side of the Zr-Ni-O system. A ternary ZrNiO_T phase occurs in an elongated phase field where O concentration varies between about 6 and 19 at.%.

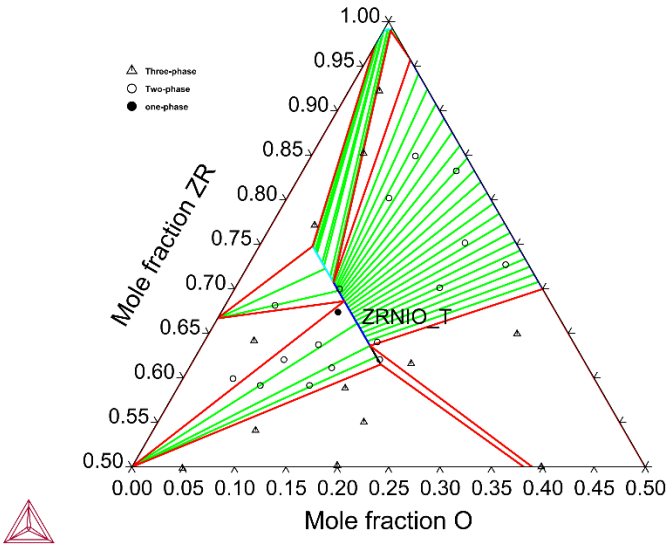

Figure 3: Calculated Zr-Ni-O isothermal section at 950 °C with experimental data from [1961Nev].

α+β → β Transition Temperatures

The plot below shows the calculated versus measured α+β → β transition temperatures at different oxygen levels in the Zr-rich region. The calculation results are well in agreement with the experimental ones.

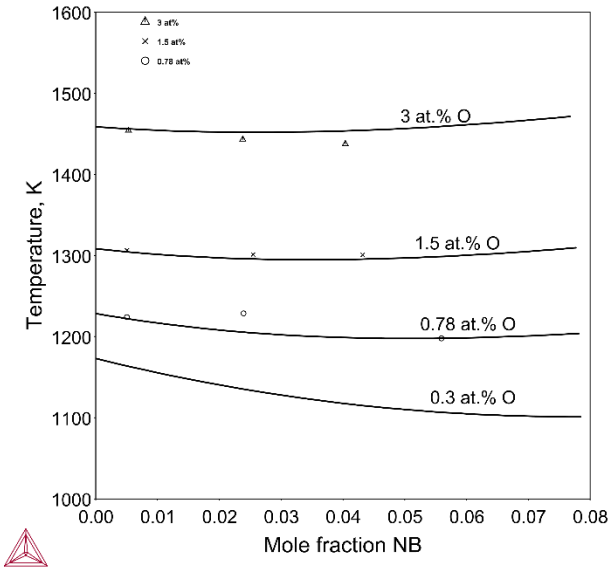

Figure 4: Calculated versus measured α+β → β transition temperature in the Zr-rich region with experimental data from [1971Hun].

References

[1961Nev] M. V. Nevitt, J. W. Downey, The Zirconium-Rich Corners of the Ternary Systems Zr-Co-O and Zr-Ni-O, Trans. Met. Soc. AIME, 221 (1961) 1014-1017.

[1971Hun] C. E. L. Hunt, P. Niessen, The continuous cooling transformation behaviour of zirconium-niobium-oxygen alloys. J. Nucl. Mater. 38, 17–25 (1971).

Hydrogen Impact on Phase Equilibria and Transition Temperatures

Hydrogen is incorporated in the TCS Zr-based Alloys Database (TCZR) where the hydrogen solubility and hydrides in binary systems and ternary Zr-Nb-H are carefully assessed. In reality, oxidation of zirconium by water releases hydrogen gas, which partly diffuses into the alloy.

H Solubility in HCP_Zr and Zr-H Phase Diagram

In this example, Figure 5 shows the calculated H solubility in HCP_Zr and Figure 6 shows the calculated Zr-H phase diagram with types of hydrides.

