Production of Thick Sheets of an Amorphous Fe_<77>P_<13>C_<10> Alloy by Incremental Solidification Method

Production of Thick Sheets of an Amorphous $Fe_{77}P_{13}C_{10}$ Alloy by Incremental Solidification Method*

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Synopsis

By using a new combined technique consisting of high-pressure gas atomization, followed by melt spinning, it has been found that an amorphous alloy sheet with a thickness as large as about 0.6 mm can be produced for an $Fe_{77}P_{13}C_{10}$ alloy. Crystallization and glass transition behaviors remain unchanged for the amorphous sheets with thicknesses ranging from 0.1 to 0.6 mm. Neither contrast revealing the interface among atomized droplets nor the precipitation of crystalline phase is seen in the sheets below about 0.6 mm thickness and the bending fracture surface consists only of a vein-like pattern. The thick amorphous alloy sheets are interpreted to result from spinning-induced incremental solidification of atomized liquid droplets supercooled up to temperatures just above T_g.

I. Introduction

Development of the technique of producing an amorphous thick sheet with a thickness above about 0.2 mm by liquid quenching for engineeringly important Fe- and Co-based alloys has strongly been desired during the last two decades. There is no information available on the production and properties of a thick amorphous alloy sheet. The largest thickness of Fe-based amorphous alloy sheet reported up to date is about 0.25 mm[1] for $Fe_{77}P_{13}C_{10}$ and $Fe_{75}Si_{10}B_{15}$ alloys. The

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thick amorphous alloy sheet has been produced by the specially designed technique[2] which enables us to keep a good thermal conductivity between molten metal and wheel even for a sheet with 0.3 to 0.4 mm by stopping the wheel revolving at a speed of 6000 rpm within a short time of 1 to 2 sec. The appropriateness of the glass-forming capacity determined by the unique method has been reconfirmed by the result that Fe-based amorphous alloy wires with high strength and good ductility have been produced in the diameter range below about 0.23 mm[3] and used as a practical material[4].

Recently, an incremental solidification[5] has attracted growing attention as a new type of direct casting method which has features between conventional casting and powder metallurgy. Advantage of the incremental solidification, i.e., solidification of small droplets which are supercooled up to temperatures just above T_g, allows us to expect that an amorphous sheet with a thickness above 0.2 mm can be produced even in Fe-P-C and Fe-Si-B systems. Expectedly, the authors have most recently succeeded in producing an amorphous Fe-P-C sheet with a thickness of about 0.6 mm by the incremental solidification method. This paper attempts to present the equipment used for the production of the thick amorphous alloy sheet and the preparation condition, morphology, thermal stability and hardness of the thick amorphous alloy sheet.

II. Experimental Procedure

An alloy of composition $Fe_{77}P_{13}C_{10}$ (at%) was used because the alloy composition had been clarified experimentally[1] to have the largest glass-forming capacity in Fe-P-C system. A mixture of pure iron (99.9 wt%), Fe-26.2 wt% P and white cast iron (Fe-4.2 wt% C) was melted under an argon atmosphere in an induction furnace and chill-cast in a copper mould to prepare the master alloys. 300 g of the alloy was charged into the atomization crucible and remelted under an argon atmosphere. The high pressure gas atomization equipment combined with a single roller spinning unit is schematically illustrated in Fig. 1. The existence of the single roller is essential to achieve the incremental solidification of the atomized small droplets. A gas nozzle with a shape similar to a Hartmann shockwave tube was designed by the authors on the basis of the information represented in Ref.(6). The roller is made from copper and the diameter is 15 cm. The shortest distance between atomized nozzle and copper wheel was fixed to be 10 cm and the rotation speed of the wheel was 7200 rpm.

The master alloy was atomized, from a temperature higher by about 200 K than the respective melting point, with argon gas at a dynamic pressure of 10 MPa. The atomized liquid droplets supercooled up to temepratures just above T_g were solidified immediately after impact against wheel and quickly build up to form an amorphous layer, resulting in the formation of thick amorphous sheets with thicknesses of 0.1 to 0.6 mm and a width of 20 mm. It is very difficult to produce a continuous amorphous sheet and the melt-spun product of atomized droplets is composed of a number of short sheets with an average length of about 70 mm. The amorphous nature and morphology of the resultant sheets were examined by X-ray diffraction, optical and scanning electron microscopy, and differential scanning calorimetry (DSC). The optical microscopy samples were prepared by etching the polished surface in a 1:19 volumetric ratio of nitric acid-methanol solution at room temperature.

