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Formation and crystallization of Al–Fe–Si amorphous alloys

R. O. SUZUKI, Y. KOMATSU, K. F. KOBAYASHI, P. H. SHINGU
Department of Metal Science and Technology, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606 Japan

Rapid solidification experiments of Al-based Al–Fe–Si ternary alloys have been performed both by the gun and single roller methods. Glass forming tendency is found to be largest near the β-phase ($Al_9Fe_2Si_2$) composition, where the amorphous state is obtained both by the gun and single roller methods. Crystallization behaviour of amorphous $AlFe_{13.0}Si_{17.4}$ alloy, near β-phase composition, followed the course of (i) the appearance of fine α-Al particles and (ii) the transformation of the matrix into β-phase. The ratio of crystallization temperature and the melting point, T_x/T_m, for $AlFe_{13.0}Si_{17.4}$ amorphous alloy is smaller than 0.5 indicating the difficulty of glass formation of these alloys.

1. Introduction

Although many alloy systems have been successfully rapidly quenched into an amorphous state, only a very few cases have been reported for aluminium-based alloys. Among these are Al–Ge [1–3] and Al–Cu [4–7] alloys, but the amorphous phases for these alloys are obtained only with a very thin portion of the sample by the gun method, which has been reported as the most effective rapid quenching method [8]. The purpose of this work is to find the glass forming composition of aluminium-based Al–Fe–Si alloys by rapid solidification both by the gun and single roller methods. The Al–Fe–Si system was chosen because this system forms several intermetallic compounds [9], and for the aluminium-based alloys, the glass forming tendency of near the compound-forming composition has been reported [3].

2. Experimental method

Samples for rapid quenching are prepared by chill casting the alloys of desired composition, using 99.99% aluminium, electrolytic iron and semiconductor grade silicon, melted in an argon atmosphere in an alumina crucible. The gun apparatus is operated in vacuum and molten alloys are ejected by high pressure argon flow onto the copper or silver substrate which is cooled by liquid nitrogen. The single roller apparatus used in the present study is a copper or stainless steel wheel of 30 cm in diameter, operated at 4000 rpm in open air. Argon gas was blown onto the wheel surface at the position next to the nozzle for the purpose of holding the tape on the wheel. Dupont 990 DSC and Rigaku DTA apparatus were used for the thermal analyses, X-ray diffractometry and JEM 200CX transmission electron microscope were used for the structure observation. Roller quenched samples were electropolished by the solution of 90% ethyl alchol and 10% perchloric acid at room temperature, while the gun quenched samples were observed without applying any thinning treatment.

3. Results and discussion

3.1. Glass forming composition

The compositions at which amorphous phases are obtained either by the gun or single roller method are shown in Fig. 1, where the equilibrium intermetallic compounds are also indicated [9]. Formation of amorphous phases at the compositions of various intermetallic compounds are confirmed by the gun method. However, by the single roller method, it was possible only at the composition of Al–13.0 at %Fe–17.4 at %Si to form an amorphous phase. This composition is near but slightly

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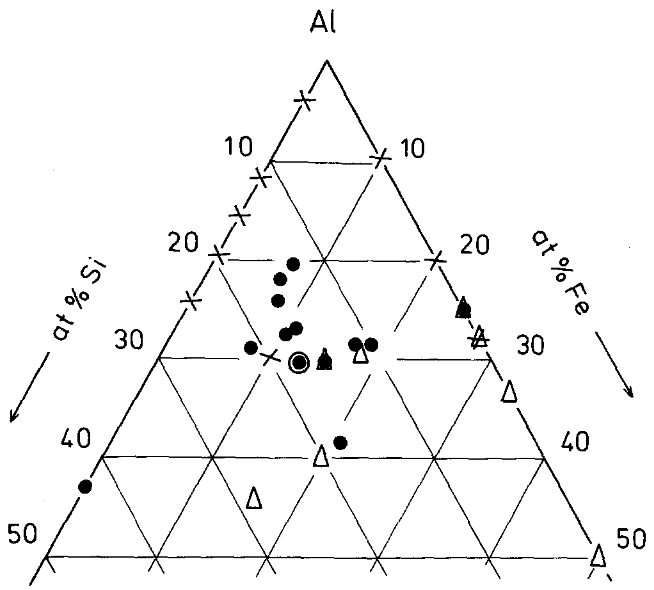

