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Structures and mechanical properties of amorphous alloy compacts prepared in an inert atmosphere

M. TAKAGI
Research and Development Department, Nippondenso Co. Ltd, Showa-cho, Kariya, Aichi 448, Japan

Y. KAWAMURA
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980, Japan

T. IMURA
Department of Mechanical Engineering, Aichi Institute of Technology, Yachigusa, Yagusa-cho, Toyota 470-03, Japan

H. SAKA
Department of Materials Science and Engineering, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

A new technique has been developed to prepare amorphous alloy compacts where all the processes, from powdering to consolidation, are carried out in an argon atmosphere. Amorphous alloy ribbons were crushed into powders at low temperature using a planetary ball mill. These powders were consolidated using a cubic-type anvil apparatus under a high hydrostatic pressure. Amorphous alloy powders and compacts thus prepared were oxidized to a much lesser extent than those prepared in air using a conventional method. The compressive strength of the compacts prepared in an argon atmosphere was higher by 30%–100% than that of those prepared conventionally in air. The strengthening mechanism is discussed based on the results of characterization of the powders and compacts.

1. Introduction

In previous studies [1–4], it was shown that many properties of amorphous alloy compacts such as mechanical ones were deteriorated by the existence of oxide films in interparticle boundaries.

In the present study, a novel method was developed where all the processes of preparation of amorphous alloy compacts, namely from powdering to consolidation, were carried out in an inert atmosphere in order to suppress the formation of oxide films in the interparticle boundaries.

Amorphous alloy ribbons were milled into powders at low temperature in an argon atmosphere, using a planetary ball mill, in order to suppress the oxidation of the powders. This milling technique utilizes the phenomenon that iron-based amorphous alloys are embrittled at low temperatures [5–7]. The powders thus obtained were consolidated under a high hydrostatic pressure in an argon atmosphere. The powders and compacts thus prepared were characterized and the results were related to the mechanical properties of the compacts.

2. Experimental procedure

The starting material was a commercial amorphous alloy ribbon of $Fe_{78}B_{13}Si_9$ (Metglas 2605S2) 25 mm wide. The ribbon was embrittled by annealing at 673 K for 90 min in vacuum, and then crushed into flakes approximately 5–10 mm in size. The flaky ribbons 4 g in weight were put in a stainless steel pot, together with seven stainless steel balls of 15 mm diameter, and the pot was sealed with an indium-coated copper O-ring to preserve an argon atmosphere even at liquid-nitrogen temperature. These procedures were carried out in an argon atmosphere in a glove box.

A pair of the pots which contained the flaky ribbons were immersed into liquid nitrogen for 15–20 min until they were cooled to liquid-nitrogen temperature. The pots were transferred quickly to a planetary ball mill (Fritsch Pulverisette 7) and milling was carried out promptly for 1 min while the temperature of the pots and flaky ribbons inside remained close to the liquid-nitrogen temperature. This operation, from cooling to milling, was repeated until the total milling time reached that desired, i.e. 1, 4, 8 or 12 min.

After the pots warmed up to room temperature, the powders were taken out of the pots and were sieved to select only those ranging from 50–100 μm in size. The selected powders were put into a platinum capsule, 5.9 mm i.d. and 5.5 mm high. The capsule was capped with a platinum disc, and then sealed with sodium

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silicate solution. These operations were also carried out in an argon atmosphere in a glove box.

The powders, while contained in the capsule in an argon atmosphere, were consolidated under a high hydrostatic pressure by a cubic-type anvil apparatus, which is shown in Fig. 1. The consolidation was carried out at a pressure of 5.4 GPa and a temperature of 723 K for 2 h. This treatment of 723 K for 2 h is just before the crystallization starts under a pressure of 5.4 GPa [2]: the crystallization temperature increases with increasing pressure [2].

