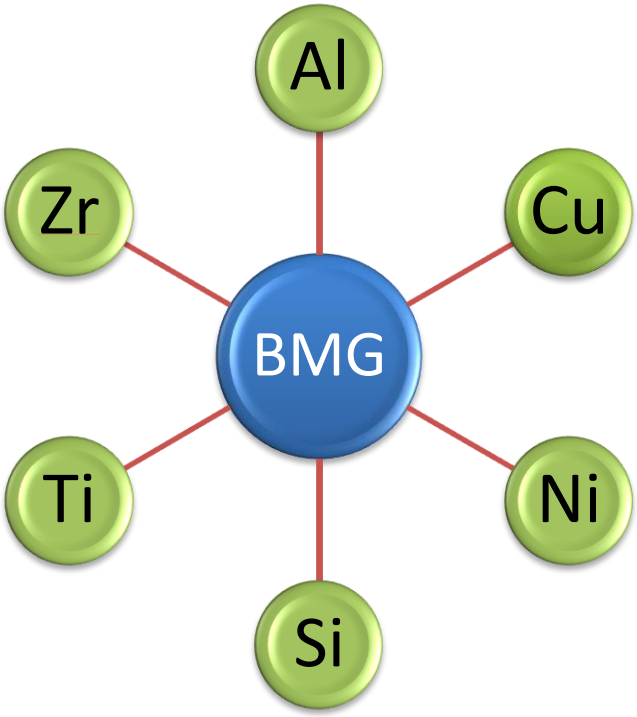
# 1. PanBMG

Thermodynamic Database for Bulk Metallic Glass

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## 1.1 Components

The PanBMG thermodynamic database, including the six elements as the following, covers all the equilibrium phases reported in the alloy system.

Al-Cu-Ni-Ti-Si-Zr

## 1.2 Suggested Composition Range

The suggested composition range for each element is listed in Table 1.1. The PanBMG database is a full description of the six-component system, which includes 15 binaries and 20 ternaries.

Table 1.1: Suggested composition range

| Element | Composition range (wt.%) |
|---|---|
| Al | 0-100 |
| Cu | 0-100 |
| Ni | 0-100 |
| Ti | 0-100 |
| Zr | 0-100 |
| Si | 0-100 |

## 1.3 Phases

Total of 122 phases are included in the database, which account for all the stable phases appearing in the alloy system. The name, the structure, and model type of major phases are given in Table 1.2. Information on all the other phases may be displayed through TDB viewer of Pandat and can be found at www.computherm.com.

Table 1.2: Phase name and related information

| Name | Lattice Size | Constituent |
|---|---|---|
| Al5CuTi2 | (0.75)(0.25) | (Al,Cu)(Ti) |
| Al5CuZr2 | (0.625)(0.125)(0.25) | (Al)(Cu)(Zr) |
| Al6Cu3Ni | (0.6)(0.3)(0.1) | (Al)(Cu)(Ni) |
| AlCu2Ti | (0.75)(0.25) | (Al,Cu)(Ti) |
| AlCu2Zr | (0.25)(0.5)(0.25) | (Al)(Cu)(Zr) |
| AlCuTi | (0.6667)(0.3333) | (Al,Cu)(Ti) |
| AlCuZr | (0.667)(0.333) | (Al,Cu)(Zr) |
| B2 | (0.5)(0.5) | (Al,Cu,Ni,Ti,Zr)(Cu,Ni,Ti,Zr,VA) |
| Bcc | (1)(3) | (Al,Cu,Ni,Si,Ti,Zr)(VA) |
| Cu2TiZr | (0.5)(0.25)(0.25) | (Cu)(Ti)(Zr) |
| Cu3Si4Zr2 | (0.3334)(0.4444)(0.2222) | (Cu)(Si)(Zr) |
| Cu4Si2Zr3 | (0.4444)(0.2222)(0.3334) | (Cu)(Si)(Zr) |
| Cu4Si4Zr3 | (0.3636)(0.3636)(0.2728) | (Cu)(Si)(Zr) |
| Fcc | (1)(1) | (Al,Cu,Ni,Si,Ti,Zr)(Va) |
| Gamma_D83 | (1)(1) | (Al,Cu,Ni,Si)(Va) |
| Hcp | (1)(0.5) | (Al,Cu,Ni,Si,Ti,Zr)(Va) |
| L12 | (0.75)(0.25)(1) | (Al,Cu,Ni,Si,Ti,Zr)(Al,Cu,Ni,Si,Ti,Zr)(Va) |
| Laves_C14 | (2)(1) | (Al,Ni,Ti)(Al,Ni,Ti) |
| Liquid | (1) | (Al,Cu,Ni,Si,Ti,Zr) |
| Ni4Si9Zr7 | (0.2)(0.45)(0.35) | (Ni)(Si)(Zr) |
| NiSiZr | (0.3333)(0.3333)(0.3334) | (Ni)(Si)(Zr) |
| NiTi | (0.5)(0.5) | (Cu,Ni)(Al,Ti,Zr) |
| NiTi2 | (0.333333)(0.666667) | (Cu,Ni)(Al,Ti) |
| NiTiZr | (1)(1)(1) | (Ni)(Ti)(Zr) |

