JOURNAL OF MATERIALS SCIENCE 22 (1987) 23–26

Preparation of amorphous composite materials

GILLES NUSSBAUM, DIETER G. AST
Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

Composite materials consisting of an amorphous $Ni_{75}B_{17}Si_8$ matrix and containing one or two reinforcing tungsten wire(s) were prepared by a modified melt-spinning technique. With this method it was possible to incorporate a single 10, 26 and 60 μm wire in the entire length of an amorphous ribbon, as well as two 26 μm wires. The process is continuous and allows the preparation of arbitrarily long composite ribbons.

1. Introduction

Because of their attractive mechanical properties, composite materials are extensively used in engineering. Thus, it is surprising that, up to now, there have been few reports on composites using metallic glasses as constituents.

A patent was filed by Narasimhan [1] on the preparation of amorphous ribbons containing hard second-phase particles for abrasive purposes. The particles were added to the charge prior to melting. Zielinski and Ast [2–5] produced ribbons of amorphous nickel-based alloys containing tungsten, silver and WC particles by injecting these particles with a flow of inert gas into the melt puddle. These authors found that the presence of a second phase could almost double the yield strength of the ribbons.

Shimanuki *et al.* [6] and Raman and Witt [7] have described how they modified a melt-spinning apparatus to produce laminated ribbons of two different amorphous compositions.

Jones [8] reports that amorphous alloys have been successfully bonded to matrices of epoxy resin and aluminium–calcium–zinc alloy. The presence of metallic glasses in mortar and cement also reinforce these materials [9].

Battelle researchers [10] have filed a patent on the preparation of amorphous ribbons reinforced by a wire, but the patent does not indicate if such materials have actually been produced.

On the other hand, ribbons containing an embedded wire are shown by Zielinski and Ast [3]. The authors simply fastened one end of the wire to a support using adhesive tape, while the other was floating freely over the drum. Upon casting, the wire was caught by the freezing melt and fed over the wheel.

This method has several disadvantages. The first one is the dimension of the apparatus when one wants to make longer ribbons (for a semi-continuous production). The absence of tension on the wire results in a lack of lateral control, and the wire may run on the surface or along one edge of ribbons prepared in this way. When we tried to introduce several wires with this method, the wires entangled and we found cross-sections of samples where as many as twelve wires were visible.

In the first section of this article, it will be shown that one or several small wires, completely embedded, do not significantly modify the cooling rate of a melt-spun ribbon. We will then describe how we modified the melt-spinning apparatus to produce amorphous ribbons containing one or several tungsten wires, and we will describe the composite ribbons obtained.

2. Heat transfers

The way in which second-phase particles modify the area of contact between the ribbon and the drum has previously been discussed [3] and similar considerations apply to wires. The relative quantity of the second phase, its wettability by the matrix and the pressure of the argon flow that extrudes the melt out of the crucible are the parameters that determine the magnitude of heat-transfer changes.

Let us assume that the wire is totally embedded, i.e. the contact between the ribbon and the drum is not modified. As in Narasimhan [1], we assume that the heat flow is perpendicular to the surface of the ribbon, but consider that the ribbon of width l contains a wire whose diameter is d. In the calculation, we replace, for reason of simplicity, the circular wire by a square one with the same section and width d. The heat transfer coefficient U_w is given by

$$\frac{U_w}{U_0} = 1 + \frac{d}{l}\frac{\pi}{4}\frac{1 - k_w/k_m}{1/hk_m d + t/d + (\pi/4)(k_w/k_m - 1)} \tag{1}$$

where l is the width and t the thickness of the ribbon, U_0 is the heat transfer coefficient in the absence of wire, k_m and k_w are the heat capacities of the matrix and the wire respectively, and h the heat transfer coefficient between the ribbon and the drum.

A limiting case would be a fibre of thickness a and width l embedded in ribbon of the same width. In this case the overall coefficient U_f is

$$\frac{U_0}{U_f} = 1 + \frac{a}{t}\frac{k_f/k_m - 1}{1/htk_m + 1} \tag{2}$$

where k_f is the heat transfer coefficient of the fibre.

