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Trans. Nonferrous Met. Soc. China 19(2009) 78-84

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Recent progress in criterions for glass forming ability

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Received 25 May 2008; accepted 9 September 2008

Abstract: The glass-forming ability(GFA) is an important factor in studying metallic glasses. So far, there are several criteria for evaluating the glass-forming ability. For predicting compositions for bulk metallic glasses, however, they show more or less accuracy and versatility for different cases. In this work, four types of criteria for the glass-forming ability are categorized and reviewed: 1) Indicators with characteristic temperatures; 2) Indicators involving structural factors; 3) Indicators based on Miedema's model; and 4) Indictors based on phase diagram. It is pointed out that a single indicator cannot be used to predict GFA of all the metallic glass systems correctly due to its limited theoretical framework, and the combination of multiple indicators shows more efficiency and accuracy. Though it is still very difficult to develop a universal indicator for GFA, recent indicators seem to be of more reliable physical meaning than those previously suggested.

Key words: glass-forming ability; metallic glass; thermodynamics; phase diagram; electronic structure

1 Introduction

Glass forming ability(GFA) is a very important terminology in studying the formation of metallic glasses. However, no standard definition has been made for this parameter up to now, and many indicators have been developed. From the engineering aspect, the lower the critical cooling rate and the larger the critical thickness are, the higher the glass forming ability of a metallic glass will be. However, it is still difficult to measure the critical cooling rate precisely, and the critical thickness strongly depends on processing parameters. Thus, characterizing the glass forming ability with easily measurable parameters is of vital importance in designing and fabricating metallic glasses.

In 1970s, two mostly used indicators for glass forming ability, supercooled liquid region $\Delta T_{xg}(\Delta T_{xg} = T_x - T_g)$, the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g) and $T_{rg}(T_{rg} = T_g/T_1)$, glass transition temperature T_g over liquidus temperature T_1), were developed[1-2]. Studies have shown that in most glassforming systems the reduced glass transition temperature T_{rg} has a better correlation with GFA than that given by $\Delta T_{xg}[3-4]$. The metallic glasses with the high GFA are known to have a T_{rg} in the range of 0.66–0.69. However, with the development of new metallic glass compositions, both indicators show unsatisfactory correlations with GFA. For example, T_{rg} is found to be unreliable to predict GFA in some Pd and Fe based metallic glasses [5–6]. As T_g , T_x , T_1 and T_m (melting point) can be easily measured from the DCS curves of metallic glasses, some new indicators based on these thermodynamic parameters were developed, such as the stability parameter, S, reported by SAAD and POULAIN[7], and $K_{\rm gl}$ proposed by HRUBY[8]. It is not until recently that a new indicator, γ , developed by LU and LIU[9–10], shows satisfactory correlations with GFA for most metallic glass systems and some oxide glasses. Since then, many other indicators based on characteristic temperatures were developed, and claimed to have better correlations with GFA than γ .

Besides the indicators based on the thermodynamic temperatures, there are plenty of other indicators for GFA. There are indicators based on structural factors. It was proposed that good glass-forming compositions should include 1) large negative enthalpy of mixing, and large atomic size difference between main 2) constitutional elements. FANG et al[11] predicted GFA considering two combined by parameters: electronegative difference and atomic size parameter. By combining a melting point depression parameter ΔT^* proposed by DONALD and DAVIDS[12], and a struc-

Foundation item: Project(50721003) supported by the Creative Research Group of National Natural Science Foundation of China Corresponding author: LIU Yong; Tel: +86-731-8836406; Tel: yonliu11@yahoo.com.cn DOI: 10.1016/S1003-6326(08)60232-0

tural parameter *P* in a form originally proposed by EGAMI and WASEDA[13], KIM et al[14–15] developed a σ indicator. Based on the electron theory in amorphous structures, an *e/a* criterion was also developed to describe GFA of metallic glasses[16–17].

Under the thermodynamic framework based on Miedema's model for calculation of enthalpy of mixing, some new indicators for GFA have also been developed [18–19]. Since the database for Miedema's model is very complete, and most empirical parameters for calculating the mixing enthalpy between two or three elements can be found, it is convenient to evaluate GFA quantitatively. The criteria are mostly built up on the principles that the composition with the lowest enthalpy of mixing or Gibbs energy at amorphous state will be the most stable metallic glass (i.e. high GFA).