Hydrogen in Zr alloys decreases α/β transus temperatures [2008Zha] and may form zirconium hydrides. The hydrides are less dense and are mechanically weaker than the alloy. The formation results in blistering and cracking of the cladding—a phenomenon known as *hydrogen embrittlement*.

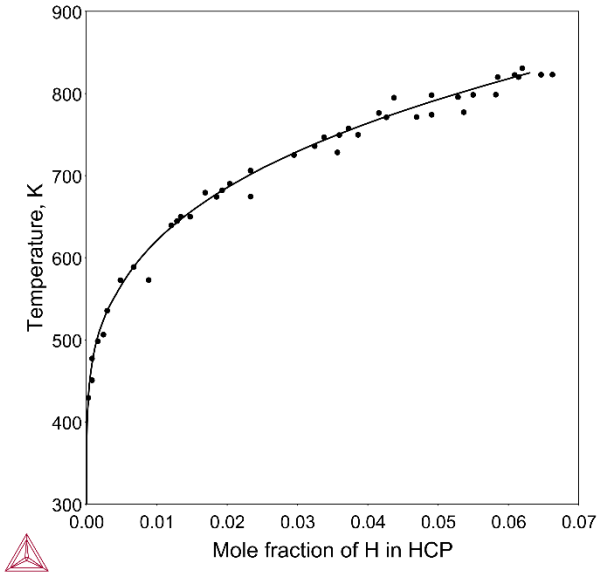

Figure 5: Calculated H solubility in HCP_Zr with published experimental data [1990Zuz].

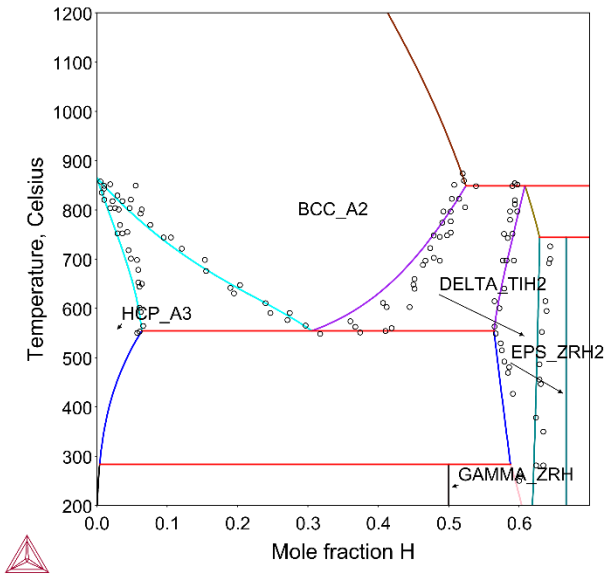

Figure 6: Calculated Zr-H phase diagram with published experimental data [1990Zuz].

Zr-H-Nb Isotherms

Figure 7 shows the calculated pressure-composition isotherms of the Zr–H–Nb system (wt.%Nb = 2.5) at different temperatures with experimental data from Sinha and Singh [1972Sin]. In the isotherms, where the pressure is composition-dependent, a single solid phase exists. On the plateaus, where the pressure is independent of composition, two solid hydride phases are in equilibrium. The phase boundary composition data, hydrogen equilibrium pressure for the two-phase region and the isobaric limit can be defined from the isotherms. In general, the agreement between calculated and experimental data is satisfactory. As the temperature decreases, the hydrogen composition increases and the equilibrium phases of the system also change.

