

Influence of chromium addition and cooling rate on Kinetic and microstructural evolution in $\text{Fe}_x\text{Cr}_{100-x}$ Metallic Glasses

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Abstract. In this study, we utilized molecular dynamics simulations with the embedded-atom approach to explore how different cooling rates and concentrations of chromium (Cr) affect the vitrification of metallic glasses (MGs) composed of a binary alloy $\text{Fe}_x\text{Cr}_{100-x}$. We assessed this impact by analyzing the glass transition temperature (T_g) and the activation enthalpy (Δh). The results reveal an interesting non-linear trend in the activation energy. Specifically, there is a sharp decrease observed at a chromium concentration of 50%, followed by a slight increase at the 75% concentration level. These kinetic observations are linked to microstructural data obtained through Voronoi polyhedral analysis (VPA). However, it's worth noting that the influence of varying cooling rates on the vitrification process appears to be relatively modest.

1 Introduction

Metallic glasses, or amorphous materials, are structures lacking a crystalline arrangement, formed when the crystallization process is obstructed. These materials have made remarkable strides, chiefly owing to their exceptional mechanical properties, notably high fracture strength and significant elastic deformation, which set them apart from crystalline materials [1]. Amorphous alloys have garnered noteworthy attention as potential biomaterials due to their advantageous trait of resisting corrosion across various forms [2]. A study has highlighted that metallic glasses based on iron display superior mechanical characteristics, including heightened strength, hardness, and corrosion resistance, in comparison to other alloy materials [3]. Examining corrosion resistance in non-metallic steels, particularly chromium, holds significant importance as it augments resistance to corrosion in challenging aqueous environments [4]. Chromium, acting as a passive promoter due to its strong oxygen bonding, enhances the durability of passive films and the expansion of oxide layers, subsequently reducing the corrosion rate in steel with an elevated chromium content [5]. Comprehending the relationship between the arrangement and dynamic characteristics of metallic glasses (MGs) is a fundamental aspect of unravelling the glass-forming ability of binary alloys. Numerous studies have been undertaken to investigate the impact of external factors on the local microstructure and properties of Fe-based binary alloys [6]. In this current investigation, we focus on analyzing two external variables: the cooling rate and the composition of the binary system. The

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phenomenon of vitrification is distinguished by the presence of a fundamental parameter known as the glass transition temperature (T_g). Determining this value allows us to calculate the activation energy, represented as Δh^* , which signifies the energy barrier that must be overcome during the transition from a liquid to a solid state. Following this, we will examine the microstructure of the binary alloy via the VPA approach. The article is structured into three main sections. Section II offers a detailed description of the system under investigation as well as an overview of the simulation methods employed in the study. In Section III, we delve into the findings obtained concerning the impacts of varying cooling rates and chromium concentrations on the activation energy and microstructural evolution of $\text{Fe}_x\text{Cr}_{100-x}$ metallic glasses. This section provides a detailed discussion of how these factors influence the studied properties. Finally, the results of this work are summarised in the conclusion section.

2 Simulation procedure

This study aimed to examine the behaviour of metallic glasses (MGs) through the application of Classical Molecular Dynamics (MD) simulations [7]. These simulations were carried out utilizing the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) programme and implemented the embedded-atom method (EAM) potential proposed by Eich et al. [8]. The EAM potential was selected for its ability to mimic the complex interatomic interactions within the alloy. Specifically, it determines the energy of each atom in the iron metal by taking into account its integration into the electron density of nearby atoms [9]. The total system's energy was calculated using the provided equation,

$$E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i,j,i \neq j} \Phi_{ij}(r_{ij}). \quad (1)$$

