Role of niobium in glass formation of Fe-Cr-Mo-C-B-Nb bulk metallic glasses

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Abstract:

A new Fe-based bulk metallic glass with superior glass forming ability, Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄, was developed based on the Fe-Cr-Mo-C-B alloy system by minor addition of niobium. The effects of niobium addition on glass formation of the Fe_{50-x}Cr₁₅Mo₁₄C₁₅B₆Nb_x (x=0, 2, 4 and 6 at.%) alloys were investigated. The optimum addition content of niobium was determined as 4 at.% by X-ray diffraction and differential scanning calorimeter analysis. A fully amorphous rod sample with 3 mm in diameter was produced by using commercial-grade raw materials and a copper mold casting technique. This alloy shows an ultimate compressive strength of 1920 MPa and Vickers hardness 1360 HV, which is two to three times that of conventional high strength steel and suggests a promising potential for applications combining outstanding corrosion and wear resistance properties. The crystallization kinetics studies found that the activation energies for glass transition, onset of crystallization and crystallization peak were higher than those of other reported Fe-based bulk metallic glasses. The value of the fragility parameter *m* for the Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy was calculated to be 34, indicating that the Fe-Cr-Mo-C-B-Nb alloy system is a strong glass former according to the Angell's classification scheme. It is inferred that

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the more sequential change in the atomic size, the generation of new atomic pairs with large negative heats of mixing and the amount of oxygen in the molten liquid neutralized into niobium oxides provide a synergetic effect for the remarkably improved glass-forming ability and thermal stability.

Keywords: Fe-based amorphous alloy; minor addition; niobium; activation energy; glass-forming ability

I. INTRODUCTION

Bulk metallic glasses (BMGs) are of current worldwide interest in materials science and engineering due to their unique properties associated with their atomic configuration, chemical bonding characteristics and electronic structure [1-5]. Among the BMG-forming alloy systems Fe-based BMGs attract considerable attention due to their high strength, high hardness and corrosion properties [6-9]. However, it is well known that the low glass forming ability (GFA) of some Fe-based alloys is a major obstacle for engineering applications. The critical cooling rate of many Fe-based metallic glasses is 10^5 K/s or even higher, limiting the shapes and synthesis production methods [10-11]. Therefore, it is necessary to improve the GFA and the manufacturability of Fe-based BMGs, and in the same direction, to understand the mechanisms of the effects of various factors on the amorphous phase formation.

Large GFA in metallic systems can be characterized by three empirical rules [12], *i.e.*, (1) a multicomponent alloy system containing three or more elements, (2) atomic radius mismatch between the components greater than 12 %, and (3) large negative heat of mixing of the constituent elements. Additionally, minor additions of some selected elements have played an important role in enhancing the GFA and thermal stability of metallic glasses since the birth of BMGs [13-16]. Hence, large efforts have been devoted to choose the minor addition elements based on the above considerations.

Fe-based metallic glasses contain from 10 to 30 at.% of metalloids. So far, the investigated minor additions for Fe-based BMGs have included: (1) variations of the metalloid content (B [17], C [18], Si [19], P [20]), (2) rare earth additions such as Sm

[21], Y [22,23], Er [24], Dy [25], Tb [26], and (3) transition metal additions such as Mo [27,28], Ni [29], Nb [30,31], Ta [31], Co [32], Cu [33]. In particular, addition of transition metals has been useful to develop new Fe-based BMGs with high GFA at low cost. Among transition metals, Pang et al. [31] studied the effect of the addition of niobium and tantalum on the GFA and corrosion resistance of melt-spun $\text{Fe}_{45}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{18}\text{B}_8$ alloys, and found that the addition of these elements enhances both properties. It has also been reported that the addition of niobium in the $\text{Fe}_{65}\text{Mn}_{13}\text{B}_{17}\text{Y}_5$ alloy [30] improves the GFA achieving a fully amorphous rod of 2 mm $\varnothing$. Herein, it is reasonable to believe that niobium has an effective role in the glass formation of Fe-based alloys. However, much more efforts should be made to further increase the GFA of Fe-based alloys by addition of niobium and to clarify the mechanisms responsible for the effect of niobium on the glass forming ability.