# 1.4 Sub-System Information

All the binary systems and ternary systems in the PanBMG database were critically assessed and thermodynamic descriptions were validated extensively against experimental information. All the equilibrium phases in each binary system and ternary system were covered in the database. Complete phase diagrams can be calculated for all binary and ternary systems in the Zr-Al-Cu-Ni-Ti-Si system. The binary systems and ternary systems included in the PanBMG database are listed in Table 1.3 and Table 1.4.

: Full description

: Full description for major phases

: Extrapolation

Table 1.3: Binary Systems Included in the PanBMG Database

| | Cu | Ni | Si | Ti | Zr |
|---|---|---|---|---|---|
| Al | Al-Cu | Al-Ni | Al-Si | Al-Ti | Al-Zr |
| Cu | | Cu-Ni | Cu-Si | Cu-Ti | Cu-Zr |
| Ni | | | Ni-Si | Ni-Ti | Ni-Zr |
| Si | | | | Si-Ti | Si-Zr |
| Ti | | | | | Ti-Zr |

Table 1.4: Ternary Systems Included in the PanBMG Database

| | Ni | Si | Ti | Zr |
|---|---|---|---|---|
| Al-Cu | Al-Cu-Ni | Al-Cu-Si | Al-Cu-Ti | Al-Cu-Zr |
| Al-Ni | | Al-Ni-Si | Al-Ni-Ti | Al-Ni-Zr |
| Al-Si | | | Al-Si-Ti | Al-Si-Zr |
| Al-Ti | | | | Al-Ti-Zr |
| Cu-Ni | | Cu-Ni-Si | Cu-Ni-Ti | Cu-Ni-Zr |
| Cu-Si | | | Cu-Si-Ti | Cu-Si-Zr |
| Cu-Ti | | | | Cu-Ti-Zr |
| Ni-Si | | | Ni-Si-Ti | Ni-Si-Zr |
| Ni-Ti | | | | Ni-Ti-Zr |
| Si-Ti | | | | Si-Ti-Zr |

# 1.5 Database Validation

The Cu-Zr binary phase diagram and the liquidus projection for Al-Ni-Zr system are shown in Figure 1.1 and Figure 1.2, respectively.