Other kinds of indicators are based on the calculations of phase diagrams. Usually good glass-forming compositions are located at or near to deep-eutectic points. This provides another way for predicting metallic glasses with high GFA. The main method involves CALPHAD thermodynamic calculation technique.

This work summarized recently developed GFA indicators based on the above-mentioned four categories, and discussed whether and how the GFA of metallic glasses can be predicted.

2 Indicators with characteristic temperatures

Glass formation is always a competing process between liquid phase and the resulting crystalline phases. If the liquid phase is stabilized upon cooling and the competing crystalline phases are difficult to precipitate out, then the glass formation of the melt would be facilitated. Thus, the GFA of a liquid virtually includes two components, i.e. liquid phase stability and the stability of the competing crystalline phases.

Since it is difficult to study the cooling process of metallic glasses, some characteristic temperatures upon heating are usually used for predicting GFA. Those temperatures include the glass transition temperature $T_{\rm g}$, crystallization temperature $T_{\rm x}$, liquidus temperature $T_{\rm 1}$ and melting point $T_{\rm m}$. Since 2000s, many indicators have been developed by combining the above parameters.

In LU and LIU's theory[9–10], the liquid phase stability can be measured by $1/2(T_g+T_l)$, which is the average of the stability of the liquids at equilibrium and metastable states, as shown in Fig.1. And the onset crystallization temperature T_x measured upon continuous reheating alone can assess the GFA under the condition that the liquids have the same liquid phase stability. To manifest the relative GFA among those liquids, T_x should be normalized to the average position of the TTT curve along the temperature axis [e.g., $1/2(T_g+T_l)$], so that all liquids have the same stabilities, as shown in Fig.1(b). Hence, the normalized T_x , denoted as γ , can be used as a gauge for GFA, which can be expressed as

$$\gamma \propto T_{\rm x} \left[\frac{1}{2(T_{\rm g} + T_{\rm l})} \right] \propto \frac{T_{\rm x}}{T_{\rm g} + T_{\rm l}} \tag{1}$$

For BMGs, the new γ value is in the range from 0.350 to 0.500, while $\Delta T_{\rm xg}$ ranges from 16.3 to 117 K and $T_{\rm rg}$ varies from 0.503 to 0.690. The new parameter γ has a better correlation with $R_{\rm c}$ (critical cooling rate) and $Z_{\rm c}$ (critical thickness) than $T_{\rm rg}$.



Fig.1 Schematic time-temperature-transformation (TTT) diagram: (a) Crystallization occuring between T_1 and T_g , and can be avoided by sufficiently cooling of the liquid (R_c); (b) Effect of T_x measured upon continuous heating for different liquids with similar T_1 and $T_g[9-10]$

Considering the fact that T_1 can be a measure of stability of the liquid and that T_x is a measure of thermal stability of the glass, MONDAL and MURTY[20] proposed a simple parameter α :

$$\alpha = \frac{T_x}{T_1}$$
 or $\beta = 1 + \alpha$ (2)

The parameter α or β holds for various metallic glasses, and also shows a good correlation with the R_c and Z_c . The parameter, as claimed, is very useful particularly in cases where a distinct T_g is not observed.

Based on theoretical calculations using the fragility concept and the nucleation theory, FAN et al[21]

proposed a dimensionless criterion, ϕ , with $T_{\rm rg}$ and $\Delta T_{\rm x}$:

$$\phi = T_{\rm rg} \left(\frac{\Delta T_{\rm x}}{T_{\rm g}} \right)^{\alpha} \tag{3}$$

where α is a constant. By linear fitting in the log $R_c - \phi$ plot for various metallic and molecular glasses, α can be optimized as 0.143.