Pang et al. [34,35] found that the Fe-Cr-Mo-C-B system exhibits an excellent corrosion resistance in aggressive HCl solutions. A detailed study of both the amorphous and partially crystallized state of $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ [6] showed also the differential contribution to corrosion resistance of the different alloy elements. In order to enhance the relevance of Fe-Cr-Mo-C-B alloys for commercial applications and fundamental research, a great number of efforts have been devoted to improve the GFA by minor additions [20,21,23-25,31]. The combination of high strength, hardness and corrosion resistance points this family of amorphous alloys as good candidates for protective amorphous coatings in highly corrosive environments. The wear loss rate is generally reduced for high values of the hardness/elastic modulus ratio [36]. Synthesis of amorphous coatings can be obtained by thermal spray techniques, and the GFA of the alloy is a fundamental parameter to avoid crystallization during the formation of the coating [37]. Within this context, we report the effect of niobium addition on the GFA, thermal stability and mechanical behavior of the corrosion resistant $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ alloy in order to improve its GFA and mechanical properties. The crystallization kinetics, the fragility parameter of the melt and the presence of Nb oxide particles were investigated for the $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=0-6$ at.%) alloys.

The role of Nb in the improvement of the alloy properties is exposed.

II. EXPERIMENTAL PROCEDURES

Multicomponent alloys with nominal compositions of $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=0, 2, 4$ and 6 at.%) were produced by arc-melting a mixture of industrial-grade Fe, Cr, Mo, C elements and a pre-melted Fe-B alloy in a Ti-gettered argon atmosphere. In order to obtain homogenous alloys, the master alloys were re-melted at least four times, and then were suck-cast into copper molds of different diameters.

Sample characterization was performed on disks cut from the produced rods. In this way, X-Ray diffraction (XRD), ultimate compressive strength and microindentation tests assess the properties of the bulk material. The amorphous nature of the as-cast samples was identified by a Bruker D8 Advance X-ray diffraction with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1541$ nm) over a 2θ range from 30° to 90° with a scanning step of 0.02° . The thermal properties associated with glass transition, supercooled liquid, crystallization and melting behavior were measured using a Netzsch 404F3 differential scanning calorimeter (DSC) at a heating rate of 20 K/min between 700 K and 1600 K. The Netzsch-Thermal-Analysis software was used to evaluate the onset temperature of the glass transition and crystallization. In order to analyze the crystallization kinetics and the fragility of the as-cast samples, the alloy specimens were heated at different heating rates ($2.5, 5, 20$, and 40 K/min) between 700 K and 1100 K. The microstructure of the as-cast samples was analyzed by a Zeiss Neon 40 scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) to assess the chemical composition, operated at 20 kV. In order to evaluate the mechanical properties of Fe-Cr-Mo-C-B-Nb system amorphous alloy, the Vickers hardness of cylindrical specimens was measured by using increasing loads from 10 to 300 g in a Shimadzu HVS-1000 digital display microhardness tester. The uniaxial compression tests of as-cast samples were performed with an Instron 4507 universal deformation machine at an initial strain rate of $0.4 \times 10^{-4} \text{ s}^{-1}$ at room temperature. The compression specimens with a diameter of 2 mm and a length of 4 mm were cut from the cast rods, and the ends of the specimens were polished

carefully to ensure parallelism.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the as-cast $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=0, 2, 4$ and 6 at.%) rod samples with diameters in the range of 1 to 3 mm, which clearly demonstrates the effect of niobium addition on the GFA of the alloy samples. As shown in Fig. 1, the 1 mm $\varnothing$ rod of the alloy without niobium addition exhibits only one sharp crystalline peak corresponding to the carbide phase $\text{M}_{23}(\text{C},\text{B})_6$ (with $\text{M}=\text{Fe},\text{Cr}$) [6] superimposed to the amorphous halo. This base alloy could not be produced in bulk amorphous rods with 1 mm $\varnothing$. Higher niobium contents allowed us to produce fully amorphous rods of 2 mm $\varnothing$ (with 2 at.% or 6 at.% of Nb) and 3 mm $\varnothing$ (with 4 at.% Nb). 3 mm $\varnothing$ rods of 2 and 6 at.% Nb content show some crystalline peaks identified as $\text{M}_{23}(\text{C},\text{B})_6$, $\eta\text{-Fe}_3\text{Mo}_3\text{C}$ and Fe_2Nb .