Figure 1 Compositions studied are shown in Al–Fe–Si ternary system where equilibrium phases are indicated by symbols (△). o: glassy state quenched by single roller method, •: glassy state quenched by gun method, X: crystalline state quenched by gun method.

deviated to a Si-rich and a Fe-deficient composition from the reported intermetallic compound, monoclinic β-phase ($Al_9Fe_2Si_2$) [10]. The fact that the formation of amorphous phase is possible by the single roller method at the composition, which is slightly deviated from the exact stoichiometric composition of the β-phase, can be explained as due to the difficulty of a massive type transformation to the crystalline state at such a composition. When the deviation from the stoichiometry is large, the appearance of other primary crystalline phases prevents the formation of a complete amorphous state.

Although the rapidly quenched samples are as brittle as the crystalline state, the X-ray diffractometries of as-rapidly quenched $AlFe_{13.0}Si_{17.4}$ both by the gun and single roller methods showed no Bragg diffraction from crystalline phases. The transmission electron micrographs of these samples are shown in Figs. 2a and b. Lack of contrast in the bright field image and the diffuse halos on the selected area diffraction pattern indicate that both samples are amorphous. The positions of the halos on the selected area diffraction pattern represented by $4\pi \sin\theta/\lambda$ were 26.7, 31.3, 49, 60 and 77 nm^{-1}. The positions of the inner two halos nearly correspond to those of (1 1 1) and (2 0 0) diffractions of fcc-Al which crystallize from the amorphous phase, 26.87 and 31.04 nm^{-1}. In transition metal based glasses the intensity of the first halo is stronger than that of the second one, which is characterized by the two split subpeaks. In $AlFe_{13.0}Si_{17.4}$ and a few compositions of these ternary alloys, the halos are composed of a pair of closely spaced inner peaks and another pair of outer peaks. The fact that the position of the inner pair of peaks is very similar to that of the Bragg diffraction peaks of aluminium crystal suggests the similarity of the basic structure between aluminum and the amorphous phase.

3.2. The thermal analysis of $AlFe_{13.0}Si_{17.4}$ amorphous alloy

Fig.3 shows the results of DSC (differential scanning calerimetry) analyses for both gun and single roller quenched samples at the heating rate of 0.33 $K\,sec^{-1}$. Crystallization takes place at temperatures corresponding to the two exothermal peaks for both cases. The gun quenched sample exhibits broader and smaller exothermal peaks indicating the non-uniformity of cooling condition compared with the sample by the single roller method. The average values of exothermal heat for the first and second peaks are listed in Table I for both samples.

The two peaks are indicated by the transmission

TABLE I Exothermal heat of crystallization for $AlFe_{13.0}Si_{17.4}$ amorphous alloy determined by DSC analysis

	First crystallization fcc α-Al	Second crystallization monoclinic β-$Al_9Fe_2Si_2$
Gun	1.46 $kJ\,mol^{-1}$	3.89 $kJ\,mol^{-1}$
Roller	2.16 $kJ\,mol^{-1}$	4.30 $kJ\,mol^{-1}$

