

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

**WEB OF SCIENCE™**Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com

Thermodynamic Approach for Amorphous Alloys from Binary to Multicomponent Systems

Lai-Chang Zhang

*The University of Western Australia
Australia*

1. Introduction

When conventional metal alloys are cooled from their molten state, atoms will quickly rearrange themselves in a long range regular and periodic manner. Therefore, conventional metallic materials have a crystalline structure in nature. The structure of amorphous alloys is very different from that of the conventional metals, where the atoms are "frozen" in a random, disordered structure when the molten liquid was cooled fast enough to frustrate the formation of crystalline structure. The first amorphous alloy, $\text{Au}_{75}\text{Si}_{25}$ (in atomic percent, at.%, throughout this chapter), was formed in 1960 (Klement et al., 1960) by using a rapid quenching technique for chilling metallic liquids at very high rate of $10^5 - 10^6$ K/s. Since then, considerable effort has been devoted to form amorphous structure through kinds of rapid solidification techniques (Suryanarayana, 1980). The research on amorphous alloys have received more development momentum in the early 1970s and 1980s when the continuous casting technique was developed for commercial manufacture of metallic glasses ribbons, lines, and sheets (Chen, 1980). However, the high cooling rate has limited the geometry of amorphous alloys in the form of thin sheets and lines. Such a small physical size (less than $50 \mu\text{m}$) has significantly limited the potential industrial/commercial applications of this new class of materials. As a result, a variety of solid-state amorphization techniques were developed in 1980s to form amorphous alloys (see two reviews as Johnson, 1986; Cahn & Zarzycki, 1991). Two terms "amorphous alloy" and "metallic glass" have been using to describe these novel materials. A widely used "amorphous alloy" is adopted in this chapter to describe any metallic alloy that does not possess crystallinity. However, this chapter still uses "metallic glass" especially for that obtained by melt quenching techniques. The first bulk metallic glass, defined as the amorphous alloys with a dimension no less than 1 mm in all directions, was discovered by Chen and Turnbull (Chen & Turnbull, 1969) in ternary Pd-Cu-Si alloy. These ternary bulk metallic glass-forming alloys have a critical cooling rate of about 100 K/s and can be obtained in the amorphous state with thickness up to 1 mm and more. Since then, especially after the presence of new bulk metallic glasses in $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ (Inoue et al., 1989) and $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ (Peker & Johnson, 1993), multicomponent bulk metallic glasses which could be prepared by direct casting at low cooling rates have been drawing increasing attention in the scientific community. A great deal of effort has been devoted to developing and characterizing bulk metallic glasses with a section thickness or diameter of a few millimetres to a few centimetres. A large variety of multicomponent bulk metallic glasses in a number of alloy systems, such as Pd-, Zr-, Mg-, Ln-, Ti-, Fe-, and Ni-based

bulk metallic glasses, have been developed via direct casting method through low cooling rates of the order of 1 – 100 K/s (Inoue, 2000; Suryanarayana & Inoue, 2011). In this method, the compositions of alloys are carefully designed to have large glass-forming ability (GFA) so that “bulk” amorphous alloys can be formed at a low cooling rate. From the requirement for high cooling rates to bypass crystallization, it is clear that metallic glasses cannot be directly cast in very large sizes. The “record” size of the bulk metallic glasses is 72 mm diameter for a $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk metallic glass (Inoue et al., 1997). Currently, amorphous alloys have a variety of uses for sports and luxury goods, electronics, medical, and defense.

2. Alloy development strategies

Amorphous alloys have become more and more attractive because of their excellent chemical, electrical, high mechanical strength, good corrosion resistance, reduced sliding friction and improved wear resistance, excellent soft and hard magnetic properties, and unique optical or electrical properties (Johnson, 1999; Inoue, 2000; Eckert et al., 2007; Wang, 2009; Xu et al., 2010; Suryanarayana & Inoue, 2011). A very large number of amorphous alloys have been synthesized from binary to ternary, quaternary, and even higher order alloy systems in the last 50 year, no matter by direct melt cooling methods or through solid-state amorphization techniques. In order to obtain the fundamental knowledge of the glass-forming ability (GFA) of multicomponent alloy systems to search for bulk metallic glasses with larger dimensions, a great number of parameters/indicators have been proposed to evaluate the GFA of amorphous alloys produced in a large number of alloy systems. Suryanarayana and Inoue have summarized these GFA parameters (Suryanarayana & Inoue, 2011), including reduced glass transition temperature T_{rg} ($=T_g/T_l$, where T_g is glass transition temperature and T_l is liquidus temperature), supercooled liquid region ΔT_x ($=T_x - T_g$, where T_x is the onset crystallization temperature), α parameter ($=T_x/T_l$), β parameter ($=1 + T_x/T_l$), γ parameter ($=T_x/(T_g + T_l)$) and so on. Although different GFA parameters were able to give a reasonably good correlation for some bulk metallic glass-forming alloy systems, not one single parameter could satisfactorily explain the glass-forming ability of all bulk metallic glass-forming alloy systems. It is noted that, all the aforementioned GFA parameters require the transformation temperatures data (i.e. glass transition temperature T_g , onset crystallization temperature T_x or liquidus temperature T_l) of an amorphous alloy. However, these transformation temperatures could be obtained only after the amorphous alloy has been formed and is reheated in thermal analysis equipment (i.e. DSC/DTA). In addition, the values of these transformation temperatures, especially the onset crystallization temperature T_x and liquidus temperature T_l are largely dependent on the heating rate that is adopted to reheat the amorphous alloys in a DSC/DTA equipment (Zhang et al., 2006).

Because of the absence of fundamental theory to predict easy glass formation, presently the search for new compositions for amorphous alloys is conducted largely by trial-and-error approach, partially guided by experimental and/or computer calculated phase diagrams and a few empirical rules. Various alloy development strategies have been proposed for multicomponent glass-forming alloys, such as Egami’s volume strain criterion (Egami & Waseda, 1984; Egami, 1997, 2003; Yan et al., 2003), Inoue’s three empirical rules (Inoue et al., 1990, 1992), and Miracle’s topological criterion (Senkov & Miracle, 2001; Miracle & Senkov, 2003). Among them, Inoue’s three empirical rules, which were formulated based on the extensive data generated on the formation of bulk metallic glasses, are the mainstay for a long time to guide the search of new bulk glass-forming alloy compositions in multicomponent

alloy systems. In fact, hundreds of multicomponent alloy compositions have been prepared in amorphous state guided by these three empirical rules. The Inoue's rules are as follows:

- The multicomponent alloy system must consist of at least three components. The formation of amorphous phase becomes easier with increasing the number of components in the alloy system.
- The atomic radius mismatch between the constituent elements must differ from each other by greater than 12%, and
- There should be large negative heats of mixing between the main components in the alloy system.

Among these criteria, the first one is based on the thermodynamic and kinetic aspects of glass formation. The increment of the number of components in an alloy will significantly increase the entropy of fusion, leading to an increase in the degree of the dense random packing of atoms. This results in a decrease in enthalpy of fusion and also an increase in the solid-liquid interface energy. As a result, these factors contribute to a decrease in the free energy of the system. The second criterion is based on the topological aspects (structure and packing of atoms), and the third one is essential for mixing of atoms (alloying to occur) and for the formation of a homogeneous amorphous phase. The combination of the significant differences in atomic sizes between the constituent elements and the negative heat of mixing is expected to result in efficient packing of clusters and consequently increase the density of random packing of atoms in the supercooled liquid state. This, in turn, leads to increased liquid-solid interface energy, and decreased atomic diffusivity, both contributing to enhanced glass formation.

Even though the Inoue's three empirical rules have received great success in the development of bulk metallic glasses, some apparent exceptions have been reported in a few alloy systems. The recently developed bulk metallic glasses in some binary alloy systems such as Ca-Al, Cu-Hf, Cu-Zr, Ni-Nb, and Pd-Si (Suryanarayana & Inoue, 2011) have apparently broken the first criterion among the Inoue's three empirical rules. Although the maximum sizes of these bulk metallic glasses in binary alloys are too small (about 1 – 2 mm), they are indeed belong to the family of bulk metallic glasses as their size is greater than the well-defined critical size of bulk metallic glass (no less than 1 mm). It is noted that the aforementioned strategies could not effectively pinpoint the chemical compositions for glass formation in multicomponent alloy systems. Therefore, the search of new compositions for bulk metallic glass-forming alloys could only rely heavily on the trial-and-error approach, which involves considerable laboratory work to find a good bulk glass-forming alloy composition. A three-dimensional search method has been developed to navigate in three-dimensional composition space for locating the best glass-forming compositions in the Mg-(Cu,Ag)-(Y,Gd) alloy system (Ma et al., 2005; Zheng et al., 2006). By combining these alloy development strategies with the knowledge of the very recently developed bulk metallic glasses, a four-step approach has been recently proposed for searching the compositions to form bulk metallic glasses in multicomponent alloy systems (Fan et al., 2010). It involves: (a) searching deep eutectic composition(s) in binary or ternary phase diagrams, (b) alloying 10-20 at.% metals showing a mutual solubility with one of the base elements, (c) selecting suitable alloying elements with large difference in atomic size and negative heat of mixing to main component, and (d) micro-alloying 1-2 at.% appropriate elements. Actually, this four-step approach is still involved in the frame of Inoue's three empirical rules.

Considering their chemical compositions, amorphous alloys are quite complex, usually containing more than 3 (mostly 4–6) constituent elements. This chemical complexity makes it very laborious to search for the best bulk glass-forming composition in each

multicomponent alloy system. Although the above-mentioned alloy development strategies have been used with some success, the search for good bulk metallic glass-forming composition guided by these strategies has not been completely satisfactory and does need tremendous laboratory work. Furthermore, phase diagrams are currently unavailable for the multicomponent alloy systems, only for up to 3 or 4 components. Since the complexity of phase diagrams increases with the component number in an alloy system, it is hard to determine the effect of the alloying elements on the existed phase diagram or the eutectic compositions (and much less about deep eutectics). It is worthy to note that the chemical compositions having the best glass-forming ability need not always lie at the eutectics and they could be located at off-eutectic compositions (Wang et al., 2005). In addition, it will be a formidable problem to determine the minimum solute content in such a high order alloy system, because the contribution of each constituent element to the volumetric strain is going to be different depending on their atomic sizes. The situation becomes more complex when one realizes that the magnitude and the sign of stress could be different for different alloying elements. Therefore, it would be great for the development of new multicomponent bulk metallic glasses if the glass-forming ability of a designated multicomponent glass-forming alloy composition could be ascertained without the necessity of doing any experiments to form the amorphous samples. It will cut down a lot of laboratory work by the current trial-and-error approach to find a good bulk glass-forming composition in a multicomponent alloy system. Therefore, a predictive approach and thermodynamic modelling (for example, through the measured or calculated heats of mixing or other thermodynamic parameters) is required to solve this problem.