From the above analysis, it can be concluded that the addition of 4 at.% of niobium optimizes the GFA of this system. In the XRD pattern of the base alloy $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$, only the carbide $\text{M}_{23}(\text{C},\text{B})_6$ crystalline phase is observed, this implies that the glass formation of the Fe-Cr-Mo-C-B alloy system competes with the growth of this phase. The competing crystalline phases include $(\text{Fe},\text{Cr})_{23}(\text{C},\text{B})_6$, $\eta\text{-Fe}_3\text{Mo}_3\text{C}$ and Fe_2Nb with the addition of niobium. A similar phenomenon also appeared in the Fe-Zr-Co-Al-Mo-B alloy system doped with yttrium [22] and the Fe-Co-Zr-Mo-W-B alloy system with nickel addition [29].

Fig. 2 exhibits the DSC traces of the central part of as-cast $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=2, 4$ and 6 at.%) alloy samples at a heating rate of 20 K/min. Table 1 summarizes the glass transition temperature T_g , onset crystallization temperature T_x , onset melting temperature T_m , liquidus temperature T_l , supercooled liquid region $\Delta T_x (=T_x - T_g)$, reduced glass transition temperature $T_{rg} (=T_g/T_l)$ as well as the parameters $\gamma (=T_x/(T_l + T_g))$ [38] and $\delta (=T_x/(T_l - T_g))$ [23,25] which have a strong relationship with the GFA of BMG alloys [13,23,38]. The alloy with 4 at.% niobium possesses the largest supercooled liquid region, $\Delta T_x=54$ K, and the higher onset crystallization temperature $T_x=883$ K, implying that the 4 at.% niobium alloy has the

highest thermal stability, in good agreement with the XRD results (Fig. 1). Such a large ΔT_x means that the supercooled liquid is rather stable upon reheating, which indicates that the $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ alloy has a great potential for plastic processing in the supercooled liquid region. The high value of the reduced glass transition temperature, $T_{rg}=0.577$, also indicates that this Fe-based BMG can be produced at a rather low critical cooling rate. This is confirmed by the γ and δ parameters whose values are above 0.35 and 1.30 [15,22,29] for all niobium containing samples, with maximum values of 0.39 and 1.455, respectively, for the 4 at.% niobium alloy. It is worthwhile to point out that the alloy sample with 4 at.% niobium addition has the lowest liquidus temperature, which indicates that the precipitation of $\text{M}_{23}(\text{C,B})_6$ (with $\text{M}=\text{Fe,Cr}$) phases is effectively hindered and the alloy composition moves closer to an eutectic point through addition of niobium in the Fe-Cr-Mo-C-B system. Consequently, the depression of the liquidus temperature leads to the enhancement of GFA and thermal stability. A similar phenomenon of liquidus temperature depression is also found to be responsible for the enhancement of GFA and thermal stability in Pd-Cu-Ni-P [39], Fe-Zr-Co-Al-Mo-B [22] and Fe-Co-Zr-Mo-W-B [29] alloy systems.

In order to evaluate the mechanical properties and the fracture behavior of the new bulk glassy $\text{Fe}_{46-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=2, 4, 6$ at.%) alloys with a diameter of 2 mm, the uniaxial compression tests and fractography analysis were performed at room temperature. All the compositions showed brittle fracture with a maximum ultimate compressive strength of 1920 MPa for the $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ rods of 2 mm $\varnothing$, as shown in Table 1. The maximum value is higher than that of $\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{18}\text{B}_5\text{Y}_2$ [23] and $\text{Fe}_{58}\text{Co}_6\text{Ni}_4\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ [29] amorphous alloys.

The appearance of the fracture surface of failed samples was observed by SEM. The fracture is along the maximum shear plane inclined by 44° with respect to the compression direction, as shown in Fig. 3, which is in good agreement with other reported BMGs [40-42]. Fig. 4 exhibits the fracture morphology of the $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ amorphous alloy with a diameter of 2 mm. Fig. 4(a) shows

the cleavage-like features composed of mirror-like regions and tear lines, indicating that the fracture occurred in a brittle manner when the local critical shear stress was exceeded. It is worth to note that though there is no plastic elongation in the compression stress-strain curve, few vein-like patterns are found in the fractography, as shown in Fig 4(b). Enhancement of the plasticity by niobium addition in other Fe-based compositions was reported in previous works [43-44]. Here, the compressive tests do not show any appreciable increase of plasticity due to niobium addition. However, a slight increase of ductility, as seems to be indicated from the fractograph analysis, may provoke important effects on the wear loss rate and other tribological properties.