The compacts and the powders prepared were characterized by various techniques. The size of the powders and density of the compacts were studied by sieving and Archimedes' method, respectively. Morphology and structure were investigated by scanning electron microscopic (SEM) observation and X-ray diffraction (XRD), respectively. Oxygen content was measured by an inert gas fusion–non-dispersive infrared absorption method. Interparticle boundaries were characterized by etching, SEM observation, electron probe micro-analysis (EPMA) and transmission electron microscopic (TEM) observation.

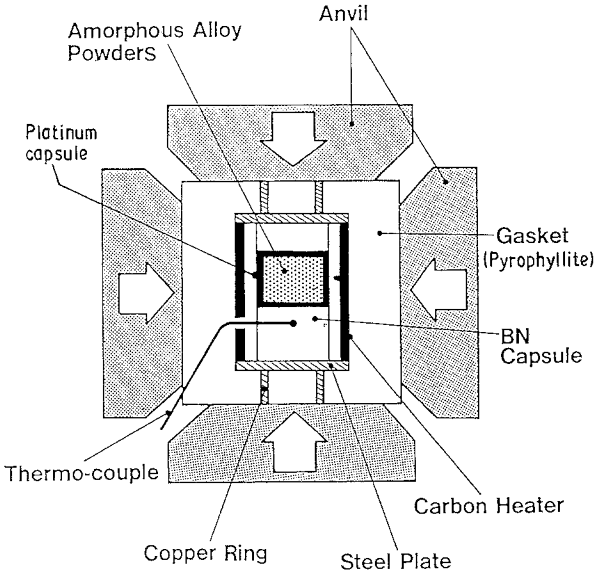

Figure 1. Schematic illustration of the consolidation technique of amorphous alloy powders under a high hydrostatic pressure in an argon atmosphere using a cubic-type anvil apparatus. Amorphous alloy powders were sealed in a platinum capsule.

Rectangular specimens 1 mm × 1 mm × 2 mm were sectioned from the compacts using a spark machine, followed by mechanical polishing. They were deformed in compression in vacuum at room temperature using two tungsten carbide platens on an Instron-type testing machine at a strain rate of $8.33 \times 10^{-5}\ \mathrm{s}^{-1}$. After the compression test, fracture surfaces were observed by SEM.

For comparison, similar analyses and measurements were carried out on the powders which were prepared at room temperature in air and also on the compacts which were consolidated in air.

3. Results

3.1. Preparation of amorphous alloy powders

The conditions under which amorphous alloy powders were prepared are summarized in Table I. Fig. 2 shows a distribution of the size of the powders as measured by sieving. The powders P2 and P5, crushed at liquid-nitrogen temperature, were remarkably smaller in size than P6, crushed at room temperature, all of which were milled for 4 min. This fact indicates that the low-temperature-milling is effective in crushing iron-based amorphous alloy ribbons.

The powder size decreased with increasing milling time up to 8 min, and then increased. This can be attributed to the reconglomeration of the powders. Comparison of the size of P2 with that of P5 reveals that the atmosphere under which crushing was carried out has little effect on the powder size.

SEM images of the amorphous alloy powders 50–100 μm in size are shown in Fig. 3. Powders P2 and P6, crushed for 4 min at low and room temperature, respectively, had flaky shape with the surfaces similar to those of the initial ribbons, although P2 (crushed at low temperature) had sharper edges than P6 (crushed at room temperature). This also indicates that the amorphous alloy is embrittled at low temperature. Powders P3 and P4, which were crushed for more than 8 min at low temperature, had more irregular shapes and surfaces than P2 and P6, and this indicated that reconglomeration of the powders had taken place during crushing. XRD studies confirmed that the amorphous structure was preserved for all the powders prepared in this study.

The results of the quantitative analysis of oxygen in the powders are also shown in Table I. The oxygen

TABLE I Summary of amorphous alloy powders prepared under different conditions and the oxygen contents of the prepared powders

Powder	Apparatus	Milling conditions		Atmosphere	Oxygen content (wt %)
		Temperature	Time (min)		
P1	P[a]	Low temp.	1	Argon	
P2	P	Low temp.	4	Argon	0.031
P3	P	Low temp.	8	Argon	0.048
P4	P	Low temp.	12	Argon	
P5	P	Low temp.	4	Air	
P6	P	Room temp.	4	Air	0.14
P7	C[b]	Room temp.	60	Air	0.15

[a] P, planetary ball mill.
[b] C, conventional ball mill.