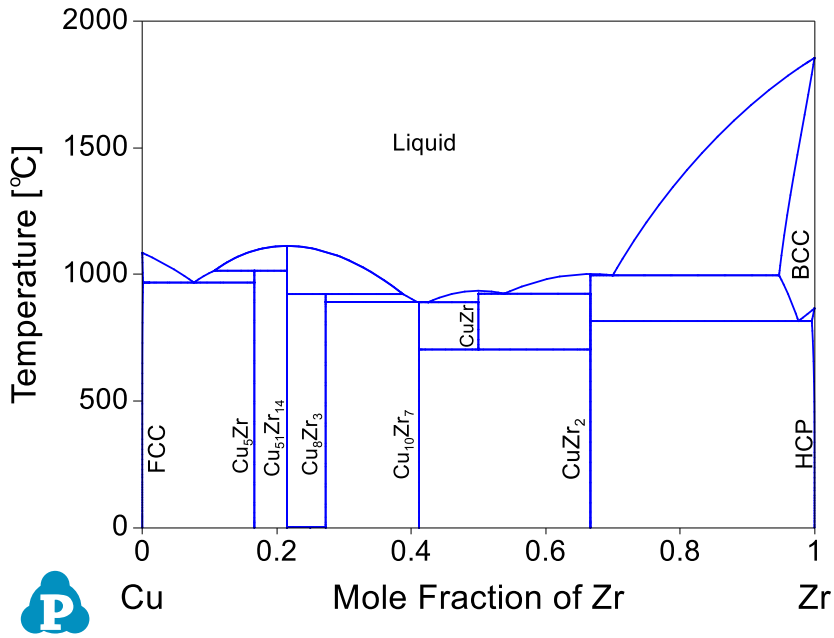


Figure 1.1: Calculated Cu-Zr phase diagram

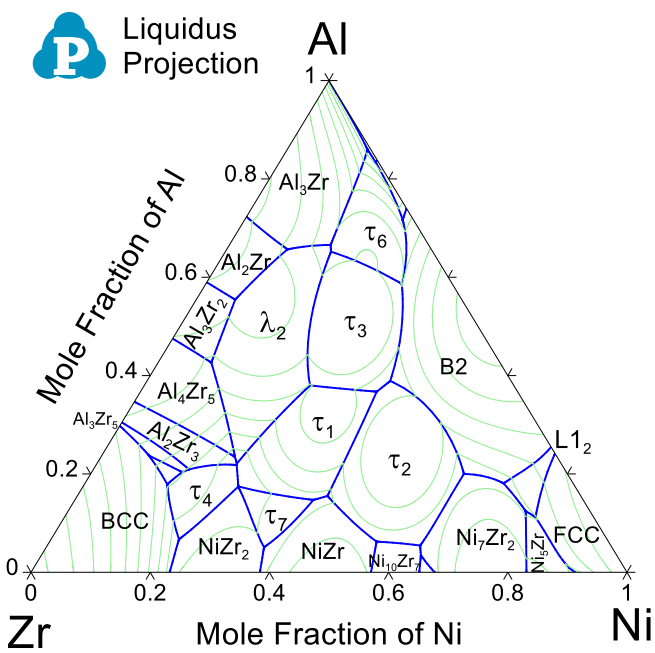


Figure 1.2: Calculated liquidus projection for Al-Ni-Zr

Some sub-quaternary systems of this database have been critically assessed and thermodynamically modeled. Figure 1.3 shows the comparison between the calculated integral enthalpy of mixing of liquid $Al_{17}Ni_{66}Si_{17}$-Cu alloys at 1575K and the experimental data from [2000Wit].

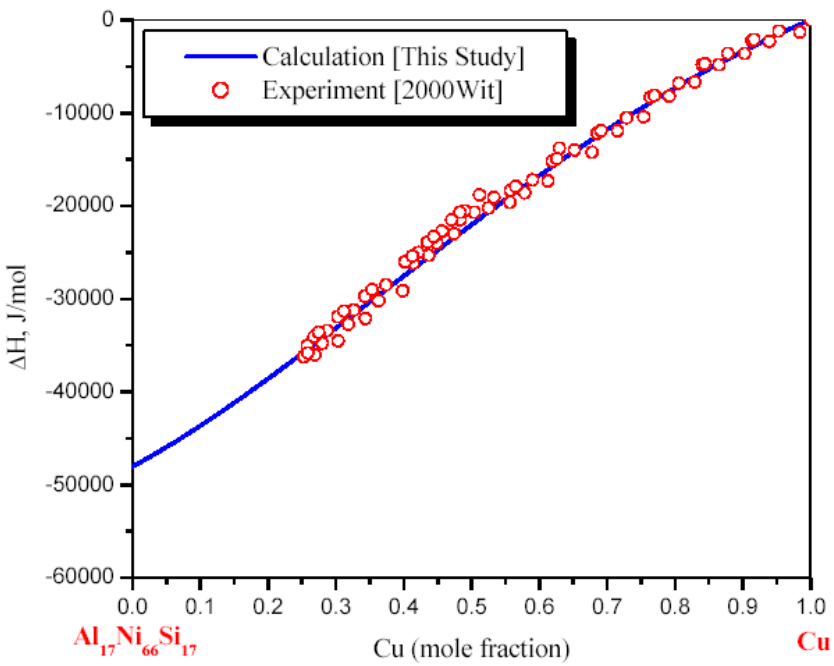


Figure 1.3: Comparison between the calculated and experimental integral enthalpy of mixing of liquid $Al_{17}Ni_{66}Si_{17}$-Cu alloys at 1575K