If we take the same values as Narasimhan [1] and Chin Huang and Fiedler [11], i.e. $h = 6.3 \times 10^5\,W\,m^{-2}K^{-1}$, $k_m = 21\,W\,mK^{-1}$, $t = 40\,\mu m$, $l = 4\,mm$

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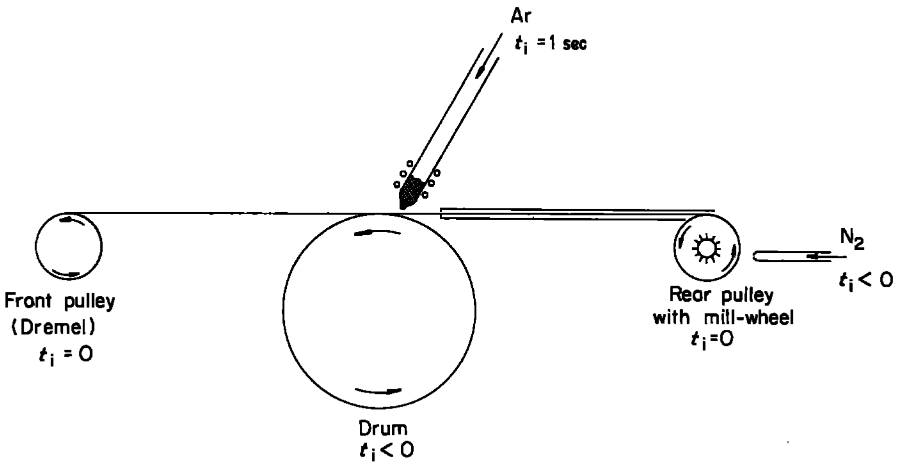

Figure 1 Schematic representation of the modified melt-spinning set-up used to prepare composite ribbons. The activating time of each device has been reported as t_i.

and $a = d = 10\,\mu$m, we see that, as for particles, the ratio U_w/U_0 remains very close to unity in the case of a wire. In the case of a ribbon U_r/U_0 will change from unity very rapidly as the thickness of the ribbon or the ratio k_f/k_m increases. In other words, the presence of one or a small number of wires, embedded in the ribbon, does not drastically change the cooling rate. The main factor remains the contact of the ribbon on the wheel surface that can account for variations as large as 60% [9, 11]. On the other hand, if a wide ribbon of fibre, or another melt-spun amorphous ribbon, must be incorporated one might consider the possibility of building a double drum set-up to improve heat extraction.

3. Description of the apparatus

In our set-up, the wire is supplied by a 2.5 in. (63.5 mm) poly(vinyl chloride) (PVC) wheel. From this wheel the wire runs over the drum, under the crucible, and is taken up by another PVC pully, similar to the first one. This pulley, thereafter called the front pulley, is driven by a small electric motor (a Dremel tool), whose speed is adjustable. To precisely locate the wire under the centre of the crucible, it is guided by a tapered quartz tube in the section between the rear pulley and the drum. The wire is unguided in the section between the casting wheel and the front pulley (Fig. 1).

In order to maintain the proper tension in the wire during acceleration and casting, an aerodynamic drag wheel was fitted on the shaft of the supply wheel. The drag exerted by this wheel was controlled by blowing argon of regulated pressure against the vanes. By trial and error, the drag was set to an optimum value which prevented entanglement and maintained a tension short of fracture in the wire. This tension keeps the wire straight and inside the ribbon.

The experiment then proceeds as a regular melt-spinning experiment. The switch activating the front pulley motor is connected to an adjustable delay relay that in turn activates the valve admitting high-pressure argon into the crucible expelling the melt. This relay delayed the opening of the valve by one second. The delay allows the wire to reach its assigned steady speed before the casting of the alloy takes place.

When the melt reaches the drum and solidifies, the wire is embedded in the freezing ribbon. Once this occurs, the speed of the wire is no longer controlled by the front pulley but by the casting drum. To prevent speed fluctuations resulting in fracture and to permit proper winding of the wire around the front pulley, the speed of the wire must be set as close as possible to the linear velocity of the casting drum.

4. Performances of the apparatus

With this apparatus we have been able to produce ribbons containing one and two tungsten wires of diameter 26 μm (Fig. 2), or one 60 μm wire, all along the ribbon. However, the two 26 μm wires, originally spooled from a single grooved supply pulley, were found to cross over many times in the cast ribbon.