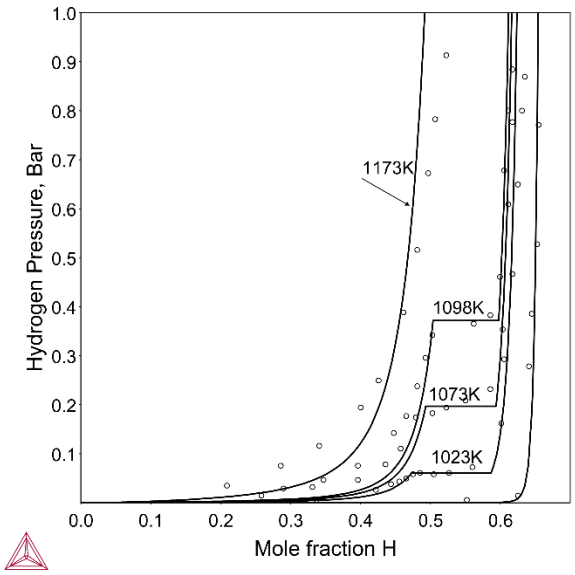

Figure 7: Calculated pressure-composition isotherms of Zr-2.5 wt.%Nb-H with experimental data from [1972Sin].

References

[1972Sin] V. K. Sinha, K. P. Singh, A pressure-composition-temperature study of Zr-Nb-H system. Metall. Trans. 3, 1581–1585 (1972).

[1990Zuz] E. Zuzek, J. P. Abriata, A. San-Martin, F. D. Manchester, The H-Zr (hydrogen-zirconium) system. Bull. Alloy Phase Diagrams. 11, 385–395 (1990).

[2008Zha] W. Zhao, Y. Liu, H. Jiang, Q. Peng, Effect of heat treatment and Nb and H contents on the phase transformation of N18 and N36 zirconium alloys. J. Alloys Compd. 462, 103–108 (2008).

Oxygen Diffusion in Zircaloy-4

Corvalan-Moya et al. [2010Cor] measured the oxygen diffusion profiles in low-Sn Zircaloy-4 at different temperatures. Diffusion Module (DICTRA) simulations were made to compare with the measured data.

The plot shows the calculation and comparison result of oxygen diffusion in BCC Zircaloy-4 at 1523 K for 309 s.

Read more about the Diffusion Module (DICTRA) on our website. If you are in Thermo-Calc, press F1 to search the help to learn about the available settings included with the Add-on Module.

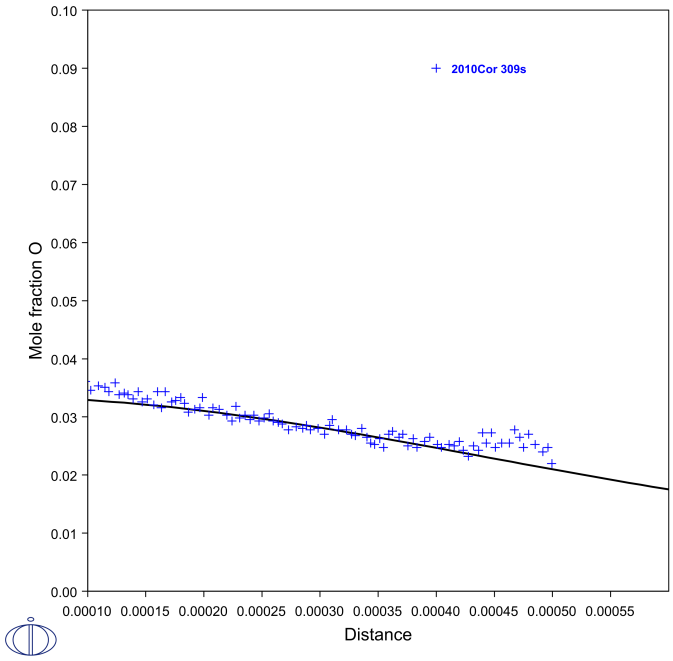

Figure 8: Calculated O diffusion profiles in Zircaloy-4 at 1523 K compared with experimental data.

Reference

[2010Cor] C. Corvalán-Moya, C. Desgranges, C. Toffolon-Masclet, C. Servant, J. C. Brachet, Numerical modeling of oxygen diffusion in the wall thickness of Low-Tin Zircaloy-4 fuel cladding tube during high temperature (1100–1250°C) steam oxidation. J. Nucl. Mater. 400, 196–204 (2010).

