Fabrication of Amorphous Alloy Sheet by Gas Melt-Spraying Method

Several studies of rapidly quenched metals fabricated by means of melt-spraying techniques have been reported^{(1)~(4)}, including the formation of an amorphous alloy of the Cu-Zr system by Giessen *et al.*⁽⁴⁾ by using a plasma melt-spraying method performed in inert gas atmosphere. The purpose of the present paper is to report the formation of amorphous alloy sheet of Fe₄₀-Ni₄₀-P₁₄-B₆ by using the oxygen-acetylene gas melt-spraying method.

There are several advantages in the melt-spraying method over the conventional melt-spinning method for the practice of rapid quenching of liquid metals. Since the melt-spraying method does not require the use of a crucible for the melting of the starting alloy, it is free from fears for the contamination during melting and the deterioration of nozzle material due to corrosion. Melt-spraying can be performed on a large cooled substrate, so that it is suitable for the production of rapidly quenched material on a large scale. However, the demerit of this method is that the material has low density due to the porosity formed during the deposition of liquid droplets.

The main difference in the present method of rapid quenching from the conventional melt-spraying method lies in the way of heat extraction from the melt-sprayed deposits. An effort was made to cool the surface of the deposits by the forced stream of liquid nitrogen down to a sufficiently low temperature so that the formed melt-sprayed deposit can act as the substrate for the rapid quenching of liquid droplets sprayed successively on it. The present method is advantageous in the formation of a thick deposit over the conventional melt-spraying method which utilizes cooling by the heat extraction to the cooled substrate through the already formed deposit layer.

The crucial point in the melt-spraying method for the formation of amorphous metals is how

to avoid the crystallisation of the already formed deposit of amorphous metals upon attachment of liquid droplets during the repeated melt-spraying. A simple consideration of heat conduction during rapid quenching⁽⁵⁾⁽⁶⁾ shows that the temperature of the substrate surface in contact with the deposited liquid film can become as high as the half temperature between the initial substrate and liquid temperatures in the case of ideal thermal contact. For a poorer thermal contact the substrate temperature will be raised to a lesser extent. If, for instance, the deposit of an amorphous metal layer formed by the first melt-spraying is cooled to 273 K prior to the successive spraying of liquid droplets of, say, 1273 K, the highest temperature that the amorphous deposit experiences, will not exceed 773 K.

A detailed experimental study of the relaxation time before crystallisation due to isothermal holding for Fe₄₀-Ni₄₀-P₁₄-B₆ amorphous alloy reported in a previous paper⁽⁷⁾ gives the relaxation time for crystallisation of 4×10^{-3} s at 773 K which is a sufficiently large value as compared with the time required for rapid quenching at a rate in the order of 10^5 to 10^6 K per second. Further work on the crystallisation of this alloy by the continuous heating experiment⁽⁸⁾ shows that the crystallisation temperature is raised by approximately 20 K as a result of the increase in the heating rate of one order of magnitude. The amorphous phase may experience a considerably high temperature without being crystallised if the heating and cooling rates are high. Thus, there are sufficient experimental and theoretical bases for the formation of a thick amorphous metal-deposit by the repeated melt-spraying method, provided the deposit is cooled to a sufficiently low temperature prior to the successive application of melt-spraying.

Fig. 1 Schematic drawing of the setup for the rapid quenching by gas melt-spraying method.

Fig. 2 X-ray diffraction patterns. (A): 300 μm thick melt-sprayed sample, (B): 150 μm thick melt-sprayed sample and (C): melt spun ribbon sample.

Experimentally, the melt-spraying was performed by using a METCO melt-spraying apparatus and a rotating copper drum 10 cm in both diameter and width cooled by a spray of liquid nitrogen as shown schematically in Fig. 1. The copper drum was rotated at a rate of 500 rpm and the liquid nitrogen flow rate was about $10^3 \text{ cm}^3/\text{min}$. The alloy sample was melted in argon atmosphere and chill cast into an ingot of 5 mm thick plate and then crushed and sieved. The powder used was in the range of 150 to 200 mesh. The melt-spraying was performed by moving the spray gun horizontally by hand. The average time interval of spraying at the same location was about one second.

Photograph 1 shows a deposited sheet taken from the copper drum, the average thickness of which is 300 μm . The X-ray diffractometry showed the existence of some extent of crystallinity in the amorphous halo background as shown by curve (A) in Fig. 2. Curve (B) is for the sample 150 μm thick and curve (C) is for

Photo. 1 Photograph of the gas melt-sprayed 300 μm thick sheet.

Photo. 2 Polished section of 300 μm thick melt-sprayed sheet (parallel to the sheet surface). Square markings are micro Vickers indentations at a weight level of 500 g.

the melt spun sample. The density of the deposits were estimated to be about 80 to 90% dense as compared with the melt spun sample by the liquid immersion method and also by the observation of the polished section by optical microscopy, as shown in Photo. 2. The differential thermal analysis curve taken by the Rigaku DSC unit for 150 μm thick sample is shown in Fig. 3. The position and the integrated peak area coincided with those for the melt spun sample within experimental error. The contraction upon crystallisation was about 0.5% which is roughly the same value as reported previously for this alloy⁽⁸⁾.

In conclusion, it has been confirmed that by

Fig. 3 DSC curve for 150 μm thick melt-sprayed sample. The scan rate is 10 K/min.

the use of conventional gas melt-spraying method the formation of amorphous metal sheet is possible. The present results indicate the possibility of producing thick amorphous metal sheet with a proper device of heat extraction from the deposit during melt-spraying.

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