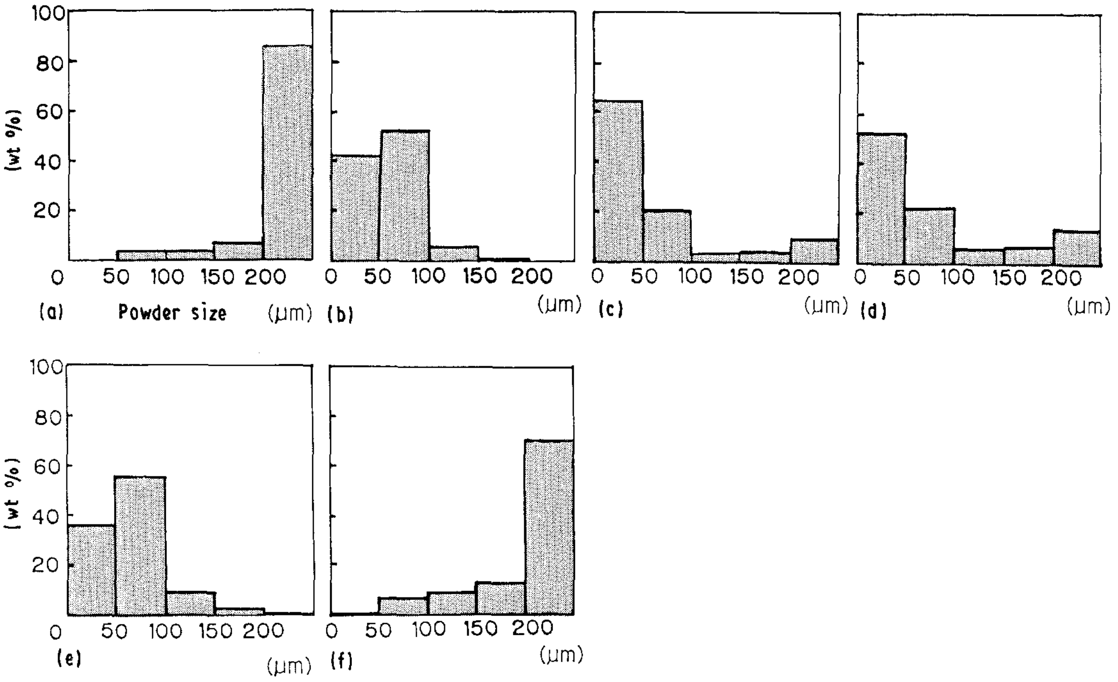

Figure 2 Size distributions of amorphous alloy powders prepared under different conditions by a planetary ball mill. (a) P1, (b) P2, (c) P3, (d) P4, (e) P5, (f) P6.