Where, Φ_{ij} signifies the energy associated with the interaction between atoms i and j when they are separated by a distance r_{ij} . On the other hand, F_i represents the energy required to embed an atom i inside a specific local site, which is specified by an electron density ρ_i . The determination of this electron density may be achieved by:

$$\rho_i = \sum_{j,j \neq i} f_j(r_{ij}), \quad (2)$$

The function $f_j(r_{ij})$ represents the electron density at the specific location of an atom i , resulting from the presence of an atom j situated at a distance of r_{ij} . The MD simulations in this study were conducted within a cubic box, employing periodic boundary conditions in all dimensions, with dimensions of $34.20 \text{ \AA} \times 34.20 \text{ \AA} \times 34.20 \text{ \AA}$. Initially, the system comprised 3925 atoms arranged in a body-centred centred (bcc) grid. To solve the Newton equations, the Verlet method in velocity form and a time step of 1 fs were utilised, chosen carefully to ensure consistent energy fluctuations throughout the experiment. Pressure was controlled using a barostat, and temperature was maintained using a Nose-Hoover thermostat [10]. A controlled heating process raised the temperature from 300 K to 3000 K at a rate of $5 \times 10^{12} \text{ K/s}$, while maintaining constant pressure without external forces, leading to a fully molten state. To investigate external factors' impact on the transition process, the molten structure was cooled from 3000 K to 300 K at varying high quenching rates in the isothermal isobaric NPT ensemble. Prior to this, a 100 picoseconds relaxation period in the liquid phase at 3000 Kelvin was performed using the Canonical NVT ensemble. Periodic atomic configuration recordings were made at 100 K intervals to study system structure changes and conduct statistical analyses. The OVITO (Open Visualization Tool) package was employed for visualizing atomic distributions and analyzing Voronoi polyhedral within the simulation box [11].

3 Results and discussion

This section explores activation energy determination and its correlation with external factors like cooling rate and chromium concentration, examining how these affect the microstructural characteristics of a simulated $\text{Fe}_x\text{Cr}_{100-x}$ system.

3.1 Kinetics properties

3.1.1 Glass transition:

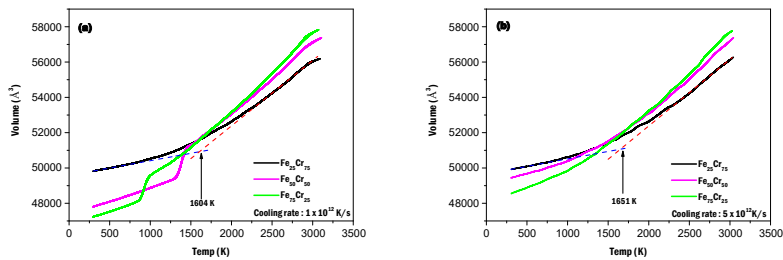


Fig. 1.Fluctuations in system volume in relation to temperature and chromium (Cr) content during the solidification process, considering two different cooling rates: (a) 10^{12}K/s and (b) $5 \times 10^{12}\text{K/s}$.

Figure 1 offers significant insights on the influence of cooling speeds and concentrations of Cr on the transformation process from a liquid state to either a glass or crystal state in the binary $\text{Fe}_x\text{-Cr}_{100-x}$ system. Figure 1(a) presents the volume-temperature curves for the studied system at various Cr concentrations $x=25\%$, $x=50\%$ and $x=75\%$. For $\text{Fe}_{25}\text{Cr}_{75}$, the curve exhibits smooth variations with temperature, characterising the liquid-to-glass transition [12]. The intersection of the linear fit of high-temperature (red dash) and low-temperature (blue dash) regimes represents the glass transition temperature (T_g). Furthermore, the plot illustrates that there is a significant decrease in volume observed at low concentrations of Cr $x = 25\%$ and $x = 50\%$, as shown in figure 2, suggesting a transition from a liquid phase to a crystalline phase. This sudden decrease in volume seen can be attributed to the dense packing of atoms inside the crystal lattice structure. This observation suggests that the presence of elevated levels of chromium (Cr) promotes the formation capacity of the iron-chromium (Fe-Cr) binary alloy known as MG, even under conditions of relatively slow cooling rates. In Figure 1(b); the graphs highlight a significant positive correlation between the cooling rate and the increase in the glass transition temperature (T_g) value. This observed linear extrapolation phenomenon is a consequence of the limited duration of rapid cooling, impeding atoms from undergoing sufficient rearrangement to form a well-organized crystalline structure [13,14]. Importantly, this extrapolation finding suggests that the trend applies to other cooling rates as well. Consequently; the Figure 1 elucidates the combined influence of both the cooling rate and the concentration of chromium (Cr) on the glass transition temperature (T_g). Specifically, T_g increases as the concentration of chromium (Cr) increases while maintaining a constant cooling rate. For a comprehensive overview of the glass transition temperature (T_g) values across various cooling rates and chromium (Cr) concentrations, please refer to Table 1. It illustrates the glass transition temperature (T_g) across various cooling rates and chromium concentrations. The table systematically presents T_g values for different combinations of these variables. Higher cooling rates are shown in the right row, while chromium

