Crystallization Kinetics of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Melt-Spun Amorphous Ribbons

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The Avrami exponent n of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbons during isothermal annealing derived from the Johnson-Mehl-Avrami equation is about 3.0 and shows good agreement with that obtained by Schloßmacher *et al.* This indicates that the main crystallization mechanism of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons is interface-controlled three-dimensional isotropic growth with early nucleation-site saturation. According to the Arrhenius relation, the activation energy for crystallization is 314 kJ/mol. This value is similar to that obtained using the Kissinger method, which implies that the crystallization during continuous heating or isothermal annealing follows a similar crystallization mechanism. [doi:10.2320/matertrans.47.2489]

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1. Introduction

TiNi-based alloys exhibiting thermoelastic martensitic transformation are known as shape memory alloys (SMAs) with good shape memory effect (SME) and superelasticity.¹⁾ Substituting Cu for Ni in binary Ti-Ni SMAs can lower the transformation hysteresis, the superelasticity hysteresis, and the flow stress level in the martensite state.²⁻⁶⁾ However, when the Cu substitution is more than 10 at.%, the alloy becomes brittle and reduces seriously the workability and shape recovery strain,^{2,7)} which restrains the applications of high Cu-content Ti-Ni-Cu ternary SMAs. In recent years, melt-spinning techniques have been utilized to fabricate high Cu-content Ti-Ni-Cu ternary SMAs to avoid the aforementioned shortage of workability. Among these SMAs, $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ (in atomic %) ribbon has been widely studied because of its high glass-forming ability, small transformation hysteresis, large transformation strain, and its one-stage B2 $\leftrightarrow$ B19 transformation compared with conventionally fabricated Ti-Ni-Cu wire.⁸⁾ Nevertheless, the as-spun Ti-Ni-Cu ribbon is amorphous and shows no SME if the ribbon is fabricated under a high cooling rate during the melt-spinning procedure. Consequently, proper thermal annealing is needed to crystallize the as-spun amorphous ribbon.

Previous studies on $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon focused on the microstructure of the partially or fully crystallized alloys, the precipitates formed after thermal treatment, and their effects on martensitic transformation.⁸⁻¹³⁾ However, reports on the crystallization kinetics of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon have been scarce.^{14,15)} Louzguine and Inoue¹⁴⁾ studied the crystallization kinetics of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon of 20 μm thick using the Johnson-Mehl-Avrami (JMA) equation. They obtained a high value of the Avrami exponent n of 5.5 and proposed that the nucleation rate was increasing during crystallization. Schloßmacher *et al.*¹⁵⁾ reported that the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon of 45 μm thick exhibited a decreasing nucleation rate during crystallization according to the

observation of transmission electron microscope (TEM). However, on the contrary, they revealed that the isothermal crystallization process measured at 693 K could be adequately described when using the Avrami exponent n of 3. Owing to the significant discrepancy of the value of the Avrami exponent n mentioned above, it is important to investigate the crystallization kinetics of the amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon in detail for the applications of either amorphous or crystalline $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. In this study, isothermal crystallization kinetics of amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt-spun ribbon is studied by means of differential scanning calorimeter (DSC). The parameters of the Avrami exponent n are evaluated to explain the nucleation and growth behaviors during the crystallization process. Additionally, the activation energy for crystallization of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon derived by the Arrhenius equation is also investigated and compared with the reported results measured by the Kissinger method.

2. Experimental Procedure

The $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbons used in this study were prepared by the Institute for Materials Research, Tohoku University, Sendai, Japan using a single-roller melt-spinning technique. The detailed procedure for specimen preparation and the amorphous characteristics of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon are demonstrated in another paper.¹⁶⁾ The crystallization kinetics of the amorphous ribbon is usually described using the JMA equation¹⁷⁻²⁰⁾ measured isothermally at different temperatures between T_g and T_x . Both the crystallization behaviors in continuous heating and isothermal annealing of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbons were conducted in a DSC equipment using TA Instrument DSC 2000 under nitrogen atmosphere. In the isothermal procedure, each $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon was first equilibrated at 673 K and subsequently heated to a set temperature between 708 and 728 K at a constant rate of 10 K/min. Then, each specimen was isothermally annealed at that set temperature for a certain time interval until the completion of crystallization.

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Fig. 1 The DSC curve of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon measured at a heating rate of 20 K/min.