The value of Vickers hardness increases from 1230HV in the Fe₅₀Cr₁₅Mo₁₄C₁₅B₆ (ribbon) to 1360 HV in the Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ (3 mm Ø rod) and to 1430 HV in the amorphous Fe₄₄Cr₁₅Mo₁₄C₁₅B₆Nb₆ (2 mm Ø rod). These are quite larger than that of other Fe-based BMG reported in the literature [25,29,30], and it is two to three times that of conventional high-strength steel. The combined increase of the GFA, ultimate compressive strength and hardness induced by niobium addition offers a promising potential for structural and wear resistant applications. Full characterization of the wear behavior of these alloys will be performed in future works.

The crystallization kinetics was investigated to further analyze the effect of niobium additions on the glass formation of the Fe-Cr-Mo-C-B system. The activation energies for the glass transition E_g , crystal nucleation E_x and crystallization growth E_p were calculated by [45]:

$$\ln \frac{Q}{T^2} = -\frac{E}{RT} + \text{constant} \quad (1)$$

where Q is the heating rate and R is the gas constant. T expresses the corresponding characteristic temperature T_g , T_x or T_p . The crystallization peak temperature T_p corresponds to the temperature of the first peak [30] in the multistage crystallization process.

Fig. 5 shows the continuous heating DSC curves of the central part of the

Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy at different heating rates of 2.5, 5, 10, 20, and 40 K/min. Through analyzing the characteristic temperature values obtained from Fig. 5, the Kissinger plots of T_g , T_x and T_p for the Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy are shown in Fig. 6. According to the slope of the Kissinger plot, the activation energies E_g , E_x and E_p for the Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy are 361 ± 5 , 580 ± 24 and 575 ± 15 kJ/mol, respectively. The activation energies E_g , E_x and E_p for the 2 at.% niobium sample are 347 ± 7 , 485 ± 27 and 481 ± 18 kJ/mol, and for the 6 at.% niobium sample are 340 ± 3 , 475 ± 26 and 470 ± 37 kJ/mol, respectively. Therefore, the alloy sample with 4 at.% niobium has the largest activation energies for the glass transition and crystallization among the samples with different niobium additions. Table 2 summarizes the activation energies of crystallization of various iron-based amorphous alloys in order to better reflect the positive impact of niobium addition on the GFA and thermal stability of the Fe-Cr-Mo-C-B alloy system. As can be seen in Table 2, the crystallization activation energies of the Fe-Cr-Mo-C-B alloy system with niobium additions are significantly larger than those of other iron-based amorphous alloys. Therefore the atom re-arrangement during crystallization from the disordered state has to overcome a higher energy barrier which enhances the thermal stability and GFA.

It is well known that the nature of the supercooled liquid is one of the principal factors affecting the GFA of metallic glasses [50]. The relaxation dynamics of the supercooled melt is often discussed in terms of the liquid fragility. The fragility parameter m evaluates the sensitivity of the liquid structure to temperature. The fragility parameter m can be defined as [51]:

$$m = \left. \frac{d \log_{10} \tau}{dT_g/T} \right|_{T=T_g} \quad (2)$$

where T is the temperature and τ is a structural-relaxation time. According to the value of the fragility parameter m , the glass forming materials can be classified into three general categories: strong, intermediate and fragile. There is a general positive correlation between good GFA and strong liquid alloys [52-53]. Generally, BMG-forming alloys belong to the relatively strong liquids with $m=30-60$, while

conventional metallic glasses are commonly classified in the medium-fragile range with $m= 50-100$ [51,54].

