A Flame-Spray Quenching Process for Continuous Production of Amorphous Powders of Fe-Ni-P-B, Ni-Si-B, and Co-Fe-B Alloys

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An experimental study for continuous production of amorphous powders by flame-spray quenching has been carried out on Fe-Ni-P-B, Ni-Si-B and Co-Fe-B alloys. The spray-quenching equipment consisted of a thermal spray gun of the oxyacetylene type, a rotating copper substrate wheel and a powder collecting system. The substrate wheel was rotated at circumferential velocities below 2.2 m/s. The progress of vitrification of the sprayed powders increased with increasing circumferential velocity of the wheel. By regulating the circumferential velocity of the wheel at approximately 2 m/s so as to suppress the lowering of the cooling rate of liquid metal impinging onto the substrate and partial crystallization of sprayed amorphous phase, once formed on the substrate, due to the flame and liquid metal stream itself from the gun, amorphous alloy powders have continuously been produced for the Fe-, Ni-, and Co-based alloys. The amorphous alloy powders produced at a circumferential velocity of 2.2 m/s were composed mostly of circular or elliptic flakes with irregular periphery. The thickness of the flaky powders was in the range from 5 to 30 μm and the particle size decreased with increasing circumferential velocity in the range below about 350 μm.

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I. Introduction

The recent development of the consolidation technique of amorphous alloys has attracted an increasing interest in amorphous alloy powders. Several techniques(1)-(6) for the production of amorphous alloy powders have been reported up to date. The present authors have also tried to prepare amorphous alloys by a flame-spray quenching process and have reported that this process is advantageous particularly in the production of amorphous alloy powders(7)(8).

The purpose of the present investigation is to study systematically under various operating parameters the method of producing amorphous alloy powders by replacing a stationary copper substrate in the spray-quenching equipment used previously by the present authors(7)(8) with a rotating copper wheel.

II. Experimental

1. Sample preparation

Alloys with compositions (at.%) Fe$_{40}$Ni$_{60}$P$_{14}$B$_{6}$, Fe$_{16}$Ni$_{64}$P$_{14}$B$_{6}$, Ni$_{75}$Si$_{3}$B$_{17}$ and Co$_{74}$Fe$_{6}$B$_{20}$ were used in the present study. Alloy powders ranging from 60 μm to 100 μm in size suitable for the spray-quenching were prepared by comminuting the alloy ingots produced, in accordance with the compositions as above, from electrolytic iron (99.9% Fe), cobalt (99.9% Co), pure nickel pellets (99.97% Ni), silicon rod (99.999% Si), iron-phosphorus alloy (27.4% P), iron-boron alloy (16.5% B), nickel-phosphorus alloy (14.5% P), nickel-boron alloy (16.0% B) and cobalt-boron alloy (17.2% B) by induction-melting and chill-casting in argon atmosphere.
2. Flame-spray quenching equipment

The spray-quenching equipment consists of four separate components as shown in Fig. 1: a thermal spray gun of the oxyacetylene type, a rotating copper substrate wheel (1200 mm OD × 1000 mm ID × 70 mm thick), a powder-brush scraper and a powder-suction collector. Here the stationary copper substrate in the previous spray-quenching equipment is replaced with the rotating copper substrate wheel so as to be applicable to continuous production of amorphous powder.

The main spray-quenching conditions were as follows; gun-substrate distance, 0.50 m; circumferential velocity of the wheel, 0.30–2.2 m/s; powder feed rate, 2.52 g/s; acetylene flow rate, 2.61 × 10⁻⁴ m³/s; oxygen flow rate, 4.72 × 10⁻⁴ m³/s; argon flow rate, 8.00 × 10⁻⁴ m³/s.

3. Check on non-crystallinity of spray-quenched powders

Non-crystallinity of spray-quenched powders was examined by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The XRD analyses were performed with Co Kα-radiation, and the DSC curve was measured at a heating rate of 1.67 × 10⁻¹ K/s under flowing argon gas (8.33 × 10⁻⁷ m³/s).

Maximum value attainable in the present quenching equipment was 2.2 m/s.

III. Results and Discussion

The copper wheel in the equipment shown in Fig. 1 was rotated at seven circumferential velocities \( V \), i.e. 0.30, 0.50, 0.75, 1.00, 1.50, 1.90, and 2.20 m/s and alloy powders with \( x = 0.50 \) and 0.80 in the \((\text{Fe}_{1-x}\text{Ni})_{80}\text{P}_{14}\text{B}_{6}\) system could be readily and continuously prepared at any such velocities. Figures 2 and 3 show typical XRD patterns taken from the powders. In Fig. 2, all the XRD traces of the \( x = 0.50 \) alloy powders reveal halo-patterns typical of an amorphous phase nearly independent of the circumferential velocity. However, Fig. 3 shows that the degree of vitrification of the \( x = 0.80 \) alloy increases with increasing circumferential velocity to \( V = 1.00 \) m/s, and the samples obtained at \( V \geq 1.00 \) m/s show the same halo-patterns as those of Fig. 2.