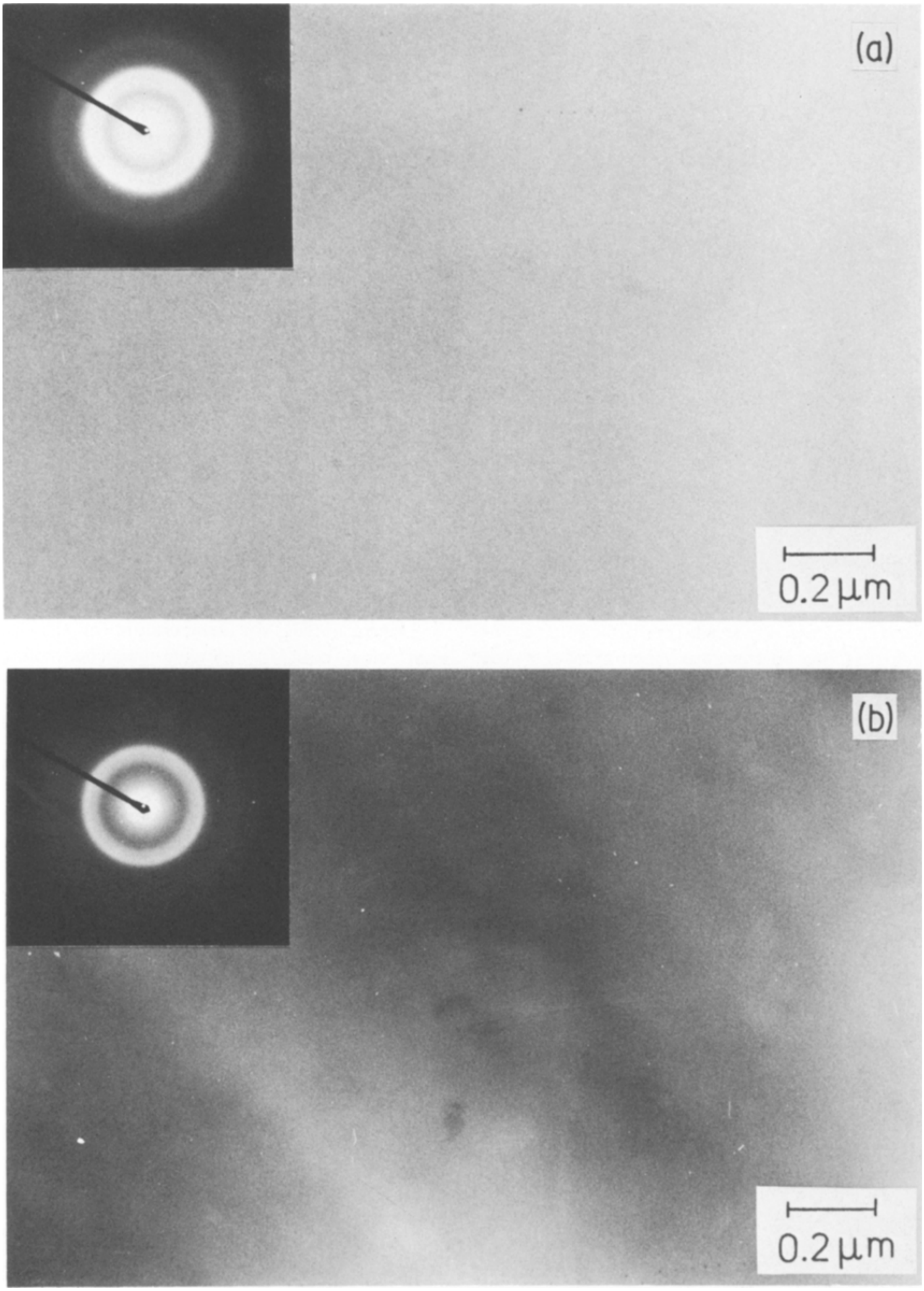

Figure 2 Transmission electron micrographs and their selected area diffraction patterns for rapidly quenched AlFe$_{13.0}$Si$_{17.4}$ alloys by single roller method (a) and gun method (b).