3. Thermodynamic approaches based on enthalpy calculation

The thermodynamic properties of alloys are very important for the understanding of the relative stability of alloys and phases. From the laws of classic thermodynamics, the thermodynamic stability of a system at constant temperature and pressure is determined by its Gibbs free energy, G . The Gibbs free energy of a system is defined as

$$G = H - TS \quad (1)$$

where H is the enthalpy, T is the absolute temperature, S is the entropy.

Thermodynamically, a system at constant temperature and pressure will be in a stable equilibrium if it has the lowest possible value of the Gibbs free energy.

Any transformation that results in a decrease in Gibbs free energy is possible. Therefore a necessary criterion for any phase transformation is

$$\Delta G = G_2 - G_1 = \Delta H - T\Delta S < 0 \quad (2)$$

where G_1 and G_2 are the free energies of the initial and final states, respectively. The transformation need not go directly to the stable equilibrium state but can pass through a whole series of intermediate metastable states.

It can be seen from the definition of G , Equation (1), that the state with the highest stability will be that with the best compromise between low enthalpy and high entropy. Thus, at low temperature metallic crystalline solids are most stable since they have the strongest atomic bonding and therefore the lowest internal energy (enthalpy). On the other hand, liquids and gases become more stable at elevated temperatures since the $-TS$ term dominates due to high atomic vibration frequency (entropy) at elevated temperatures. Therefore, amorphous

phase becomes more “stable” when its Gibbs free energy is lower than that of the competing crystalline phase. In other words, the Gibbs free energy change $\Delta G (= G_{\text{amorphous}} - G_{\text{crystalline}})$ becomes negative.

There are several ways to obtain thermodynamic properties of an alloy. One possibility is the experimental investigation. However, it is impossible for some alloys to conduct the experimental measurements due to both technological difficulties and high cost and huge time consumption. So, systematic prediction via theory is a significant and effective approach to obtain thermodynamic properties of alloys, especially for multicomponent alloys. Strictly speaking, it is the Gibbs free energy rather than the enthalpy that should be considered to determine the stability of a phase. However, the contribution from entropy is much smaller than that from enthalpy in solid compounds, and therefore the entropy contribution to the free energy term is neglected, and only the enthalpy term is regarded as an indicator of the stability of an alloy (Suryanarayana & Inoue, 2011). A number of methods, both computational and experimental, have been devised to estimate the formation enthalpies of alloys. In order to cast a wide search net for prospective alloys or alloy modifications, a rapid means of estimating the formation enthalpies would greatly speed up the discovery of the good glass formers in multicomponent alloy systems. The following four types of theoretical methods have been used to estimate the formation of amorphous structure in multicomponent alloy systems.

- First principles calculations, within the framework of density-functional theory,
- Statistical mechanics based approaches, using atomistic simulation techniques like ab-initio calculations, molecular dynamics simulations and Monte Carlo methods,
- Solution thermodynamics, based on extrapolation of experimental data, as in the CALPHAD (which stands for CALculation of PHase Diagrams) method, and
- Semi-empirical methods like Miedema’s semi-empirical model, or the BFS (Bozzolo-Ferrante-Smith) model, which is in turn based on the equivalent crystal theory.

Each of these methods has its own pros and cons (Ray et al., 2008). First-principles calculations can yield highly accurate values, however, they also have a high computing cost and require prior information on the crystal structure. There are great amounts of calculations to be performed for the prediction of the formation enthalpy of a binary alloy using the first principles, and this amount increases rapidly with increasing the number of component. Atomistic simulations of energy can be carried out using harmonic methods, which can be used only for solid phases. But, some parameters such as vibrational frequencies necessary in these methods could only be obtained from the quasiharmonic lattice theory. The CALPHAD method is based on expressing the thermodynamic variables as a polynomial function of temperature. Extensive database of these functions is largely required for multicomponent alloys. In absence of such a database the CALPHAD approach cannot be used. Amongst the semi-empirical approaches, the Miedema’s approach is perhaps the most commonly used one. The Miedema’s method can be adapted for extremely fast calculation of enthalpies, although these semi-empirical approaches are not as accurate as ab-initio techniques. However, in situations where a large number of alloys have to be considered in absence of a prior thermodynamic database, an approach like the Miedema’s model could provide an excellent starting point.

4. Thermodynamic approach for amorphous alloys via Miedema’s model

The stability of any given phase is determined by its Gibbs free energy with reference to the competing phases. Thus, an amorphous phase will be stable if its Gibbs free energy is lower

than that of the competing crystalline phase(s) in the glass-forming alloy systems. Miedema (de Boer et al., 1988; Bakker, 1998) has developed a semi-empirical method to calculate the enthalpies of the formation of liquid, solid solutions, intermetallic compounds, and amorphous phases in alloys based on the chemical, elastic, structural, and topological effects. So far, the Miedema's semi-empirical model is a simple and powerful way to calculate the mixing enthalpy of alloys. The Miedema's semi-empirical model was primarily developed for binary alloy systems, and it has been subsequently extended for ternary alloy systems (Gallego et al., 1990) and for quaternary or higher order alloy systems (Zhang et al., 2007). Regarding the applications of the Miedema's model to amorphous alloys, it could be used for predicting the glass-forming ability, glass-forming composition range, onset crystallization temperature, glass transition temperature and so on. This section only gives two application examples for the predictions of the glass-forming composition range (GFR) and glass-forming ability (GFA), and the applications for others could be retrieved in literatures (for examples, de Boer et al., 1988; Bakker, 1998; Takeuchi & Inoue, 2001).

4.1 The original Miedema's model for binary alloys

In general, the formation enthalpy of an alloy consists of the following four common parts depending on the type of the alloy

$$\Delta H = \Delta H^{chemical} + \Delta H^{elastic} + \Delta H^{structure} + \Delta H^{topological} \quad (3)$$

The first part $\Delta H^{chemical}$ is the enthalpy of chemical mixing. The Miedema's model uses only three quantities, attached to each element, that determine enthalpy changes upon alloying: molar volume, electronegativity and the electron density at the boundary of the Wigner-Seitz cell. All parameters and constants used in the model are estimated and tabulated by Miedema and can be found in literatures (de Boer et al., 1988; Bakker, 1998). In Miedema's model, atoms are conceived as "blocks" of the element (de Boer et al., 1988). These blocks represent Wigner-Seitz cells or, in general, they correspond to the Voronoi or Laguerre polyhedra. In this picture, when bringing dissimilar atoms into contact, energy effects occur at the interface, where the two polyhedra are in contact, and will correspondingly be proportional to the area of this interface. Thus, for dilute solution of atoms A in an excess of atoms B, this area is proportional to $V_A^{2/3}$, where V_A is the molar volume of A.

A second quantity that plays a role in the enthalpy change upon alloying is a sort of potential that is felt by the outer electrons of the atom. It resembles the electronegativity and is denoted by φ (Pauling, 1960). The potential φ gives the energy $-e\varphi$ that is needed for bringing such an electron with negative charge e to infinity, so it has a positive sign and is expressed in Volt. This energy is proportional to $-(\varphi_A - \varphi_B)^2$, because an amount of electronic charge $\Delta Z \propto |-\varphi_A - \varphi_B|$ is transferred over this "potential" difference with a corresponding energy gain of $|\Delta Z \cdot \Delta\varphi|$. The square $-(\varphi_A - \varphi_B)^2$ is also clear from the fact that the enthalpy effect is the same. In both cases the same amount of electronic charge is transferred, no matter the electronic charge is transferred from A to B or the other way. This energy contribution is called negative part of the enthalpy upon alloying $\Delta H_{A \text{ in } B}^{interfacial}$ (negative part). The actual values of the φ 's, used in Miedema's model are slight modifications of measured values, within experimental error, in order to obtain a set of parameters that adequately describe the alloying behavior. A second term in the enthalpy is "the density at the boundary of the Wigner-Seitz cell" and is denoted by n_{WS} . This value is always positive and represents the positive term in the mixing enthalpy $\Delta H_{A \text{ in } B}^{interfacial}$ (positive part). The origin of the positive term in the

enthalpy lies in the fact that, when solving an A atom in a B host a discontinuity in n_{WS} is created, which is not allowed so that the discontinuity should be smoothed at the boundary by bringing electrons to higher energy levels, which explains the positive sign of this contribution. The enthalpy change is proportional to $(n_{WSA}^{1/3} - n_{WSB}^{1/3})^2$ and is, for a similar reason as previously outlined, a squared difference (Bakker, 1998). The sum of positive and negative parts may be either positive or negative in sign, depending on the relative absolute values of both parts. Miedema has found in a semi-empirical way the dependence between these three quantities and the chemical (interfacial) enthalpy for solving one mole of transition metal A in an excess of transition metal B

$$\Delta H^{chemical}(A \text{ in } B) = \frac{V_A^{2/3}}{(n_{WS}^{-1/3})_{average}} \{-P(\Delta\phi)^2 + Q(\Delta n_{WS}^{1/3})^2 + R\} \quad (4)$$

where P , Q and R are empirical constants for a given group of metals. P and Q are proportionality constants, and constant R is connected with the hybridization of d -type wave functions with p -type wave functions if transition metals and non-transition metals become nearest neighbours in an alloy. The term "chemical" refers to the effects due to electron transfer and smoothing of the electron density at the boundary of the Wigner-Seitz cell.

In the case of *random, dilute solution* of two elements having equal molar volumes (A in B with fractions c_A and c_B correspondingly) the chemical enthalpy effect upon the formation of an alloy is

$$\Delta H^{chemical}(1 \text{ mole of } A) = c_B \Delta H^{chem}(A \text{ in } B) \quad (5)$$

since the average contact of atoms A with atoms B is given by c_B .