Since the major application of the PanBMG database is to predict the composition region of low-lying liquidus surfaces of the Zr-Al-Cu-Ni-Si-Ti system where bulk metallic glass (BMG) tends to form, the database is validated by comparing the predicted composition region with the low-lying liquidus surfaces and experimentally identified bulk metallic glass forming region. The low-lying liquidus surfaces are indicated by the temperatures of the invariant reactions occurring on the liquidus surface, which can be automatically calculated by Pandat. Examples of these comparisons for Zr-Cu-Ni-Ti and Zr-Al-Cu-Ni-Ti are given below.

Using the PanBMG database, the invariant temperatures for all the five-phase equilibria in the Cu-Ni-Ti-Zr alloys with one of these phases being a liquid

phase were calculated. Figure 1.4 compares the calculated liquid composition of the invariant reactions with the lowest temperatures and experimentally identified regions for BMG formation [2001Yan]. As shown in Figure 1.4, the calculated liquid compositions of these invariant reactions are denoted as solid circles and the experimentally identified BMG forming compositions by Lin and Johnson [1995Lin] are denoted by open squares.

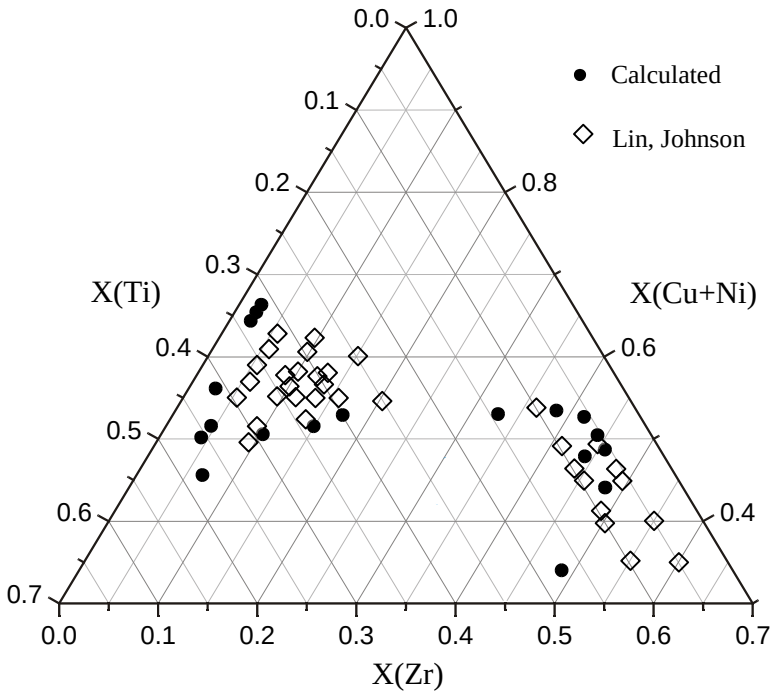


Figure 1.4: Comparison of the thermodynamically predicted and experimentally identified [1995Lin] liquid compositions of the five-phase invariant reactions with one of phases being liquid in the Zr-Cu-Ni-Ti system

Figure 1.5 shows that thermodynamically predicted liquid alloy compositions with low-lying liquidus surface illustrate a region of the quinary composition space, in which a series of new Zr-rich alloys were subsequently found experimentally to form bulk metallic glasses with diameters up to 14mm by using the conventional copper mold dropping casting (or suction casting) method. Five representative novel glass-forming alloys are denoted as G1-G5 in Figure 1.5 as well. Strikingly, the calculated compositional region is noted to be in good agreement with those experimental results [1999Joh, 1996Xin,

2000Pel, 1999Xin, 2003Zha, 2005Cao, 2005Ma] (presented as green dots in Figure 1.5).

