

Solid State Amorphisation of the Platinum Metals

A REVIEW OF SOME RECENT PUBLICATIONS

The absence of crystal defects such as grain boundaries and dislocations in amorphous metals makes them interesting both for basic research and in many applications. The amorphous state tends to confer improved mechanical strength, high wear-, corrosion- and electrical-resistance, and soft magnetic behaviour. Amorphous materials can combine a range of these physical and magnetic properties which, due to the absence of specific intermetallic compounds, can be varied continuously by altering the composition of the alloy.

Until recently amorphous metallic materials were associated with rapid quenching of the melt, which is the usual method of preparation. Recently however, it has been demonstrated that it is possible to form amorphous alloys by reactions which occur in the solid state. An appreciable number of the solid state amorphisation reactions which have been studied to date, including some of the very earliest, have involved alloys of the platinum group metals.

The first solid state amorphisation reaction was reported in 1983, this being the reaction of hydrogen with crystalline Zr_3Rh leading to the formation of an amorphous hydride compound (1). At around the same time another group of investigators succeeded in producing an amorphous rhodium-silicon material by annealing a polycrystalline rhodium and an amorphous silicon bilayer at a temperature of 300°C (2). Following this it was shown that a similar process could occur in wholly polycrystalline metallic systems, when an amorphous alloy was formed by diffusion at the interface between thin layers (300Å) of gold and lanthanum, at temperatures between 50 and 80°C (3).

In melt spinning processes glass formation is expected to occur at compositions corresponding to deep eutectic points in the phase diagram. However, solid state amorphisation reactions

tend to take place at compositions which correspond to intermetallic compounds with high melting points.

A solid state amorphisation process depends critically on the fact that the amorphous phase has a free energy which is lower than the non-equilibrium state of the crystalline solid. Thus a thermodynamic driving force for the formation of the glassy phase exists. In solid state amorphisation by diffusion from thin layers, this driving force results from the large negative heat of mixing of the individual elements. The formation of the metastable amorphous phase, rather than more stable equilibrium crystalline phases, occurs as a result of kinetic considerations. For instance, solid state amorphisation between thin layers is more likely to occur where the diffusion of one element into the other is fast when compared with the self-diffusion of the elements. In this way the amorphous alloy forms long before the collective rearrangement of the two species, which is necessary for intermetallic nucleation, can occur.

Thin Film Diffusive Couples Incorporating Platinum Metals

Two recent papers from Cornell University, New York, deal with the formation, by solid state amorphisation, of glassy platinum-aluminium alloys by diffusion from thin films of the elemental metals.

In the first of these papers, platinum-aluminium thin film samples were prepared on sodium chloride substrates and oxidised silicon wafers by electron beam evaporation techniques, at a pressure of 5×10^{-7} Torr (4). Two types of sample were prepared: the first a co-evaporated platinum-aluminium amorphous alloy, 77 nm thick, overlaid with a 47 nm thick crystalline layer of pure aluminium, and the second a polycrystalline platinum-aluminium bilayer.

Heating the co-evaporated platinum-aluminium/aluminium sample rapidly to 220°C caused a number of transformed regions to form and grow. These result from the formation of amorphous islands in the still largely crystalline aluminium overlayer. All the amorphous regions appear to form simultaneously and thereafter their number remains constant. Complete amorphisation was achieved at a temperature of 450°C, at which point all the remaining aluminium was incorporated in the amorphous phase. The non-uniformity of the reaction was attributed to the presence of a non-uniform alumina layer at the aluminium/platinum-aluminium interface.

Observations of the platinum-aluminium bilayer showed that an amorphous layer was present between the two as-deposited polycrystalline films, indicating that transformation to the glassy phase can occur at temperatures around 70°C. As the temperature was raised, the amorphous region grew until limited by the crystallisation of the Al_3Pt_2 intermetallic compound at 450°C.

The composition of the amorphous phase varied between 60 and 75 atomic per cent aluminium.

In the second paper concerning solid state amorphisation of platinum-aluminium, multilayers comprising three aluminium layers (outside layers 15–25 nm thick and inside layer 20–35 nm thick) separated by two platinum layers (10 nm thick) were examined (5).

Amorphisation was achieved by heating the sample at a rate of 5°C/min and then holding it at 200°C for 15 minutes. Three samples were treated in this way, and subsequently heated to higher temperatures until crystallisation commenced. In the first sample, of measured composition 24 ± 4 atomic per cent platinum, the crystallisation temperature was around 360°C and the dominant phase was $\text{Pt}_8\text{Al}_{21}$. The second sample, containing 25 ± 4 atomic per cent platinum, crystallised at around 270°C to form, mainly, the PtAl_2 intermetallic compound. The third sample, of composition 36 ± 4 atomic per cent platinum, crystallised at the still lower temperature of 230°C to form mostly Pt_7Al_3 . Thus it was concluded that solid state amorphisation does occur in the platinum-aluminium

system at compositions between those of the equilibrium compounds $\text{Pt}_8\text{Al}_{21}$ and Pt_7Al_3 .