Or, the same per 1 mole of atoms ("A plus B"):

$$\Delta H^{chemical}(1 \text{ mole of atoms}) = c_A c_B \Delta H^{chemical}(A \text{ in } B) \quad (6)$$

In the case of the atoms with different sizes the surface area is also different for atoms A and atoms B. Therefore, Miedema introduced the concept of surface fraction or "surface concentration" as

$$c_A^S = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \quad (7)$$

$$c_A^S + c_B^S = 1 \quad (8)$$

And in this case one obtains

$$\Delta H^{chemical}(1 \text{ mole of atoms}) = c_A c_B^S \Delta H^{chemical}(A \text{ in } B) \quad (9)$$

It is clear that in an ordered compound the surface contact between atoms A and atoms B is larger than that in a completely disordered alloy. Miedema denoted the degree to which atoms A are in contact with atoms B by f_B^A . Comparison of the experimental and calculated enthalpies has shown that f_B^A could be well described by $f_B^A = c_B^S [1 + \gamma (c_A^S c_B^S)^2]$, where $\gamma = 0$ for completely disordered alloys, $\gamma = 8$ for intermetallic compounds and $\gamma = 5$ for amorphous alloys (Weeber, 1987). Therefore, the Equation (9) can be generalized and rewritten in the form

$$\Delta H^{chemical} = c_A f_B^A \frac{V_A^{2/3}}{(n_{WS}^{-1/3})_{average}} \{-P(\Delta\phi)^2 + Q(\Delta n_{WS}^{1/3})^2 + R\} \quad (10)$$

The second term $\Delta H^{elastic}$ in Equation (3) is elastic enthalpy representing the so called size mismatch enthalpy. In solid solutions, where atoms of different sizes have to occupy equivalent lattice positions, an additional positive contribution to the alloying enthalpy arises due to lattice deformations necessary to accommodate atoms of different sizes. In order to estimate the mismatch enthalpy Miedema used continuum elastic theory of Eshelby and Friedel (Eshelby, 1956) and received the following equation for the elastic part of the enthalpy upon alloying

$$\Delta H^{elastic}(A \text{ in } B) = \frac{2K_A G_B (V_A - V_B)^2}{4G_B V_A + 3K_A V_B} \quad (11)$$

where K is the bulk modulus, G is the shear modulus and V is the molar volume. Elastic enthalpy is essential for solid solutions only, when solute atoms are randomly distributed in the lattice of the solvent. In contrast, in liquids and in solid ordered equilibrium phases this energy is almost non-existent.

The $\Delta H^{structure}$ contribution appears, according Miedema, in the solid solutions and reflects the preference for the transition metals in the $3d$ series to crystallize in one of the main crystallographic structures body-centered cubic (bcc), face-centered cubic (fcc) or hexagonal closely packed (hcp), depending on Z , the number of valence electrons per atom. Miedema constructed, partly on the basis of band-structure calculations, partly on empirical findings of the structural stabilities for bcc, fcc and hcp structures of metals (de Boer et al., 1988; Bakker, 1998).

Since the crystal structure of a pure transition element depends on the number of valence electrons Z of the metal, the solution of one mole of atoms A in excess of atoms B leads in fact to the transformation A to B from a structural point of view and the corresponding energy change can be written as $E_{\sigma,B} - E_{\sigma,A}$. But atoms A , which are virtually transformed into atoms B have a different number of electrons than atoms B themselves. Therefore, the total number of electrons per atom in an alloy also differs from the value of pure atoms B and the structural enthalpy will change by an amount $(Z_A - Z_B) \frac{\partial E_{\sigma,B}}{\partial Z}$. Thereby the total structural enthalpy change per mole of solvent atoms is determined by

$$\Delta H^{structure}(A \text{ in } B) = (Z_A - Z_B) \frac{\partial E_{\sigma,B}}{\partial Z} + (E_{\sigma,B} - E_{\sigma,A}) \quad (12)$$

The last term $\Delta H^{topological}$ in Equation (3) is called topological enthalpy. For liquids the topological enthalpy, accounting for the difference between the crystalline state and the liquid state is the heat of fusion with the magnitude of about $R\bar{T}_m$, where $R = 8.31 \text{ J K}^{-1}$ is the gas constant and \bar{T}_m is the average of the two melting temperatures.

In amorphous alloys a certain degree of relaxation towards the solid state exists, so that the enthalpy contribution will be lower. It has been proposed as (Bakker et al., 1995)

$$\Delta H^{topological} = 3.5 \times 10^{-3} \cdot (c_A T_{m,A} + c_B T_{m,B}), \text{ kJ mol}^{-1} \quad (13)$$

According to this one can write the formation enthalpies of different types of alloys in the following forms

$$\Delta H^{liquid} = \Delta H^{chemical} \quad (14)$$

$$\Delta H^{solid\ solution} = \Delta H^{chemical} + \Delta H^{elastic} + \Delta H^{structure} \quad (15)$$

$$\Delta H^{compound} = \Delta H^{chemical} \quad (16)$$

$$\Delta H^{amorphous} = \Delta H^{chemical} + H^{topological} \quad (17)$$

All previous equations can be applied for only one type of concentrated binary alloys: intermetallic compounds, and for random, dilute solutions, but not for concentrated solutions. Miedema solved this problem by just averaging according to the following equations:

$$\Delta H^{chemical} = c_A c_B [f_B^A \Delta H^{chemical}(A\ in\ B) + f_A^B \Delta H^{chemical}(B\ in\ A)] \quad (18)$$

$$\Delta H^{elastic} = c_A c_B [c_B \Delta H^{elastic}(A\ in\ B) + c_A \Delta H^{elastic}(B\ in\ A)] \quad (19)$$

$$\Delta H^{structure} = E_{\sigma}^{structure}(\langle Z \rangle) - E_{\sigma}^{ref}(\langle Z \rangle) \quad (20)$$

where $\langle Z \rangle$ is the average number of valence electrons, $E_{\sigma}^{structure}(\langle Z \rangle)$ is the value of E_{σ} for the most stable structure with $\langle Z \rangle$ electrons per atom, $E_{\sigma}^{ref}(\langle Z \rangle)$ is a linear extrapolation between the lattice stabilities of the two relevant metals in their equilibrium states.

One of the well-known applications of the Miedema's model is to predict the glass-forming composition range (GFR) in glass-forming alloy systems. In general, by comparing the enthalpy difference between the formation enthalpy of the amorphous phase ($\Delta H^{amorphous}$) and that of the solid solution ($\Delta H^{solid\ solution}$) or intermetallic compounds ($\Delta H^{compound}$), the glass-forming range can be estimated. That is, if the enthalpy of the formation of the amorphous phase is lower than that of the solid solution or that of the intermetallic compounds, the amorphous phase is preferentially formed, otherwise, when considering metastable equilibrium conditions, the solid solution or intermetallic compounds are easily formed ("general method"). Or, the glass-forming range can also be estimated using the "common tangent method", *i.e.* using two common tangents between the enthalpy curves of the amorphous phase and the competitive crystalline phases such as the solid solutions and/or the intermetallic compounds (Weeber & Bakker, 1988). The compositions where the formation enthalpy curve of the amorphous phase attains the lowest absolute values then define the glass-forming composition range. In contrast, the compositions between the common tangents give an estimate for the two-phase region where the amorphous phase coexists with crystalline phases. The Miedema's model was applied to predict the glass-forming composition ranges in a series of binary alloy systems (Weeber et al., 1988), such as Cu-Ti, Ni-Ti, Ni-Zr, Ni-Nb, and so on. Fig. 1 gives an example of the calculated enthalpies of amorphous phase and that of the terminal solid solutions in the Ni-Ti binary alloy system. The predicted glass-forming composition range in the Ni-Ti system is 24 - 77 at.% Ni, which is in well agreement with the experimental glass-forming composition range (28 - 72 at.% Ni) prepared by mechanical alloying. Table 1 summarizes the predicted glass-forming composition ranges determined by applying the Miedema's model and the experimental results under mechanical alloying in several binary alloy systems. It shows that, in binary alloy systems, the determined glass-forming composition ranges by the Miedema's model are in accordance with those obtained from experimental observations.

Alloy	Predicted range	Measured range
Ni-Ti	24 - 77 at.% Ni	28 - 72 at.% Ni
Ni-Zr	24 - 83 at.% Ni	20 - 80 at.% Ni
Ni-Nb	31 - 80 at.% Ni	20 - 80 at.% Ni
Cu-Ti	28 - 75 at.% Cu	10 - 87 at.% Cu
Fe-Zr	27 - 79 at.% Fe	30 - 78 at.% Fe
Pd-Ti	20 - 54 at.% Pd	15 - 58 at.% Pd
Cu-Hf	29 - 79 at.% Cu	30 - > 70 at.% Cu
Ni-Hf	25 - 84 at.% Ni	15 - 65 at.% Ni

Table 1. Some examples of the predicted glass-forming composition ranges in binary alloy systems, determined by using the Miedema's model, and the measured composition ranges under mechanical alloying. (Reprinted from Weeber et al., 1988. With permission)

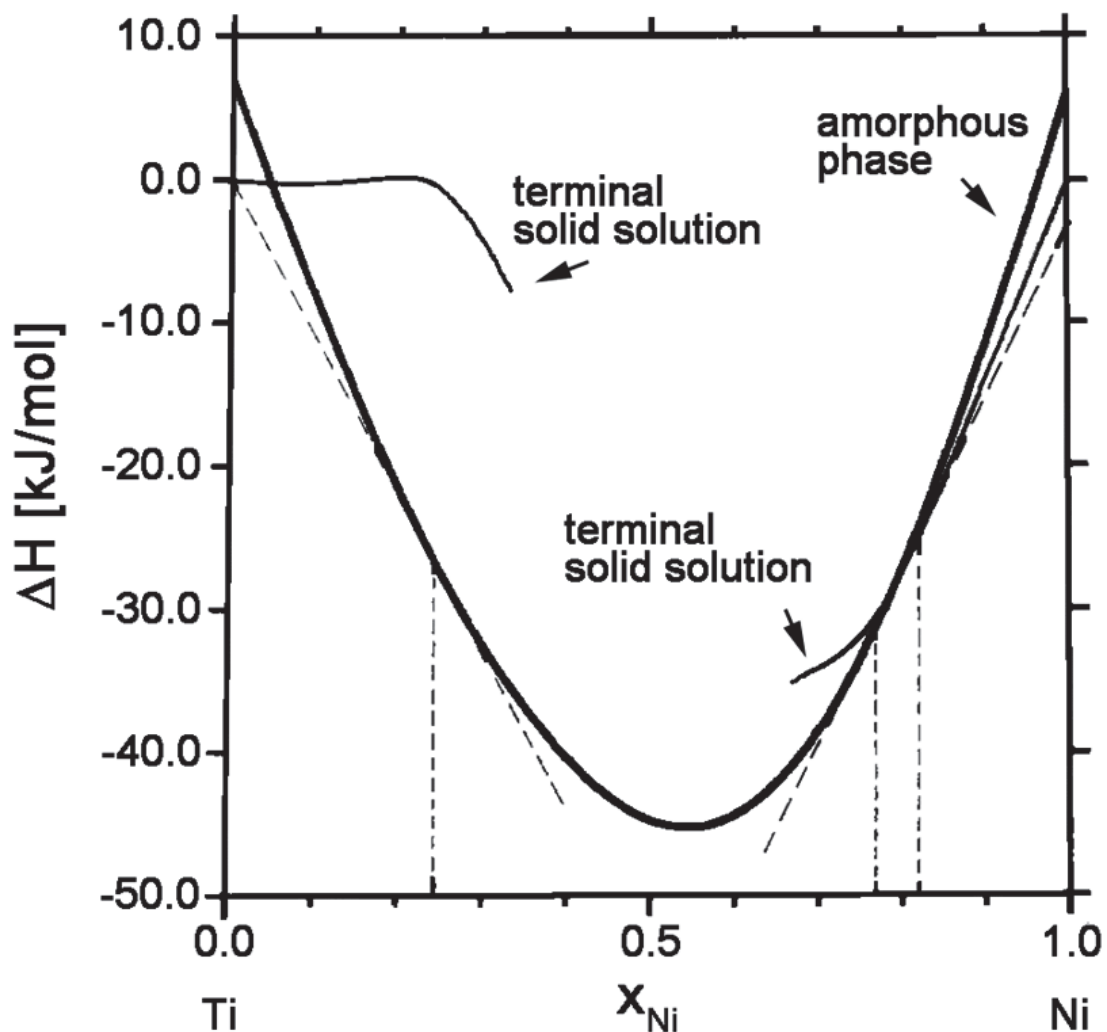


Fig. 1. Enthalpy diagram by the Miedema's model for the amorphous phase and the terminal solid solutions in the Ni-Ti system. The glass-forming composition range, defined by using double common tangents method, is 24 - 77 at.% Ni (Reprinted from Weeber et al., 1988. With permission)