Fig. 7 shows the variation of the inverse heating rate Q^{-1} with the inverse glass transition temperatures T_g^{-1} in an Angell plot. The T_g scale has been normalized by the lowest T_g corresponding to a heating rate of $Q=2.5$ K/min. At relatively low heating rates, the T_g -variation of Q^{-1} can be fitted by a Vogel-Fulcher-Tammann (VFT) equation [55]:

$$Q^{-1} = A \exp\left(\frac{DT_0}{T - T_0}\right) \quad (3)$$

where D , A and T_0 are fitting parameters and T expresses T_g measured at different heating rates Q . Through the VFT fitting, the fragility parameter m can be calculated by [54]:

$$m = \frac{DT_0 T_g}{(T_g - T_0)^2 \ln 10} \quad (4)$$

As a result, the value of the fragility parameter m for the $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ alloy is determined to be 34. Comparison with other excellent glass-forming alloys, such as $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.4}\text{Ni}_{10}\text{Be}_{27.5}$ ($m=34$) [56], $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ ($m=41$) [57], $\text{Y}_{56}\text{Al}_{24}\text{Co}_{20}$ ($m=42$) [58], $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ ($m=52$) [59] and $\text{Pt}_{60}\text{Ni}_{15}\text{P}_{25}$ ($m=54$) [51], shows that the fragility parameter of $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ is among the lowest values found for metallic glass-forming melts. Indeed, $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ falls into the strong glass-former category according to Angell's classification. There are few reported values of the fragility parameter for Fe-based metallic glasses. In the case of Fe-Nb-Al-Ga-P-C-B and (Fe,Co)-Si-Al-Ga-P-C-B systems [60], the fragility parameters of good-glass forming compositions were $m \sim 35$, while poor glass-forming alloys showed higher values up to $m \sim 60$. The m values of the $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=2, 4$ and 6 at.%) alloys indicate that these metallic melts have the high viscosity necessary to inhibit crystallization during the quenching process. However, the similar values found in all three compositions (see Fig. 7) cannot explain the differences in GFA between them, which have to be ascribed to other effects.

Fig. 8 shows back-scattered SEM micrographs for the central part of (a) $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ and (b) $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ alloy samples of 3 mm $\varnothing$. As can be seen in Fig. 8a, the $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ alloy sample contains a great number of dark dendrite phases showing that the $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ alloy sample of 3 mm $\varnothing$ is partially crystalline. The composition of these dendrites was measured by EDS and shows iron enrichment, indicating that they presumably correspond to the Fe-rich $\text{M}_{23}(\text{C},\text{B})_6$ phase. In the SEM image of the 3 mm $\varnothing$ $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ sample only a few white spherical particles are observed embedded in the amorphous matrix. For this case, Fig. 9 shows the elemental map of iron, chromium, molybdenum, niobium and oxygen evidencing that the constituent elements are homogeneously distributed in the amorphous matrix. By comparing the positions of the white particles in the back-scattered SEM image in Fig. 9 (a) and the elemental maps (Fig. 9b-f), it can be observed that they correspond to zones rich in niobium and oxygen. This suggests that the white particles correspond to niobium oxides. The content of niobium in the remaining matrix is estimated from the EDS analysis to be 3.9 at.%.

Improvement of the GFA in metallic glasses through oxygen scavenging by some elements has been reported in different systems, such as Zr-Al-Ni-Cu [61] and Fe-Zr-Co-Mo-W-B [22] doped with yttrium, Zr-Al-Ti-Cu-Ni microalloyed with 0.1 at.%B + 0.2 at.%Si + 0.1 at.%Pb [62] and Fe-Cr-Mo-C-B doped with Sm [21]. The presence of niobium oxide particles suggests that a similar phenomenon is observed in the alloys characterized in this work. Niobium scavenges oxygen and forms niobium oxides during the melting and casting processes. Therefore, the content of oxygen in the remaining liquid is decreased by addition of niobium, resulting in a substantial improvement of the GFA of the Fe-Cr-Mo-C-B system.

From the above analyses, it can be established that the niobium addition improves the glass formation of the Fe-Cr-Mo-C-B-Nb system in two ways. On the one hand, the addition of niobium is effective for increasing the degree of satisfaction of the three Inoue's empirical rules. Niobium has the largest atomic radius of 1.43 Å among all constituent elements and, consequently, the addition of niobium causes a more

sequential change in the atomic size: Nb (1.43 Å) > Mo (1.36 Å) > Cr (1.25 Å) > Fe (1.24 Å) > B (0.9 Å) > C (0.77 Å) [63]. Secondly, the addition of niobium generates new atomic pairs with large negative heats of mixing such as Nb-C: -102 kJ/mol and Nb-B: -54 kJ/mol [63]. These two effects contribute to frustrate the nucleation of crystalline phases until the concentration of niobium is large enough to allow the formation of the Fe₂Nb phase. It is worth to note that the remaining crystalline phases - (Fe,Cr)₂₃(C,B)₆ and η-Fe₃Mo₃C - are the main crystallization products expected in the Fe-Cr-Mo-C-B family of metallic glasses [6] and they appear in both high and low niobium content alloys.