The tungsten wire we used had a fracture strength of 400 kg mm^{-2} at room temperature. The forces exerted on the wire depend on the acceleration of the front pulley and the inertia of the supply wheel. In our set-up they exceed the breaking strength of a single 10 μm wire.

In order to both separate two wires and incorporate a single 10 μm wire in the ribbons we carried out the following modifications:

(i) We replaced the rear single-groove pulley by a double-groove PVC pulley.

(ii) When casting with two wires, we kept the two wires separate until they reached the front pulley.

(iii) Later, to facilitate the spooling up of the as-cast ribbon, we replaced the front pulley by a lightweight

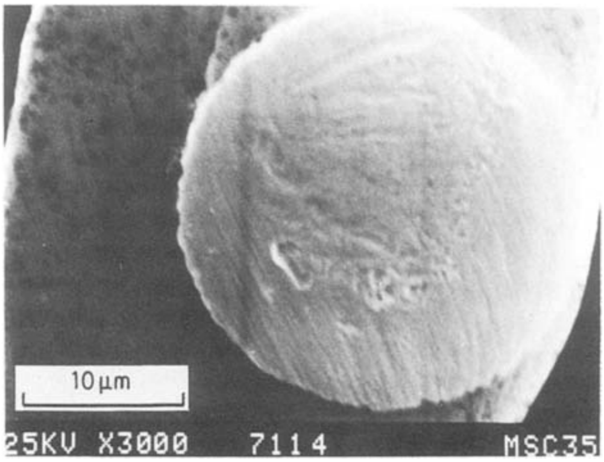

Figure 2 SEM cross-section of an amorphous ribbon containing a single 26 μm tungsten wire.

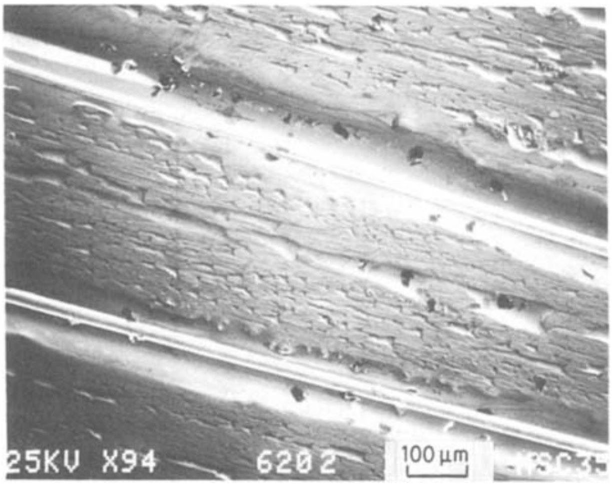

Figure 3 SEM micrograph of the dull (wheel) surface of a ribbon containing two 26 μm tungsten wires. The total length of the section where the wires were embedded was about 1.8 m.

drum of the same diameter but 60 mm wide. By adjusting the apparatus, we were able to produce ductile amorphous ribbons of good surface morphology with cast-in tungsten wires, wound on the drum [12]. With this new set-up, we produced ribbons containing two 26 μm wires, separated all the way along (Fig. 3) without any crossings.

(iv) Next, we separated the dual function of the wire(s), which serves as a mechanical coupling between front and rear pulley and as a reinforcing fibre. This was done by using a section of sturdy 60 μm wire to couple the two pulleys temporarily during the acceleration phase. This wire bypassed the casting drum. In this way, single 10 μm wires could be embedded into ribbons (Fig. 4).

5. Ribbon morphology

The samples prepared were inspected by optical microscopy as well as by scanning electron microscopy, using a JEOL JSM 35 microscope, which was also used to study composition in the electron diffraction and X-ray spectroscopy (EDS) mode. Both surfaces of the ribbons and cross-sections were investigated.