Recently, by combining with a new glass-forming ability parameter, the Miedema's model has been used as a guide to searching for the best glass-forming ability composition in binary alloy systems (Xia et al., 2006a, 2006b, 2006c). It is argued that the formation of a metallic glass should involve two aspects (Xia et al., 2006a). While glass formation requires that the Gibbs free energy of the hypothetical amorphous phase is lower than that of the competing crystalline phases (mostly intermetallic compounds and sometimes solid solution depending alloy systems), the resistance to crystallization is dependent on the difference in the Gibbs free energies of the amorphous phase and intermetallic compounds. Therefore, the first aspect is the thermodynamic driving force for glass formation ($-\Delta H^{amorphous}$). The larger this value is, the easier is the glass formation. The other aspect is the resistance for glass formation against crystallization ($\Delta H^{amorphous} - \Delta H^{competing\ phase}$). The smaller this value is, the higher is the stability of the amorphous phase. The $\Delta H^{competing\ phase}$ could be $\Delta H^{solid\ solution}$ or $\Delta H^{compound}$ depending on the actual competing phases in an alloy system. Based on this, a γ^* parameter was proposed as a measure of glass-forming ability of alloy systems, defined as

$$\gamma^* = GFA \propto \frac{-\Delta H^{amorphous}}{\Delta H^{amorphous} - \Delta H^{competing\ phase}} = \frac{\Delta H^{amorphous}}{\Delta H^{competing\ phase} - \Delta H^{amorphous}} \quad (21)$$

The greater is the value of γ^* the higher is the glass-forming ability of the alloy. The formation enthalpy ΔH as a function of compositions for an amorphous phase and all the competing phases could be calculated by the Miedema's model. Using the aforementioned approach, one could determine the glass-forming composition ranges in which different phases are stable. Afterwards, by calculating the γ^* parameter within this determined composition range in which the amorphous phase is stable, the best glass-forming composition could be estimated when the γ^* parameter reaches a maximum value.

Xia et al. (Xia et al., 2006a) has applied the above method to search the best glass-forming composition in the Ni-Nb system, as shown in Fig. 2. The plots of γ^* with composition indicates that the best glass former lies at the composition around Ni_{61.5}Nb_{38.5}, where the γ^* reaches its largest value. Experimental studies of the glass-forming ability on Ni_{100-x}Nb_x alloys, at short intervals of 0.5 at.% in the composition range of $x = 37.5 - 40.5$ at.% Nb, have shown that the alloy Ni₆₂Nb₃₈ has the best glass-forming ability among the investigated compositions. The predicted composition is roughly in agreement with the experimental observations. The small difference in the experimental and predicted compositions was attributed to the fact that the entropy term was neglected in the calculations. Similar work on Cu-Hf alloys (Xia et al., 2006b) and Cu-Zr alloys (Xia et al., 2006c) have confirmed that this method is practical for predicting the best glass-forming compositions, at least in the studied binary alloy systems.

4.2 Extended Miedema's model for ternary alloys

Gallego et al. (Gallego et al., 1990) approximated the formation enthalpy in ternary system as a sum of the formation enthalpies of the respective binary alloy systems. This extended model has been largely used in ternary alloy systems and has received considerable success. However, such an approach has neglected the role of ternary interaction parameters and the relative compositions of the individual binaries, since the partitioning coefficients need not be the same for all the binaries. A number of work has attempted to improve on this extended Miedema's approach to multicomponent glass-forming alloy systems (Goncalves & Almeida, 1996; Zhang & Jesser, 2002; Herbst, 2002; Shindo et al., 2002; de Tandler et al.,

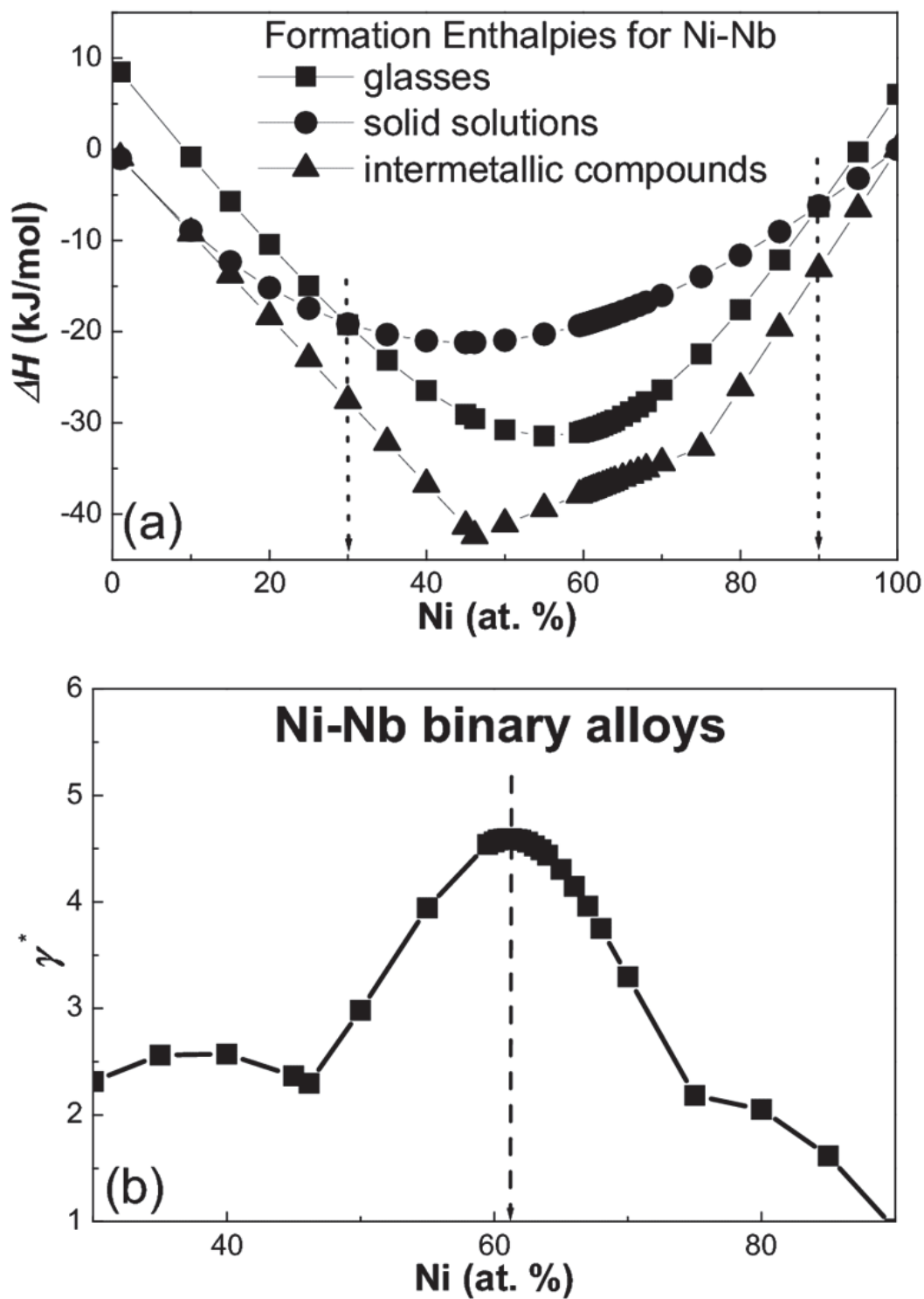


Fig. 2. (a) Plots of calculated enthalpies of the amorphous phase and competing crystalline phases in the Ni-Nb system. At any given compositions, the phase with the lowest enthalpy will be the most stable phase. The amorphous phase is stable at the compositions between the two dash lines. (b) Plot of γ^* parameter as a function of composition in the Ni-Nb system. Note that the largest value of γ^* lies at the best glass-forming composition. (Reprinted from Xia et al., 2006a. With permission)

2006; Ouyang et al., 2006a, 2006b; Zhang et al., 2007; Bera et al., 2007; Wang et al., 2007). All these amended extensions have their own pros and cons.

Goncalves and Almeida (Goncalves & Almeida, 1996) devised an ingenious approach for the estimation of enthalpies based on the relative positions of atoms. This approach was devised for MgCu₂, MgZn₂, CaCu₅ structure types. In principle the approach can be extended to other structure types as well, once the crystallographic information is available. However, this approach cannot be applied in absence of relevant crystallographic information. Herbst (Herbst, 2002) used an extended version of the Miedema's model to predict the hydrogen content in ternary hydrides. However, this approach had to establish and incorporate polynomial fits based on the data for a large number of hydrides. Hence this approach is not a general approach and cannot be applied directly to multicomponent glass-forming alloy systems. Zhang and Jesser (Zhang & Jesser, 2002) attempted to extend the original Miedema's model using the same approach as Gallego et al. (Gallego et al., 1990) while incorporating an additional strain energy component. The strain energy was calculated using the Eshelby's model (Eshelby, 1956). However, the Eshelby's model is a continuum approach, devised to treat the stresses arising from inclusions and hence, strictly speaking, cannot be applied to alloying at atomistic levels. De Tandler et al. (de Tandler et al., 2006) also adopted an approach similar to Gallego et al. (Gallego et al., 1990) while adding an entropy component to estimate the Gibbs free energy. Ouyang et al. (Ouyang et al., 2006a, 2006b) used a geometric approach similar to Toop's approach (Saunders & Miodownik, 1998). However, it is known that Toop's approach is largely applicable to ionic solids rather than metallic materials. Bera et al. (Bera et al., 2007) estimated the formation enthalpies using a pseudo-binary approach. However, their approach was based on crystallography and hence cannot be used in absence of crystallographic information. Among all these amended extensions, the extended method by Gallego et al. (Gallego et al., 1990) has so far received the most success for ternary alloy systems. Therefore, this chapter only describes the extended method by Miedema's model by Gallego et al. (Gallego et al., 1990).