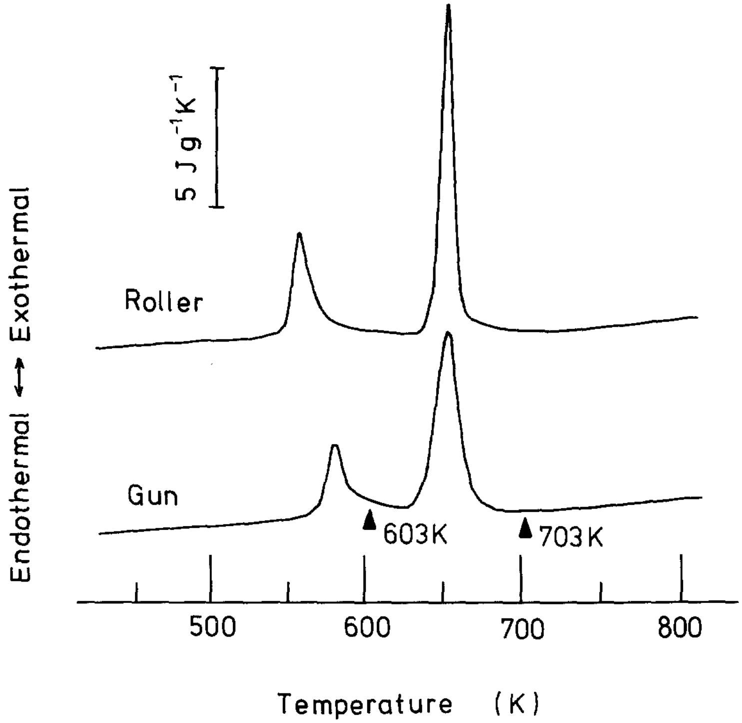

Figure 3 DSC curves for alloys of $AlFe_{13.0}Si_{17.4}$ quenched by the gun method and single roller method with the heating rate of $0.33\,K\,sec^{-1}$.

electron microscopy and X-ray diffraction measurements as due to the appearance of f c c α-phase (lower temperature peak) and monoclinic β-phase [10] (higher temperature peak), respectively. Figs. 4a and b show the structure and the diffraction patterns of the gun quenched samples after annealing up to the temperature between the first and second peak (603 K), and to the temperature higher than the second peak (703 K), respectively. These samples were heated up at the same rate as the DSC analyses shown in Fig. 3.

The fact that the temperature of the first exothermal peak for the gun quenched sample is higher than that for the roller quenched one may be explained as due to the depletion of aluminium by oxidation. It is experimentally confirmed for the gun quenched samples in this ternary system that the temperature of the first exothermal peak becomes closer to the second peak as the composition is set closer to the stoichiometric β-$Al_9Fe_2Si_2$.

Fig. 5 shows the change in the peak tempera-

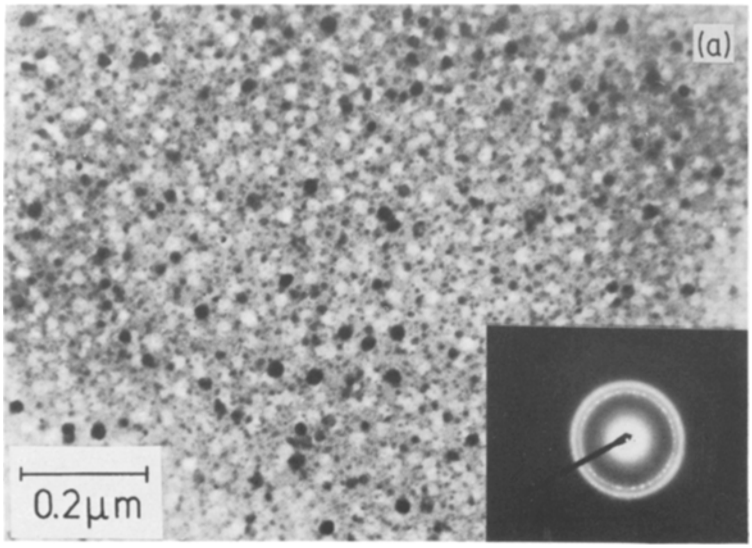

Figure 4 Transmission electron micrographs and their selected area diffraction patterns of $AlFe_{13.0}Si_{17.4}$ amorphous alloy after heated up to 603 K (a) and to 703 K (b) at the rate of $0.33\,K\,sec^{-1}$.