Precipitate Growth in Zircaloy-4

Calculations have been made using the current versions of TCS Zr-based Alloys Database (TCZR) and TCS Zr-alloys Mobility Database (MOBZR) and the Add-On Precipitation Module (TC-PRISMA) to compare with the precipitation and growth of the C14 phase Zr(Fe, Cr)2 in Zircaloy-4 alloy as studied by [1990Gro].

When setting up the calculation, a **General** precipitate growth model was selected since Fe and Zr have remarkable diffusivity differences. A mobility enhancement prefactor (0.03) is also used.

The resulting plot compares the mean radius of the spherical C14 precipitate phase calculated from the Precipitation Module (TC-PRISMA) with the data from [1990Gro].

Read more about the Precipitation Module (TC-PRISMA) on our website. If you are in Thermo-Calc, press F1 to search the help to learn about the available settings included with the Add-on Module.

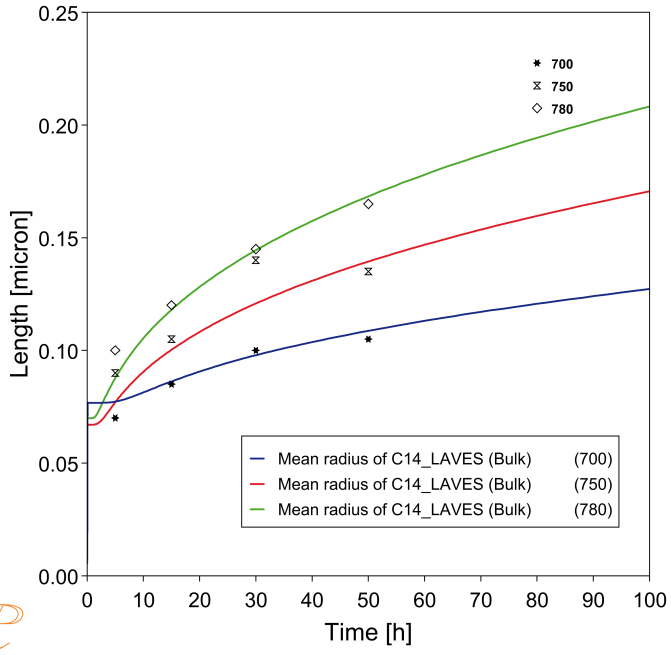

Figure 9: Mean radius of C14 for different heat treatments.

Reference

[1990Gro] J. P. Gros, J. F. Wadier, Precipitate growth kinetics in Zircaloy-4. J. Nucl. Mater. 172, 85–96 (1990).

TCZR Calculation Examples

In this section:

Binary Phase Diagrams

You can use the TCS Zr-based Alloys Database (TCZR) to plot binary phase diagrams in Thermo-Calc. Each assessed binary system is modeled to accurately describe experimental phase diagram data available in the literature.

These examples show a selection of the important assessed systems that are the building blocks of the database itself when applying the CALPHAD method.

Learn more on our website about the CALPHAD Method and how it is applied to the Thermo-Calc databases.

Cr-Zr

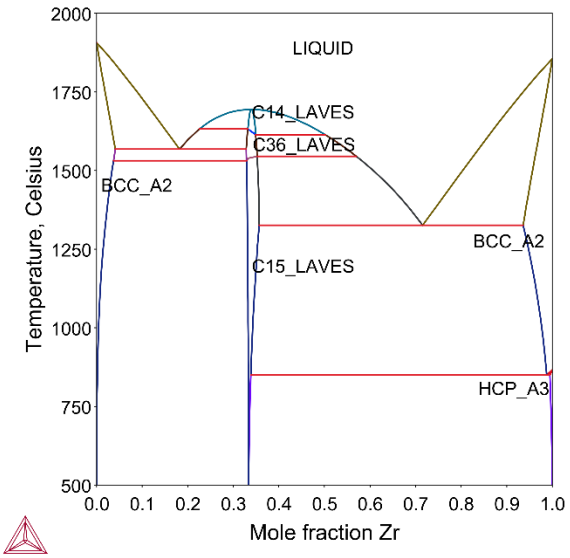

Figure 10: Calculated Cr-Zr phase diagram.