In a ternary alloy system A-B-C, the formation enthalpies of each phase could be defined as:

$$\Delta H_{ABC} = \Delta H_{AB} + \Delta H_{AC} + \Delta H_{BC} \quad (22)$$

As a result, the formation enthalpies the amorphous phase are given by the equations:

$$\Delta H_{ABC}^{amorphous} = \Delta H_{ABC}^{chemical} + \Delta H_{ABC}^{topological} \quad (23)$$

$$\Delta H_{ABC}^{chemical} = \Delta H_{AB}^{chemical} + \Delta H_{AC}^{chemical} + \Delta H_{BC}^{chemical} \quad (24)$$

$$\Delta H_{ij}^{chemical} = c_i \cdot c_j \left(c_j \cdot \Delta H_{i \text{ in } j}^{interface} + c_i \cdot \Delta H_{j \text{ in } i}^{interface} \right) \quad (25)$$

$$\Delta H^{topological} = 3.5 \times 10^{-3} \cdot \sum_{i=1}^3 c_i \cdot T_{m,i} , \text{ kJ mol}^{-1} \quad (26)$$

where $\Delta H^{amorphous}$ is the formation enthalpy of the amorphous phase, $\Delta H_{ABC}^{chemical}$ is the enthalpy of chemical mixing defined by Equations (24) and (25), $\Delta H^{topological}$ is defined by Equation (26), where c_i is the composition of the i^{th} components whose melting temperatures are $T_{m,i}$. The factor $\{1 + \gamma \cdot (c_i^s \cdot c_j^s)^2\}$ needs to be multiplied to Equation (25) as previously in binary alloy systems when short-range order (SRO) exists in the amorphous phase (Weeber, 1987) (γ is called an SRO parameter, $\gamma = 5$ is the usual case), where c_i^s is the surface fraction of the cell. Here, c_i^s is developed for a multicomponent alloy system as

$$c_i^S = \frac{c_i V_i^{2/3}}{\sum_i c_i V_i^{2/3}} \quad (27)$$

where V_i is the molar volume of the component. These values were taken from the literature (Niessen et al., 1983).

Based on the formation enthalpy of intermetallic compound in a binary alloy system (Equation 16) and the enthalpy of chemical mixing in ternary alloy system (Equation 24) the formation enthalpy of intermetallic compound in a ternary alloy system is defined as:

$$\Delta H^{compound} = \Delta H_{AB}^{chemical} + \Delta H_{AC}^{chemical} + \Delta H_{BC}^{chemical} \quad (28)$$

The structural contribution to the enthalpy of solid solution, arising from the difference between the valences and crystal structures of the solute and the solvent, is expected to have only a minor effect and can be almost negligible in determining the glass-forming composition range (Lopez et al., 1987; Bakker, 1998) when compared with the elastic energy contribution. Also, it is difficult to calculate this structural contribution in multicomponent alloy systems and so it was not considered in the calculations. Hence, the formation enthalpies of a solid solution phase can be derived from

$$\Delta H_{ABC}^{solid\ solution} = \Delta H_{ABC}^{chemical} + \Delta H_{ABC}^{elastic}(solid\ solution) \quad (29)$$

where $\Delta H_{ABC}^{chemical}$ is the enthalpy of chemical mixing, as shown in Equation (24). $\Delta H_{ABC}^{elastic}(solid\ solution)$ is the elastic enthalpy arising from the atomic size mismatch, expressed as Equations (30) - (32)

$$\Delta H_{ABC}^{elastic}(solid\ solution) = \Delta H_{AB}^{elastic} + \Delta H_{AC}^{elastic} + \Delta H_{BC}^{elastic} \quad (30)$$

$$\Delta H_{ij}^{elastic} = c_i \cdot c_j (c_j \cdot \Delta H_{i\ in\ j}^{elastic} + c_i \cdot \Delta H_{j\ in\ i}^{elastic}) \quad (31)$$

$$\Delta H_{i\ in\ j}^{elastic} = \frac{2K_i G_j (V_i^* - V_j^*)^2}{3K_i V_j^* + 4G_j V_i^*} \quad (32)$$

Here, K_i is the bulk modulus of the solute, G_j is the shear modulus of the solvent, and V_i^* and V_j^* are the modified molar volumes of the solute and the solvent, respectively, corrected for charge transfer effects (Bakker, 1985):

$$\Delta V_i = \frac{P_0 V_i^{2/3} (\phi_i^* - \phi_j^*)}{(n_{WS}^i)^{-1/3} + (n_{WS}^j)^{-1/3}} \cdot \left| (n_{WS}^i)^{-1} - (n_{WS}^j)^{-1} \right| \quad (33)$$

V_i is the molar volume of pure component i , the ϕ^* parameters are the electronegativity (in volts) and the n_{WS} parameters are the electron densities at the Wigner-Seitz cell boundary (in density units). The parameter P_0 has been found empirically to be 1.5 (Bakker, 1985). All numerical values of the parameters are available in the literature de Boer et al., 1998.

In order to verify the applicability of this extended Miedema's model, Gallego et al. (Gallego et al., 1990) has compared the glass-forming composition ranges in the Co-rich region in Co-Zr-M (M = Nb, W, Mo, V and Cr) ternary alloys. The calculated composition ranges by the extended Miedema's model are close to the values of the minimum solute concentrations for glass formation derived from the Ueno-Waseda equation.

Murty et al. (Murty et al., 1992) applied this extended model to the ternary Ti-Ni-Cu alloy system to calculate the glass-forming composition range, as shown in Fig. 3. The calculated glass-forming composition ranges in this ternary alloy system are $x = 0 - 30$ and $58 - 60$ for

$\text{Ti}_{40}\text{Ni}_{60-x}\text{Cu}_x$, $x = 0 - 24$ and $49 - 50$ for $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ and $x = 0 - 15$ for $\text{Ti}_{60}\text{Ni}_{40-x}\text{Cu}_x$. These calculated results are in general agreement with those experimental observations by mechanical alloying.

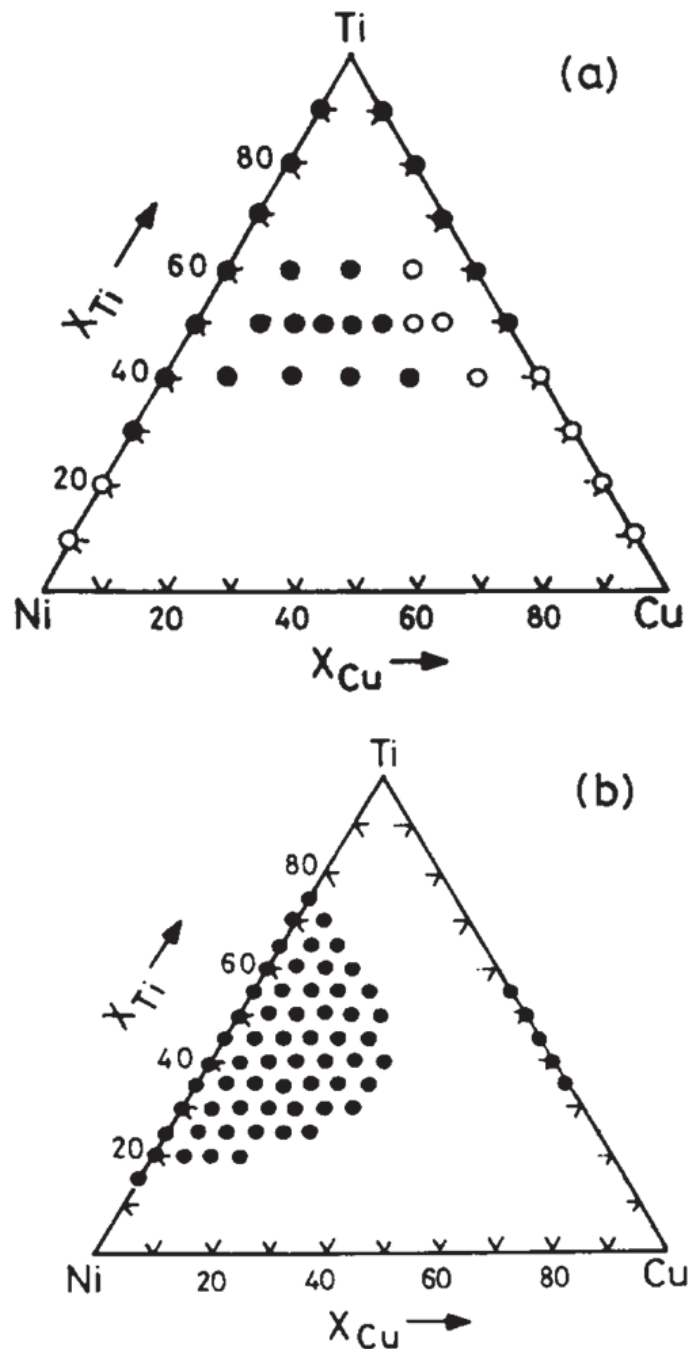


Fig. 3. Comparison of (a) experimental and (b) calculated glass-forming composition ranges in Ti-Ni-Cu alloy system (Reprinted from Murty et al., 1992. With permission)

Takeuchi and Inoue (Takeuchi & Inoue, 2001) used the Miedema's model to determine the stability of the amorphous phase and estimate the glass-forming composition range. By carrying out the calculations for 335 glass-forming ternary alloy systems except for Al-Cu-Fe, Al-Mo-Si and Au-Ge-Si, it is showed that the calculated results are in agreement with the

experimental data for Cu-Ni- and Al-Ti- based ternary alloy systems. An example is shown in Fig. 4 (a). But, the calculated glass-forming composition ranges in Zr-, La-, Fe-, and Mg-based ternary alloy systems were overestimated, as shown in Fig. 4 (b), because of the simplification inherent in their model. The authors has also noted that the factors that influence the glass-forming composition range are $\Delta H^{interface}$, $\Delta H^{elastic}$, T_m , viscosity, diffusion, short-range order, intermediate phases, and so on. They have compared the glass forming composition ranges obtained by considering and those obtained by ignoring the short-range order factor in amorphous phase, which is expressed as the $\{1 + \gamma \cdot (c_i^s \cdot c_j^s)^2\}$. Figs. 4 (c) and (d) show an example of the effect of short-range order factor on the glass-forming composition range. By considering the short-range order factor, the calculated glass-forming ranges in the Al-Ni-Zr system are much closer to the experimental observations, especially for the compositions near the Al-rich corner and the Al-Zr binary subsystem. It is interesting to note that the short-range order has different influences on the glass formation in different alloy systems. For examples, the short-range order has little change in the glass forming range in the B-Fe-Zr and La-Mg-Ni systems. In contrast, ignoring the short range order factor has led to the absence in the glass-forming range in the Ni-P-Pd system.