There are other indicators based on TURBULL's classical nucleation and growth theory. In this framework, the homogeneous nucleation rate, I, and the growth rate, U, of a crystalline phase formed from an undercooled liquid can be expressed by[22]

$$I = \frac{10^{30}}{\eta} \exp\left[\frac{-16\pi}{3} \frac{\alpha^3 \Delta S_{\rm f} T^2}{R(T_{\rm l} - T)^2}\right]$$
(4)

and

$$U = \frac{10^2 f}{\eta} \left[1 - \exp(-\frac{\Delta S_{\rm f} (T_{\rm l} - T)}{RT}) \right]$$
(5)

where η is the viscosity, *f* is the fraction of nucleation sites at the growth interface, α is a factor which depends on the atomic arrangement at the interface and has a value close to unity, ΔS_f is the change in entropy per mole of alloy due to melting, *T* is the temperature of the melt and *R* is the universal gas constant. According to the two equations, the important parameters governing the GFA are η and $T/(T_1-T)$. Consequently, two new parameters were proposed[23–24]:

$$\delta = \frac{T_{\rm x}}{T_{\rm l} - T_{\rm g}} \tag{6}$$

and

$$\beta = \frac{T_{\rm x} \cdot T_{\rm g}}{\left(T_{\rm l} - T_{\rm x}\right)^2} \tag{7}$$

By calculating the characteristic temperatures of tens of metallic glass compositions and correlating with the critical thickness, both parameters were claimed to have a better fitting than other parameter thus developed.

The critical cooling rate is a very important parameter in studying GFA. It is usually determined by the nose method in TTT diagrams[25]. However, the critical values thus calculated are typically one order of magnitude greater than experimentally determined values [26]. By using the kinetic theory of Johnson-Mehl-Avrami-Kolmogorov (JMAK), ZANOTTO et al[27] derived and calculated the critical cooling rate, X_c , by employing the cooling curve of DTA or DCS, and proposed the critical cooling rate q_{cr} :

$$q_{\rm cr} = \sqrt{\frac{gN_{\rm s}}{X_{\rm c}}} \left| \int_{T_{\rm m}}^{T_{\rm g}} \mu(T) \mathrm{d}T \right| \tag{8}$$

By comparing q_{cr} with several GFA indicators, it is indicated that only those indicators involving T_x , T_g , T_1 (or T_m) have good correlations with the critical cooling rate.

3 Indicators involving structural factors

Atomic structures in liquids are believed to have an intrinsic influence on the GFA of metallic glasses. A relatively dense atomic structure in liquids may restrain the occurrence of crystallization. The dense atomic structures include local short-range order(SRO) and medium-range order(MRO)[28]. The density of atomic arrangement is governed by two factors: atomic packing and atomic bonding. Atomic packing involves some geometrical parameters, such as atomic size ratio and size of clusters, while atomic bonding is more related to the electronic structures, such as the electronegativity and Fermi surface-Brillouin zone interaction.

common practice to design high GFA compositions is to choose alloying elements with appropriate atomic size ratios, for example, a wide atomic size distribution, with uniform separation of the sizes[29]. In such a way, the random atomic packing density will be increased in the liquids. MIRACLE [30-31] proposed a comprehensive efficient cluster packing model for metallic glasses consisting of ≤ 4 topologically distinct cluster with solute at their centers. The ECP model is based on the fact that the best glass-forming systems usually have a higher density that is typically 99.5% or more of the crystalline density in the same composition range. However, geometrically atomic packing behavior related with atomic size ratio cannot be the only parameter indicating the GFA, and usually is combined with other factors, such as thermodynamic and electronic structure characteristics.

EGAMI and WASEDA[13] have suggested the following criterion for the formation of the amorphous phase in binary alloy systems based on the atomic scale elasticity theory:

$$x_{\rm B}^{\rm min} \left| \frac{(v_{\rm B} - v_{\rm A})}{v_{\rm A}} \right| = x_{\rm B}^{\rm min} \left| (\frac{r_{\rm B}}{r_{\rm A}})^3 - 1 \right| \approx 0.1$$
(9)

where x_B^{min} is the minimum solute content, and v_i and r_i (*i*=A, B) are atomic volume and atomic radius, respectively. The larger the atomic size difference is, the smaller the amount of solute is required to form an amorphous phase. It is expected that GFA increases with increasing the overall atomic size mismatch. Based on Eq.(4), KIM et al[32] extended the overall effect of atomic size mismatch on GFA to ternary alloys by using the following P' parameter:

$$P' = \frac{x_{\rm B}}{x_{\rm B} + x_{\rm C}} \left| \frac{(v_{\rm B} - v_{\rm A})}{v_{\rm A}} \right| + \frac{x_{\rm C}}{x_{\rm B} + x_{\rm C}} \left| \frac{(v_{\rm C} - v_{\rm A})}{v_{\rm A}} \right|$$
(10)