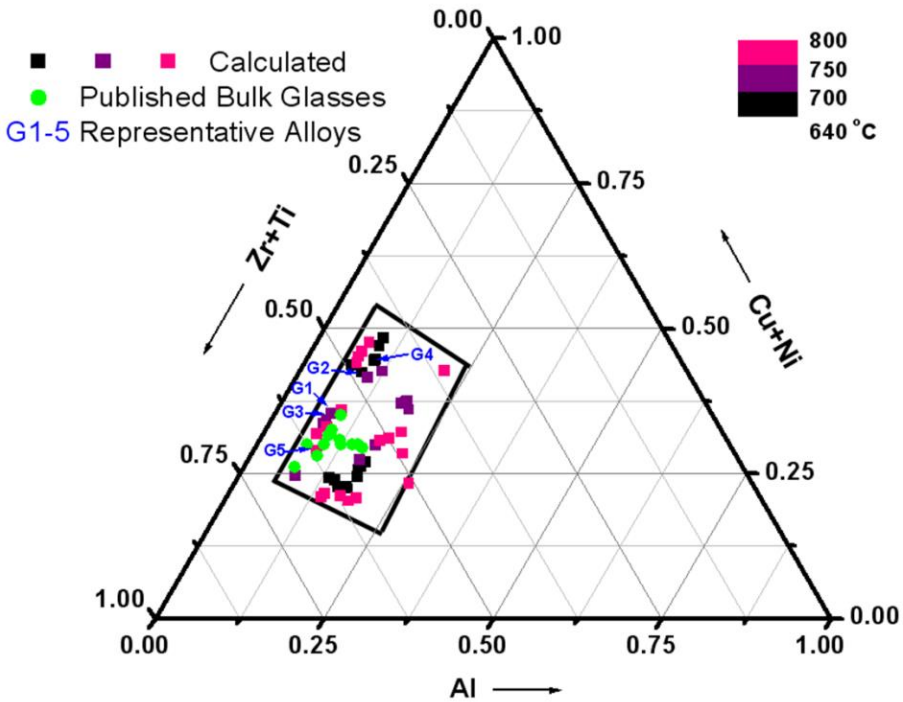


Figure 1.5: Comparison of the thermodynamically predicted and experimentally identified liquid compositions of the six-phase invariant equilibria with one of phases being liquid in the Zr-Al-Cu-Ni-Ti system

Figure 1.6 shows a calculated isopleth of the quinary Zr-Al–Cu–Ni–Ti phase diagram with 8.5%Al, 31.3%Cu, and 4.0%Ni, using the PanBMG database. The concentration of Ti varies from 0 to 15% with a corresponding concentration of Zr from 56.2% to 41.2%. In other words, Ti was used to partially replace Zr in a quaternary base alloy $Zr_{56.2}Cu_{31.3}Ni_{4.0}Al_{8.5}$. This quaternary alloy was identified to be a bulk glass-forming alloy (with a critical casting diameter for glass formation of *6 mm*) based on the calculated low-lying liquidus surface of the quaternary Zr–Al-Cu-Ni system. As shown in this isopleth, the calculated liquidus at the origin of the compositional coordinate, i.e., the base alloy $Zr_{56.2}Cu_{31.3}Ni_{4.0}Al_{8.5}$, decreases rapidly to a minimum of about 4.9%Ti and then increases again. Thus, the liquidus depression reaches a maximum of 102K at 4.9%Ti replacement. Accordingly, a series of alloys of $Zr_{56.2-x}Ti_xCu_{31.3}Ni_{4.0}Al_{8.5}$

with values of $x$ varying from 0 to 12, were prepared with the expectation that the alloy with 4.9%Ti would exhibit the highest Glass Forming Ability (GFA). This prediction was approved by experimental results as shown in Figure 1.7.