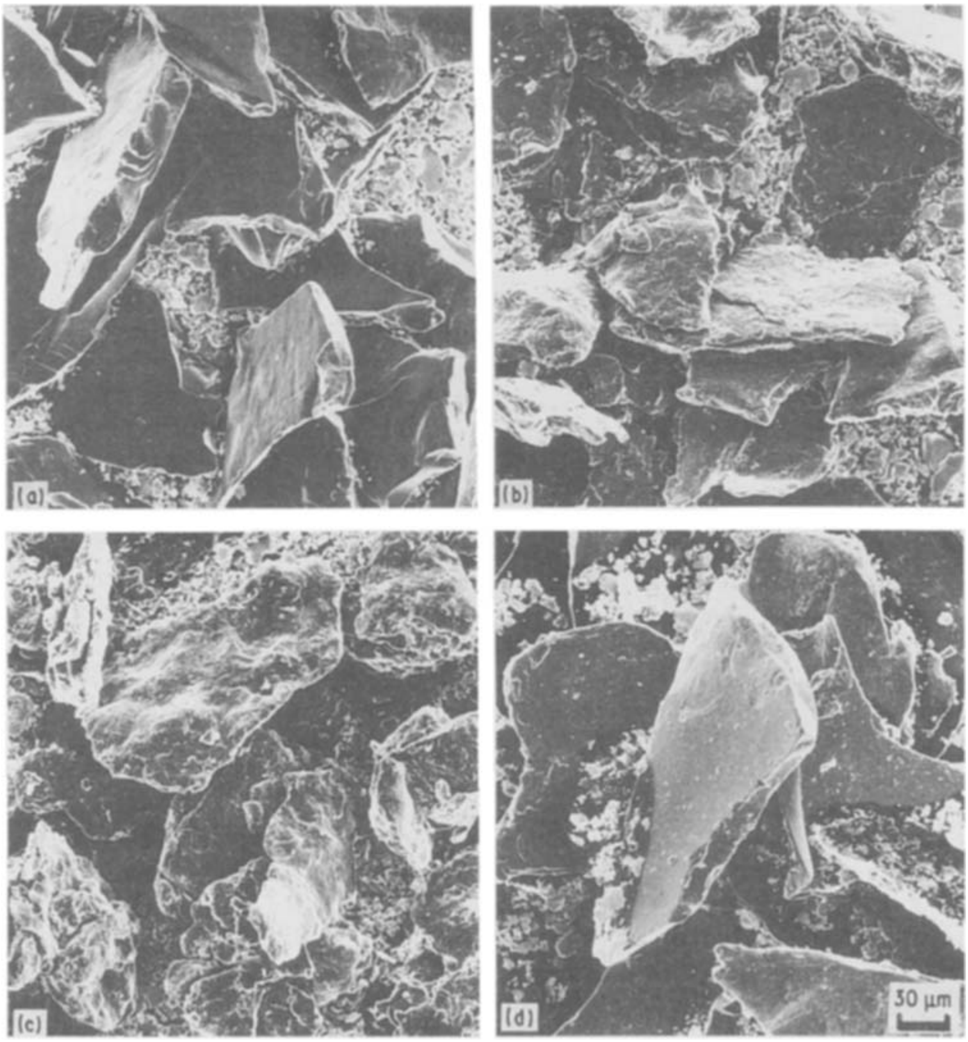

Figure 3 Scanning electron micrographs of amorphous alloy powders 50–100 µm in size. (a) P2, (b) P3, (c) P4, (d) P6.

content of the powders prepared by low-temperature milling in an argon atmosphere was lower by a factor of three to five than that of those prepared in air. It can be said that the low-temperature milling in an argon atmosphere suppressed the oxidation of amorphous alloy powders significantly, although, when the milling time became longer, the oxygen content increased slightly.

3.2. Preparation of amorphous alloy compacts

Amorphous alloy powders thus prepared were consolidated in an argon atmosphere under a high hydrostatic pressure at a temperature just below the crystallization temperature. An X-ray diffraction showed that the compacts had amorphous structure. The bulky amorphous alloy compacts prepared in this study are summarized in Table II, where the compacts prepared in air are also included for comparison.

Fig. 4a–d shows optical micrographs of the cross-sections of the amorphous alloy compacts, etched for 10 s with 6% nital. In B1 and B2, which were consolidated in an argon atmosphere, interparticle boundaries between powders appeared faintly, while in B3 and B4, which were consolidated in air, interparticle boundaries appeared clearly as dark lines. Fig. 4e–h shows SEM images of the cross-sections of the amorphous alloy compacts before etching. The interparticle boundaries could be observed in B3 and B4, but hardly in B1 and B2. These results are in good agreement with those of the optical microscopic observation.

No pores were observed in B4 but some were observed in B1, B2 and B3. Actually B4 had 100% density of the parent ribbon, while B1, B2 and B3 had 98%–99% density. These pores may be attributed to the residual gases sealed in the platinum capsule.