The effect of niobium improving the topological and chemical stability of the glass and inhibiting the nucleation of the competing crystalline phases is also evidenced by the low fragility parameters and the high crystallization activation energies. The fragility parameter *m* of the Fe-Cr-Mo-C-B-Nb melts shows a relatively low value among that of other excellent glass-forming alloys, indicating that Fe-Cr-Mo-C-B-Nb alloys are strong metallic liquids, and they possess a high degree of topological and chemical short-range order and a high packing density. Moreover, this may indicate a small amount of free volume and a significant short-range ordering as well as low thermal and electrical conductivity inside the bulk metallic glass [64]. All these effects due to a high degree of electron localization and directional bonding.

Furthermore, the activation energy for crystallization, E_p , of the Fe-Cr-Mo-C-B-Nb system is larger than that of other iron-based amorphous alloys. This indicates the formation of a dense random packed structure with low atomic mobility due to the addition of 4 at.% of niobium. The excess of niobium in the 6 at.% niobium alloy is manifested by the relative reduction of E_p and the appearance of the Fe₂Nb phase.

On the other hand, the niobium atom possesses the second strongest affinity with the oxygen atom among all constituent elements in the Fe-Cr-Mo-C-B-Nb alloy system. The standard molar enthalpies of formation of the most stable oxides of the constituent elements are -1899.5 (Nb₂O₅), -1531 (Cr₃O₄), -1273.5 kJ/mol (B₂O₃),

-1118.4 (Fe₃O₄), -745.1 (MoO₃) and -393.5 (CO₂) [65]. While considering the enthalpies of formation per mole of atomic oxygen for every constituent element, the enthalpies of formation are -382.8 (Cr₃O₄), -379.9 (Nb₂O₅), -279.6 (Fe₃O₄), -254.7 (B₂O₃), -248.4 (MoO₃) and -196.8 kJ/mol (CO₂), thus showing that niobium oxide has the second highest enthalpy of formation. Therefore, the formation of niobium and chromium oxides is thermodynamically favored by considering this approach. As it is well known, the formation of stable chromium oxides and oxi-hydroxides provides high corrosion resistance in this kind of systems [6]. On the other hand, the formation of niobium oxides, as the ones identified here by EDS, can be favored in the melt due to the different activities of the elements in the alloy and the specific experimental conditions. During the melting and casting processes, it is plausible that oxygen in the molten liquid is partially neutralized into niobium oxides, thus stabilizing the remaining liquid. Therefore, a proper substitution of a small fraction of iron by niobium in the Fe₅₀Cr₁₅Mo₁₄C₁₅B₆ alloy system can significantly enhance its thermal stability and glass-forming ability.

IV. CONCLUSIONS

The GFA and thermal stability of the Fe-Cr-Mo-C-B alloys can be significantly enhanced by substituting a certain amount of iron by niobium. The indicative parameters of GFA, ΔT_x , T_{rg} , γ and δ show that the optimum content of niobium addition is 4 at.% among the Fe_{50-x}Cr₁₅Mo₁₄C₁₅B₆Nb_x (x=0, 2, 4 and 6 at.%) alloys. The Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy can be formed as fully amorphous rod with a diameter of 3 mm. This composition has the larger ultimate compression strength, 1920 MPa, and a Vickers Hardness of 1360 HV, two to three times that of conventional high strength steel. The glass transition and crystallization activation energies of the Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy are calculated as 361±5, 580±24 and 575±15 kJ/mol for T_g , T_x and T_p , respectively. These activation energies are much larger than those of other reported Fe-based bulk metallic glasses. Thus, the Fe-Cr-Mo-C-B-Nb system has a higher energy barrier for crystallization compared with that of other iron-based amorphous alloys. The fragility parameter m for the

Fe₄₆Cr₁₅Mo₁₄C₁₅B₆Nb₄ alloy is 34, indicating that this alloy can be classified as a strong metallic liquid. According to the analysis presented in this work, the more sequential change in the atomic size, the generation of new atomic pairs with large negative heats of mixing and the amount of oxygen in the molten liquid neutralized by formation of niobium oxides are likely the main reasons for the significant enhancement of GFA and thermal stability.