concentrations decrease from high to low along the top column. Each cell contains a specific T_g value, indicating the temperature at which the material undergoes the glass transition. Analysing this data helps reveal the relationship between cooling rates, chromium concentrations, and the material's glass transition behaviour. Additionally, increasing chromium concentration results in higher viscosity, facilitating the transition to a vitreous state at elevated temperatures and inhibiting free volume formation, as depicted in Figure 1 (b), leading to an elevated T_g .

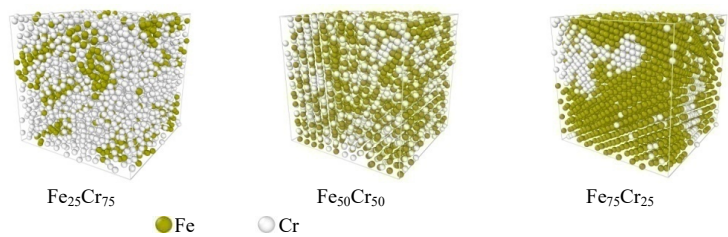


Fig. 2. 3D visualisation assisted with OVITO of Fe_x-Cr_{100-x} . With varying chromium content at room temperature (300K) and a cooling rate of $1 \times 10^{12} K/s$, the varied shapes of the system's glassy and crystal states are illustrated.

Table 1. Evolution of T_g of Fe_x-Cr_{100-x} vs. cooling rate and Cr concentration and activation energy of different Cr concentrations.

Fe_xCr_{100-x}	Glass temperature transition			
	$5 \times 10^{12} K/s$	$1 \times 10^{13} K/s$	$5 \times 10^{13} K/s$	$1 \times 10^{14} K/s$
$Fe_{25}Cr_{75}$	1650.43 K	1809.90 K	1820.65 K	1833.65 K
$Fe_{50}Cr_{50}$	1413.25 K	1612.86 K	1620,56 K	1631.91 K
$Fe_{75}Cr_{25}$	1402.23 K	1509.68 K	1516,90 K	1521.80 K

3.1.2 Activation energy

Metallic glasses exist in a metastable state, making them prone to transitioning to a lower energy state, typically the crystalline form, when provided with sufficient energy. The energy required for this transition is commonly referred to as activation enthalpy or activation energy. Moynihan established a relationship between the glass transition temperature and the cooling or heating rate (b_c) of a material to analyze the energy involved in the crystallization process and the transition from a glassy state to a crystalline structure. According to the theoretical framework presented, this association can be expressed as [15]:

$$-\frac{d \ln(b_c)}{d(1/T_g)} = -\frac{\Delta h^*}{R}$$

(3)

In the given context, R is the universal gas constant, whereas Δh^* denotes the energy associated with molecular mobility and atomic rearrangement occurring at the glass transition temperature T_g . Taking into account different Cr concentrations, Figure 3 is an

Arrhenius figure that illustrates the link between the glass transition temperature and the logarithm of the cooling rate for $\text{Fe}_x\text{-Cr}_{100-x}$. The narratives mostly centre around the activation energy associated with this particular relationship. The inclination of the graphed line provides insight into the activation energy of the $\text{Fe}_x\text{-Cr}_{100-x}$ system. A more pronounced incline indicates an elevated activation energy, hence indicating that the substance necessitates a greater amount of energy for the transition to take place. Conversely, a more gradual incline denotes lower activation energy, so suggesting that the substance may undergo the transition with more ease.