The distribution of iron, silicon and oxygen in the amorphous alloy compacts was determined by EPMA, and is shown in Fig. 5. Sharp peaks of oxygen were observed in B3 and B4; these peaks correspond to oxide films existing in the interparticle boundaries in B3 and B4. In the case of B1 and B2, such sharp peaks of oxygen were not observed.

In Table II, the results of the quantitative analysis of oxygen in amorphous alloy compacts are shown as measured by an inert gas fusion–non-dispersive

TABLE II Summary of amorphous alloy compacts prepared from different powders under various conditions, together with the oxygen contents of the prepared compacts, the density and the compressive strength

Compact	Powder	Consolidation conditions		Oxygen content (wt %)	Compressive strength (GPa)	Density (%)
		Atmosphere	Platinum capsule			
B1	P2(argon, P[a])	Argon	Used	0.037	1.51	98.9
B2	P3(argon, P)	Argon	Used	0.057	2.28	98.7
B3	P6(air, P)	Air	Used	0.14	0.81	98.4
B4	P7(air, C[b])	Air	Not Used	0.16	1.15	100
B5	P2(argon, P)	Air	Not Used	0.16		

[a] P, planetary ball mill.

[b] C, conventional ball mill.

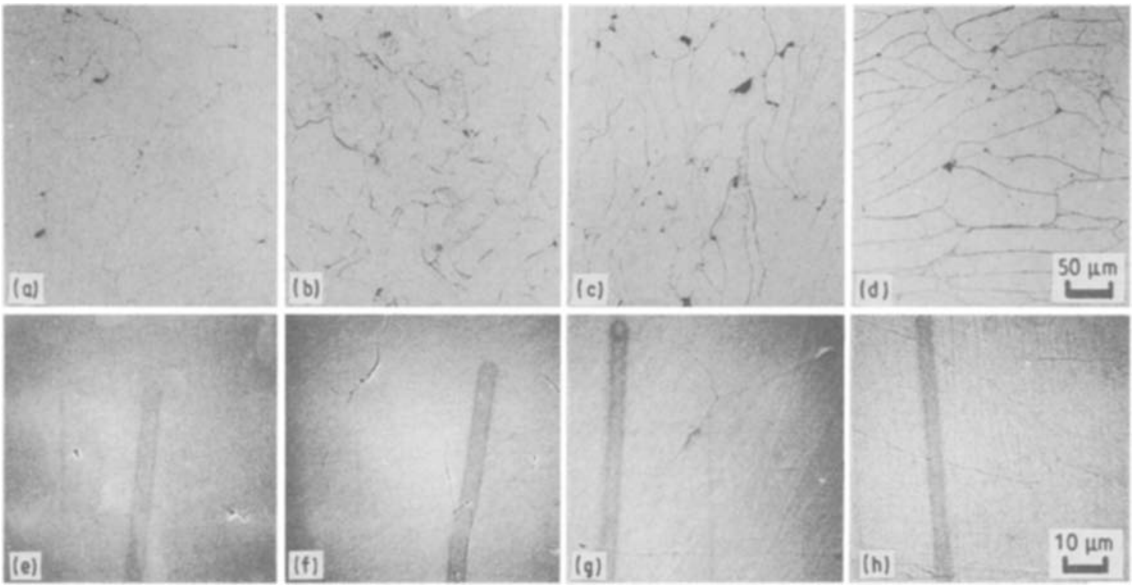

Figure 4 Micrographs of cross-sections of amorphous alloy compacts. (a–d) Optical micrographs after being etched for 10 s with 6% nital; (e–h) scanning electron micrographs after being mechanically polished but without being etched. Dark lines about 8 µm wide are contamination deposits along which chemical analyses were carried out by EPMA (see Fig.5). (a, e) B1, (b, f) B2, (c, g) B3, (d, h) B4.