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Figure captions

Fig. 1. XRD patterns of the as-cast $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=0, 2, 4$ and 6 at.%) alloys.

Fig. 2. DSC traces of the central part of $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=2, 4$ and 6 at.%) alloys at a heating rate of 20 K/min.

Fig. 3. Outer surface of as-cast glassy $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ rod ($\varnothing = 2$ mm) subjected to compressive fracture.

Fig. 4. Secondary electron SEM images of failed as-cast $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ glassy rods ($\varnothing = 2$ mm) (a) tear lines and mirror-like region; (b) micro vein-like region.

FIG. 5. DSC traces obtained from the central part of $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ alloy at different heating rates of $2.5, 5, 10, 20$ and 40 K/min.

FIG. 6. Kissinger plots of T_g , T_x and T_p for $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ alloy sample of 3 mm $\varnothing$.

Fig. 7. Arrhenius plot of the variation of the inverse heating rate Q^{-1} with the inverse glass transition temperature T_g for the $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ alloy. The solid lines show the strong ($m = 16$) and very fragile ($m = 200$) kinetic behavior limits.

Fig. 8. Back-scattered SEM image of the central part of (a) $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ and (b) $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ alloy sample of 3 mm $\varnothing$. Region A: amorphous matrix; B: niobium oxides.

Fig. 9. (a) Back-scattered SEM image of the central part of $\text{Fe}_{46}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_4$ amorphous alloy ($\varnothing = 3$ mm); Corresponding elemental maps showing the distribution of (b) Fe, (c) Cr, (d) Mo, (e) Nb and (f) O.

Table captions

Table 1. Thermal properties, ultimate compressive strength and Vickers hardness of the central part of $\text{Fe}_{50-x}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Nb}_x$ ($x=0, 2, 4, 6$ at.%) alloys.

Table 2. Activation energies of crystallization of several iron-based amorphous alloys calculated by the Kissinger method.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Table 1

Composition (at.%)	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT_x (K)	T_{rg}	γ	δ	Ultimate Compressive Strength (MPa)	Hardness HV
Fe ₅₀ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆	-	-	1382	1483	-	-	-	-		1230±30
Fe ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Nb ₂	826	878	1362	1451	52	0.569	0.386	1.405	926	1290±30
Fe ₄₆ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Nb ₄	829	883	1367	1436	54	0.577	0.39	1.455	1920	1360±50
Fe ₄₄ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Nb ₆	830	874	1343	1460	44	0.568	0.382	1.387	1573	1430±50

Table 2

Alloy	E_p (kJ·mol ⁻¹)	References
Fe ₅₅ Cr ₁₈ Mo ₇ C ₄ B ₁₆	322±5	46
Fe ₅₂ Cr ₁₈ Mo ₇ C ₄ B ₁₆ Nb ₃	332±5	46
Fe ₆₁ Co ₅ Zr ₈ Cr ₂ Mo ₇ B ₁₅ Y ₂	289.2	47
Fe ₅₀ Cr ₁₄ Mo ₁₄ C ₁₄ B ₆ Y ₂	348.4±2.6	25
Fe ₅₀ Cr ₁₄ Mo ₁₄ C ₁₄ B ₆ Dy ₂	358.3±2.8	25
Fe ₇₀ Nb ₂ Al ₅ Ga ₂ P ₁₁ C ₆ B ₄	422	48
Fe _{76.5} Si _{13.5} CuB ₉	280±20	49
Fe ₇₀ Cr ₁₀ Si ₅ B ₁₅	260±25	49
Fe ₇₅ Mo ₃ Si ₉ B ₁₃	325±30	49
Fe _{73.5} Si _{13.5} Cu ₁ Nb ₃ B ₉	360±30	49
Fe ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Nb ₂	481±18	this work
Fe ₄₆ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Nb ₄	575±15	this work
Fe ₄₄ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Nb ₆	470±37	this work