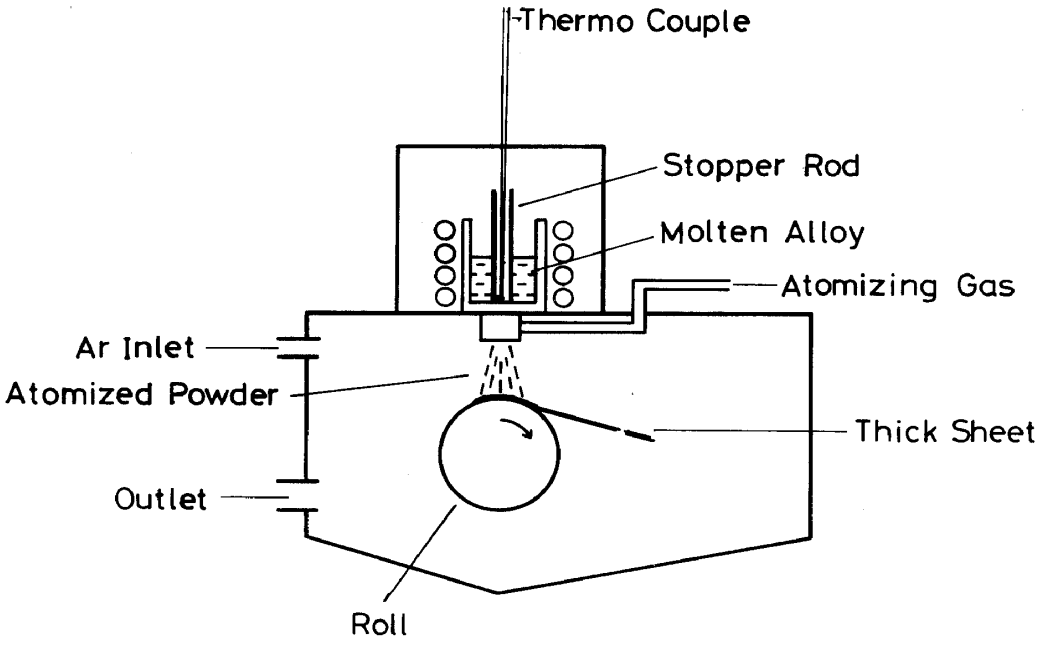

Fig. 1 Schematic illustration of newly constructed equipment consisting mainly of high-pressure gas atomization and melt-spinning parts.

III. Results and Discussion

Figure 2 shows the cross-sectional structure of an amorphous $Fe_{77}P_{13}C_{10}$ sheet with a maximum thickness of about 0.65 mm. The optical micrograph was taken in a deeply etched state where a crystalline phase, if present, would be distinctly detected. No contrast revealing the existence of crystalline phases is seen even in the freely solidified surface area, indicating clearly that a homogeneously amorphous phase is formed over the entire cross-sectional area even in the sheet with a thickness as large as about 0.65 mm. From this result, it is concluded that the incremental solidification resulting from the combined process of high-pressure argon atomization, followed by melt spinning can produce a thick amorphous alloy sheet with a thickness above 0.2 mm. Although some pores with sizes of 1 to 20 μm are observed, it is notable that no contrast revealing the deposited trace of atomized powders is seen over the entire thickness range. The smooth contrast of the cross-sectional structure indicates that almost all the atomized droplets are in a liquid state when they are flattened with the wheel and the splatted liquid pieces are intermixed within an extremely short time before solidification to an amorphous structure.