Fe-Zr

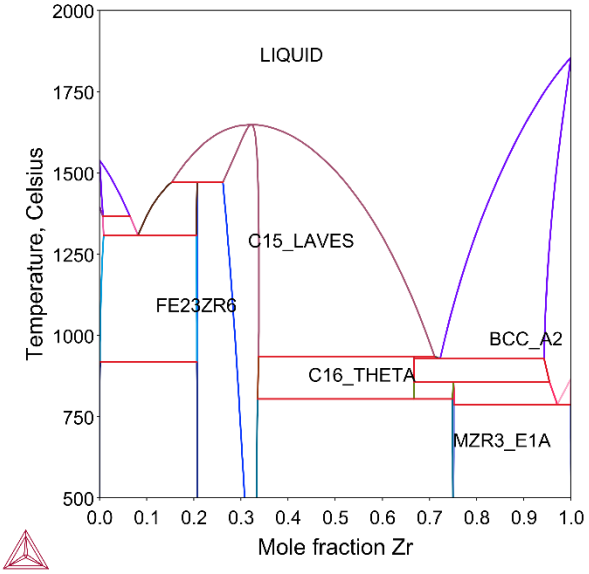

Figure 11: Calculated Fe-Zr phase diagram.

Nb-Zr

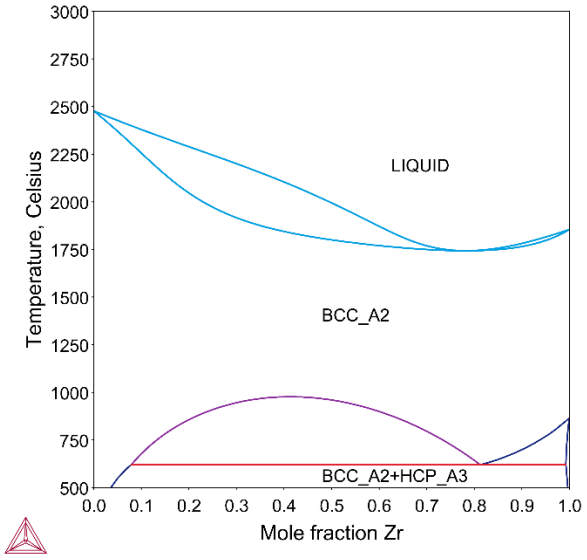

Figure 12: Calculated Nb-Zr phase diagram.

Zr-O

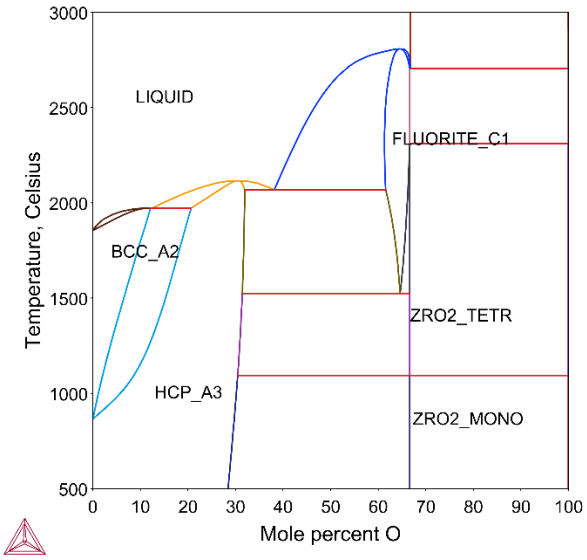

Figure 13: Calculated Zr-O phase diagram.

Ternary Phase Diagrams

You can use the TCS Zr-based Alloys Database (TCZR) to plot ternary phase diagrams in Thermo-Calc. Each assessed ternary system is modeled to accurately describe experimental phase diagram data available in the literature.

These examples show a selection of the important assessed systems that are the building blocks of the database itself when applying the CALPHAD method.