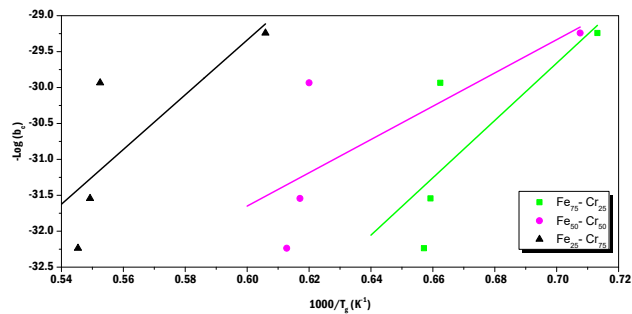


Fig. 3.Arrhenius plot of $-\ln(b_c)$ vs. $1000/T_g$ for different Chromium concentration.

Table 2 highlights a notable correlation between the concentration of Chromium (Cr) and the corresponding activation enthalpy. Generally, an increase in Chromium concentration is accompanied by a decrease in the activation enthalpy. However, at a concentration of 50%, there is a significant decrease in the activation energy, indicating that the glass transition is more favourable compared to concentrations below this point but higher than the value observed at a concentration of 75%. Consequently, the binary alloy $\text{Fe}_{50}\text{Cr}_{50}$ can be categorized as a eutectic system. To clarify, it can be observed that when the chromium concentration is 50%, the energy required for the transition to the glassy state is comparatively lower than that of concentrations at 25% and 75%. This phenomenon has been substantiated by several empirical investigations, as shown by studies conducted by various researchers [16,17].

Table 2. Activation enthalpy (Δh^*) of glass transition in binary $\text{Fe}_x\text{-Cr}_{100-x}$ system.

Cr Concentration	$\text{Fe}_{75}\text{Cr}_{25}$	$\text{Fe}_{50}\text{Cr}_{50}$	$\text{Fe}_{25}\text{Cr}_{75}$
Δh^* (kJ/mol)	331.87	192.59	316.59
$\delta \pm$ (kJ/mol)	23.19	13.98	21.32

3.2 Analysis of microstructure evolution with VPA

To get a more thorough comprehension of the local structure at a microscale in liquids and vitreous states, the Voronoi polyhedral analysis (VPA) method, initially introduced by Finney [18,19], is employed in this section. This partitions three-dimensional space into multiple polyhedra centered on individual atoms. These polyhedra consist primarily of

triangles n_3 , quadrilaterals n_4 , pentagons n_5 , and hexagons n_6 . Using Voronoi indices denoted as $\langle n_3, n_4, n_5, n_6 \rangle$ where n_i represents the number of i-edged faces in the VP, it is possible to characterise the local structures of these polyhedra. The Voronoi indices are also a measure of the total coordination number $CN = \sum_i n_i$, which permits differentiation and classification of the type of polyhedron surrounding a central atom within a specified cutoff distance [20]. Hwang et al. [21] further classified the various forms of VP into three distinct groups: crystal-like clusters ($\langle 0,4,4,x \rangle$), mixed-like clusters ($\langle 0,3,7,x \rangle$ and $\langle 0,3,6,x \rangle$), and icosahedral-like clusters ($\langle 0,1,10,x \rangle$, $\langle 0,2,8,x \rangle$, and $\langle 0,0,12,x \rangle$), where x typically takes on values between 0 and 6. A stack of these VPs, which constitutes a Voronoi tessellation, forms metallic glass. Figure 4 illustrates the distribution of Voronoi Polyhedra (VPs), which undergo significant changes during the cooling process [22]. Consequently, we can observe that the VPs that make up the vitreous state are typically the icosahedral-like $\langle 0,0,12,x \rangle$, $\langle 0,1,10,x \rangle$ and $\langle 0,2,8,x \rangle$, as well as the crystal-like $\langle 0,4,4,6 \rangle$. However, the abundance of icosahedral-like VPs is particularly noteworthy.