The exothermic heat of crystallization \( \Delta H_c \) of \( \text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_{6} \) amorphous alloy powders was determined to be 4.40 kJ/mol at a circumferential velocity of 1.00 m/s.
tial velocity of 0.30 m/s ($V=0.30\text{ m/s}$) and 4.47 kJ/mol at $V=2.20\text{ m/s}$ and that of Fe$_{16}$Ni$_{64}$P$_{14}$B$_6$ amorphous alloy powders 4.67 kJ/mol at $V=1.00\text{ m/s}$ and 4.62 kJ/mol at $V=2.20\text{ m/s}$. Since $\Delta H_c$ of the $x=0.50$ amorphous ribbon, prepared by melt-spinning, has been reported to be 4.25 kJ/mol$^{(9)}$, the $\Delta H_c$ values of the alloy powders prepared at $V=0.30$ and 2.20 m/s are within an experimental error in good agreement with the previous data$^{(9)}$. $\Delta H_c$ for an amorphous alloy is empirically known to be about 30 percent of the heat of fusion $\Delta H_m$.$^{(10)}$ In our earlier paper$^{(8)}$, $\Delta H_m$ values of the $x=0.50$ and 0.80 alloys were evaluated to be 10.27 kJ/mol and 10.63 kJ/mol, respectively. Consequently, the $\Delta H_c$ values are about 40% of $\Delta H_m$, in accordance with the previous ratio of $\Delta H_c/\Delta H_m$. Therefore, the powder samples revealing typical amorphous halo-patterns in Figs. 2 and 3 are judged to be composed of an amorphous single phase.

Here since the circumferential velocity is regarded as corresponding to the gun traverse rate (GTR) in the spray-quenching equipment with a stationary copper substrate$^{(7)(8)}$, the XRD patterns shown in Fig. 3, i.e. the ones with some peaks representing partial crystallinity in the samples produced at $V \leq 0.75\text{ m/s}$, appear to be consistent with the XRD pattern of the sample with the same composition ($x=0.80$) prepared at GTR = 0.7 m/s shown in Fig. 2 in Ref. (7).

In view of the influence of circumferential velocity on vitrification of sprayed products, it is considered that the heat amount per unit time on the substrate supplied from the flame and liquid spray-stream itself from the gun increases with decreasing circumferential velocity and that the increase in the heat amount results in lowering of the cooling rate of liquid metal stream. Additionally, in the case of low circumferential velocity of the substrate wheel, there seems to be the possibility that sprayed products, once vitrified on the substrate, are reheated by the flame and liquid metal stream itself from the gun and partly transform to crystalline form during the spray-quenching.

The average thickness $t_f$ of sprayed flaky powders was determined by microscopic measurement of cross-section of them mounted on epoxy-resin as follows; 24 $\mu$m ($V=0.30\text{ m/s}$) and 19 $\mu$m ($V=2.20\text{ m/s}$) for the $x=0.50$ alloy; 20 $\mu$m ($V=0.30\text{ m/s}$) and 14 $\mu$m ($V=2.20\text{ m/s}$) for the $x=0.80$ alloy. Thus, $t_f$ of the $x=0.80$ alloy is smaller than that of the $x=0.50$ alloy at both the circumferential velocities.

It is well known that the fluidity of a liquid alloy increases with increase in the degree of superheat, namely, the superheat above the melting temperature $T_m$.$^{(11)}$ $T_m$, determined by differential thermal analysis, of the $x=0.50$ and 0.80 alloys was 1180 K and 1143 K, respectively. Since the condition of spray-quenching is the same for both alloys, the temperature of each spray liquid stream can be considered to be nearly equal. Accordingly it is thought that the fluidity of the $x=0.80$ liquid alloy subjected to greater superheat is larger than that of the $x=0.50$ alloy.

Furthermore, in the previous work$^{(12)}$ on
crystallization of amorphous \((\text{Fe}_{1-x}\text{Ni}_x)_{80}\text{P}_{14}\text{B}_6\) alloy system, we have reported that the fluidity of this liquid alloy system is expected to increase with increasing nickel content, on the basis of compositional dependence of the fluidity of binary Fe–Ni liquid alloy. Thus, the variation of \(t_f\) with nickel content, determined as above, is also supported from the above discussion concerning the fluidity of the \(x=0.50\) and 0.80 alloys.

