

Semi-Empirical Modelling of Glass Forming Ranges for Y-Co-Si System

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Glass forming abilities of a ternary Y-Co-Si system were determined on the basis of combined semi-empirical Miedema's and geometric models. The enthalpy of amorphous and solid solution phases formation, along with the mismatch entropy and GFA parameter, were analysed to indicate compositions with the highest ability for the amorphization. The large atomic radii difference between constituents, especially Y and Si, is the deciding factor of GFA. Compositions ranged between $Y_{33}Si_{67}$ and $Y_{45}Si_{55}$ are the best glass formers.

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1. Introduction

One of the main aims in the field of metallic glasses is the determination of glass forming ability (GFA) which reflects the tendency for amorphous phase formation. A large number of empirically-based criteria has been developed up to date. In last decade some modifications and extensions of the semi-empirical Miedema's model were used to determine GFA and glass forming ranges (GFR) of alloys [1, 2]. Usually Miedema's theory has been developed to determine formation enthalpies of binary systems. Thermodynamic properties of multinary alloys must be calculated by extrapolation of quantities obtained for their sub-binaries. The asymmetric geometric model was used by us [3] to calculate the GFR for ternary Y-Co-Si system. Rare-earth and cobalt based amorphous alloys exhibit the spectra of complex magnetic properties as for example itinerant electron metamagnetism and exchange-enhanced Pauli paramagnetism [4].

2. Calculation method

The calculation basis of the semi-empirical approach is the Miedema's model [5, 6], also called macroscopic-atom model. In determination of glass forming ability, total free energy of amorphous phase and its solid solution counterpart need to be compared, as two competing states. Values calculated for sub-binaries must be extrapolated to determine the glass forming ranges of ternary and other multinary alloys. In this work, the asymmetric geometric model [7], proposed for ternary intermetallics and solid solutions, is applied to calculate the formation enthalpy of the solid solutions ΔH^{ss} and amorphous alloys ΔH^{am} , and also the formation enthalpy difference between both counterparts ΔH^{am-ss} . Additionally, the effect of atomic radius differences, which is important in glassy state formation processes, is estimated by a normalized mismatch entropy S_{σ}/k_B . GFA can be also char-

acterized quantitatively by glass forming ability parameter ΔP_{HS} [8]. The used approach is described in more details in Ref. 3.

3. Results and discussion

Formation enthalpies of amorphous phase ΔH^{am} and solid solution ΔH^{ss} were calculated for the whole range of compositions with the step of 1 at.% for Y-Co-Si alloys. The determined values, along with the difference between both quantities ΔH^{am-ss} , are shown in Fig. 1 in the form of contour maps. At first, it should be underlined that lower formation energy of amorphous phase, as compared to the crystalline one, promotes the glassy state formation. The lowest ΔH^{am} values were calculated for Y-Si binary system. The enthalpy of formation reaches almost -58 kJ/mol for $Y_{45}Si_{55}$. Highly negative enthalpy of amorphous phase formation for the mentioned composition is consistent with previous results obtained for Y-Co-B [9]. Large negative values of interfacial enthalpies equal to -318 kJ/mol (Y in Si) and -216 kJ/mol (Si in Y) [5] are responsible for such significant effect. The amorphization process is favored in this system due to the homogeneity and reduced phase separation in undercooled liquid. Y-Co, Co-Si and ternary Y-Co-Si alloys, excluding several compositions in the corners of the phase diagram, are also predicted to form amorphous phase, despite of less negative values of ΔH^{am} . ΔH^{ss} contour map is different from that of amorphous alloys, mainly on Y-Co edge, due to the highly positive elastic energy (more than 30 kJ/mol for $Y_{50}Co_{50}$). This contribution is connected with the misfit of two types of atoms and depends, among other quantities, on shear and bulk moduli values. By taking into account only the difference between ΔH^{ss} and ΔH^{am} (Fig. 1c), it could be deduced that the best glass formers are lying on Y-Co edge. Notwithstanding, as it was mentioned, elastic enthalpy plays a main role in this case and could overwhelm other contributions and dim the overall results. On the basis of ΔH^{am-ss} values, as it represents the driving force for amorphization, one may expect the lowest GFA for the compositions in the corners of phase diagram and

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Co-Si binary alloys. This is consistent with experimental reports, in which the majority of Co-Si amorphous phases were synthesized as thin films, where the quenching process is more rapid than in other synthesis techniques [10]. According to previous results ([11] and references therein), the Co-Si amorphous structure is stable for more than 30 at.% of Si. It is rather consistent with the results obtained from our calculations for binary system, which places the glass forming range between 42 and 64 at.% of Si.