3. Results and Discussion

3.1 Crystallization behavior under a constant heating rate and isothermal annealing

Figure 1 shows the DSC heating curve of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon obtained at a constant heating rate of 20 K/min. As can be seen, the DSC curve shows a glass transition temperature (T_g) of 673 K and a single exothermic peak corresponding to a crystallization temperature (T_x) of 733 K. Moreover, from Fig. 1, there is an extended super-cooled liquid region between T_g and T_x . Therefore, the study of isothermal crystallization kinetics of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was chosen at different temperatures between 708 and 728 K. Figure 2 plots the isothermal DSC curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon during isothermal annealing at different temperatures. In Fig. 2, each DSC curve shows a single exothermic peak after a certain period of incubation. It is assumed that the volume fraction up to any time t is proportional to the area fraction of the exothermic peak. As a result, the crystallized volume fraction during isothermal annealing can be determined by measuring the area fraction of the exothermic single peak. Here, all the DSC measurement results and the integrating peak areas were analyzed and calculated using TA Universal Analysis DSC software. In addition, the crystalline volume fractions for at least 150 different time intervals were calculated during each crystallization process and their results as a function of annealing time obtained at different temperatures are shown in Fig. 3.

3.2 Avrami exponent n and reaction rate constant k

The JMA equation describes the isothermal crystallization kinetics of the amorphous alloys as:

$$X = 1 - \exp\{-[k(t - \tau)]^n\} \quad (1)$$

where X is the crystallized volume fraction (%), τ is the incubation time for the crystallization taken as the time interval between the sample reaching the isothermal temperature and the initiation of crystallization, n is the Avrami exponent and k is the reaction constant. Here, the incubation time τ is defined as the time interval between the time when the specimen reaches the annealing temperature and the time

Fig. 2 The isothermal DSC curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon measured at different isothermal annealing temperatures.

Fig. 3 The crystallized volume fraction as a function of annealing time for $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon measured at different isothermal annealing temperatures.

when the specimen reaches 1% crystallized volume fraction. The reaction rate constant, k is a function of annealing temperature and can be described by the Arrhenius relation:

$$k = k_0 \exp[-E_C/RT] \quad (2)$$

where k_0 is a constant and E_C is the apparent activation energy for crystallization. According to eq. (1), the values of k and n can be determined using the following equation.

$$\ln[\ln(1/(1 - X))] = n \ln k + n \ln(t - \tau) \quad (3)$$

By plotting $\ln[\ln(1/(1 - X))]$ against $\ln(t - \tau)$ measured from Fig. 3, one can obtain the JMA plots for different temperatures as shown in Fig. 4. The data for $12 < X < 85$ (%) in each different temperature curve show almost a straight line. Therefore, the values of the Avrami exponent, n and reaction constant, k can be obtained from the slopes and the intercepts of the straight lines shown in Fig. 4. The detailed results of the calculated Avrami exponent, n and reaction constant, k are listed in Table 1 together with the incubation time, τ . As shown in Table 1, the incubation time, τ decreases with increasing annealing temperature. On the other hand, the reaction constant, k increases with increasing annealing temperature. Furthermore, the calculated Avrami

Fig. 4 The JMA plots for the crystallization of Ti₅₀Ni₂₅Cu₂₅ amorphous ribbon measured at different isothermal annealing temperatures.

Table 1 The kinetics parameters of Ti₅₀Ni₂₅Cu₂₅ amorphous ribbon during isothermal annealing at different temperatures.

Annealing Temperature, T/K	708	713	718	723	728
Incubation time, τ/min	16.35	8.33	3.61	1.68	0.85
Avrami exponent, n	3.35	3.01	3.02	3.38	3.35
Reaction constant, k/min^{-1}	0.20	0.24	0.32	0.47	0.90

exponent n for different temperatures ranges from 3.01 to 3.38. According to Ref. (20), the Avrami exponent of $n = 3$ implies that the main crystallization mechanism is interface-controlled three-dimensional isotropic growth and early nucleation-site saturation. Therefore, the crystallization kinetics of Ti₅₀Ni₂₅Cu₂₅ amorphous ribbon treated by isothermal annealing at different temperatures between T_g and T_x may follow the same crystallization mechanism because all Avrami exponents n derived at different temperatures are close to 3. This result shows good agreement with the crystallization studies reported by Schloßmacher *et al.*^{9,15)} which used TEM microstructural observation for the specimen isothermally crystallized at a constant temperature of 693 K. On the other hand, the relatively high average value of the Avrami exponent n of 5.5 reported by Louzguine and Inoue¹⁴⁾ is not observed in this study. Such high value implies an increase in the nucleation rate. However, this crystallization mechanism disagrees with the result of TEM microstructural observations reported by Schloßmacher *et al.*^{9,15)} According to Ref. 14), a high heating rate of 100 K/min was used before isothermal annealing. On the other hand, a lower heating rate of 10 K/min was used in this study to eliminate the influence of overshooting and fluctuating temperatures in the initial stage of isothermal annealing and the JMA isothermal analysis. Therefore, the different heating rates may account for the conflicting values of Avrami exponent n calculated in this study and that reported by Louzguine and Inoue.¹⁴⁾

