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A new thermodynamic parameter to predict glass forming ability in iron based multi-component systems containing zirconium

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ABSTRACT

A new thermodynamic parameter P_{HSS} ($P_{HSS} = \Delta H^C(\Delta S_\sigma/k_B)(\Delta S_C/R)$) is proposed, to describe and predict the glass forming ability (GFA) of Fe based alloys. Here ΔH^C is the chemical enthalpy of mixing, ΔS_σ is the mismatch entropy and ΔS_C is the configurational entropy. The P_{HSS} parameter incorporates enthalpy of mixing, size mismatch and the number of elements in the systems which influence GFA significantly. It was observed from rapid solidification processing (RSP) and mechanical alloying (MA) studies that, all alloys with P_{HSS} in between −0.55 kJ/mol to −6.00 kJ/mol would form glass in the Fe–Zr–B system. MA and RSP experiments on multi-component Fe–Cr–Ni–Zr–B alloys indicated that P_{HSS} is a better parameter to predict GFA of the system than P_{HS}, a parameter used in earlier studies. It was also observed that bulk metallic glass (BMG) forming alloys can be observed in between a P_{HSS} range of −3.00 kJ/mol to −6.00 kJ/mol, with the maximum thickness of the BMG increasing with decreasing P_{HSS} within the above range.

1. Introduction

Metallic glasses are important engineering materials due to their unique physical, mechanical and chemical properties owing to lack of translational periodicity and absence of defects such as dislocations and grain boundaries [1]. Since the discovery of the first metallic glass in the Au–Si system [2] by RSP, considerable research was focussed on understanding the GFA of metallic systems. The aim of the research was to decrease the critical cooling rate to obtain glasses in 'bulk', to use them for many practical applications.

Over time, several qualitative and quantitative criteria were developed to describe GFA. Based on thermodynamic and kinetic considerations for the suppression of nucleation, Turnbull [3] proposed the first GFA criterion called reduced glass transition temperature, $T_{rg} = T_g/T_l$, where T_g is the glass transition temperature and T_l is the liquidus temperature of the alloy. Alloys with $T_{rg} > 2/3$, imply high melt viscosity and low melting point, were found to have high GFA. Subsequently, it was discovered that by eliminating heterogeneous nucleation sites, millimetre to centimetre thick glasses could be made in Pd- based alloy systems at low critical cooling rates, which were termed as BMG's [4]. It was realised that internal factors, such as the number, atomic size and chemical nature of elements play an important role in glass formation, rather than external factors related to processing, such as the cooling rate [5].

Inoue [5] proposed that an alloy melt would form a BMG if (i) it has more than 3 elements, (ii) the size difference among the species is greater than 12%, and (iii) the enthalpy of mixing in the liquid state is negative. All these factors lead to efficient packing in the liquid, bringing it energetically closer to its crystalline counterpart. This would increase the viscosity, thereby restricting atomic mobility. Decreased atomic mobility suppresses the nucleation and stabilize the liquid to low temperatures, which would then 'configurationally freeze' into a glass upon cooling. Exceptions to Inoue's three empirical criteria were also reported [6]. However, the majority of BMG's were found to obey Inoue's empirical rules and these rules can be treated as general guidelines to identify good glass forming compositions.

Several parameters were proposed to describe GFA since Turnbull's T_{rg} such a $\Delta T_x = T_x - T_g$, (here T_x is the crystallization onset temperature while heating) [7], $\gamma = T_x/(T_g + T_l)$ [8], $\alpha = T_x/T_l$ and $\beta = 1 + \alpha$ [9], as well as $\delta = T_x/(T_l - T_g)$ [10]. Most of the parameters proposed are based on thermochemical properties of glasses. They

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are not predictive in nature, as they require the synthesis of the glassy alloys first. There were also attempts to predict GFA and glass forming compositions from solution thermodynamics [11]. Most of these attempts are limited to binary or ternary alloys. Other approaches were also proposed to predict the glass forming compositions, for instance, models based on the size difference among the constituent species [12], and topological models based on efficient cluster packing [13].

Recently a combined thermodynamic and topological approach was proposed by Bhatt et al. [14], wherein a product of enthalpy of chemical mixing and entropy of mismatch yielded a parameter named as P_{HS} which was used for predicting GFA in a number of Zr and Cu based systems [14,15]. This approach was also extended to Fe based systems recently [16,17]. While modelling, the effect of the number of components was considered only in a qualitative manner in the earlier reports [16,17]. This would limit the direct applicability of the P_{HS} parameter to multi-component systems. A general model incorporating all the above three parameters (enthalpy of mixing, mismatch entropy and configurational entropy) would be more helpful in pinpointing the glass forming compositions in multi-component systems. In the present study, an attempt has been made to identify a new thermodynamic GFA parameter, incorporating the above three parameters. With the help of these new GFA parameter and experimental data on amorphous alloys, the glass forming composition ranges have been identified in the Fe–Zr–B system. Predictability of GFA with P_{HS} and the new parameter has been compared in Fe based multi-component systems. Model predictions have been validated by the synthesis of select alloys by MA and RSP routes.