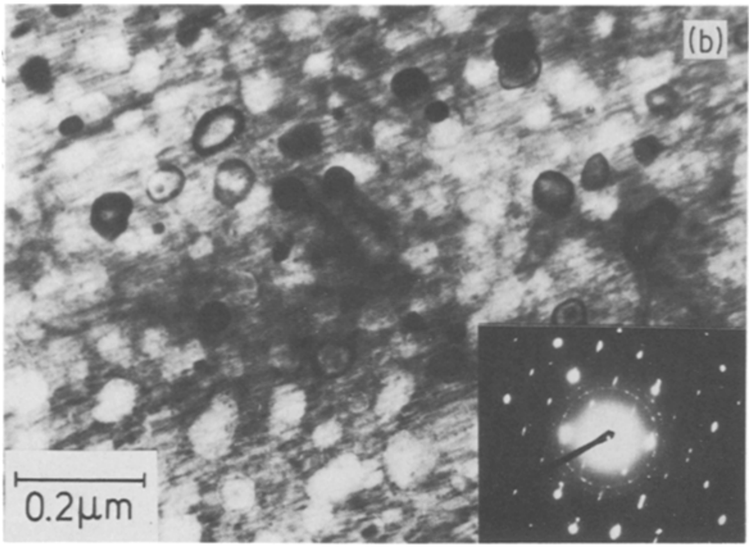

Figure 4 Continued

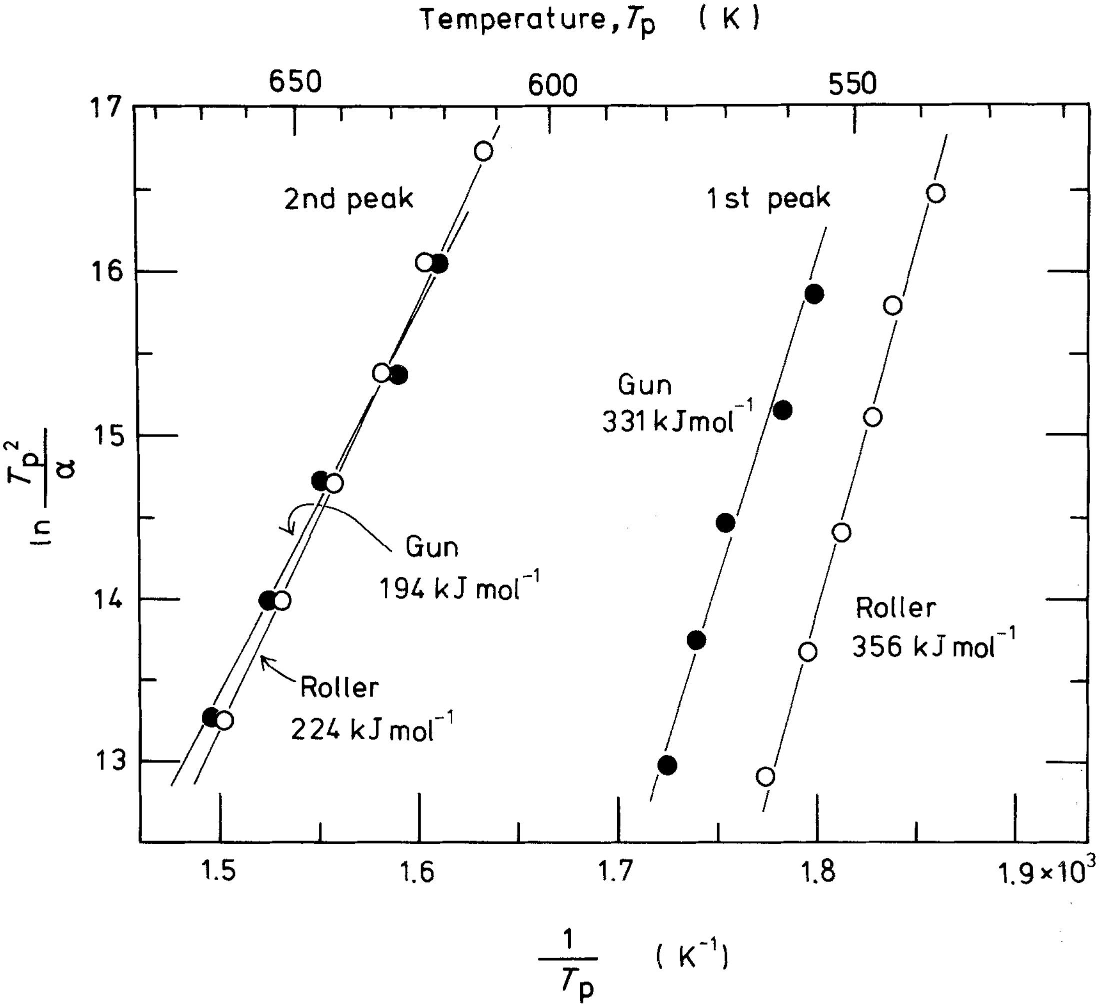

Figure 5 Kissinger plot of exothermal peak temperatures for the determination of activation energies of crystallization processes of $AlFe_{13.0}Si_{17.4}$ amorphous alloy.