The P' parameter represents the effective atomic mismatch of each solute atom, which depends on alloy system and composition. Then P' parameter was combined with a thermodynamic parameter ΔT^* , to form a new σ parameter for predicting GFA:

$$\sigma = \Delta T^* \times P' \tag{11}$$

 ΔT^* is a dimensionless melting temperature depression parameter to evaluate GFA of metallic glasses, introduced by DONALD and DAVIDS[12]:

$$\Delta T^* = \frac{T_{\rm m}^{\rm mix} - T_{\rm l}}{T_{\rm m}^{\rm mix}} \tag{12}$$

where T_1 is a liquidus temperature; and $T_{st}^{\text{mix}} = \sum_{i}^{n} x_i \cdot T_m^i$ with x_i and T_m^i standing for the molar fraction and melting point, respectively of the *i*th component in an *n*-component alloy system. ΔT^* for the most glass forming alloys such as Fe- and Ni-based metallic glasses has been reported to be larger than 0.2[12]. By combining the two parameters, the σ parameter shows good correlation with GFA (the maximum diameter) in some ternary bulk metallic glasses[14–15].

FANG et al[11] combined the atomic size parameter δ and the electronegativity difference Δx to evaluate GFA:

$$\Delta x = \sqrt{\sum_{i=1}^{n} C_i (x_i - \bar{x})^2}, \, \bar{x} = \sum_{i=1}^{n} C_i x_i$$
(13)

$$\delta = \sqrt{\sum_{i=1}^{n} C_i (1 - \frac{r_i}{\bar{r}})^2}, \ \bar{r} = \sum_{i=1}^{n} C_i r_i$$
(14)

where *n* is the number of component in the alloy system; C_i , x_i and r_i are the atomic percentage, Pauling electronegativity and covalent atomic radius of element *i*, respectively. It is demonstrated that there is a linear relationship between the parameters and BMG thermal stability (T_{xg}).

LIU et al[33] expanded the two parameter criteria to seven, including two electronegativity difference parameters (*L* and *L'*), three atomic size ratio parameters (*W*, *W'* and λ_n), a valence electron difference *Y* and a reduced melting temperature $T_{\rm rm}$. Then the seven parameters are combined to calculate Z_c , R_c , $T_{\rm xg}$ and other characteristic parameters by linear fitting. The combined criterion provides a good guideline for predicting BMGs with a high GFA.

4 Indicators based on Miedema's model

Thermodynamic calculation provides another way to develop indicators for GFA. The Miedema's model is an empirical theory for calculating enthalpy of mixing in various binary systems both for the liquid and solid state [34–35]. Since the metallic glass formation process is controlled by thermodynamic factors, this theory was firstly used to predict the composition range of amorphous binary transition metal alloys[36–37].

The Miedema's model involves the calculations of the formation enthalpy of amorphous phase(ΔH^{amor}), solid solutions (ΔH^{SS}), and intermetallic compounds (ΔH^{inter}) according to the following equations [38]:

$$\Delta H^{\text{amor}} = \Delta H^{\text{chem}}(\text{amor}) + \Delta H^{\text{topo}}$$
(15)

$$\Delta H^{\rm ss} = \Delta H^{\rm chem}(SS) + \Delta H^{\rm elastic} + \Delta H^{\rm structure}$$
(16)

$$\Delta H^{\text{inter}} = \Delta H^{\text{chem}} (\text{inter})$$
(17)

where $\Delta H^{\text{chem}}(\text{amor})$ is the chemical mixing enthalpy of the amorphous state, ΔH^{topo} is the topology enthalpy of a glass, $\Delta H^{\text{chem}}(\text{SS})$ is the chemical mixing enthalpy of a solid solution, $\Delta H^{\text{elastic}}$ is the elastic enthalpy of the solid solution calculated based on the continuous elastic model, $\Delta H^{\text{structure}}$ is the structure enthalpy induced by the structural changes, and $\Delta H^{\text{chem}}(\text{inter})$ is the chemical mixing enthalpy of an intermetallic compound. In Zr-Ni-Al ternary system, 4.0 kJ/mol $<|\Delta H^{\text{SS}}-\Delta H^{\text{am}}| < 7.0$ kJ/mol corresponds to $\Delta T_{\text{xg}} > 50$ K[39]. The enthalpy difference between the solid solution and the amorphous phase contributes to the driving force for crystallization. Thus, the smaller the difference is, the higher the GFA of alloys will be.