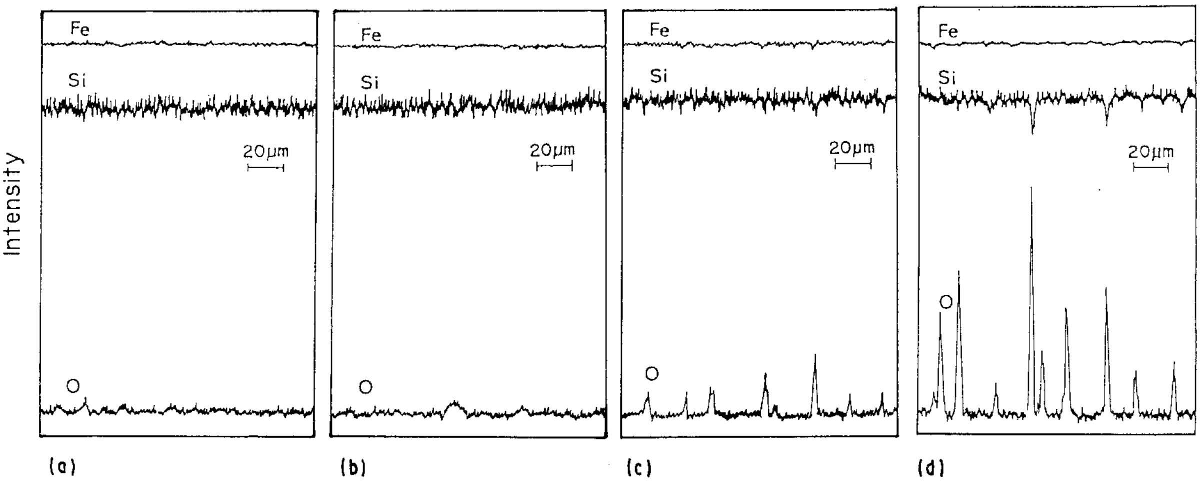

Figure 5 The amounts of iron, silicon and oxygen in the cross-sections of amorphous alloy compacts analysed by EPMA. (a) B1, (b) B2, (c) B3, (d) B4.

infrared absorption method. Oxygen contents in B1 or B2 were lower than those in B3 or B4 by a factor of three to five. This is in good agreement with the results on the distribution of oxygen measured by EPMA.

Comparison of Tables I and II shows that the oxygen contents of amorphous alloy compacts were low only when both processes of powdering and consolidation were carried out in an argon atmosphere. This can be seen clearly in the case of B5; compact B5 was consolidated in air from amorphous alloy powders P2 which had been prepared by low-temperature milling for 4 min in an argon atmosphere. The oxygen content in B5 was as high as that of B3 which was treated in air throughout all the processes.

3.3. TEM observation of interparticle boundaries in amorphous alloy compacts

TEM observation was carried out in order to characterize the interparticle boundaries in amorphous alloy compacts. Fig. 6 shows TEM images of the vicinity of interparticle boundaries in compacts (a)B1, (b)B2 and (c)B4. In B4, which was consolidated in air from the powders milled at room temperature, crystallized regions (denoted Cry.), composed of many microcrystals smaller than 10 nm in size, existed near the interparticle boundaries, the width ranging from 100–200 nm. These microcrystals seemed to be formed by a local temperature rise in the surfaces of the powders while being milled at room temperature. In B1 and B2, which were prepared from powders milled in an argon atmosphere at low temperature, such crystallized regions were observed only rarely.

It is evident that nucleation of crystals at the surfaces of the powders during milling was suppressed at low temperature and that the oxidation during milling and consolidation was suppressed in an inert atmosphere. Region A shown in Fig. 6a and b corresponds to direct bonding between Fe–B–Si amorphous powders themselves. Such regions were hardly observed in B4. The region O shown in Fig. 6a was amorphous phase and may be an oxide film.