3.3 Activation energy E_C of crystallization derived from JMA equation

Figure 5 plots the $\ln k$ as a function of $1/T$ where $\ln k$ is calculated from Fig. 4. As can be seen, a straight line is

Fig. 5 $\ln k$ vs. $1/T$ plot of crystallization data calculated from Fig. 3. The slope of the fitting line indicates an activation energy of $E_C = 314 \text{ kJ/mol}$.

Fig. 6 Variation of the local activation energy with the crystallized volume fraction for Ti₅₀Ni₂₅Cu₂₅ amorphous ribbon.

obtained and its slope corresponds to the activation energy for crystallization E_C of eq. (2). From Fig. 5, the calculated value of E_C is 314 kJ/mol. Besides eq. (2), the activation energy can also be evaluated by the isothermal sigmoid curves of crystallized volume fraction versus annealing time at different temperatures. During the isothermal process, when the crystallized volume fraction is X , the transformation time, $t(X)$ is related to the annealing temperature as described by the Arrhenius relationship:²⁰⁾

$$t(X) = t_0 \exp[E_C(X)/RT] \quad (4)$$

where t_0 is a time constant, and $E_C(X)$ is the local activation energy. We plot $\ln[t(X)]$ vs. $1/T$ using the experimental data of $t(X)$ at different temperatures of Fig. 3, an approximately straight line is obtained and the slope of the line corresponds to the value of $E_C(X)$. Figure 6 shows the plot of measured $E_C(X)$ values calculated from Fig. 3 as a function of X for the Ti₅₀Ni₂₅Cu₂₅ amorphous ribbon. As shown in Fig. 6, the value of $E_C(X)$ decreases rapidly

from about 461 kJ/mol at $X = 3\%$ to about 305 kJ/mol at $X = 20\%$, and then increases gradually in the succession of crystallization for $21\% < X < 98\%$. The extremely high value of $E_C(x)$ in the initial crystallization stage is due to the large activation energy needed for the primary crystallites nucleating from the amorphous matrix. Additionally, the activation energy for the whole crystallization process can also be obtained from the isothermal experiment by taking the time at which the transformed fraction is 50%.²¹⁾

$$t_{0.5} = t_0 \exp[E_C/RT] \quad (5)$$

where $t_{0.5}$ is the time at which the crystallized fraction is 50% and E_C is the activation energy of the whole crystallization process. From Fig. 6, the E_C value calculated at $t_{0.5}$ is about 313 kJ/mol, which is in good agreement with that obtained from Fig. 5 (314 kJ/mol). These E_C values are also similar to those derived from the Kissinger method, reported by Louzguine and Inoue ($E_C = 306$ kJ/mol),¹⁴⁾ Schloßmacher *et al.* ($E_C = 374$ kJ/mol)¹⁵⁾ and Chang *et al.* ($E_C = 341$ kJ/mol).¹⁶⁾ These E_C results demonstrate the fact that both the Kissinger analysis and the JMA approach can be utilized to determine the activation energy for crystallization process. At the same time, these E_C results also imply that the crystallization during continuous heating or isothermal annealing follows a similar crystallization mechanism.

4. Conclusions

The Avrami exponents n of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon during isothermal annealing were determined to be 3.01–3.38 using the Johnson-Mehl-Avrami equation. This indicates that the main crystallization mechanism in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon is interface-controlled three-dimensional isotropic growth with early nucleation-site saturation. The crystallization behavior derived from the JMA equation also shows good agreement with that obtained by Schloßmacher *et al.* According to the Arrhenius relation, the measured activation energy, E_C for the crystallization of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ amorphous ribbon is 314 kJ/mol. The high value of local activation energy, $E_C(X)$ in the initial crystallization stage is owing to the large activation energy needed for the primary crystallites nucleating from the amorphous matrix. The activation energy, E_C calculated by the Arrhenius relation is similar to that obtained by the Kissinger method. This characteristic implies that the

crystallization during continuous heating or isothermal annealing follows a similar crystallization mechanism.

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