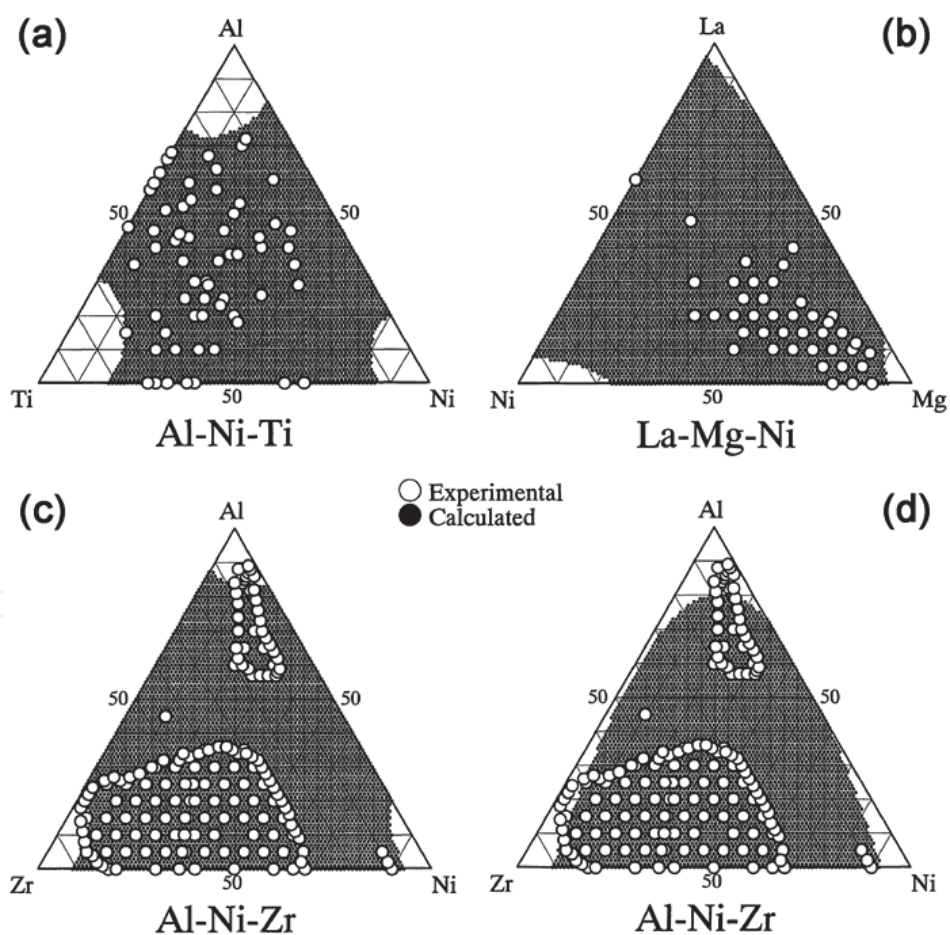


Fig. 4. Experimental and calculated glass-forming composition ranges for different alloy systems under the conditions where the short-range is (a)-(c) considered and (d) ignored. It is noted that the short-range order factor has different influences on the calculated glass-forming composition range. (Reprinted from Takeuchi & Inoue, 2001. With permission)

4.3 Extended Miedema's model for quaternary and more complex alloy systems

From the aforementioned alloy development strategies for multicomponent amorphous alloys in Section 2, one finds that the fourth and later alloying elements, take only about 1-2 at.% in the alloy, which are actually dilute solution in a ternary alloy. In addition, the components in all the multicomponent glass-forming alloy systems could be divided into three types of elements based on their atomic size and chemical affinity (Takeuchi & Inoue, 2001). Therefore, the quaternary or higher order alloy systems could be regarded as pseudo-ternary or occasionally as pseudo-quaternary alloy systems. As a result, the extended Miedema's model could be applied to quaternary or higher order alloy systems, as long as such high order alloy systems are discreetly conceived as pseudo-ternary alloy systems based on the chemical affinity of the components.

Zhang et al. (Zhang et al., 2007) has successfully presented this pseudo-ternary solution method to the Ti-Zr-Nb-Cu-Ni-Al multicomponent alloy system consisting of 6 constituent elements. It is suggested to divide the elements in the alloy system into three groups based on their chemical affinity and afterwards to calculate the formation enthalpy of the alloys using the Miedema's formula for ternary alloys in Section 4.2. As an example, the Ti-Zr-Nb-Cu-Ni-Al alloy system can be considered as a pseudo-ternary alloy system, where (Ti,Zr,Nb) may be regarded as A, (Cu,Ni) as B and Al as C, respectively. The corresponding parameters of each pseudo-component (*i.e.* A, B, and C) can be calculated using the confusion principle, as the elements in each pseudo-component are infinite soluble each other. According to the experimental observations (Zhang et al., 2007), the competitive crystalline phases in the course of the formation of the amorphous phase in this high order alloy system are only solid solutions (*i.e.* Cu and (Nb,Zr) solid solutions). Therefore, the formation enthalpies of the amorphous phase and the solid solutions are calculated to determine the glass-forming range, as shown in Fig. 5. Comparing with the formation enthalpies of the solid solution and that of the amorphous phase in this (Ti,Zr,Nb)-(Cu,Ni)-Al pseudo-ternary alloy system, the calculated glass-forming composition range corresponds to a (Ti,Zr,Nb) content of about from 21 to 51 at.% using the double tangent method (see GFR A in Fig. 5). In contrast, when using the general method, the calculated glass-forming composition range is estimated as 12 - 63 at.% (Ti,Zr,Nb) (see GFR B in Fig. 5). From the experiments, an amorphous phase was formed by mechanical alloying for the powder mixtures with a (Ti,Zr,Nb) content of 20 - 60 at.%. Both calculated glass-forming ranges are comparable to the experimental results. Therefore, the Miedema's model can be successfully applied to calculate the glass-forming composition range in complex alloy systems composed of more than four components, as long as by appropriately regarding the complex alloy systems as pseudo-ternary alloy systems.

Due to the complexity of ternary and higher order multicomponent alloy systems, the calculations may be not precisely in agreement with the experimental observations. On the other hand, it is expensive and time-consuming to experimentally measure the formation enthalpy of such complex alloys. Therefore, there is a significant need for simple and reliable theoretical calculation. Because of more complexity arising from large component number in multicomponent alloy systems, the extended Miedema's model becomes definitely more complex than the original binary one. The larger the component number in an alloy is, the more complex is the extended Miedema's model and at the same time the less accurate is the calculation. The extended Miedema's model by Gallego et. al. (Gallego et al., 1990) has neglected the third and subsequent interaction parameter and the relative composition of the individual binaries and calculated the formation enthalpy as a sum of corresponding binary alloys (such as the Equation 22 in the Section 4.2). As previously

described at the beginning in the Section 4.2, there exist some other proposed extensions of the Miedema's model for multicomponent alloy systems. The values of the formation enthalpy from these extensions deviate more or less from the experimental observations (Kokotin 2010), which will significantly influence the precision when applying the extended Miedema's model to higher order alloy systems.

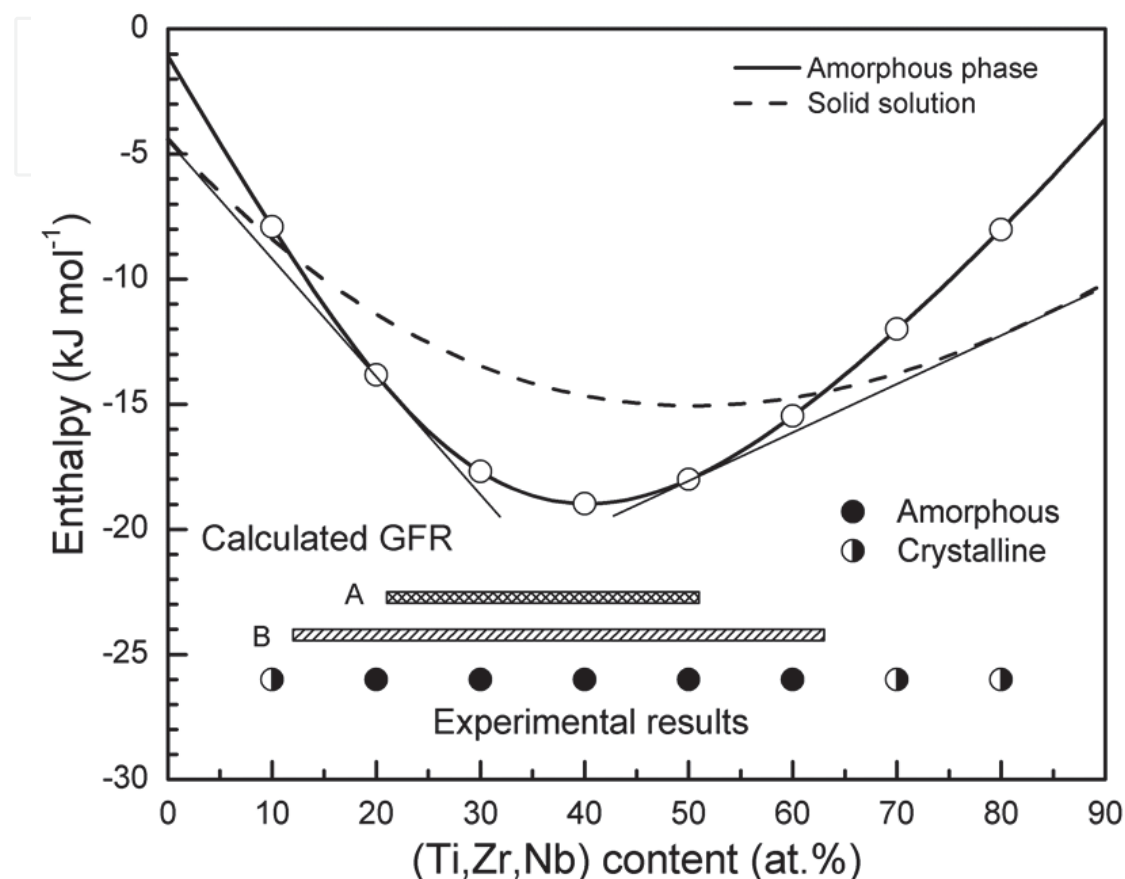


Fig. 5. Calculated enthalpy diagrams of the pseudo-ternary $(\text{Ti,Zr,Nb})_x(\text{CuNi})_{90-x}\text{Al}_{10}$ alloy system. The calculated glass-forming composition range (GFR) and the experimentally determined GFR are plotted together for comparison. GFR A and B are estimated using the common tangent method and the general method, respectively. Both calculated glass-forming composition ranges are in agreement with the experimental observations. It proves that the Miedema's model can be successfully applied to complex alloy systems composed of more than four components. (Reprinted from Zhang et al., 2007. With permission)

5. Conclusions

Due to complexity arising from large component number, the fundamental understanding of the formation, structure and properties becomes more and more difficult with increasing the component number in the multicomponent glass-forming alloy systems. The Miedema's semi-empirical model enables us to make fast predictions for values of several effects in alloys, such as for glass-forming ability and for glass forming composition range from binary to ternary and higher order multicomponent alloy systems. The calculated results are well agreement with the experimental observations. By supplemented by suitable

parameters and/or procedures, the application of the Miedema's semi-empirical model and extensions to estimate the formation enthalpies would greatly speed up the search for prospective alloys or alloy modifications for multicomponent glass-forming alloys.