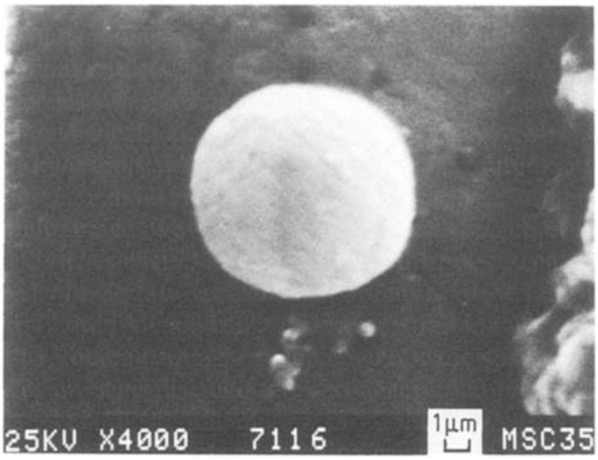

Figure 4 SEM cross-section of a ribbon containing a single 10 μm tungsten wire. To prepare this sample, about 60 cm long, a larger wire was used to start the supply wheel.

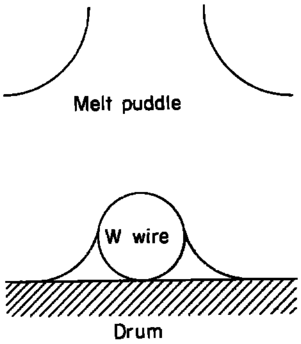

Figure 5 Ribbon–drum contact under the crucible while incorporating a wire in an amorphous ribbon.

5.1. Unaided examination

Ribbons 30 to 40 μm thick containing 26 μm wires tended to split along the wires. Some brittle zones and even holes were also seen along the wires. This indicates that the presence of the wire does modify the cooling rate of some zones of the ribbons, by creating voids between the ribbon and the drum, most likely by dragging air along and thus altering the ribbon–drum contact. Similar features were observed on the ribbons cast with a single 60 μm wire.

However, by reducing the speed of rotation of the drum to 1200 r.p.m. (surface speed of 20 m sec^{-1}), we were able to produce thicker ribbons (50 to 60 μm). The wire, still 26 μm in diameter, was no longer visible in its entire length on the dull (wheel) surface of the ribbon but could occasionally be seen on the free surface and, in other sections, was totally embedded. These ribbons were not fragile along the wire, nor did they contain any defects such as holes or brittle zones. For comparison, the critical thickness for formation of $Ni_{75}B_{17}Si_8$ amorphous ribbon is 225 μm [13].

5.2. Microscopy of the samples

The optical microscopy of the dull surface of ribbons containing one or two 26 μm wires revealed that, at those sections where the wire was not embedded, a strip of surrounding material appeared as shiny as the free surface (Fig. 3). It is believed that this shiny strip was solidified at a lower cooling rate, possibly because air entrapment prevented good contact with the drum. The tiny area of contact between the wire and the drum does not allow the wire to evacuate the heat of the surrounding area.

It can be seen in Fig. 5 that the presence of the wire can substantially reduce the cross-section of a thin ribbon. Also, due to the slower cooling rate of the material in the shiny strip, some crystallites might form there, subsequently embrittling the ribbon. A large wire, or two entangled wires, can produce a comparatively wide strip of slower cooled material.

X-ray analysis showed no widening of the matrix–Tungsten interface. In such a short time (about 2×10^{-4} sec [14]), no reaction nor diffusion is expected between the melt and the wire.

6. Summary and conclusion

A modified melt-spinning set-up was used to cast composite ribbons at speeds close to 20 m sec^{-1}. In this material the matrix is amorphous and the added phase is on one or two tungsten wires, 10 to 60 μm in diameter.

It appears that any kind of wire or continuous fibre of such dimensions could be embedded in an amorphous ribbon, if wetted by the melt. Non-wetting fibres, such as carbon fibres, have so far not been successfully incorporated. Efforts are now under way to modify the carbon-fibre surface to increase its wettability.

With few modifications, it should be possible to drive another amorphous ribbon and hopefully reproduce the results of Zielinski and Ast [4, 5].

The mechanical properties of the ribbons containing wires have not been investigated. Such studies, especially on composites with a crystallized matrix, are planned since mechanical data on the matrix behaviour at elevated temperature are available [12, 15].

Acknowledgements

This research was sponsored by the Office of Naval Research under Contract N00014-85-K-0006. The Material Science Center at Cornell provided additional funds and operates the central TEM facility used to study the microstructure. G.N. was also partly supported by the French Minister of Foreign Affairs.

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Received 16 October
and accepted 9 December 1985