2. Experimental details

MA was carried out in a Retsch planetary high energy ball mill model PM 400. A 250 ml capacity WC vial and 10 mm diameter WC balls were used during MA. In most of the milling experiments a ball to powder weight ratio of 10:1 was used. Elemental powder blends mainly consisting of Fe, Zr, B, Cr, Ni with a particle size of less than 50 μm with purity >99% were loaded into milling vials and milling was carried out at a disk speed of 300 rpm. Toluene was used as a process control agent. Milling was interrupted every 30 min for cooling of vials for 30 min. Samples were collected at regular intervals to monitor the progress of amorphisation.

For RSP experiments, select Fe based alloy ingots were prepared by arc-melting. The arc-melting chamber was evacuated to a pressure of $\sim 10^{-4}$ mbar and then back filled with high purity Ar. RSP was also carried out in an Ar filled chamber that was evacuated prior to Ar filling. Induction melted alloy was injected onto a copper wheel rotating at 2400 rpm to obtain ribbons of ~3 mm width and 20–50 μm thickness.

The phases present in the MA powders and RSP ribbons were examined using X-ray diffraction (XRD) with a Panalytical X Pert Pro X-ray diffractometer with the Bragg–Brentano geometry using Cu-Kα radiation ($\lambda = 0.15406$ nm). Phase identification was carried out using ICDD PDF 4+ database. The microstructure

Table 1
GFA parameter calculation results for binary to multi-component alloys in Fe–Cr–Ni–Zr–B system.

Composition	ΔH^C, kJ/mol	$\Delta S_\sigma/k_B$	$\Delta S_C/R$	P_{HS}, kJ/mol	P_{HSS}, kJ/mol
$Fe_{80}B_{20}$	−9.05	0.20	0.50	−1.84	−0.91
$Fe_{70}Zr_{10}B_{20}$	−14.79	0.38	0.80	−5.65	−4.49
$(Fe_{0.82}Cr_{0.18})_{70}Zr_{10}B_{20}$	−11.52	0.38	1.13	−4.40	−4.97
$(Fe_{0.74}Cr_{0.18}\ Ni_{0.08})_{70}Zr_{10}B_{20}$	−10.23	0.38	1.31	−3.92	−5.13

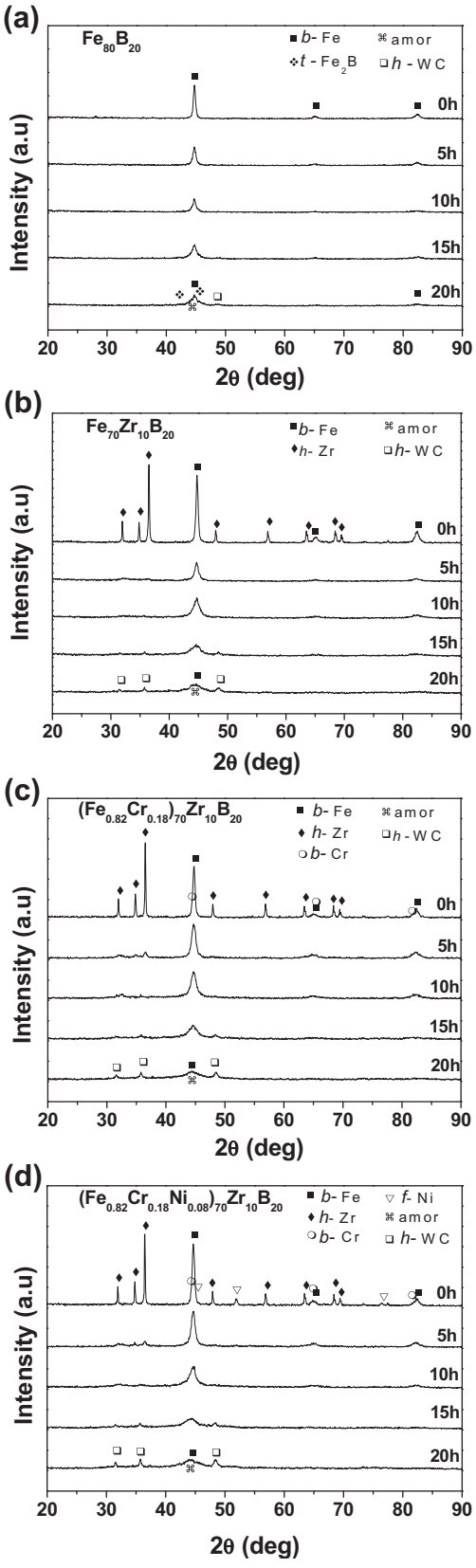

Fig. 1. XRD patterns of mechanically alloyed powder blends with nominal compositions of (a) $Fe_{80}B_{20}$, (b) $Fe_{70}Zr_{10}B_{20}$, (c) $(Fe_{0.82}Cr_{0.18})_{70}Zr_{10}B_{20}$ and (d) $(Fe_{0.82}Cr_{0.18}Ni_{0.08})_{70}Zr_{10}B_{20}$.