Various Miedema's model extensions could lead to deviations of the calculated values of the formation enthalpy from the experimental data. These deviations will reduce the precision when application the model is incorporated with other parameters/procedures for multicomponent glass-forming alloy systems. From this reason, more suitable modification and justification of the Miedema's semi-empirical model is needed, especially for multicomponent alloy systems.

6. Acknowledgments

The author is grateful to J. Eckert, K.B. Kim, H.B. Lu, P. Yu, W.Y. Zhang, and M. Calin for their stimulating discussions. Financial support provided by Research Services of The University of Western Australia (through UWA Research Development Award Scheme) is gratefully acknowledged.

7. References

- Bakker, H. (1985). Fast Metal Impurity Diffusion in Metals and The Miedema Model. *Journal of the Less-Common Metals*, Vol. 105, No. 1, (January 1985), pp. 129-138, ISSN 0022-5088
- Bakker, H., Zhou, G.F., & Yang, H. (1995). Mechanically Driven Disorder and Phase Transformation in Alloys. *Progress in Materials Science*, Vol. 39, No. 3, (July 1995), pp. 159-241, ISSN 0079-6425
- Bakker, H. (1998). *Enthalpies in Alloys: Miedema's Semi-empirical Model*, Trans Tech Publication Ltd, ISBN 0-87849-783-8, Switzerland
- Bera, S., Mazumdar, S., Ramgopal, M., Bhattacharyya, S., & Manna, I. (2007). Prediction of Enthalpy of Formation and Gibbs Energy Change in Pseudo-Binary (Ti-Zr)(Fe-Cr)(2) and Pseudo-Ternary (Ti-Zr)(Fe-Cr)(2)-H System Using Extended Miedema Model. *Journal of Materials Science*, Vol. 42, No. 10, (May 2007), pp. 3645-3650, ISSN 0022-2461
- Bozzolo, G., Ferrante, J., & Smith, J.R. (1992). Method for Calculating Alloy Energetics. *Physical Review B*, Vol. 45, No. 1, (January 1992), pp. pp. 493-496, ISSN 1098-0121
- Cahn, R.W., & Zarzycki, J. (1991). *Glasses and Amorphous Materials*, Vol. 9 of *Materials Science and Technology: A Comprehensive Treatment*. Wiley, John, & Sons Incorporated, ISBN 783527268221, Weinheim, Germany
- Chen, H.S. (1980). Glassy Metals. *Reports on Progress in Physics*, Vol. 43, No. 4, (January 1980), pp. 353-432, ISSN 0034-4885
- Chen, H.S., & Turnbull, D. (1969). Formation, Stability and Structure of Palladium-Silicon Based Alloy Glasses. *Acta Metallurgica*, Vol. 17, No. 8, (August 1969), pp. 1021-1031, ISSN 0001-6160
- Cocco, G., Soletta, I., Enyo, S., Magini, M., & Cowlam N. (1990). On The Amorphisation Reactions of CuTi by Mechanical Alloying. *Journal de Physique Colloques*, Vol. 51, No. C4, (July 1990), pp. 181-187, ISSN 0449-1947

- de Boer, F.R., Boom, R., Mattens, W.C.M., Miedema, A.R., & Niessen A.K. (1988). *Cohesion in Metals: Transition Metal Alloys*, Elsevier, ISBN 0-444-87098-9, North-Holland, Amsterdam
- de Tandler, R.H., Soriano, M.R., Pepe, M.E., Kovacs, J.A., Vicente, E.E., & Alonso, J.A. (2006). Calculation of Metastable Free-Energy Diagrams and Glass Formation in The Mg-Cu-Y Alloy and Its Boundary Binaries Using The Miedema Model. *Intermetallics*, Vol. 14, No. 3, (March 2006), pp. 297-307, ISSN 0966-9795
- Dinsdale, A.T. (1991). SGTE Data for Pure Elements. *Calphad*, Vol. 15, No. 4, (October-December 1991), pp. 317-425, ISSN 0364-5916
- Eckert, J., Das, J., Pauly, S., & Duhamel, C. (2007). Mechanical Properties of Bulk Metallic Glasses and Composites. *Journal of Materials Research*, Vol. 22, No. 2, (February 2007), pp. 285-301, ISSN 0884-2914
- Egami, T., & Waseda, Y. (1984). Atomic Size Effect on The Formability of Metallic Glasses. *Journal of Non-Crystalline Solids*, Vol. 64, No. 1-2, (April 1984), pp. 113-134, ISSN 0022-3093
- Egami, T. (1997). Universal Criterion for Metallic Glass Formation. *Materials Science and Engineering A*, Vol. 226-228, No. 1-2, (June 1997), pp. 261-267, ISSN 0921-5093
- Egami, T. (2003). Atomistic Mechanism of Bulk Metallic Glass Formation. *Journal of Non-Crystalline Solids*, Vol. 317, No. 1-2, (March 2003), pp. 30-33, ISSN 0022-3093
- Eshelby, J.D. (1956). The Continuum Theory of Lattice Defects, In: *Solid State Physics Vol. 3: Advances in Research and Applications*, Seitz, F., & Turnbull, D., pp. 79-144, Academic Press, ISBN 9780126077032, New York, USA
- Fan, G.J., Zhao, J.C., & Liaw, P.K. (2010). A Four-Step Approach to The Multicomponent Bulk-Metallic Glass Formation. *Journal of Alloys and Compounds*, Vol. 497, No. 1-2, (May 2010), pp. 24-27, ISSN 0925-8388
- Gallego, L.J., Somoza, J.A., & Alonso, J.A. (1990). Glass-Formation in Ternary Transition-Metal Alloys. *Journal of Physics-Condensed Matter*, Vol. 2, No. 29, (July 1990), pp. 6245-6250, ISSN 0953-8984
- Goncalves, A.P., & Almeida, M. (1996). Extended Miedema Model: Predicting The Formation Enthalpies of Intermetallic Phases with More Than Two Elements. *Physica B*, Vol. 228, No. 3-4, (November 1996), pp. 289-294, ISSN 0921-4526
- Herbst, J.F. (2002). On Extending Miedema's Model to Predict Hydrogen Content in Binary and Ternary Hydrides. *Journal of Alloys and Compounds*, Vol. 337 No. 1-2, (May 2002), pp. 99-107, ISSN 0925-8388
- Hohenberg, P., & Kohn, W. (1964). Inhomogeneous Electron Gas. *Physical Review*, Vol. 136, No. 3B, (November 1964), pp. B864-B871, ISSN 0163-1829
- Inoue, A., Kita, K., Zhang, T., & Masumoto, T. (1989). An Amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ Alloy Prepared by Water Quenching. *Materials Transactions JIM*, Vol. 30, No. 9, (September 1989), pp. 722-725, ISSN 1345-9678
- Inoue, A., Yamaguchi, H., Zhang, T., & Masumoto, T. (1990). Al-La-Cu Amorphous-Alloys with A Wide Supercooled Liquid Region. *Materials Transactions JIM*, Vol. 31, No. 2, (February 1990), pp. 104-109, ISSN 1345-9678
- Inoue, A., Nakamura, T., Nishiyama, N., & Masumoto, T. (1992). Mg-Cu-Y Bulk Amorphous-Alloys with High-Tensile Strength Produced by A High-Pressure Die-

- Casting Method. *Materials Transactions JIM*, Vol. 33, No. 10, (October 1992), pp. 937-945, ISSN 1345-9678
- Inoue, A., Nishiyama, N., & Kimura, H. (1997). Preparation and Thermal Stability of Bulk Amorphous Pd₄₀Cu₃₀Ni₁₀P₂₀ Alloy Cylinder of 72 mm in Diameter. *Materials Transactions JIM*, Vol. 38, No. 2, (February 1997), pp. 179-183, ISSN 1345-9678
- Inoue, A. (2000). Stabilization of Metallic Supercooled Liquid and Bulk Amorphous Alloys. *Acta Materialia*, Vol. 48, No. 1, (January 2000), pp. 279-306, ISSN 1359-6454
- Inoue, A., & Takeuchi, A. (2002). Recent Progress in Bulk Glassy Alloys. *Materials Transactions*, Vol. 43, No. 8, (August 2002), pp. 1892-1906, ISSN 1345-9678
- Johnson, W.L. (1986). Thermodynamic and Kinetic Aspects of The Crystal to Glass Transformation in Metallic Materials. *Progress in Materials Science*, Vol 30, No. 2, (January 1986), pp. 81-134, ISSN: 0079-6425
- Johnson, W.L. (1999). Bulk Glass-Forming Metallic Alloys: Science and Technology. *MRS Bulletin*, Vol. 24, No. 10, (October 1999), pp. 42-56, ISSN 0883-7694
- Klement, W., Willens, R.H., & Duwez, P. (1960). Non-crystalline Structure in Solidified Gold-Silicon Alloys. *Nature*, Vol. 187, No. 4740, (September 1960), pp. 869-870, ISSN 0028-0836
- Kokotin, V. (2010). *Polyhedra-Based Analysis of Computer Simulated Amorphous Structures*. PhD thesis, Technical University Dresden, Germany
- Lopez, J.M., Alonso, J.A., & Gallego, L.J. (1987). Determination of The Glass-Forming Concentration Range in Binary-Alloys from A Semiempirical Theory - Application to Zr-Based Alloys. *Physical Review B*, Vol. 36, No. 7, (July 1987), pp. 3716-3722, ISSN 1098-0121
- Ma, H., Shi, L.L., Xu, J., Li, Y., & Ma E. (2005). Discovering Inch-Diameter Metallic Glasses in Three-Dimensional Composition Space. *Applied Physics Letters*, Vol 87, No. 18, (October 2005), pp. 181915, ISSN 0003-6951
- Miedema, A.R., de Chatel, P.F., & de Boer, F.R. (1980). Cohesion in Alloys - Fundamentals of A Semi-Empirical Model. *Physica B, & C*, Vol. 100, No. 1, (January 1980), pp. 1-28, ISSN 0378-4371
- Miracle, D.B., & Senkov, O.N. (2003). Topological Criterion for Metallic Glass Formation. *Materials Science and Engineering A*, Vol. 347, No. 1-2, (April 2003), pp. 50-58, ISSN 21-5093
- Murty, B.S., Ranganathan, S., & Rao, M.M. (1992). Solid-State Amorphization in Binary Ti-Ni, Ti-Cu and Ternary Ti-Ni-Cu System by Mechanical Alloying. *Materials Science Engineering A*, Vol. 149, No. 2, (January 1992), pp. 231-240, ISSN 0921-5093
- Niessen, A.K., de Boer, F.R., Boom, R., de Chatel, P.F., Matterna, W.C.M., & Miedema, A.R. (1983). Model Predictions for The Enthalpy of Formation of Transition Metal Alloys II. *Calphad*, Vol. 7, No. 1, (January-March 1983) pp. 51-70, ISSN 0364-5916
- Ouyang, Y.F., Zhong, X.P., Du, Y., Feng, Y.P., & He, Y.H. (2006a). Enthalpies of Formation for The Al-Cu-Ni-Zr Quaternary Alloys Calculated via A Combined Approach of Geometric Model and Miedema Theory. *Journal of Alloys and Compounds*, Vol. 420, No. 1-2, (August 2006), pp. 175-181, ISSN 0925-8388