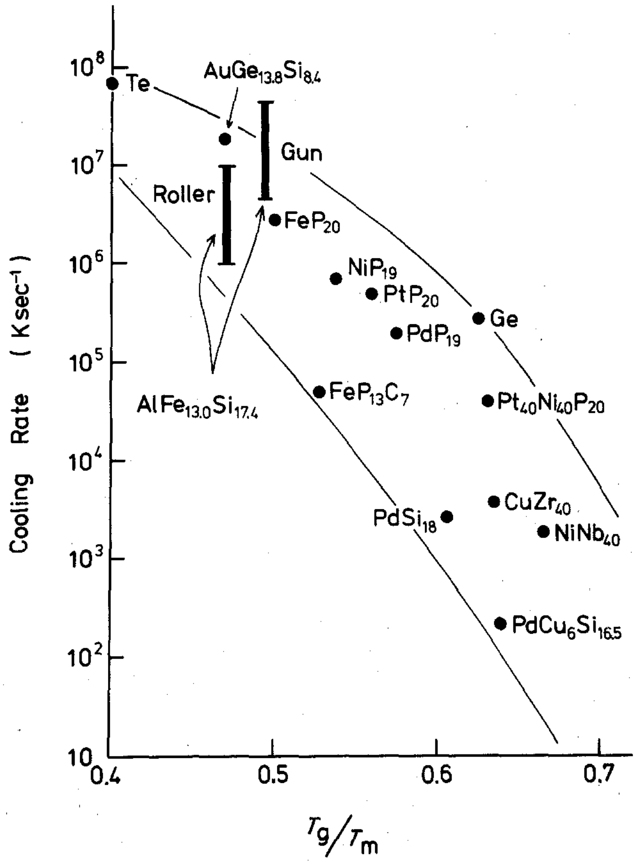

Figure 6 Relationship between the critical cooling rate and the ratio of the glass temperature and the melting point (T_g/T_m) for various amorphous alloys. Two curves indicate the theoretical estimation by Davies *et al.* [13, 14].

ture, T_p, due to the change in the heating rate, α, of DSC analyses. By the application of Kissinger's analysis [11, 12],

$$\ln \frac{T_p^2}{\alpha} = \frac{E}{R \cdot T_p} + \ln \frac{\tau_0 \cdot E}{R} \qquad (1)$$

the apparent activation energy, E, for these peaks are obtained as indicated in Fig. 5. The activation energy for the lower temperature peak is larger than that for the higher temperature peak. Such difference in activation energy may be understood as due to the necessity of long range diffusion process for α-Al-phase formation compared with the in situ massive transformation for the case of β-phase formation from amorphous matrix.

The ratio of the temperature of the first crystallization peak at the heating rate of 0.33 $\mathrm{K\,sec^{-1}}$, 543 K, and the liquidus temperature, 1152 ± 5 K, T_p/T_m, is 0.47. When this value is compared with the T_g/T_m values of other glass forming alloys, the critical cooling rate for amorphous phase formation is estimated to be as large as 10^6 to $10^7\,\mathrm{K\,sec^{-1}}$, as shown in Fig. 6 [13, 14].

When the critical cooling rate is used in place of the heating rate in Kissinger's Equation (1) a rough estimation of the minimum undercooling required for the retention of glassy state down to the room temperature by the rapid quenching becomes possible. The extention of the position of the first crystallization peak of the roller quenched sample shown in Fig. 5 to the heating rate of $5 \times 10^6\,\mathrm{K\,sec^{-1}}$ gives the crystallization temperature of 702 K. When this temperature is compared with the liquidus temperature of this alloy, the minimum undercooling necessary to avoid the crystallization is estimated as 450 K. Such a large undercooling again indicates the difficulty of glass formation of this aluminum based alloy.

4. Conclusions

Rapid solidification experiments of aluminium based Al–Fe–Si ternary alloys have been performed both by the gun and single roller methods. The following results were obtained.

1. At the composition of Al–13.0 at% Fe–17.4 at% Si an amorphous phase is obtained both by the gun and single roller methods.

2. Crystallization behaviour of the amorphous phase followed the course of the appearance of α-Al phase (lower temperature) and monoclinic β-phase (higher temperature). Average values of exothermal heat for the first and second phases are 2.2 and $4.3\,\text{kJ}\,\text{mol}^{-1}$, respectively, for the single roller quenched sample.

3. Difficulty of glass formation of the aluminium alloys is shown by the small value of the ratio of the crystallization temperature and the melting point, T_p/T_m.

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