In both of the above publications the authors comment that at least one of the essential criteria for solid state amorphisation, namely a negative enthalpy of mixing of the constituent elements, is met in the platinum-aluminium system. However the proposed kinetic criterion for solid state amorphisation predicts the anomalous diffusion of one element. The first of the two papers reported the low temperature dissolution of aluminium in a co-evaporated platinum-aluminium alloy, indicating its role as the faster diffusing species. However, the aluminium impurity diffusion and platinum self-diffusion coefficients are within the same order of magnitude over a wide temperature range, showing that the proposed kinetic requirement for glassy phase formation at low temperatures is not satisfied.

Ball-Milled Alloys Containing Platinum Metals

Mechanical alloying was developed some years ago as a method of combining particular metals and non-metals, which were difficult to combine by more conventional methods. A typical mechanical alloying process involves the use of a high energy ball mill in which the metallic powder particles are repeatedly trapped by colliding balls, causing major deformation and cold welding. The successive deformation and welding of grains leads to a progressively refined lamellar-type of grain structure.

Reports of the production of glassy materials by ball milling elemental powders together suggest that the mechanism is essentially solid state amorphisation occurring by interdiffusion within layered composite powders. In solid state amorphisation reactions caused by ball milling intermetallic powders, the situation is slightly different. In this case the ball milling process must introduce sufficient free energy to render the intermetallic unstable with respect to the glassy phase. Diffusion can then occur at an increased rate due to local temperature rises caused by the milling action.

A recent publication from the University of Amsterdam reported the amorphisation of

palladium-zirconium alloys by ball milling (6). In these experiments a range of palladium-zirconium alloys were prepared by arc melting the constituents together, then crushing and milling the ingot. Milling was carried out under argon to prevent oxidation. The products of the milling process were examined by X-ray diffraction which showed that single phase amorphous $\text{Pd}_x\text{Zr}_{100-x}$ alloys were obtained, for $x > 45$. The upper limit for x was certainly greater than 60. For $x < 45$ a two phase material consisting of an amorphous phase and PdZr_2 intermetallic was formed.

In a further publication the same group of investigators considered the amorphisation of platinum-zirconium alloys by a high-energy ball milling process. Using X-ray diffraction and differential thermal analysis, they established the feasibility of amorphising $\text{Pt}_{33}\text{Zr}_{67}$ and $\text{Pt}_{50}\text{Zr}_{50}$ alloys by ball milling for about 270 hours, under an argon atmosphere (7).

Studies of the palladium/platinum-zirconium system represent an extreme test of the current models describing solid state amorphisation by ball milling (8). Palladium and platinum display the largest heats of mixing, and therefore form with zirconium the most stable intermetallic compounds. Despite the stability of the crystalline phases the ball milling process is still able to produce the metastable glassy state.

Future Work

The dimensions of amorphous materials which can be produced by the melt spinning route are limited by the need for extremely rapid quenching. Solid state amorphisation by diffusion from thin layers is similarly constrained by the thickness of a single amorphous layer, but it is possible to use a composite structure to produce a bulk glassy material. In the same way, solid state amorphisation by ball milling offers the possibility of producing bulk glassy alloys by an industrial scale process. The unusually high exothermic alloying reactions of the platinum group metals, with a range of other elements, and their correspondingly stable intermetallic compounds, do not in any way preclude their participation in such amorphisation reactions. In fact, the high

negative heat of mixing of a variety of metals with the platinum group metals appears to favour solid state amorphisation reactions, and is likely to ensure the inclusion of the platinum group metals in future work in this area. M.L.D.

References

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Palladium in a Thin-Film Hydrogen Sensor

There is a growing interest in the development of solid state devices for use as chemical sensors, and following the significant progress made in hydrogenated amorphous silicon thin-film transistor technology, the possibility of using devices based upon this as sensors has become very attractive.

A recent letter from the Istituto di Elettronica dello Stato Solido, CNR, Italy, describes the development of a palladium-gate thin-film transistor as a hydrogen sensor (L. Mariucci, A. Pecora, C. Puglia, C. Reita, G. Petrocco and G. Fortunato, *Jpn. J. Appl. Phys., Part 2 Lett.*, 1990, **29**, (12), L2357-L2359).

Although the electrical characteristics of a top-gate device are inferior to those of a bottom-gate one, the former was selected to meet the requirement of a gate electrode in direct contact with the environment. A 100 nm thick layer of palladium was sputter deposited onto the 9 nm thick silicon nitride employed as the gate insulator. This enables the device to respond in a relatively fast time and in a relatively stable and reproducible manner to hydrogen, and the investigation has shown that such devices are good enough for application as hydrogen sensors.