Learn more on our website about the CALPHAD Method and how it is applied to the Thermo-Calc databases.

When working in Thermo-Calc with ternary diagrams you use either the Ternary Calculator (in Graphical Mode) or the Ternary module (in Console Mode). The fundamental calculation engine is the same but you access the settings in different ways.

Cr-Nb-Zr

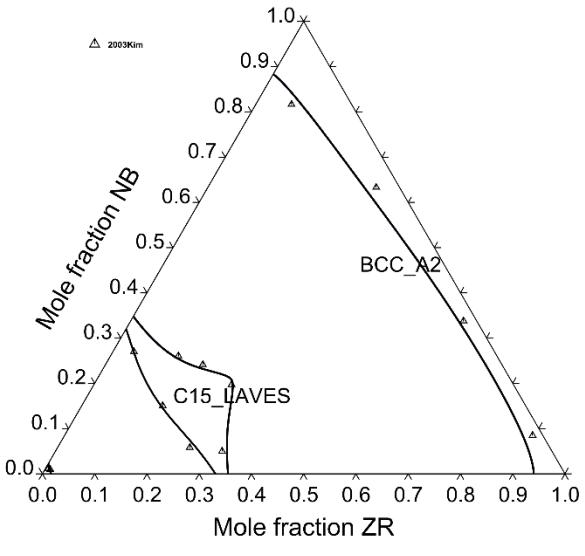

Figure 14: Calculated Cr-Nb-Zr isothermal section at 1573 K.

Fe-Sn-Zr

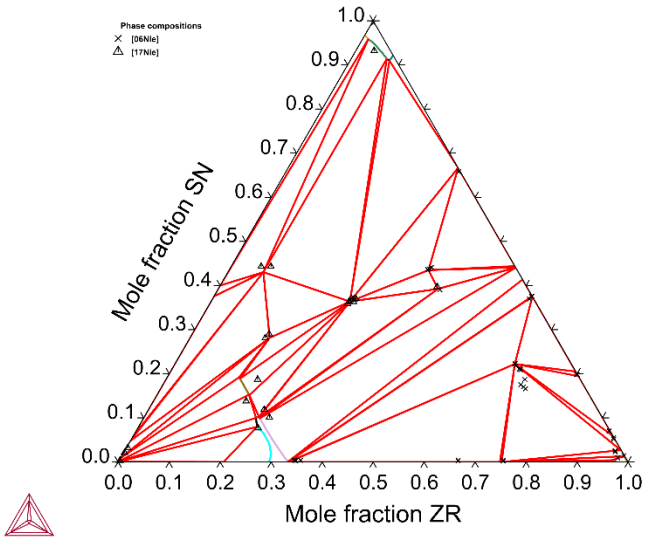

Figure 15: Calculated Fe-Sn-Zr isothermal section at 1073 K with experimental phase compositions determined by [2006Nie] and [2017Nie].

Fe86N14-Zr Alloys

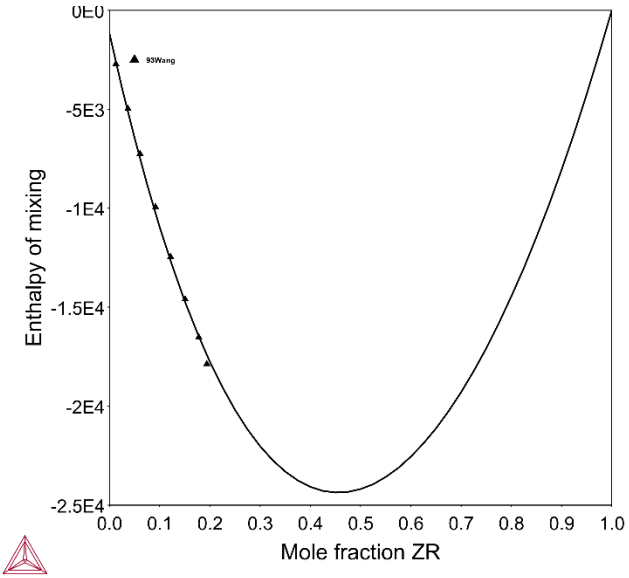

Figure 16: Calculated enthalpy of mixing of liquid Fe86N14-Zr alloys at 1873 K with experimental data from [1993Wan].