3.4. Compressive strength of amorphous alloy compacts

The amorphous alloy compacts were deformed in compression at room temperature. The stress–strain curves are shown in Fig. 7. In all the cases studied,

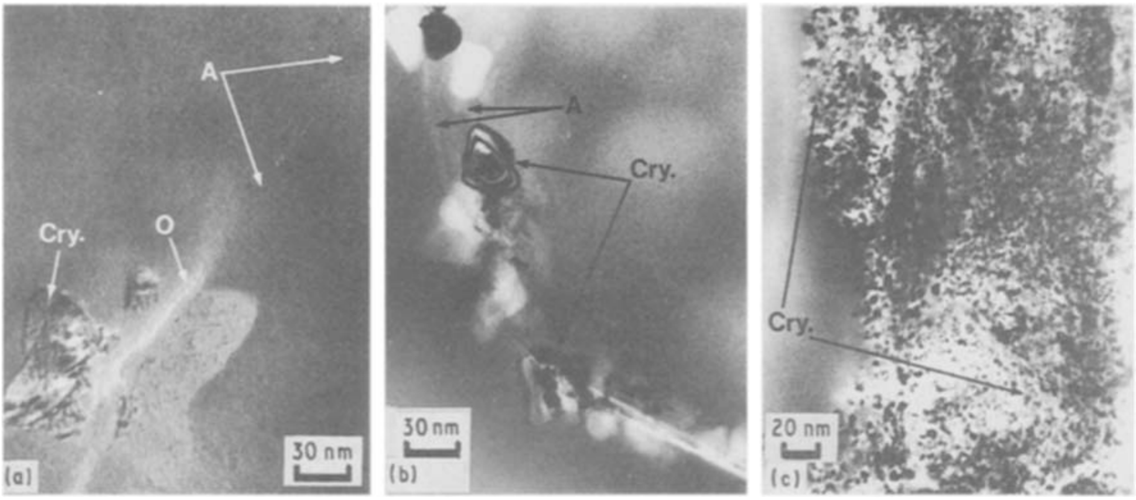

Figure 6 Transmission electron micrographs of interparticle boundaries in amorphous alloy compacts. (a) B1, (b) B2, (c) B4.

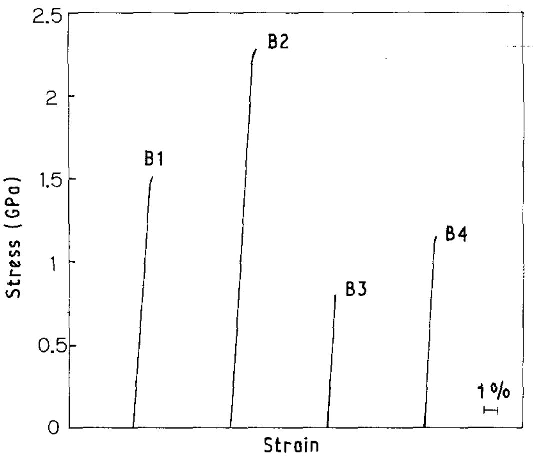

Figure 7 Stress–strain curves of amorphous alloy compacts as measured in compression tests at room temperature. $\varepsilon = 8.33 \times 10^{-5}\,s^{-1}$.

specimens fractured before plastic deformation occurred. Compacts B1 and B2, prepared in an argon atmosphere, had higher strength than B3 and B4, prepared in air. In particular, B2, which was prepared from P3 milled for 8 min, showed the highest value of 2.28 GPa.

SEM images of the fracture surface of the compacts are shown in Fig. 8. In the fracture surfaces of B3 and B4, the shape of the original powder particles could be recognized; this indicates that interparticle fracture was dominant. In the case of B2, which had the highest strength, flat fracture surfaces with vein patterns stretched by shear stress were observed; this indicates that transparticle fracture was dominant. The morphology of the fracture surface of B1 is between these two extremes, and showed a mixture of transparticle and interparticle fracture.

These features of the morphology of the fracture surfaces are in good agreement with the measurement of the compressive strength.

4. Discussion

It is clear that the strength of amorphous alloy compacts is improved substantially by reducing the amounts of oxide films and microcrystals at the interfaces. This can be seen from the fact that the strengths of B1 and B2 are higher than those of B3 and B4 (cf. Fig. 7 and Table II). In this respect, the present technique is very useful in preparing high-strength amorphous alloy compacts.