According to Fig. 3 in Ref. (7), it is shown that the glass formability, approximately defined in terms of the reduced crystallization temperature \(T_x/T_m\), of the \(x=0.50\) and 0.80 alloys is almost the same; \(T_x\) is the crystallization temperature of each amorphous alloy. Consequently, the \(x=0.80\) liquid alloy, which deposits in thinner thickness, i.e. more rapidly solidifies, on the substrate, appears to vitrify more easily compared with the \(x=0.50\) alloy at each circumferential velocity, provided that the increase in fluidity with nickel content for the former alloy, as discussed above, does not largely affect the glass formability. This implies that the partial crystallinity in the XRD patterns revealed at low circumferential velocity shown in Fig. 3 can not be explained from the difference in the \(t_f\) value between these alloys. So the relation between \(t_f\) and \(V\) was not examined systematically in the present work, though \(V\)-dependence of \(t_f\) is apparent as described above.

In the earlier paper(8), we have determined the activation energy for crystallization \(E_c\) and the crystallization temperature \(T_x\) of these amorphous alloys as follows; 393 kJ/mol, 680 K for the \(x=0.50\) alloy and 345 kJ/mol, 662 K for \(x=0.80\) alloy. Since the values of \(E_c\) and \(T_x\) are regarded as measures of the thermal stability of an amorphous alloy, these results are thought to be an indication that the thermal stability of the \(x=0.80\) alloy is lower in comparison with the \(x=0.50\) alloy.

Therefore, the difference between the XRD patterns seen in Figs. 2 and 3 seems to reflect the difference in the thermal stability between the alloys having \(x=0.50\) and 0.80 in amorphous state, associated with the activation energy for crystallization and the crystallization temperature. This suggests that also in the case of alloys, like the \(x=0.80\) alloy, whose thermal stability in amorphous state is comparatively low, continuous production of the amorphous powders by the present spray-quenching equipment is achieved by increase in the circumferential velocity of the wheel.

Figure 4 shows typical XRD patterns for spray-quenched \(\text{Ni}_{75}\text{Si}_{18}\text{B}_{17}\) and \(\text{Co}_{74}\text{Fe}_6\text{B}_{20}\) powders prepared at \(V=2.20\) m/s by using the present spray-quenching equipment. The average thickness of flaky powders were 25 \(\mu\)m for \(\text{Ni}_{75}\text{Si}_{18}\text{B}_{17}\) and 23 \(\mu\)m for \(\text{Co}_{74}\text{Fe}_6\text{B}_{20}\), and such quenched powders of both alloys also could continuously be prepared at \(V=2.20\) m/s as in the case of the iron-nickel base alloys, but systematic experiments under different circumferential velocities were not performed. Since the almost halo-patterns typical of amorphous materials are observed in both alloy samples, the cooling rate of liquid metal streams at the circumferential velocity of about 2 m/s is high enough to fully cause the vitrification of these alloys.

Although the average thickness of spray-quenched flaky powders varied with alloy composition and circumferential velocity, that of powders obtained at \(V=2.20\) m/s was in the range from 5 to 30 \(\mu\)m. Although the characteristics of these particles are dependent on the circumferential velocity as described later in details, the alloy powders were composed basically of nearly circular or elliptic flakes with an irregularly star-shaped periphery.
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(Fig. 5). Figure 5 shows a scanning electron micrograph of amorphous Fe₄₀Ni₄₀P₁₄B₆ powders produced at V=2.20 m/s.

Table 1 lists the particle size and size distribution of the powders prepared at different circumferential velocities for the x=0.50 alloy which were amorphous at all the velocities. The yield of the amorphous powders produced at a circumferential velocity of 2.20 m/s was about 75 mass% of total weight of material supplied for the gun. The table also shows that the fraction of smaller particles increases with increasing circumferential velocity and at about 2 m/s most of the powders are below 350 μm in diameter. Although variation of such powder characteristics of other alloy systems with the circumferential velocity of the wheel was not examined, the diameter of the powders prepared at 2.20 m/s also ranged below 350 μm.

To characterize metal powder, the specific surface $S_w$ of the powder is often used. Such data in the case of amorphous alloy powders are especially important, because they might be used as catalyzers or raw material for consolidation. Figure 6 shows the change in specific surface of the $x=0.50$ alloy samples as a function of the circumferential velocity. Here $S_w$ was determined by permeametry using the Fisher subsieve sizer instrument. As the circumferential velocity increases, the specific surface increases largely in the range below 0.70–1.00 m/s and then gradually.