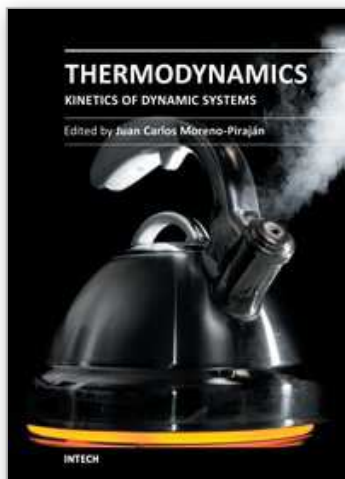
- Ouyang, Y.F., Zhong, X.P., Du, Y., Jin, Z.P., He, Y.H., Yuan, Z.H. (2006b). Formation Enthalpies of Fe–Al–RE Ternary Alloys Calculated with A Geometric Model and Miedema's Theory. *Journal of Alloys and Compounds*, Vol. 416, No. 1-2, (June 2006), pp. 148-154, , ISSN 0925-8388
- Pauling, L. (1960). *The Nature of The Chemical Bond*, 3rd Edition, Cornell University Press, ISBN 0-8014-0333-2, Ithaca, USA
- Peker, A., & Johnson, W.L. (1993). A Highly Processable Metallic Glass: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$. *Applied Physics Letters*, Vol 63, No. 17, (October 1993), pp. 2342-2344, ISSN 0003-6951
- Politis, C., & Johnson, W.L. (1986). Preparation of Amorphous $Ti_{1-x}Cu_x$ ($0.10 < x < 0.87$) by Mechanical Alloying. *Journal of Applied Physics*, Vol. 60, No. 3, (August 1986), pp. 1147-1151, ISSN 0021-8979
- Ray, P.K., Akinc, M., & Kramer, M.J. (2008). Estimation of Formation Enthalpies Using An Extended Miedema Approach. *Proceeding of 22nd Annual Conference on Fossil Energy Materials*, Pittsburgh, PA, USA, July 2008
- Ray, P.K., Akinc, M., & Kramer, M.J. (2010). Applications of An Extended Miedema's Model for Ternary Alloys. *Journal of Alloys and Compounds*, Vol. 489, No. 2, (January 2010), pp. 357-361, ISSN 0925-8388
- Rickman, J.M., & LeSar, R. (2002). Free-Energy Calculations in Materials Research. *Annual Review of Materials Research*, Vol. 32, No. 1, (January 2002) pp. 195-217, ISSN 1531-7331
- Saunders, N., & Miodownik, A.P. (1998). *CALPHAD: Calculation of Phase Diagrams – A Comprehensive Guide*, Pergamon, ISBN 0-08-042129-6, New York, USA
- Schwarz, R.B., Petrich, R.R., & Saw, C.K. (1985). The Synthesis of Amorphous Ni-Ti Alloy Powders by Mechanical Alloying. *Journal of Non-Crystalline Solids*, Vol. 76, No. 2-3, (December 1985), pp. 281-302, ISSN 0022-3093
- Senkov, O.N., & Miracle, D.B. (2001). Effect of The Atomic Size Distribution on Glass Forming Ability of Amorphous Metallic Alloys. *Materials Research Bulletin*, Vol. 36, No. 12, (October 2001), pp. 2183-2198, ISSN 0025-5408
- Shindo, T., Waseda, Y., & Inoue, A. (2002). Prediction of Glass-Forming Composition Ranges in Zr-Ni-Al alloys. *Mateirlas Transactions*, Vol. 43, No.10, (October 2002), pp. 2502-2508, ISSN 1345-9678
- Smith, J.R., & Banerjea, A. (1987). New Approach to Calculation of Total Energies of Solids with Defects - Surface-Energy Anisotropies. *Physical Review Letters*, Vol. 59, No. 21, (November 1987), pp. 2451-2454, ISSN 0031-9007
- Suryanarayana, C. (1980). *Rapidly Quenched Metals - A Bibliography 1973–1979*. Plenum, ISBN 0904357228, New York, USA
- Suryanarayana, C., & Inoue, A. (2011). *Bulk Metallic Glasses*. CRC Press, ISBN 978-1-4200-8597-6, Boca Raton, London, New York
- Takeuchi, A., & Inoue, A. (2001). Calculations of Amorphous-Forming Composition Range for Ternary Alloy Systems and Analyses of Stabilization of Amorphous Phase and Amorphous-Forming Ability. *Materials Transactions*, Vol. 42, No. 7, (July 2001), pp. 1435-1444, ISSN 1345-9678

- Wang, D., Tan, H., & Li, Y. (2005). Multiple Maxima of GFA in Three Adjacent Eutectics in Zr-Cu-Al Alloy System - A Metallographic Way to Pinpoint The Best Glass Forming Alloys. *Acta Materialia*, Vol. 53, No. 10, (June 2005), pp. 2969-2979, ISSN 1359-6454
- Wang, W.C., Li, J.H., Yan, H.F., & Liu, B.X. (2007). A Thermodynamic Model Proposed for Calculating The Standard Formation Enthalpies of Ternary Alloy Systems. *Scripta Materialia*, Vol. 56, No. 11, (June 2007), pp. 975-978, ISSN 1359-6462.
- Wang, W.H. (2009). Bulk Metallic Glasses with Functional Physical Properties. *Advanced Materials*, Vol. 21, No. 45, (December 2009), pp. 4524-4544, ISSN 0935-9648
- Weeber, A.W. (1987). Application of The Miedema Model to Formation Enthalpies and Crystallization Temperatures of Amorphous Alloys. *Journal of Physics F Metal Physics*, Vol. 17, No. 4, (April 1987), pp. 809-813, ISSN 0305-4608
- Weeber, A.W., & Bakker, H. (1988). Extension of the Glass-Forming Range of Ni-Zr by Mechanical Alloying. *Journal of Physics F Metal Physics*, Vol. 18, No. 7, (July 1988), pp. 1359-1369, ISSN 0305-4608
- Weeber, A.W., Loeff, P.I., & Bakker, H. (1988). Glass-Forming Range of Transition Metal-Transition Metal Alloys Prepared by Mechanical Alloying. *Journal of the Less-Common Metals*, Vol. 145, (December 1988), pp. 293-299, ISSN 0022-5088
- Xia, L., Li, W.H., Fang, S.S., Wei, B.C., & Dong, Y.D. (2006a). Binary Ni-Nb Bulk Metallic Glasses. *Journal of Applied Physics*, Vol 99, No. 2, (January 2006), pp. 026103, ISSN 0021-8979
- Xia, L., Ding, D., Shan, S.T., & Dong, Y.D. (2006b). The Glass Forming Ability of Cu-Rich Cu-Hf Binary Alloys. *Journal of Physics-Condensed Matter*, Vol. 18, No. 15, (April 2006), pp. 3543-3548, ISSN 0953-8984
- Xia, L., Fang, S.S., Wang, Q., Dong, Y.D., & Liu, C.T. (2006c). Thermodynamic Modeling of Glass Formation in Metallic Glasses. *Applied Physics Letters*, Vol. 88, No. 17, (April 2006), pp. 171905, ISSN 0003-6951
- Xu, J., Ramamurty, U., & Ma E. (2010). The Fracture Toughness of Bulk Metallic Glasses. *JOM*, Vol. 62, No. 4, (April 2010), pp. 10-18, ISSN 1047-4838
- Yan, Z.J., Li, J.F., He, S.R., & Zhou, Y.H. (2003). Evaluation of The Optimum Solute Concentration for Good Glass Forming Ability in Multicomponent Metallic Glasses. *Materials Research Bulletin*, Vol. 38, No. 4, (March 2003), pp. 681-689, ISSN 0025-5408
- Zhang, B.W., & Jesser, W.A. (2002). Formation Energy of Ternary Alloy Systems Calculated by An Extended Miedema Model. *Physica B*, Vol. 315, No. 1-3, (April 2002), pp. 123-132, ISSN 0921-4526
- Zhang, L.C., Xu, J., & Ma, E. (2006). Consolidation and Properties of Ti-based Bulk Amorphous Alloy by Equal Channel Angle Extrusion. *Materials Science and Engineering A*, Vol. 434, No. 1-2, (October 2006), pp. 280-288, ISSN 0921-5093.
- Zhang, L.C., Kim, K.B., Yu, P., Zhang, W.Y., Kunz, U., & Eckert, J. (2007). Amorphization in Mechanically Alloyed (Ti, Zr, Nb)-(Cu, Ni)-Al Equiatomic Alloys. *Journal of Alloys and Compounds*, Vol. 428, No. 1-2, (January 2007), pp. 157-163, ISSN 0925-8388

Zheng, Q., Ma, H., Ma, E., & Xu, J. (2006). Mg-Cu-(Y, Nd) Pseudo-Ternary Bulk Metallic Glasses: The Effects of Nd on Glass-Forming Ability and Plasticity. *Scripta Materialia*, Vol. 55, No. 6, (September 2006), pp. 541-544, ISSN 1359-6462

IntechOpen

IntechOpen



Thermodynamics - Kinetics of Dynamic Systems

Edited by Dr. Juan Carlos Moreno Piraján

ISBN 978-953-307-627-0

Hard cover, 402 pages

Publisher InTech

Published online 22, September, 2011

Published in print edition September, 2011

Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Lai-Chang Zhang (2011). Thermodynamic Approach for Amorphous Alloys from Binary to Multicomponent Systems, *Thermodynamics - Kinetics of Dynamic Systems*, Dr. Juan Carlos Moreno Piraján (Ed.), ISBN: 978-953-307-627-0, InTech, Available from: <http://www.intechopen.com/books/thermodynamics-kinetics-of-dynamic-systems/thermodynamic-approach-for-amorphous-alloys-from-binary-to-multicomponent-systems>

INTECH

open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen