

Article

Crystallization Kinetics of Hypo, Hyper and Eutectic Ni–Nb Glassy Alloys

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Abstract: This study presents the thermal and kinetic behavior of Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} binary glassy alloys. The alloys ingots were obtained through an electric arc furnace and the ribbons using the melt-spinning technique at two different wheel speeds, 8 and 25 m/s. The non-isothermal study was carried out by means of Differential Scanning Calorimetry (DSC) at five different heating rates: 12.5, 15, 17.5, 20, and 22.5 K/min. X-ray Diffraction (XRD) analysis showed a fully glassy phase for all ribbons for all compositions. For both wheel speeds, the ribbons with higher Nb content were significantly thinner than those with less content. The activation energies were calculated from the Kissinger method, showing the tendency $E_{p1} > E_{x1} > E_g$, where E_{p1} , E_x and E_g denote the activation energies of first peak temperature, the first crystallization onset and glass transition, respectively. The Flynn–Wall–Ozawa model displayed a close correlation with heating rates, ribbon thicknesses, and composition. The Nb content enhanced the glassy stability since the activation energy required for crystallization increased at higher Nb concentrations.

Keywords: Ni–Nb; thermal behavior; activation energy; crystallization kinetics; ribbon thicknesses



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1. Introduction

Ni-based metallic glasses have received significant attention due to scientific and technological potential since the first successful synthesis of glassy phase in binary alloys such as the Ni–Nb system [1]. The physical and chemical properties of the Ni–Nb system are diversified and increased when obtained in form of glassy ribbons, which improve their magnetic properties such as ferromagnetism (either extremely soft or moderately hard magnetism) and can therefore be used as materials for engineering applications, i.e., micro-gear motors and pressure sensors [2,3].

The formation of Ni–Nb metallic glasses depends on the chemical composition (30–60 at.%Nb), shape (ribbons, rods, tubes), and dimensions (thickness, diameter) [4]. These types of alloys, like other metallic glasses, do not exhibit an atomic medium- and long-range order and thus provide high thermal stability, high compressive strength, relatively good plasticity, and high corrosion resistance properties [5].

The glass-forming ability (GFA) is an important descriptor to obtaining Ni–Nb metallic glasses [6]. The GFA is the ability of an alloy melt to generate a glassy phase due to rapid solidification; there is significant interest in identifying thermal parameters that lead to the formation of metallic glass, combining the stability of the liquid phase with the resistance of the glassy phase to crystallization [7–9]. The formation of metallic glasses was based on the

following empirical rules [10]: (1) multicomponent systems, (2) difference in atomic radii greater than 12%, (3) negative heat of mixing, and (4) deep eutectic; this rule is based on the T_{rg} criterion is defined as $T_{rg} = T_g/T_l$ and is the ratio of the glass transition temperature to the melting temperature [11]. However, some Cu–Hf [12], Cu–Zr [13], and Ni–Nb [14] binary alloys are the exception to these rules since they can produce a fully glassy phase. In Ni–Nb metallic glasses, this was attributed to chemical and thermodynamic factors, i.e., the radii of Ni = 1.25 Å and Nb = 1.47 Å, and mixing energy of -143 kJ/mol [15]. Therefore, the diffusion of the atoms becomes slower during the crystallization process, so the nucleation and crystallization are suppressed [16]. It has been reported that the crystallization process, with a poly-tetrahedral interatomic arrangement in the glassy state. Here, the bond-angle distributions result from the radii and chemical order difference, producing an icosahedral-like distribution [17].

Most of the research carried out on the Ni–Nb system presents compositions that are close to the eutectic point, i.e., Ni_xNb_{100-x} ($x = 59.5, 60.5, 61$ and 62.5 at.%) in order to obtain metallic glasses in the form ribbons, rods, powders and coatings [18–22]. The study of these alloys was limited to production, solidification, and vitrification and a comprehensive GFA investigation directed towards the thermal behavior, i.e., where similar thermal parameter values were reported, i.e., $T_g = 870$ – 890 K, $T_{x1} = 910$ – 940 , $T_{p1} = 920$ – 960 , $\Delta T_x = 23$ – 40 , $T_{rg} = \sim 0.58$, $\gamma = \sim 0.4$ [23,24] were the characteristic temperatures are denoted by T_g is the glass transition temperature, T_{x1} is the first onset crystallization temperature, the second crystallization temperature is T_{x2} , the super-cooled liquid region ($\Delta T_x = T_{x1} - T_g$) and crystallization peaks T_{p1} , T_{p2} and T_{p3} .

Moreover, the crystallization process (two or three steps) [25,26], elucidation of crystalline phases (Ni_3Nb and Ni_6Nb_7) at the first peak of crystallization of the alloys [27], and atomic distributions and structure [28,29] were also assessed. This binary alloy presents particularities in the crystallization process, such as those studied by Lesz et al.; the thermal parameters in rods and ribbons of $Ni_{62}Nb_{38}$ composition showed similar T_g , T_{rg} and γ values for both geometries. Despite the importance of the Ni–Nb glassy alloy system, the crystallization kinetics of any alloy system and the crystallization kinetics of any alloys have not been reported.

The crystallization kinetic analysis enables calculation of the activation energy (E_a) in different stages of crystallization as T_g , T_{x1} , T_{p1} , and their associated activation energies, i.e., E_g , E_{x1} , E_{p1} . Differential scanning calorimetry (DSC) is typically employed to carry out this study; this technique also helps determine the glassy alloys thermal data, i.e., crystallization time, phase transformations temperatures, and heat flow absorbed or released with them [30]. Several experimental procedures have been developed to calculate activation energies in order to investigate chemical and physical transformations, such as crystallization [31]. Among them, the Kissinger methods consists of carrying out a series of experiments where small amounts of samples are subjected to different heating rates. The exothermic peak is taken as a constant conversion point for measuring each heating rate [32,33].

As mentioned above, the crystallization kinetic study of Ni–Nb alloys in the eutectic zone, i.e., between 26.5 and 50 (Nb at.%) with different ribbon thicknesses, has not been previously reported. Therefore, this work aims to kinetically analyze $Ni_{58.5}Nb_{41.5}$, $Ni_{59.5}Nb_{40.5}$, and $Ni_{60.5}Nb_{39.5}$ hypo, hyper and eutectic alloys and assess the effect of material thickness and composition on the crystallization behavior. In addition, the energy required to carry out the glass transition and crystallization process (E_g , E_p , and E_x) through Kissinger and Flynn–Wall–Ozawa models was also assessed.

2. Materials and Methods

Binary alloy ingots with nominal compositions of $Ni_{58.5}Nb_{41.5}$ (hypereutectic), $Ni_{59.5}Nb_{40.5}$ (eutectic), and $Ni_{60.5}Nb_{39.5}$ (hypoeutectic) (at.%) were prepared by arc melting (Edmund Bühler GmbH, Bodelshausen, Germany), with pure Ni (99.98%) and Nb (99.95%) elements under an argon (Ar) atmosphere. The ingots were remelted five times to achieve

a homogeneous composition. The weight loss of each ingot was less than 0.2% during the alloying process. The glassy alloys ribbons were produced by a melt-spinner (Edmund Bühler GmbH, Bodelshausen, Germany), which consists of continuous casting of the liquid alloys on the surface of a rotating copper wheel under a helium (He) atmosphere. The casting conditions included two tangential speeds, i.e., 8 and 25 m/s, with an injection pressure of 0.3 bar. The diameter of the quartz crucible nozzle was 0.8 mm. The distance between the nozzle and copper wheel was 5 mm. The crystalline phases of the ingots and the glassy phase of the ribbons (shiny surface) were examined by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer (Rigaku, Tokyo, Japan), model Ultima IV with CuK α radiation. In Ar flow, the thermal stability of the glassy alloys was investigated using a Differential Scanning Calorimeter SDT Q600 (TA Instruments, New Castle, DE, USA). Non-isothermal DSC conditions were used, with five heating rates: 12.5, 15, 17.5, 20, and 22.5 K/min. Three experiments for each sample were carried out for statistical purposes.

3. Results

3.1. Structural Characterization

3.1.1. Ingots Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} Alloys

The XRD patterns of Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} alloys ingots (1 cm diameter) are shown in Figure 1 the crystalline Ni₆Nb₇ and Ni₃Nb phases were identified by comparison with a data base (JCPDS 04-004-3644 and 04-012-8012, respectively). These phases agreed well with those reported for the present alloys [34]. Furthermore, the eutectic reaction of Ni_{59.5}Nb_{40.5} alloy revealed distinct peaks associated with both phases, representing this reaction when cooling, i.e., L $\rightarrow$ Ni₃Nb + Ni₆Nb₇ [35]. It can be observed that for the Ni–Nb alloy system, with a small variation in composition (1 at.% Nb) a significant change in crystal growth of phases it was evident. On the other hand, the Ni_{60.5}Nb_{39.5} alloy showed more peaks associated with the Ni₃Nb orthorhombic phase. These results proved the chemical homogeneity of the alloys, as when studying alloys with small chemical composition differences (>1 at.%), the chemical homogeneity of the ingot is critical for the analysis. XRF analyses were also carried out to support this argument, giving a global composition (at.%) of Ni = 59.56% and Nb = 40.44% (eutectic), Ni = 60.54% Nb = 39.46% (hypoeutectic) and Ni = 58.58% and Nb = 41.42% (hypereutectic). The observed small differences between the nominal, and experimental compositions are in the sensibility limit of the equipment, thus hypo, hyper and eutectic compositions were obtained.

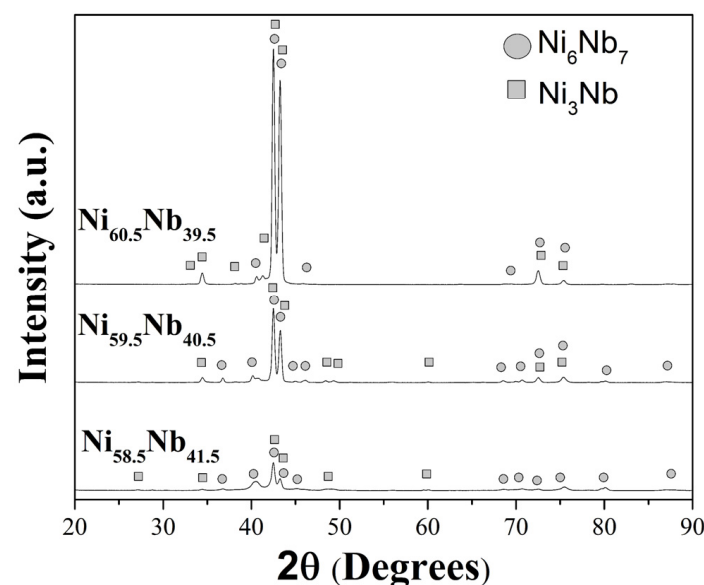


Figure 1. XRD patterns of ingots Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} alloys.

3.1.2. Ribbons Cast at 8 m/s and 25 m/s

The XRD patterns of 105, 130, and 140 μm ribbon thickness of the $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloys (8 m/s) are shown in Figure 2a; the XRD patterns of these ribbons exhibited only one broad diffused peak without any diffraction peaks related to any crystalline phase. This confirms the formation of a fully glassy phase for each alloy composition ribbon. In addition, the slight shift of the peak maxima to the right was observed, indicating a cell contraction resulting from the drop of the amount of Nb in the alloys, attributed to the difference in atomic radii. Figure 2b shows the XRD patterns of 45, 50, and 60 μm thickness of $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloys cast at 25 m/s, respectively. This figure also exhibits only one broad peak, with an observed cell contraction, also attributed to the amount of Nb in the investigated alloys. However, the shift for this casting condition was more evident, attributed to the higher cooling rate.

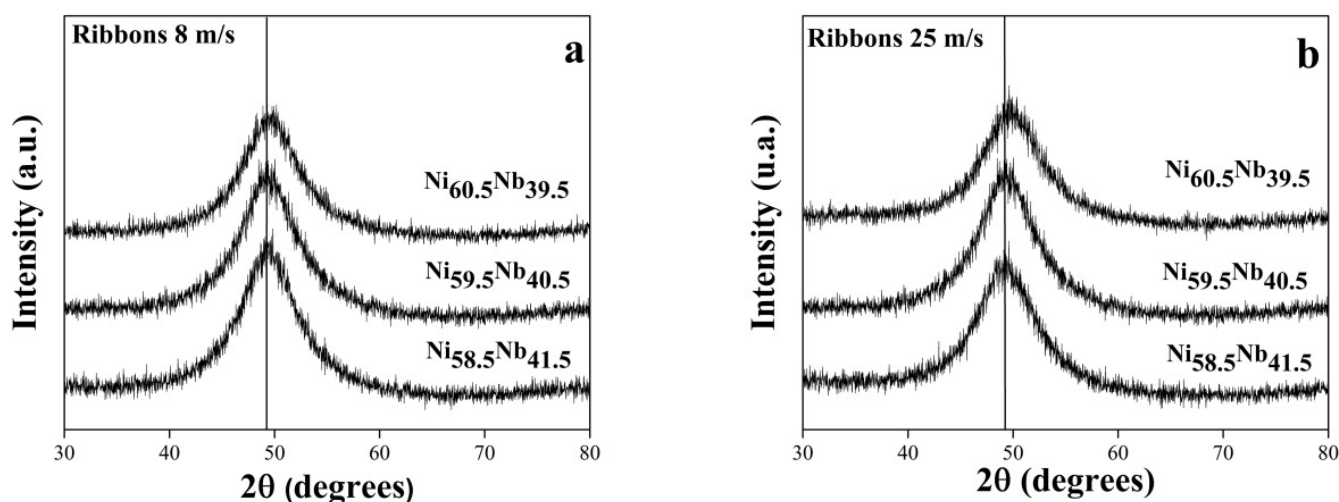


Figure 2. (a,b). XRD patterns of ribbons cast at 8 and 25 m/s for the $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$ and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloys.

3.2. Thermal Characterization

Figure 3 shows the non-isothermal analysis, at a heating rate of 20 K/min, for the 8 and 25 m/s cast ribbons. All ribbon thicknesses were fully vitreous. The GFA could be explained in terms of the “Post-Mortem” thermal criteria for glass formation, i.e., the reduced glass transition temperature, T_{rg} . This parameter is considered an indicator of a good glass former, as it considers nucleation kinetics and viscosity. Values of T_{rg} ranging from 0.4 to 0.7 indicate that the homogeneous nucleation has been suppressed, and therefore there are conditions of forming a fully glassy phase [36]. Another parameter to consider for evaluating glass formation and stability is γ , which considers T_g , T_x , and T_l to predict glass formation and is defined as $\gamma = T_x / (T_g + T_l)$, whose ideal value is 0.5 [37]. As mentioned above, Figure 3 shows the non-isothermal analysis curves for $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ glassy alloys and their calculated thermal parameters, i.e., T_g , T_{x1} , T_{x2} , $\Delta T_x = T_{x1} - T_g$, T_{p1} , T_{p2} and T_{p3} .

3.2.1. Hypereutectic $\text{Ni}_{58.5}\text{Nb}_{41.5}$ Alloy

Figure 4 shows the thermograms for cast ribbons at heating rates of 12.5, 15, 17.5, 20, 22.5 K/min; a summary of the obtained values is shown in Tables 1 and 2. The characteristic temperatures of the 105 μm ribbon are shown in Figure 4a, a shift to the right of the thermogram due to the heating rates was observed. The glass transition temperature (T_g) changed from 884 K to 896 K, for 12.5 K/min and 22.5 K/min, respectively. The onset crystallization temperature (T_{x1}) from 902 to 910 K. The exothermic peaks showed a displacement from $T_{p1} = 923$ to 929 K and $T_{p2} = 990$ to 1005 K and $\Delta T_x = 14$ to 18 K. Similarly, the thermograms for 45 μm ribbon are shown in Figure 4b. The temperatures obtained for

this composition were from $T_g = 885$ (12.5 K/min) to 896 K (K/min). The change from T_{x1} 904 to 911 K, T_{p1} from 921 to 927 K and T_{p2} from 980 to 994 K. The magnitude of $\Delta T_x = 15$ to 19 K, in both ribbons was the smallest values for all studied alloys. On the other hand, the temperatures associated with the 45 μm ribbon showed the same shift of the signals to the right but less marked, associated with the thickness of the ribbons, as other parameters were kept constant, i.e., composition, heating rates, atmosphere, etc.

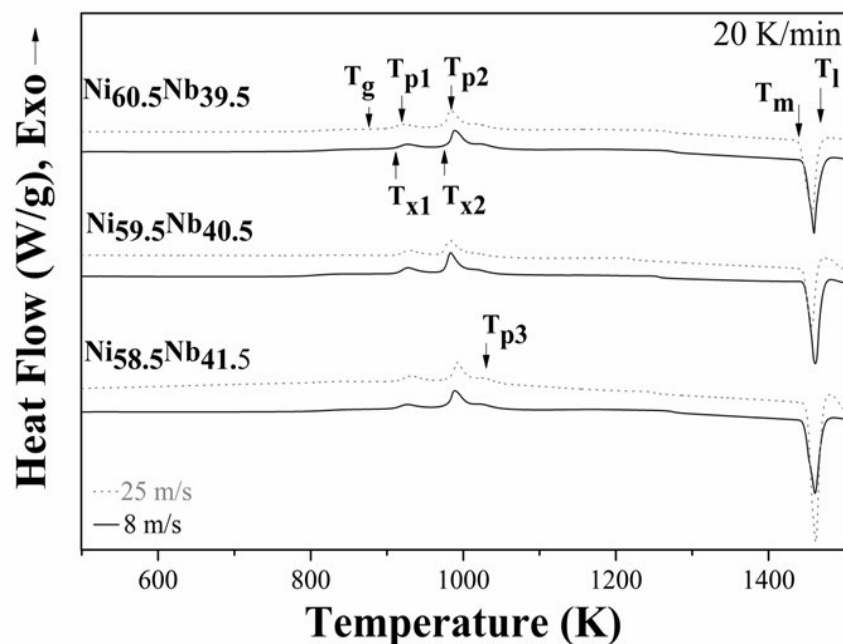


Figure 3. DSC curves of $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ ribbons at a heating rate of 20 K/min.

The crystallization in this $\text{Ni}_{58.5}\text{Nb}_{41.5}$ hyper eutectic alloy composition of both ribbon thicknesses was characterized for the presence of two exothermic peaks, indicating that the crystallization process was carried out in two steps. Furthermore, the thickness and thermal behavior of the $\text{Ni}_{58.5}\text{Nb}_{41.5}$ glassy alloy was also attributed to Nb content, i.e., type of metallic bonds, atomic radii, and d-electrons of transition metals.

3.2.2. Eutectic $\text{Ni}_{59.5}\text{Nb}_{40.5}$ Alloy

The thermal analysis of 130 μm glassy ribbons for the $\text{Ni}_{59.5}\text{Nb}_{40.5}$ eutectic composition is shown in Figure 4c, their thermal parameters are summarized in Table 1. Similar behavior was also observed, i.e., the values of the calculated thermal shifted to the right of thermogram, for instance: from 876 to 890 K in T_g , T_{x1} from 911 to 920 K in, T_{p1} from 924 to 931 K in and T_{p2} from 977 to 991 K (for 12.5 K/min and 22.5 K/min, respectively). For this alloy composition, the magnitude of ΔT_x was 30 to 35 K, being the highest value of the studied alloy compositions. Figure 4d shows the glassy ribbons thermograms with a thickness of 50 μm ribbons. Here, a slight shift to the right of thermograms was also observed; however, this shift occurred at slightly lower temperatures ($T_g = 872$ to 884 K. The $T_{x1} = 913$ –921 K. The $T_{p1} = 927$ –934 K and $T_{p2} = 979$ –989 K). The crystallization behavior for this alloy was also carried out in two steps, for both glassy ribbon thicknesses (130 and 50 μm). This result is consistent with the nature of the eutectic composition ($\text{Ni}_{59.5}\text{Nb}_{40.5}$). According to the phase diagram, after heating from the glassy phase, the nucleation of Ni_6Nb_7 and Ni_3Nb phases is likely.

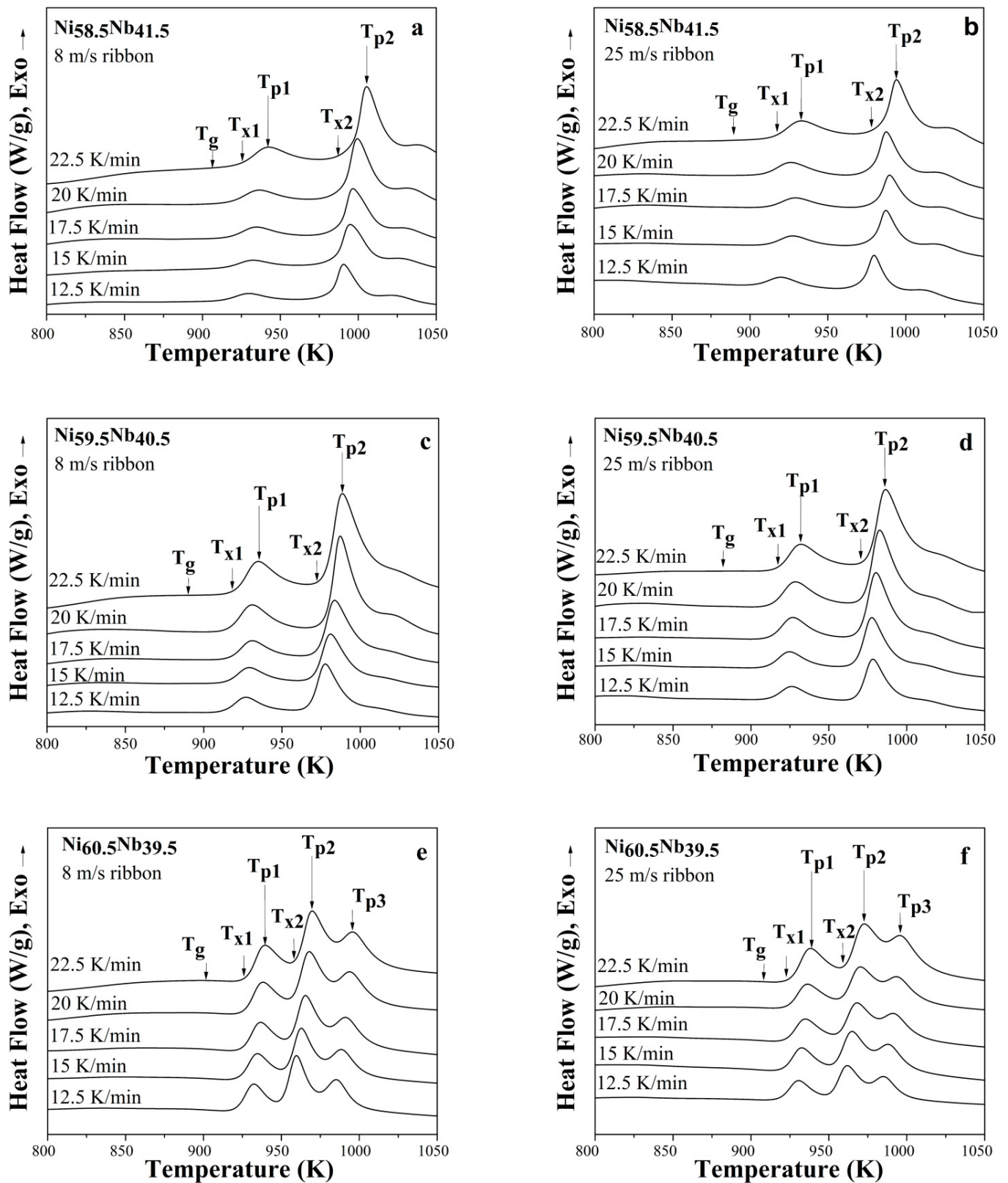


Figure 4. (a–f). DSC curves of Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} alloy ribbons cast at 8 and 25 m/s.

Table 1. Thermal parameters of Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} ribbons cast at 8 m/s.

Alloy	Heating Rate (K/min)	T _g (K)	T _{x1} (K)	T _{p1} (K)	T _{x2} (K)	T _{p2} (K)	T _{p3} (K)	ΔT _x (K)	T _m (K)	T _l (K)	T _{rg}	γ	Thickness (μm)
Ni _{58.5} Nb _{41.5}	12.5	884	902	923	982	990	—	18			0.60	0.39	105
	15	887	905	925	985	995	—	18			0.60	0.39	
	17.5	890	907	927	988	999	—	17	1447	1472	0.60	0.39	
	20	893	909	928	991	1002	—	16			0.61	0.39	
	22.5	896	910	929	993	1005	—	14			0.61	0.39	
Ni _{59.5} Nb _{40.5}	12.5	876	911	924	969	977	—	35			0.60	0.39	130
	15	880	914	926	972	981	—	34			0.60	0.39	
	17.5	884	916	928	974	985	—	32	1445	1472	0.60	0.39	
	20	887	918	929	976	988	—	31			0.60	0.39	
	22.5	890	920	931	978	991	—	30			0.60	0.39	
Ni _{60.5} Nb _{39.5}	12.5	887	920	929	951	960	977	28			0.60	0.39	140
	15	891	922	931	954	963	980	27			0.60	0.39	
	17.5	895	925	933	956	965	983	27	1449	1474	0.61	0.39	
	20	899	927	935	958	968	986	27			0.61	0.39	
	22.5	902	929	936	960	970	988	26			0.61	0.39	

Table 2. Thermal parameters of Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5}, and Ni_{60.5}Nb_{39.5} ribbons cast at 25 m/s.

Alloy	Heating Rate (K/min)	T _g (K)	T _{x1} (K)	T _{p1} (K)	T _{x2} (K)	T _{p2} (K)	T _{p3} (K)	ΔT _x (K)	T _m (K)	T _l (K)	T _{rg}	γ	Thickness (μm)
Ni _{58.5} Nb _{41.5}	12.5	885	904	921	969	980	—	19			0.60	0.38	45
	15	888	906	923	977	987	—	18			0.60	0.38	
	17.5	891	908	925	979	990	—	17	1450	1471	0.60	0.38	
	20	894	910	926	975	987	—	16			0.61	0.38	
	22.5	896	911	927	982	994	—	15			0.61	0.38	
Ni _{59.5} Nb _{40.5}	12.5	872	913	927	968	979	—	41			0.60	0.39	50
	15	875	915	929	972	982	—	40			0.60	0.39	
	17.5	878	917	931	967	977	—	39	1447	1466	0.60	0.39	
	20	881	919	932	972	982	—	38			0.60	0.39	
	22.5	884	921	934	978	989	—	37			0.60	0.39	
Ni _{60.5} Nb _{39.5}	12.5	893	918	930	962	986	995	25			0.61	0.39	60
	15	898	920	932	964	988	997	22			0.61	0.39	
	17.5	901	922	934	967	992	1003	21	1450	1469	0.61	0.39	
	20	904	924	936	970	994	1007	20			0.61	0.39	
	22.5	907	926	937	972	997	1012	19			0.61	0.39	

3.2.3. Hypoeutectic Ni_{59.5}Nb_{40.5} Alloy

Figure 4e shows the thermogram curves of the 140 μm Ni_{60.5}Nb_{39.5} hypoeutectic alloy ribbon. This composition also showed the same behavior as the previous hyper and eutectic glassy ribbons. The temperatures also shifted from 887 to 902 K in T_g, 920–929 K in T_{x1}. On the contrary to the hyper and eutectic alloys, three crystallization peak temperatures were observed. The crystallization peaks temperatures were T_{p1} = 929–936 K, T_{p2} = 960–970 K, and T_{p3} = 977–988 K (for 12.5 K/min and 22.5 K/min, respectively), the magnitude of ΔT_x was 26 to 28 K (Table 1). Figure 4f shows the thermograms for thinner ribbons (60 μm). For the heating rates used in the study, the T_g values were 893 to 907 K, T_{x1} = 918 to 926 K observing three crystallization peak temperatures, T_{p1} = 930 to 937 K, T_{p2} = 986 to 997 K and T_{p3} = 995 to 1012 K and ΔT_x = 19 to 25 K (Table 2). The thermal parameters' correlation on the heating rates was evident, as they shifted progressively to a higher value. The Ni_{60.5}Nb_{39.5} alloy exhibited three exothermic peaks, implying a more complex crystallization process than hyper and eutectic glassy alloys. Additionally, with the thickness of the ribbon, the temperature associated to the third peak, attached to T_{p2}, occurred in a

lagged fashion. It is important to point out that this peak was produced at even 1 at.% Nb difference, being possibly attributed to the more disordered glassy structure.

3.3. Iso-Conversional Kinetics

The thermal analysis results were processed through the iso-conversional methods or models, e.g., Kissinger [32] and Flynn–Wall–Ozawa [38]. The obtained data effectively elucidate the crystallization reactions behavior carried out during the heating process, i.e., consecutive reaction steps or a combination with the viscosity variation [39].

3.3.1. Kissinger Method for Ribbons Cast at 8 and 25 m/s

The Kissinger method can be applied for a number of other thermally activated events, i.e., precipitation, crystallization, etc. The Kissinger method can be expressed using the following equation [33].

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

where β is heating rate, T is the characteristic temperature at the specific heating rate (T_g , T_{x1} and T_{p1}), E_a is the activation energy, R is the universal gas constant.

Figure 5a–f, shows the Kissinger plots for ribbons cast at 8 m/s and 25 m/s. The data from the slopes of the straight lines in the plots and the activation energy values are shown in Table 3. The activation energies were calculated for the hyper, hypo and eutectic alloy compositions using the Kissinger method. The energies calculated were the activation energy of the glass transition, activation energy of the first crystallization onset, and first peak temperature (E_g , E_{x1} , E_{p1} , respectively). In general terms, the results obtained for the calculated activation energies exhibited the following order: $E_a(\text{Ni}_{58.5}\text{Nb}_{41.5}) > E_a(\text{Ni}_{59.5}\text{Nb}_{40.5}) > E_a(\text{Ni}_{60.5}\text{Nb}_{39.5})$. The magnitude of E_g for the 25 m/s ribbons varied from 330 kJ/mol (hypereutectic alloy) to 266 kJ/mol (hypoeutectic alloy), confirming that the rearrangement of the atoms required less energy to carry out the transition from a glassy to a crystallized alloy, i.e., nucleation and grain growth. The activation energies for E_{x1} and E_{p1} are reduced when decreasing the Nb content; for instance, for the 25 m/s ribbons, the calculated values from the hyper to hypoeutectic alloys ranged from $E_{x1} = 554$ kJ/mol to 517 K/mol and E_{p1} from 688 to 587 kJ/mol. The activation energies calculated with the Kissinger method in this investigation are close to those reported by Collins et al. [40], where $E_{p1} = 628$ kJ/mol (30–40 μm) and Pratten et al. [41] where $E_{p1} = 600$ kJ/mol (50 μm) for ribbons of $\text{Ni}_{60}\text{Nb}_{40}$ alloy composition. These activation energy tendency values were also observed for the thicker ribbons. It was confirmed that in these types of alloys, with complex crystallization systems, more energy is required to grow the Ni_3Nb and Ni_6Nb_7 phases than the activation energy of nucleation E_{x1} of the same phases. Therefore, it was observed that the most stable alloy had the highest amount of Nb (hypereutectic alloy). In terms of thickness, the alloy ribbons cast at higher wheel speed showed the highest activation energies and, therefore, they are more stable, as more energy will be required to form a crystallized phase.

Table 3. Activation energies E_g , E_{x1} and E_{p1} for the crystallization of $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$ and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ glassy ribbons cast at 8 and 25 m/s (Kissinger method).

Alloy	Ribbon (m/s)	E_g	E_{x1}	E_{p1}
		(kJ/mol)		
$\text{Ni}_{58.5}\text{Nb}_{41.5}$	8	306	477	649
	25	330	538	665
$\text{Ni}_{59.5}\text{Nb}_{40.5}$	8	256	447	597
	25	298	520	601
$\text{Ni}_{60.5}\text{Nb}_{39.5}$	8	241	435	565
	25	266	502	571

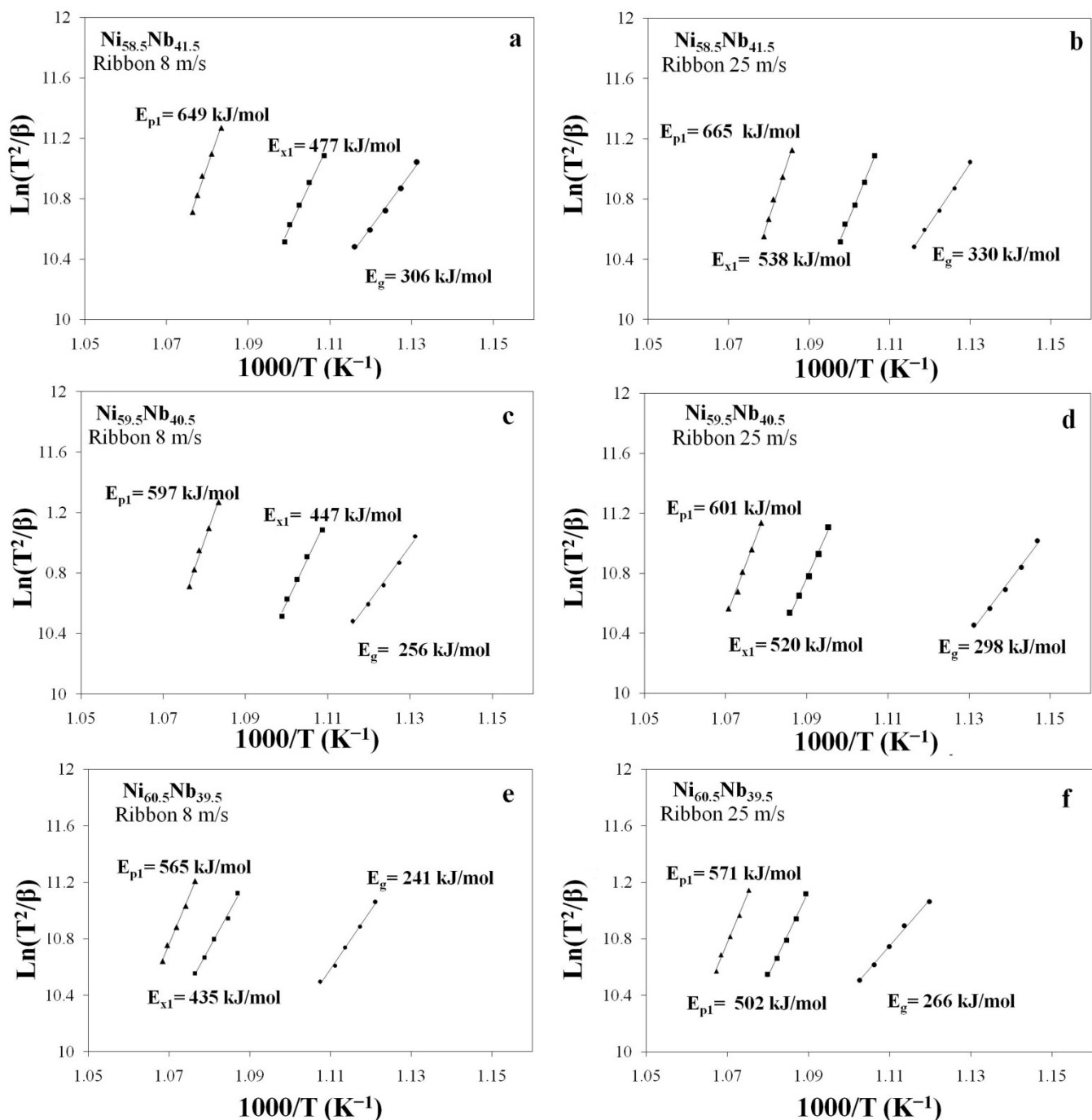


Figure 5. (a–f). Kissinger plots of $\ln(\beta/T^2)$ vs. $1000/T$ ($T = T_g, T_{x1}$ and T_{p1}) from 8 m/s (a,c,e) and 25 m/s (b,d,f) ribbons of Ni_{58.5}Nb_{41.5}, Ni_{59.5}Nb_{40.5} and Ni_{60.5}Nb_{39.5} alloys.

3.3.2. Kissinger Method for Ribbons Cast at 8 and 25 m/s

Another accepted model to describe the crystallization kinetics in metallic glasses is the Flynn–Wall–Ozawa (FWO) model. This model has also been used to calculate the activation energy of the crystallization process. The FWO model shows the dependence of $\ln(\beta)$ vs. $1000/T$ and calculates the activation energy (E_a). The model is represented in following equation [42].

$$\ln(\beta) = -\frac{E_a}{RT} + \text{constant} \quad (2)$$

where β is the heating rate, T is the characteristic temperature at the specific heating rate (T_g , T_{x1} and T_{p1}), E_a is the activation energy, R is the universal gas constant.

Figure 6a–f, shows the FWO plots for cast ribbons at 8 m/s and 25 m/s. The activation energies values are summarized in Table 4. The activation energy (E_a) was calculated from $\ln(\beta)$ vs. $1/T$ of the FWO model. These results indicated that the activation energy (E_g , E_{x1} , and E_{p1}) decreased as a function of Nb content; for instance: for the $\text{Ni}_{58.5}\text{Nb}_{41.5}$ alloy (ribbon 25 m/s), E_{p1} was 554 kJ/mol and for $\text{Ni}_{60.5}\text{Nb}_{39.5}$ E_{p1} was 517 kJ/mol. In terms of ribbon thicknesses, the activation energies (E_g , E_{x1} , and E_{p1}) increased as the tangential Cu wheel speed raised (thinner ribbons). The Kissinger and FWO models confirmed that a lower energy E_g (endothermic peak) is required to carry out the glass transition, rearranging the atoms before the glassy alloy crystallization (first order phase transformation). On the other hand, the behavior of the E_x for the first stage of crystallization (exothermic peaks) showed smaller values than for E_p . Therefore, the nucleation of Ni_6Nb_7 and Ni_3Nb crystalline phases requires less energy than that needed for grain growth. The values obtained through the FWO model showed that the activation energies are slightly higher than those calculated from the Kissinger method, being attributed to the normalization generated by T^2 included in Equation (1). Furthermore, as the FWO model is an approximation method, deduced for complex crystallization systems, it has an error between 1 and 4% with respect to the Doyle approximation [38].

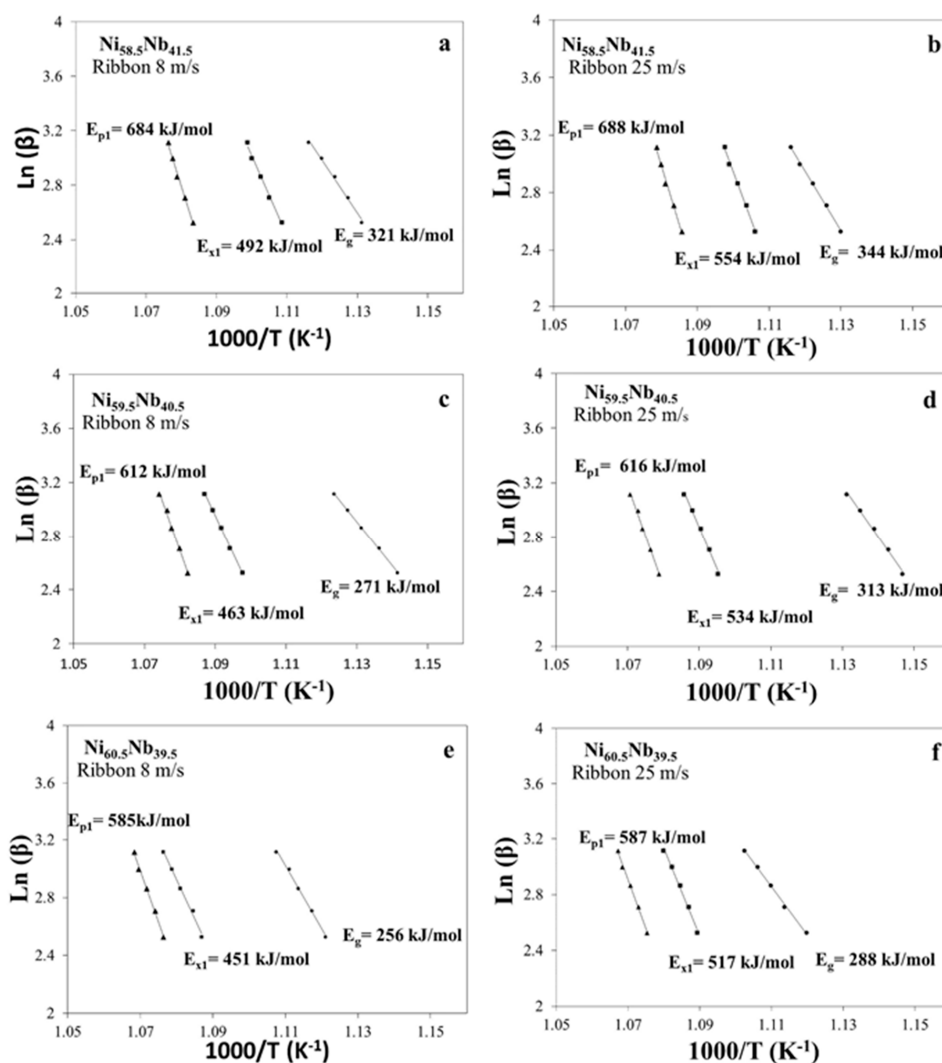


Figure 6. (a–f). Flynn–Wall–Ozawa calculated with $\ln(\beta/T^2)$ vs. $1000/T$ ($T = T_g$, T_{x1} and T_{p1}) for 8 m/s (a,c,e) and 25 m/s (b,d,f) cast ribbons for the $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloys.

Table 4. Activation energies E_g , E_{x1} , and E_{p1} for 8 and 25 m/s cast ribbons for the $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloys (FWO model).

Alloy	Ribbon (m/s)	E_g	E_{x1}	E_{p1}
		(kJ/mol)		
$\text{Ni}_{58.5}\text{Nb}_{41.5}$	8	321	492	684
	25	344	554	688
$\text{Ni}_{59.5}\text{Nb}_{40.5}$	8	271	463	612
	25	313	534	616
$\text{Ni}_{60.5}\text{Nb}_{39.5}$	8	256	451	585
	25	288	517	587

3.4. Crystallization Fraction

As is well known, the crystallization volume fraction is directly proportional to the fractional area of the exothermic heat flow peak area. Therefore, the crystallization fraction, α , was determined by the equation “ $\alpha = A_T/A$ ”, where A_T is the fraction area of crystallization peak between the onset of crystallization time (t_0) and time t A is the total area of the exothermic crystallization peak. Figure 7a–f shows the correlation of α vs. temperature for the $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$, and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloy ribbons cast at 8 m/s and 25 m/s. Here, the crystallization process displayed three stages: (1) slow nucleation for $\alpha < 0.1$, (2) a stable crystallization reaction when temperature increased (grain grow), i.e., $0.1 < \alpha < 0.9$, and (3) a slow crystallization reaction when $\alpha > 0.9$. The apparent crystallization fraction showed an α displacement to the right as a function of the heating rates. All curves showed the characteristic sigmoid behavior, i.e., the curves become steeper at higher heating rates. Eventually, the glassy samples will transform from a metastable to a stable state. In other words, the sigmoid shape of the curve indicates a slow phase transformation process at the early and late crystallization stages ($\alpha < 0.2$ and $\alpha > 0.8$). The initial part of the crystallization process could be attributed to the relatively high activation energy involved in the crystallization process. When the activation energy decreased, the transformation rate increased. The curve separations could be related to energy accumulation, i.e., the curve will be displaced even further to the right at a higher heating rate. At a low heating rate, the crystal nucleus size would be larger than at higher rating rates.

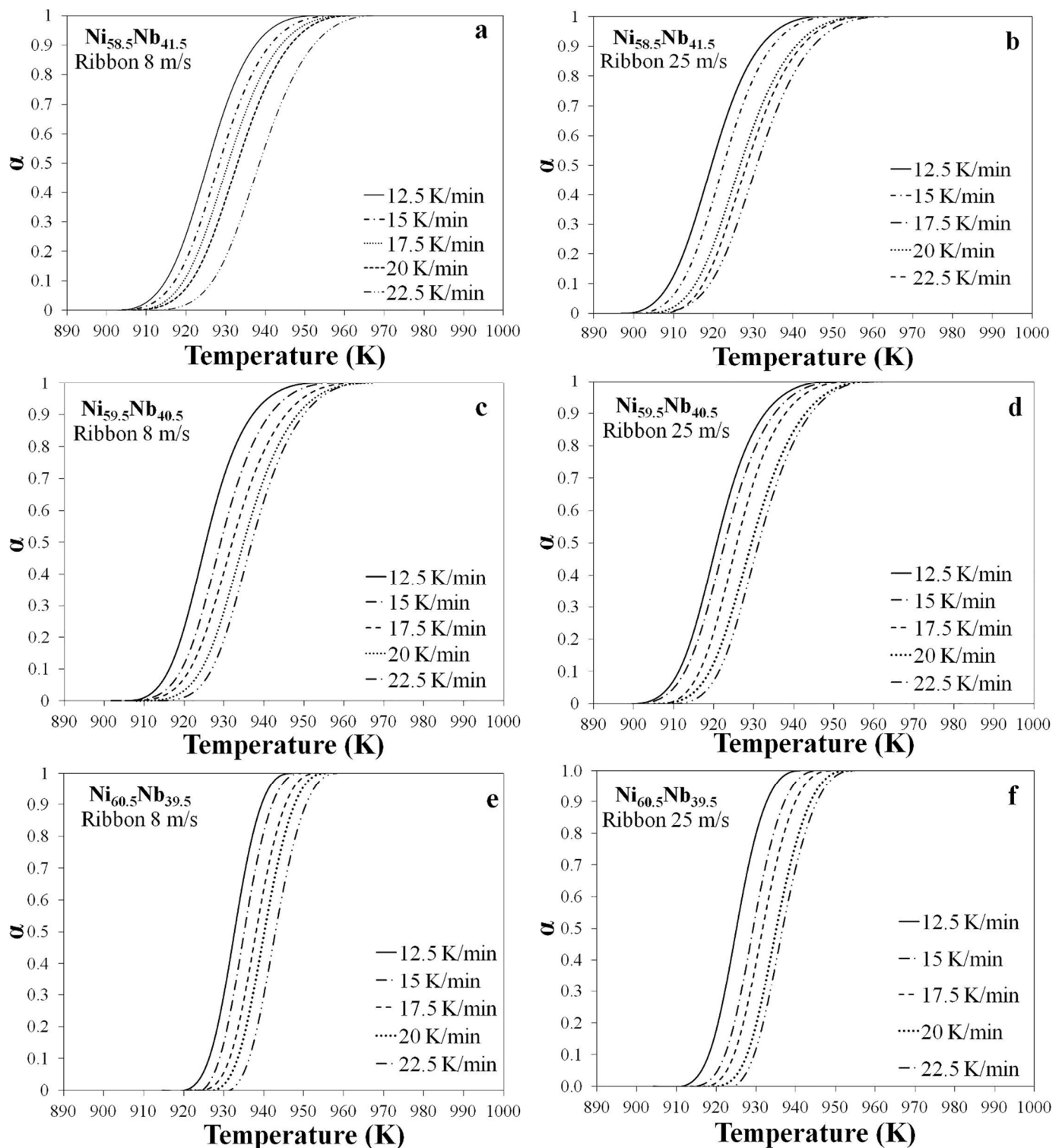


Figure 7. (a–f). Plots α vs. Nb%, from 8 m/s and 25 m/s ribbons of $\text{Ni}_{58.5}\text{Nb}_{41.5}$, $\text{Ni}_{59.5}\text{Nb}_{40.5}$ and $\text{Ni}_{60.5}\text{Nb}_{39.5}$ alloys.

4. Conclusions

It has been experimentally demonstrated that the hypo, hyper and eutectic alloys showed a fully glassy phase in both ribbon thicknesses. A heating rate dependence of T_{rg} and γ was observed. In all cases, these thermal parameters shifted progressively to a higher value. The magnitude of $T_{\text{rg}} = \sim 0.60$ and $\gamma = \sim 0.40$ showed similar behavior

in all studied alloys. In terms of thermal stability, the non-isothermal study revealed that the crystallization process takes place in two steps at Nb concentrations of 41.5 and 40.5 at.%. However, at Nb = 39.5% a third crystallization peak was observed, indicating a more complex crystallization process. These results proved that the alloy with the highest amount of Nb (hypereutectic alloy) required less temperature to crystallize. Thickness also played an important role, as the ribbons cast at higher wheel speed showed the highest activation energy, indicating that more energy will be required to form crystallized phases. In addition, with the Nb additions, the thermal stability increased, suppressing the nucleation and grain growth. This could be an indicative that, at least for this alloy, the probability of forming a bulk metallic glass is high. The activation energy (E_g , E_{x1} , and E_{p1}) is a function of Nb content. The $Ni_{58.5}Nb_{41.5}$ alloy showed the highest activation energies values in both thicknesses. This study also showed that the highest thermal stability demonstrated with the Kissinger method and Flynn–Wall–Ozawa models corresponded to alloys with high Nb content. These models also confirmed that less energy E_g (endothermic peak) is required to carry out the glass transition. Finally, the nucleation of Ni_6Nb_7 and Ni_3Nb crystalline phases required less energy than grain growth.

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