In order to establish a correlation between the kinetic study (section 1) and the evolution of the microstructure (section 2), we explore how these Voronoi Polyhedra (VPs) evolve in response to changes in the cooling rate and chromium concentration. Figure 5 presented illustrate an almost non-linear pattern in the evolution of the dominant VPs' percentage over time. These results are consistent with the findings obtained in the kinetic aspect of the study. Specifically, it was demonstrated that at the $Fe_{50}Cr_{50}$ concentration level, there is a decrease in the proportion of crystal-like VP structures, accompanied by an increase in the occurrence of icosahedral (Ico) VP structures. This observation provides compelling evidence for a significant reduction in the enthalpy of vitrification when the chromium content reaches 50%. In other words, the system exhibits a preference for the formation of Ico VPs over crystal-like VPs [23].

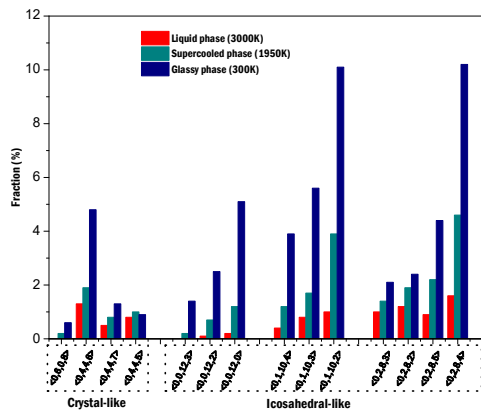


Fig. 4. Voronoi polyhedral distribution in the binary $Fe_{75}Cr_{25}$ system in a liquid, supercooled, and vitreous state with a cooling rate of 10^{13} K/s.

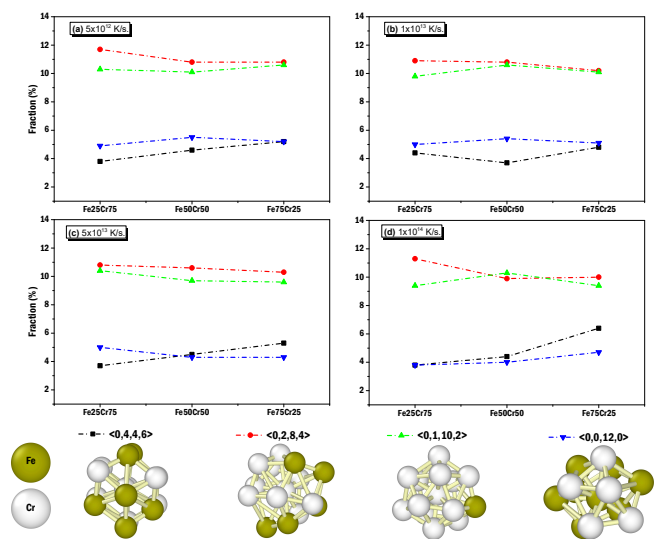


Fig. 5. Voronoi polyhedral distribution of the glassy state (300K) of the binary Fe_xCr_{100-x} over various cooling rate and Cr content.

Conclusion

In summary, this study demonstrates the substantial influence of Chromium concentration and quenching rate on the kinetic and microstructural transformations within binary Fe-Cr metallic glasses. The investigation of the glass transition mechanism in this binary system involved assessing the T_g value and the Δh^* energy barrier, enabling a comprehensive examination of the effects of varying chromium concentrations. The results unveiled a direct relationship between chromium concentration and the vitrification energy barrier, with lower chromium content corresponding to a higher energy barrier for vitrification. Notably, the 50% chromium concentration exhibited a unique characteristic, with the largest Δh^* value, surpassing even the values observed at 25% and 75% chromium concentrations. The analysis of the microstructure's evolution using VPA also revealed a non-linear pattern in the proportion of Icosahedral and crystal-like Voronoi Polyhedra, with the Icosahedral structures exhibiting higher favourability at the 50% concentration. These findings complement the kinetic analysis, which suggests that Icosahedral structures are often associated with metal glass production.

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