However, it must be said that the present technique, as it is, is insufficient to remove oxide films and microcrystals at the interfaces completely. This is clear from micrographs shown in Figs 4 and 6, and also from the results of elemental analyses (Table II and Fig. 5). Under these circumstances, the morphology of the starting powders may also affect the strength of the resulting compacts considerably. For example, the strength of B2 is higher than that of B1 by a factor of 1.5 (cf. Fig. 7 and Table II), despite the fact that the amount of oxygen in B2 is slightly higher than in B1. This simply indicates that the amount of oxygen, and hence oxide films at the interface, is not the sole factor controlling the strength of amorphous alloy compacts.

B1 was made of P2, while B2 was made of P3 (Table II). Both P2 and P3 were milled at low temperature in an argon atmosphere, but the former was milled for 4 min and the latter for 8 min (Table I). The surface morphology of P3 was much more complicated than that of P2 (cf. Fig. 3). As a result, the microstructure of B2 was more complicated than that of B1 (compare Fig. 4a and b), and this suggests that mechanical interlocking between powders is stronger in B2 than in B1. Therefore, the strength of B2 is probably higher than that of B1, and this is exactly what was observed.

5. Conclusions

A new technique was developed where all the processes for preparing amorphous alloy compacts were carried out in an argon atmosphere, and the properties of the powders and compacts thus prepared were studied. The following results were obtained.

1. When amorphous alloy powders were prepared by crushing amorphous alloy ribbons at liquid-nitrogen temperature in an argon atmosphere using a planetary ball mill, oxidation and crystallization at the surfaces of the powders were suppressed significantly, compared with those crushed at room temperature in air.

2. Oxidation and crystallization at the interparticle boundaries could be suppressed only when all the processes, from powdering to consolidation, were carried out in an inert atmosphere. The oxygen content of those compacts which were processed in an argon

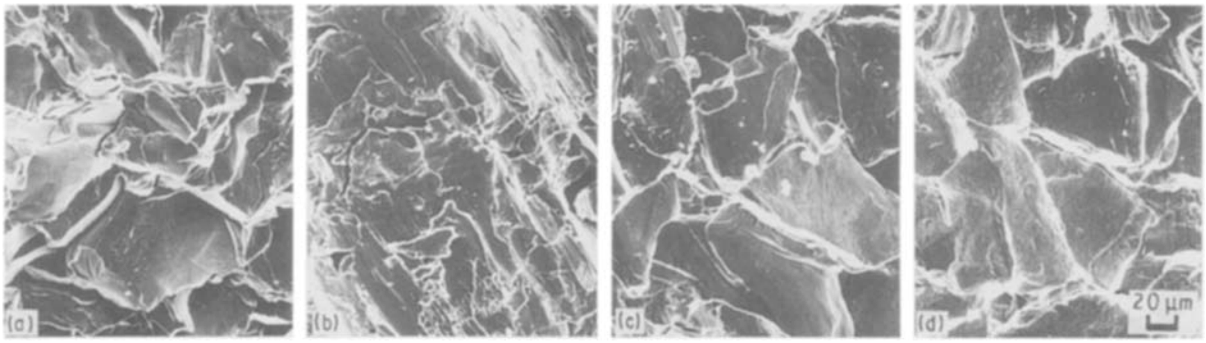

Figure 8 Scanning electron micrographs of fracture surfaces of amorphous alloy compacts after compression tests. (a) B1, (b) B2, (c) B3, (d) B4.

atmosphere was lower by a factor of three to five than that of those prepared conventionally in air.

3. Compressive strength of these amorphous alloy compacts, which were processed in an argon atmosphere, was higher by a factor of 130%–200% than that of the compacts prepared in air.

4. It is concluded that suppression of oxidation and crystallization at the interparticle interfaces is crucial to improve the strength of amorphous alloy compacts.

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