For binary Zr-Cu system, taking into account of both enthalpy of the formation for the amorphous phase and the enthalpy difference between the intermetallic phase and the amorphous phase, XIA et al[18] proposed a parameter γ^* to evaluate GFA, which can be expressed as

$$\gamma^* = \text{GFA} \propto \frac{\Delta H^{\text{amor}}}{\Delta H^{\text{inter}} - \Delta H^{\text{amor}}}$$
(18)

The higher the absolute value of ΔH^{amor} is, the better the GFA is; and the smaller the enthalpy difference between the intermetallic phase and the amorphous phase is, the better the GFA is[18]. By combining the parameter γ^* and a topological instability " λ criterion", OLIVERIA et al[40] predicted the glass-formation compositions in Al-Ni-Y system. Under the same ideology, JI et al[41] proposed a γ' parameter to determine GFA:

$$\gamma' = \text{GFA} \propto \frac{\Delta H^{\text{liq}} \Delta H^{\text{amor}}}{(\Delta H^{\text{inter}})^2}$$
(19)

TAKEUCHI and INOUE[19] also calculated the mixing enthalpy (ΔH) and mismatch entropy (S_{σ}) of glass forming alloys and thus obtained critical values of ΔH and S_{σ} for high GFA of multicomponent metallic glasses. BASU et al[42] used the same approach to identify glass- formation compositions in (Zr,Ti, Hf)-(Cu, Ni) binary and ternary systems. The mixing enthalpy varies between -13 and -45 kJ/mol and the normalized mismatch entropy varies between 0.13 and 0.15.

Recently, RAO et al[43] calculated the Gibbs-energy change with the help of Miedema, MIRACLE, mismatch entropy, and configurational entropy models, and identified the best glass-formation composition by drawing iso-Gibbs-energy change contours in quinary systems, as shown in Fig.2.



Fig.2 Iso-free energy contour map for Zr-Ti-Ni-Cu-Al system showing composition with highest negative $\Delta G[43]$

5 Indictors based on phase diagram

The glass formation compositions usually located near to eutectic points. Thus it is possible to predict GFA by looking at deep eutectic points. Several studies have been made by examining binary phase diagrams in order to find binary metallic glasses along eutectics, or to extrapolate binary information for ternary alloys design. It was found that the locations of eutectics and the compositions having a good GFA are similar[44]. LI et at[45] reported their observations of bulk metallic glass formation by pinpointing ternary eutectic compositions:

$$L \rightarrow \tau_5 + ZrCu + Cu_{10}Zr_7 \tag{20}$$

in the Zr-Cu-Al system. Therefore, calculating liquidus temperature profiles with the aim of searching for eutectics is useful to predict compositions with a good GFA. By considering this, CHENEY and VECCHINO [46] proposed a α parameter, quatitatively describing the depth of a eutectic, to evaluate GFA. The α parameter, as a measure of the depth of a eutectic, is related to a weighted liquidus temperature. The calculation of α parameter is shown in the following equation:

$$\alpha = \frac{\sum_{i=1}^{n} x_i T_i}{T_1} \tag{21}$$

The weighted liquidus temperature is the numerator, where x_i is the atomic fraction of element *i*, T_i is the melting temperature of element *i*, and *n* is the number of elements. A eutectic will generate a α higher than unity, and a deep eutectic will produce a high α value. The calculation is illustrated for the case of the La-Ni-Al alloy in the ternary diagram, as shown in Fig.3. The α parameter provides a more complete understanding of the thermodynamics of glass-formation ability than the liquidus temperature alone. It is found that the glass-forming composition is located in the region with a α parameter larger than 1, and the best glass formers may have a α parameter larger than 1.5. Recently, CHENEY and VECCHINO[47] combined the liquidus-based model with a model depicting the chemical short-range order (CSRO) to evaluate GFA of various metallic glass systems. It is found that metallic glass compositions tend to locate at or near to deep eutectics, but also have an optimized structural topology.