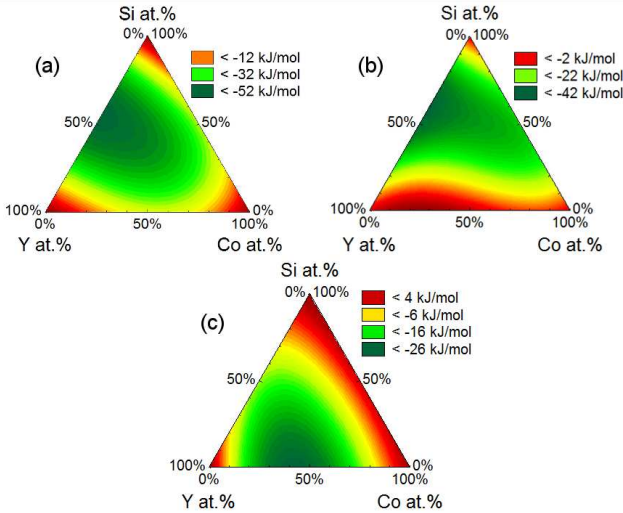


Fig. 1. Contour maps of (a) the formation enthalpy of amorphous alloy, (b) the formation enthalpy of solid solution and (c) the difference between both quantities ΔH^{am-ss} , calculated for ternary Y-Co-Si system.

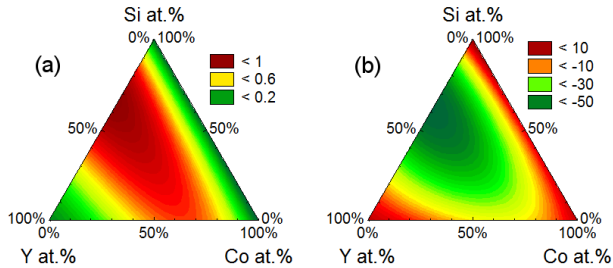


Fig. 2. Contour maps of (a) the normalized mismatch entropy and (b) glass forming ability parameter, calculated for Y-Co-Si system.

The basis for all described effects is the large difference in atomic radii of the constituents. It has an impact on the contributions connected with atomic size mismatch and topological disorder (elastic and topological enthalpy). The results obtained for normalized mismatch entropy S_σ/k_B confirm those findings (Fig. 2a). The S_σ/k_B of Y-Co-Si system reaches 0.99 for $Y_{33}Si_{67}$ (large difference in atomic radius of both constituents) and for the vast number of compositions (95.7%) exceeds the 0.1 value which is the canonic limit for alloys with significant GFA [12]. Glass forming ability parameter ΔP_{HS} combines the entropy and chemical enthalpy (see

Fig. 2b). The ΔP_{HS} results are similar with those of formation enthalpy of amorphous alloys and normalized mismatch entropy, as can be seen from the comparison of Fig. 1a, Fig. 2a and Fig. 2b. Alloys with the highest glass forming ability represent the binary Y-Si system. Additional alloying element is supposed to promote the vitrification. In accordance with that, ternary alloys should be the best glass formers. However, undertaken analysis of Y-Co-Si system suggests that the large atomic radii difference between constituents (especially Y and Si) is the deciding factor. The best GFA compositions are $Y_{39}Si_{61}$, $Y_{33}Si_{67}$ and $Y_{45}Si_{55}$, determined on the basis of ΔP_{HS} , S_σ/k_B and ΔH^{am} analysis, respectively. It should be underlined that the results were obtained on the basis of thermodynamic approach and the kinetics of the glass formation could have a strong impact on preferred alloys compositions.

4. Conclusions

It was found that the effect of additional alloying element is less pronounced than the large atomic radii difference between the alloy constituents. Basing on different quantities (ΔH^{am} , ΔP_{HS} , S_σ/k_B) the best GFA compositions are ranged between $Y_{33}Si_{67}$ and $Y_{45}Si_{55}$.

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