With the aim of clarifying the maximum thickness for the formation of an amorphous sheet by the present combined process, the cross-sectional structure of $Fe_{77}P_{13}C_{10}$ alloy sheets with larger thicknesses was examined with an optical microscope. The optical micrograph shown in Fig. 3 reveals clearly that a crystalline phase is formed at a distance of about 0.6 mm from the wheel-contacted surface and hence the maximum thickness for the glass formation for the sheet with about 0.9 mm thickness by the present process is about 0.6 mm. The rectangular marks in Fig. 3 represent Vickers indentations and the hardness increases significantly by the structural change from amorphous to crystalline phase. Additionally, no appreciable crack is seen in the vicinity of the indentations, indicating that the thick amorphous sheet does not have an extremely brittle nature. Although no theoretical estimation has been made on the result that the critical thickness is about 0.6 mm, the formation of crystalline phase at a distance of about 0.6 mm from the wheel-contacted surface is probably due to the disappearance of the cooling effect caused by the copper wheel.

In addition to the identification of an amorphous nature by optical microscopy, X-ray diffraction analysis was made as a function of sample thickness for the $Fe_{77}P_{13}C_{10}$ samples. Figure 4 shows the X-ray

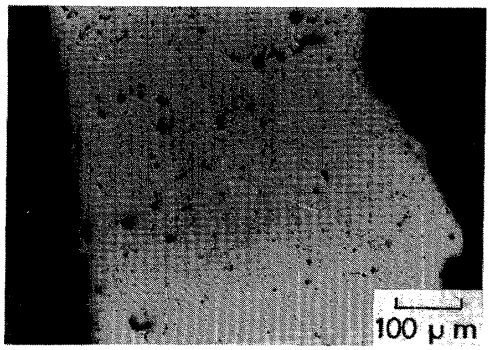

Fig. 2 Optical micrograph showing the cross-sectional structure of $Fe_{77}P_{13}C_{10}$ sheet with a thickness of about 0.65 mm produced by melt spinning of atomized liquid droplets.

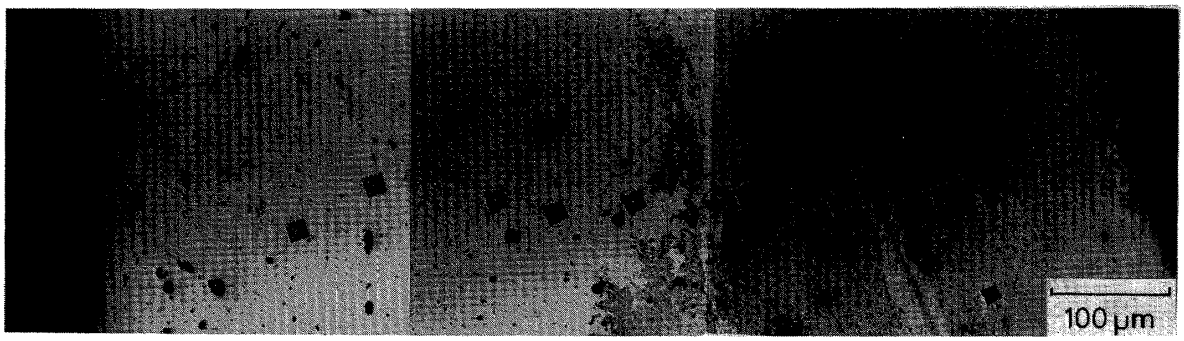

Fig. 3 Optical micrograph showing the cross-sectional structure of $Fe_{77}P_{13}C_{10}$ sheet with a thickness of about 0.9 mm produced by melt spinning of atomized liquid droplets.

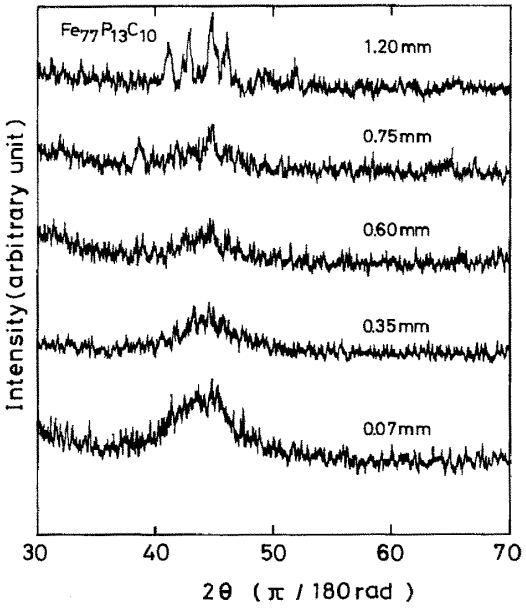

Fig. 4 X-ray diffraction patterns showing the as-quenched structure of $Fe_{77}P_{13}C_{10}$ sheets with different thicknesses produced by melt spinning of atomized liquid droplets.