Ni-Sn-Zr

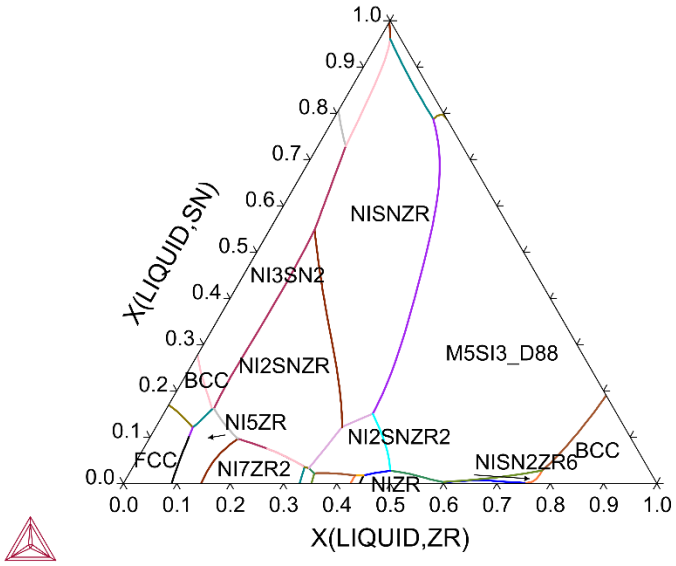

Figure 17: Calculated Ni-Sn-Zr liquidus projection.

References

[1993Wan] H. Wang, R. Lück, B. Predel, Thermodynamic investigation on liquid iron-nickel-zirconium alloys. J. Phase Equilibria. 14, 48–53 (1993).

[2003Kim] W.-Y. Kim, T. Takasugi, Laves phase fields in Cr–Zr–Nb and Cr–Zr–Hf alloy systems. Scr. Mater. 48, 559–563 (2003).

[2006Nie] N. Nieva, D. Arias, Experimental partial phase diagram of the Zr–Sn–Fe system. J. Nucl. Mater. 359, 29–40 (2006).

[2017Nie] N. Nieva, C. Corvalán, M. J. Jiménez, A. Gómez, C. Arreguez, J.-M. Joubert, D. Arias, Phase diagram of the Fe-Sn-Zr system at 800 °C. J. Nucl. Mater. 487, 186–191 (2017).

Viscosity: Ni-Zr and Fe-Zr

The viscosity thermophysical property data is included with the TCS Zr-based Alloys Database (TCZR).

For more information about the various thermophysical models, and when in Thermo-Calc, press F1 to search the online help. The details are found under a *General Reference* section.

You can find information on our website about the properties that can be calculated with Thermo-Calc and the Add-on Modules. Additional resources are added on a regular basis so keep checking back or subscribe to our newsletter.

Ni-Zr

The dynamic viscosity of the Ni-Zr system has been studied extensively [1998Ohs; 2014Joh; 2017Ohi]. Except for the values reported by Ohishi et al. [2017Ohi], the other measurements are in agreement with each other. The calculated viscosity curves after assessing this system based on the experimental data are shown in the following figure.