In order to examine the change in the shape of the as-sprayed deposits with circumferential velocity, copper discs 12.7 mm in diameter and 5 mm in thickness were fixed on the copper substrate of the wheel with tape, and the $x=0.50$ alloy was spray-quenched on these discs at various circumferential velocities of the wheel. The as-sprayed deposits were observed with a scanning electron microscope. The results are schematically depicted in Fig. 6. While at higher circumferential velocity near 2 m/s liquid metal droplets in stream separately impinge on the substrate and then solidify in the form of almost circular or elliptic flakes with rather irregular periphery, such metal

![Fig. 5 Scanning electron micrograph of amorphous Fe₄₀Ni₄₀P₁₄B₆ alloy powders spray-quenched at V=2.20 m/s.](image)

![Fig. 6 Variation of the specific surface $S_w$ of powder particle and as-sprayed deposit shape with circumferential velocity of rotating wheel.](image)

| $V$ m/s | Size distribution, mass% |
|---------|--------------------------|
|         | Size range, μm           |
|         | <177 | 177–350 | 350–590 | 590–840 | 840< |
| 0.30    | 17   | 23      | 27      | 13      | 20   |
| 0.50    | 18   | 37      | 28      | 10      | 10   |
| 0.75    | 26   | 44      | 24      | 5       | 1    |
| 1.00    | 32   | 46      | 21      | 1       | tr.  |
| 1.50    | 39   | 50      | 11      | tr.     | 0    |
| 1.90    | 39   | 49      | 11      | 1       | tr.  |
| 2.20    | 58   | 40      | 2       | 0       | 0    |
droplets begin to overlap partly on the substrate at a decreased circumferential velocity near 0.75 m/s and at a velocity as low as 0.30 m/s most of them lap over, forming very irregularly flaky deposits. This appears to explain qualitatively the $S_a$ vs $V$ relation where a critical range is seen near 0.70-1.00 m/s.

In Fig. 2 in Ref. (7), some peaks revealing partial crystallinity were seen in the XRD patterns of $(Fe_{1-x}Ni_x)_{80}P_{14}B_6$ powders spray-quenched at GTR = 0.70 m/s, in a similar way to the data (Fig. 3) for the XRD patterns of the $x = 0.80$ alloy samples prepared at the circumferential velocities below 1.00 m/s. These results seem to be associated also with the fact that in the case of the circumferential velocity or gun traverse rate below 1.0 m/s, liquid metal droplets in stream from the gun, when impinge on the substrate, start to overlap one another on the substrate.

It was shown from the above results that amorphous alloy powders are produced by regulating moderately the circumferential velocity of the wheel in the spray-quenching equipment without performing additional operations like cryogen blowing onto the substrate. The present process is expected to be hopeful as a continuous production process of amorphous alloy powders with flaky shape.

IV. Conclusion

A study for the production of amorphous alloy powders has been performed for $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{16}Ni_{64}P_{14}B_6$, $Ni_{75}Si_{8}B_{17}$, and $Co_{74}Fe_{6}B_{20}$ systems and the following points are concluded:

1) The progress of vitrification of the sprayed alloy powders increases with the circumferential velocity of the rotating substrate wheel. When the circumferential velocity is regulated at approximately 2 m/s, amorphous powders of all the alloys studied are produced.

2) The amorphous alloy powders produced at a circumferential velocity of 2.2 m/s are composed basically of nearly circular or elliptic flakes 5-30 $\mu$m thick with rather irregular periphery, and the particle size decreases with increasing circumferential velocity, mostly being below about 350 $\mu$m at the circumferential velocity near 2 m/s.

3) In view of the simple constitution of this quenching equipment as well as the easiness of its operation, the present spray-quenching process is highly promising in the production of amorphous alloy powders.

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REFERENCES

(1) T. Yamaguchi and K. Narita: IEEE Trans. Magn., MAG-13 (1977), 1621.
(2) S. A. Miller and R. J. Murphy: Scripta Met., 13 (1979), 673.
(3) H. Ishii, M. Naka and T. Masumoto: Sci. Rep. RITU, A29 (1981), 343.
(4) T. Masumoto, I. Ohnaka, A. Inoue and M. Hagiwara: Scripta Met., 15 (1981), 293.
(5) A. E. Berkowitz and J. L. Walter: Mat. Sci. Eng., 55 (1982), 275.
(6) T. Sato, T. Ichiyama, T. Noda and K. Kumai: Bulletin Japan Inst. Metals, 24 (1985), 509.
(7) H. Miura, S. Isa, K. Omuro and N. Tanigami: Trans. JIM, 22 (1981), 597.
(8) H. Miura, S. Isa and K. Omuro: Trans. JIM, 25 (1984), 284.
(9) F. E. Luborsky: Mater. Sci. Eng., 28 (1977), 139.
(10) F. Spaepen and D. Turnbull: Rapidly Quenched Metals, Ed. by N. J. Grant and B. C. Giessen, The MIT Press, Cambridge, Massachusetts, (1976), p. 205.
(11) R. A. Flinn: Fundamentals of Metal Casting, Addison-Wesley Pub. Co., Inc., (1963) p. 87.
(12) H. Miura and S. Isa: J. Non-Crystalline Solids, 68 (1984), 255.
(13) F. V. Lenel: Powder Metallurgy, Principles and Applications, Metal Powder Industries Federation, Princeton, New Jersey, (1980), p. 59.