diffraction patterns taken from the freely solidified surface side of $Fe_{77}P_{13}C_{10}$ sheets with different thicknesses of 0.1 to 1.2 mm. The structure comprises an amorphous phase for the sheets below 0.60 mm in thickness and a crystalline phase consisting of αFe and $Fe_3(P,C)$ for the sheets above 0.75 mm in thickness. No appreciable difference in the broad diffraction peaks due to the amorphous structure was seen for the sheets with 0.07, 0.35 and 0.60 mm thickness, indicating the formation of a similarly amorphous phase in the sheets below 0.6 mm thickness.

The formation of an amorphous thick sheet is also confirmed from SEM observation of the bending fracture surface of the thick sheet (≃0.55 mm thickness). As shown in Fig. 5, the fracture surface consists only of a vein-like pattern similar to that for amorphous alloy ribbons produced by liquid quenching and no fine shell pattern characteristic to thermally embrittled and hydrogen-embrittled amorphous alloys is observed. The fracture surface appearance suggests that the thick amorphous Fe-P-C sheet has rather good ductility, even though the sheet fractures during bending deformation. Furthermore, neither an evidence of splat boundaries nor large pores are observed over the fracture surface, indicating that the thick amorphous sheet has a rather high product density in the as-splatted state.

Thus, the X-ray diffraction and SEM data also show that the critical thickness for formation of an amorphous $Fe_{77}P_{13}C_{10}$ sheet by the present process is in the vicinity of 0.6 mm, being consistent with the result (Figs. 2 and 3) obtained by optical microscopy. The critical thickness is 2.4 times as large as the largest value (≃0.25 mm)[1] obtained by the modified single roller melt spinning method. The significant difference indicates clearly that the combined process of high-pressure gas atomization and melt spinning leading to incremental solidification is useful for the production of a thick amorphous sheet.

Figure 6 shows the DSC curves of $Fe_{77}P_{13}C_{10}$ amorphous sheets with thicknesses ranging from 0.037 to 1.43 mm measured at a heating rate of 40 K/min, along with the data for the Fe-P-C amorphous ribbon with a thickness of 0.02 mm produced only by the melt-spinning method. The amorphous phase transforms to crystalline phases accompanied by a sharp exothermic reaction with the onset tempeature of about 743 K, and there is no appreciable difference in the crystallization temperature(T_x), corresponding to the exothermic onset temperature, and the exothermic reaction behavior with sheet thickness. T_x, and glass transition temperature (T_g) and the heat of crystallization (ΔH_x) of $Fe_{77}P_{13}C_{10}$ amorphous sheets as a function of sample thickness are

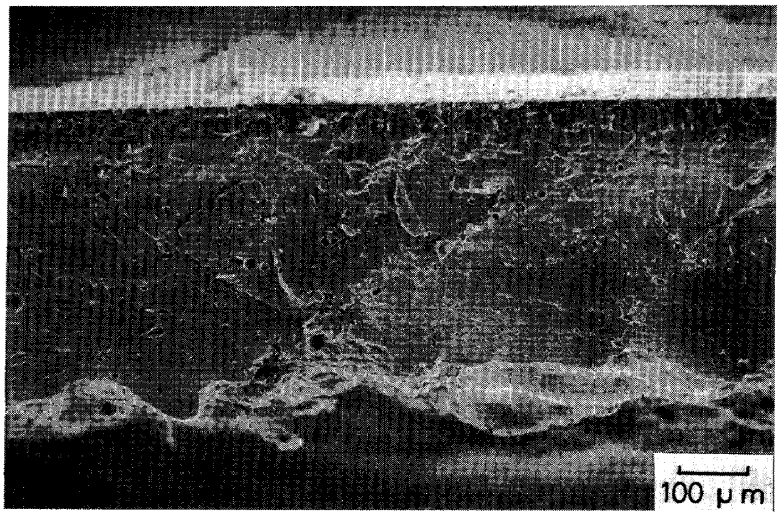

Fig. 5 Scanning electron micrograph showing the fracture surface appearance of an amorphous $Fe_{77}P_{13}C_{10}$ sheet with a thickness of about 0.55 mm produced by melt apinning of atomized liquid droplets.

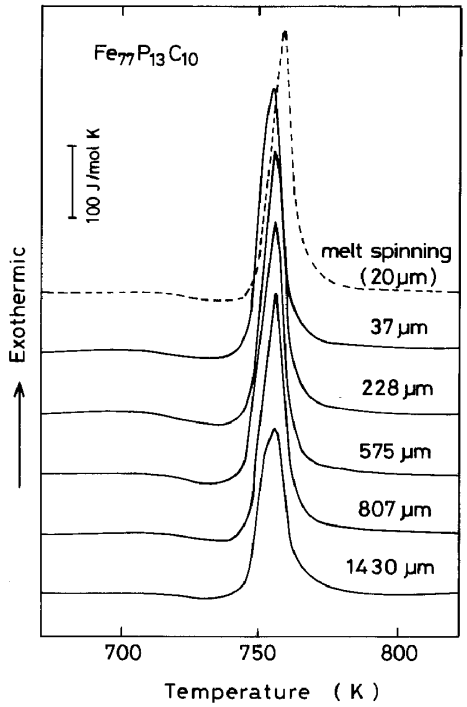

Fig. 6 Differential scanning calorimetry curves of amorphous $Fe_{77}P_{13}C_{10}$ sheets with different thicknesses produced by melt spinning of atomized liquid droplets. The data for the amorphous ribbon produced by melt spinning are also shown for comparison.

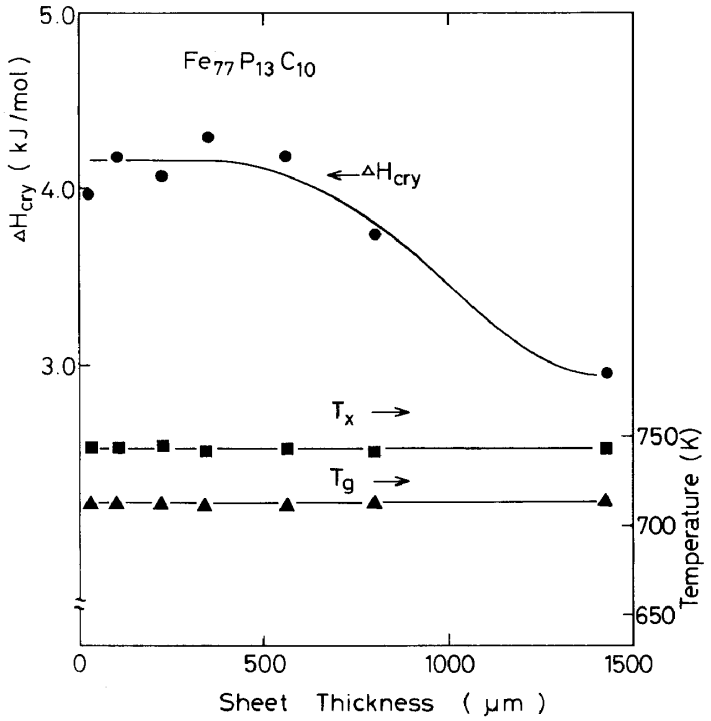

Fig. 7 Changes in T_x, T_g and ΔH_x as a function of sheet thickness for amorphous $Fe_{77}P_{13}C_{10}$ sheets produced by melt spinning of atomized liquid droplets.

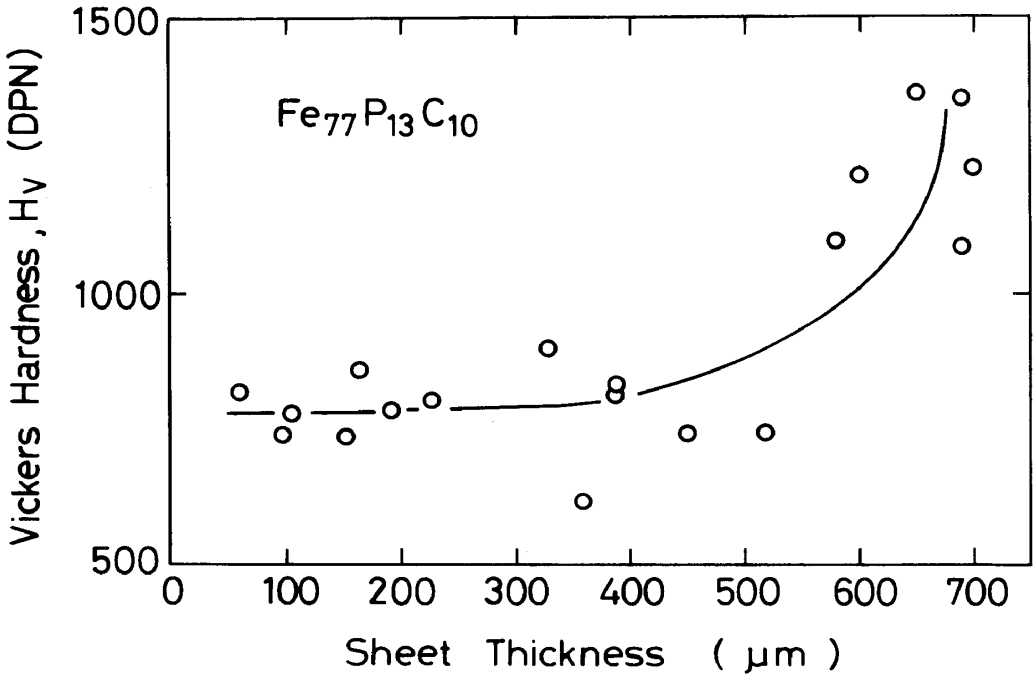

Fig. 8 Change in Vickers microhardness (H_v) as a function of sheet thickness for amorphous $Fe_{77}P_{13}C_{10}$ sheets produced by melt spinning of atomized liquid droplets.

plotted in Fig. 7. The T_x, T_g and ΔH_x values are 743 K, 711 K and 4.2 kJ/mol, respectively, for the amorphous sheet with about 0.6 mm thickness, being comparable to that (4.1 kJ/mol) of the amorphous ribbon sample. With further increasing sheet thickness, T_x and T_g remain constant and ΔH_x decreases significantly in the vicinity of about 0.8 mm thickness. The thickness agrees roughly with the critical thickness where the phase transition from amorphous to crystalline structure takes place and hence the decrease in ΔH_x is interpreted as due to the mixture of crystalline and amorphous phases. Figure 8 shows the change in Vickers microhardness (H_v) with the distance from roller-contacted surface for $Fe_{77}P_{13}C_{10}$ sheets with thicknesses ranging from 0.3 to 0.9 mm. The H_v values are about 770 DPN and no systematic change in H_v with sample thickness is seen in the thickness range below about 0.6 mm, indicating that there is no significant change in the amorphous structure for the sheets with thicknesses ranging from 0.02 to 0.6 mm.

IV. Conclusion

The new rapid quenching process consisting of high-pressure argon atomization and melt spinning was found to give rise to the formation of an amorphous Fe-P-C sheet with a thickness as large as about 0.6 mm. The formation of the extremely thick amorphous alloy sheet is probably because of the incremental solidification of atomized small droplets supercooled up to temperatures just above T_g by impact against wheel. Furthermore, the thick amorphous sheet has nearly the same values of T_x, T_g and ΔH_x as those for the melt-spun ribbon with a thickness of about 0.02 mm and hence it is concluded that there is no significant difference in the amorphous structure between the thick amorphous sheet with $\simeq$0.6 mm thickness and the melt-spun ribbon with $\simeq$0.02 mm thickness. The clarification of the mechanisms of the stack and peeling of the thick sheet on the revolving wheel is in progress because it is expected to offer an information for the production of a continuous thick sheet.

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