Fig.3 Example plot (La-Ni-Al system) of alpha parameter, actual (calculated based on thermodynamics), and ideal (weighted) liquidus profile[46]

The formation of metallic glass is the result of the suppression of the crystallization process during cooling. Therefore, the best glass formation composition may also be termed as the composition with the minimum driving force for crystallization. By using phase diagrams, if the driving forces or competitive growth behaviors for the crystallization of all the intermetallic or eutectic phases can be depicted, the optimum glass-forming composition

may be derived. By studying the competitive growth rate of different eutectics, MA and CHANG[48] proposed a critical glass-forming velocity (v_c) for ternary eutectic systems:

$$v_{\rm c} = \left(\frac{T_{\rm l}^x - T_{\rm g}}{K_{\rm x}}\right)^2 \propto \left(1 - T_{\rm rg}\right)^2 \tag{22}$$

where T_1^x is the liquidus temperature, K_x is the growth constant for *x*. The growth limitation of eutectic is crucial for locating/optimizing best glass-formers in eutectic systems. The difference between the eutectic temperature T_e and the glass transition temperature T_g will affect the GFA, but the growth rate of eutectics affects the GFA more effectively.

By using the CALPHAD method, KIM et al[49] calculated the Gibbs energy of all the intermetallic phases in the Cu-Ti-Zr system, and use the minimum Gibbs energy (entropy of formation) as the lowest driving force for crystallization, and for deriving compositions with a high GFA.

Like molecular glasses, many metallic glasses were reported to separate phase in the glass state prior to crystallization, even in the liquid state [50]. A solution in a ternary system can decompose into two solutions with different compositions even if the mixing enthalpy is all negative, when the mixing enthalpy in one of the three binary systems is significantly more negative compared with the others. This means that there is a possibility of a liquid phase separation even in a god glass-forming alloy. By considering that the glass-forming ability is low in the phase separating compositions, ABE et al[51] calculated the liquid phase miscibility gap in ternary glass-forming system using the sub-regular solution model to evaluate the GFA. They predicted the liquid phase miscibility gap at low temperatures in most ternary bulk metallic glass systems, and found out that the glass-forming region usually does not overlap with the phase separation region.

6 Is it possible to predict GFA precisely?

As mentioned above, glass-forming ability involves two aspects: the stability of the liquid structure and the resistance to crystallization. The former is related to the thermodynamic factors, and the latter to the kinetic factors. Owing to the difficulties in measuring thermodynamic parameters directly from the liquid state, most indicators involve parameters measured or calculated from the solid state. Also, as there is still much to be known on the liquid structure, no strictly deduced theoretical factors for GFA are available yet, and most indicators currently used are only phenomenological. However, some recent developments may predict GFA more accurately in both thermodynamic and kinetic aspects. For example, by the CALPHAD technique, glass-forming in some multi-component alloy systems can be well described, and new glass-forming composition regions can be predicted[52]. Also, the topological structures of the liquid state and the amorphous phase have been studied intensively and much progress has been made[31]. The electronstatic levitation technique makes it possible to study the glass-forming liquids in wider temperature range[53]. The TTT diagrams and some other kinetic factors can be conveniently determined for the liquid structures.

However, more and more researchers believe that one single indicator cannot be used to predict GFA of all the metallic glass systems due to its limited theoretical framework. For example, γ parameter is capable of representing the GFA of most alloys, but it is less accurate in assessing the GFA of the compositions whose decisive competing crystalline phase upon cooling is different from that upon heating[54]. The indicators based on structural parameters do not involve kinetic factors, and thus, cannot be used alone to predict GFA [55]. The indicators based on Miedema's model may be lack of precision in calculation due to limited data and/or error in the empirical data[40]. Another problem with the evaluation of GFA is the standards, which are the critical cooling rate and the critical size of BMGs. The critical cooling rate is usually determined by the nose method in TTT diagrams, and it is one order magnitude greater than the experimental ones; while the critical size is highly influenced by experimental conditions and sometimes is full of artifacts. Therefore, the combination of multiple indicators may be a way more effective to evaluate GFA of BMGs.

Finally, the formation of metallic glass is a non-equilibrium process, and studies in view of equilibrium theories may lead to incorrect results. Thus, it is still a long way to develop proper indicators for GFA, which are theoretically strict and composed of very simple and fundamental parameters.

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