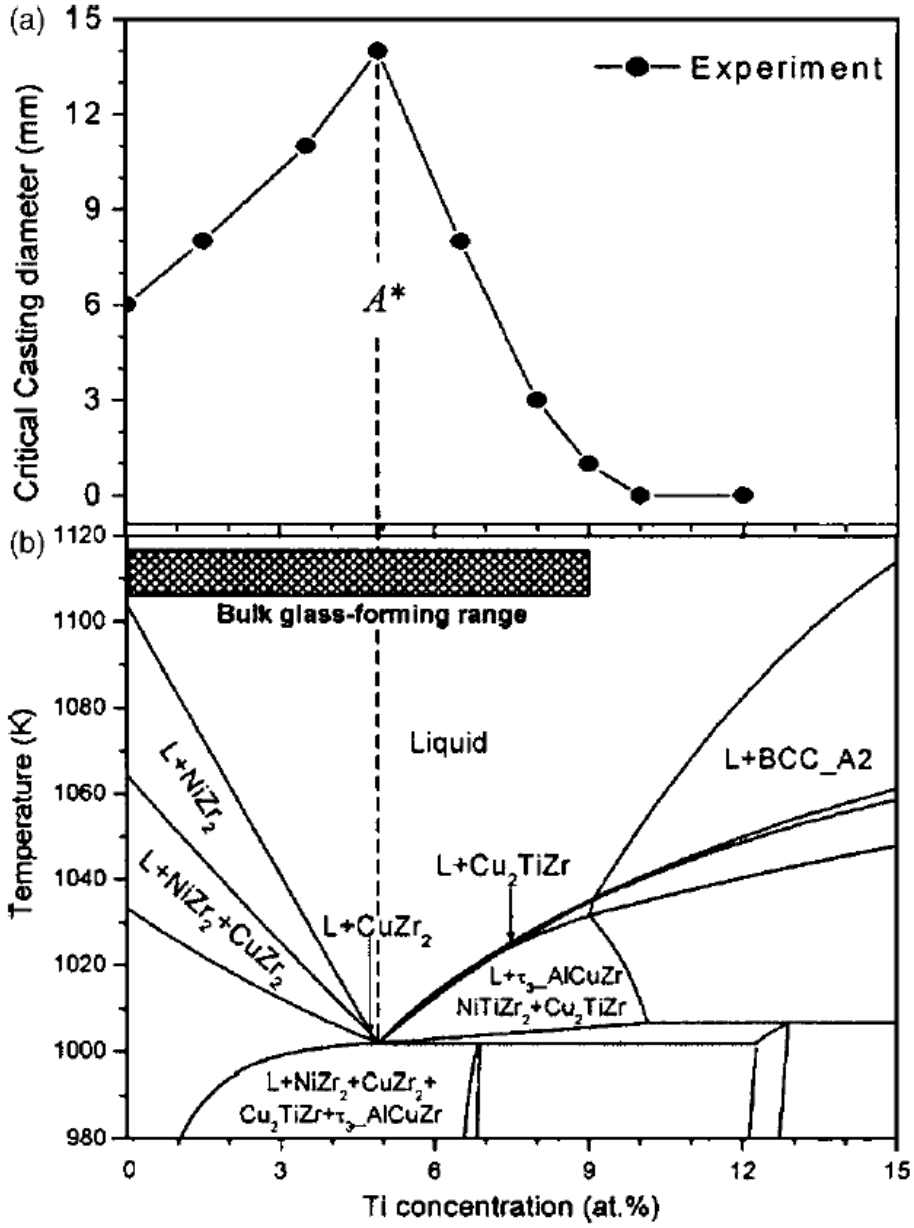


Figure 1.6: (a) The critical casting diameter as a function of Ti concentration in a series of alloys $Zr_{56.2-x}Ti_xCu_{31.3}Ni_{4.0}Al_{8.5}$(x=0–12), showing A* (containing 4.9%Ti) is the bulkiest glass-forming alloy; (b) The calculated isopleth with the compositions of Cu, Ni, and Al fixed at 31.3%, 4.0%, and 8.5%, respectively. The shaded area denotes the experimentally observed bulk glass-forming range

Figure 1.7: Surface appearance of the glassy alloys rods obtained in the study based on the thermodynamic calculations [2005Cao]

# 1.6 References

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