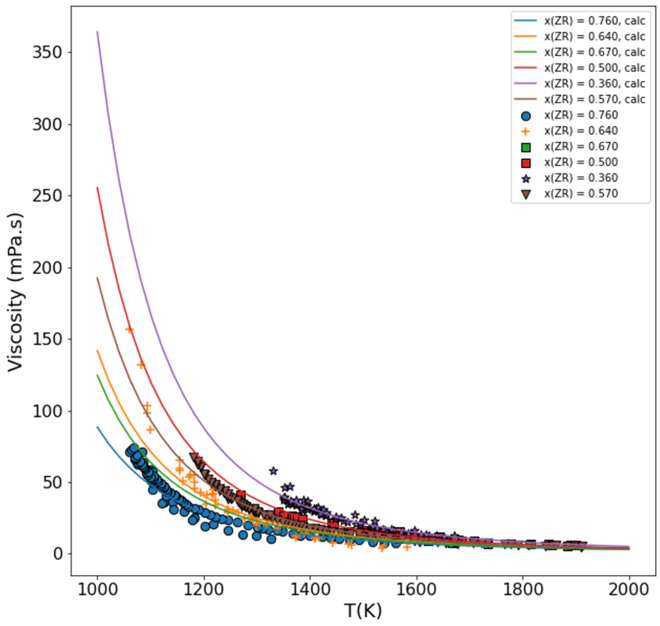

Figure 18: Dynamic viscosity of Ni-Zr binary alloys at various compositions compared with experimental data from [1998Ohs; 2014Joh].

Fe-Zr

The calculated dynamic viscosity of the Fe-Zr system along with experimental data is shown below.

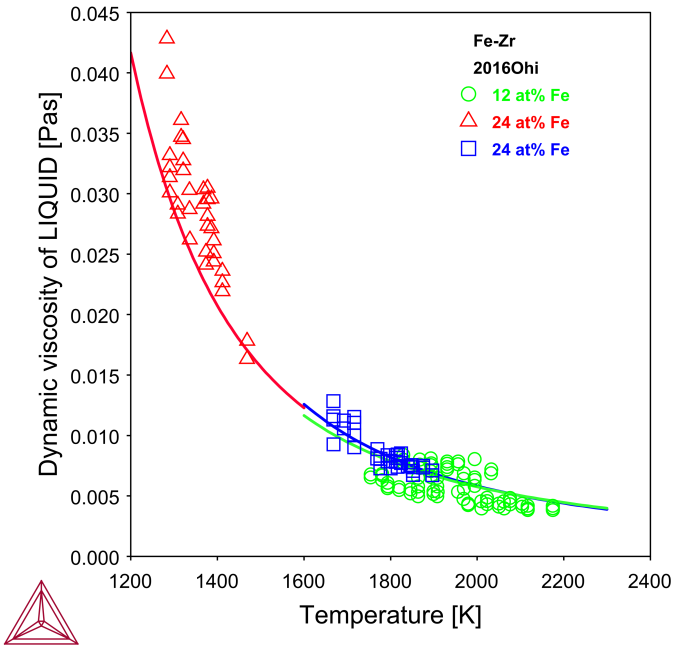

Figure 19: Calculated dynamic viscosity of Fe-Zr compared with experimental data from [2016Ohi].

References

[1998Ohs] K. Ohsaka, S. K. Chung, and W. K. Rhim, Specific volumes and viscosities of the Ni–Zr alloys and their correlation with the glass formability of the alloys, Acta Mater., vol. 46, no. 13, pp. 4535–4542 (1998).

[2014Joh] M. L. Johnson, N. A. Mauro, A. J. Vogt, M. E. Blodgett, C. Pueblo, and K. F. Kelton, Structural evolution and thermophysical properties of ZrxNi100−x metallic liquids and glasses, J. Non. Cryst. Solids, vol. 405, pp. 211–218 (2014).

[2016Ohi] Y. Ohishi, H. Muta, K. Kurosaki, J. T. Okada, T. Ishikawa, Y. Watanabe, S. Yamanaka, Thermophysical properties of molten core materials: Zr–Fe alloys measured by electrostatic levitation. J. Nucl. Sci. Technol. 53, 1943–1950 (2016).

[2017Ohi] Y. Ohishi, T. Kondo, T. Ishikawa, J. T. Okada, Y. Watanabe, H. Muta, K. Kurosaki, S. Yamanaka, Physical properties of molten core materials: Zr-Ni and Zr-Cr alloys measured by electrostatic levitation. J. Nucl. Mater. 485, 129–136 (2017).