

Vitreous Palladium Alloys

LOW-TEMPERATURE MEASUREMENT IN A NUCLEAR ENVIRONMENT

The philosophy of conventional resistance thermometry places considerable emphasis on the ability of metallic sensing elements to be used and retained in a state which approaches crystalline perfection. The high-purity wires are carefully supported to avoid strain and are also carefully annealed to eliminate lattice defects. Only in this way can the relationship between temperature and electrical resistance be uniquely defined, and platinum is still primarily responsible for embodying this relationship in concrete form. Departures from this policy of perfection have hitherto been fairly marginal and have involved, for example, very slight alloying with other noble metals to strengthen the platinum wire for industrial applications, or perhaps the use of iron-rhodium alloys for low-temperature applications (1) where pure platinum behaves in an anomalous manner.

An alternative approach to the problems of resistance thermometry is obviously required in those situations where ionising radiations are encountered and where heavy neutron fluxes inflict permanent and progressive damage on conventional metallic sensing elements. A viewpoint diametrically opposed to conventional ideas suggests that the best resistance element for low-temperature measurement in a high neutron flux would already contain so many lattice defects that radiation damage could be ignored and any irreversible strains which occurred would have only a marginal defect upon measuring accuracy.

Vitreous Alloys for Resistance Thermometry

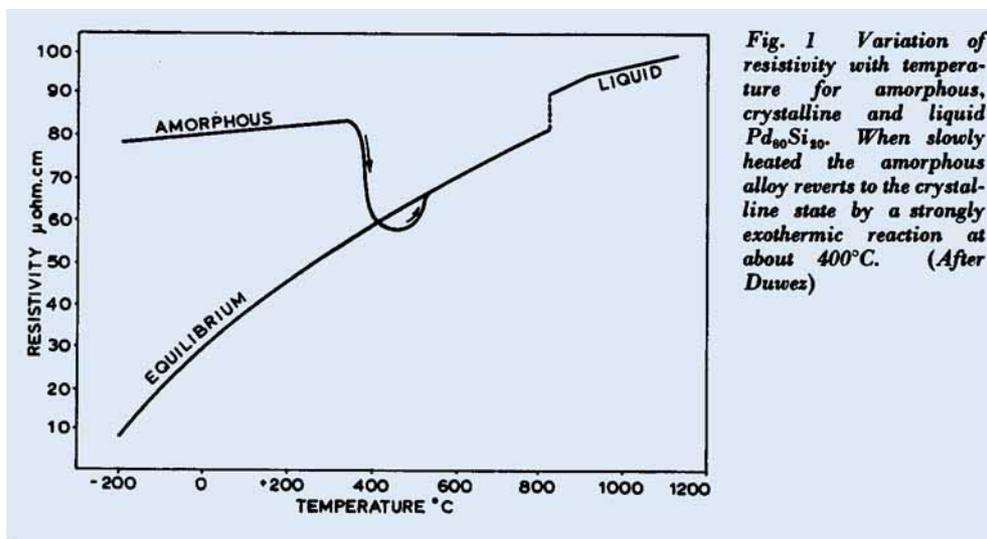
Liquid metals have a completely random structure which is not seriously affected by radiation damage. If this random or amorphous structure could be frozen into a solid

state it would form, therefore, a resistance element containing the maximum possible number of lattice defects and would, therefore, be relatively immune to radiation damage. The implications of this approach have been recently explored by C. R. Tallman (2) of the Los Alamos Laboratory of the University of California during the development of the nuclear rocket engines needed for the Nerva and Rover programmes. Severe problems were encountered in the measurement of cryogenic temperatures in these engines. In addition to damage caused by neutron bombardment, internal gamma heating caused errors which sometimes approached several tens of degrees, and it became necessary, therefore, to consider amorphous alloy resistance elements which were less severely affected than crystalline wires by neutrons and gamma fluxes.

Amorphous Noble Metal Alloys

The possibility of retaining, by extremely rapid solidification, the amorphous structure of liquid metals was first demonstrated in 1960 by Duwez et al. (3). The gold-silicon amorphous foils then produced were quite unstable at room temperature and some decomposition occurred even during X-ray examination. It was soon established, however, that those alloys most likely to respond to the rapid quenching treatment were those forming low melting point eutectics, and in particular those in which the packing density in the liquid state was higher than in the crystalline form so that expansion occurred on solidification. Typical examples of such alloys occurred in the gold-silicon, gold-germanium and gold-tin systems (4, 5).

Low melting point eutectics are also formed in the binary alloys of platinum and silicon, in platinum alloyed with germanium or anti-



mony, and in the alloys of rhodium with germanium (6). From all these platinum metal systems amorphous material can be retained by the extremely rapid solidification of compositions close to the eutectic. Among these binary alloys the palladium-silicon eutectic composition is noteworthy because of the stability of the vitreous phases obtained by solidification at cooling rates of the order of 10^5 deg C per second and above.

Although the palladium-silicon diagram is now known to be more complicated than was hitherto supposed (7), all the alloys containing 10 to 30 atomic per cent of silicon have a strong tendency to undercool (8). Amorphous phases can be successfully retained by rapidly quenching palladium alloys containing from 15 to 23 atomic per cent of silicon.

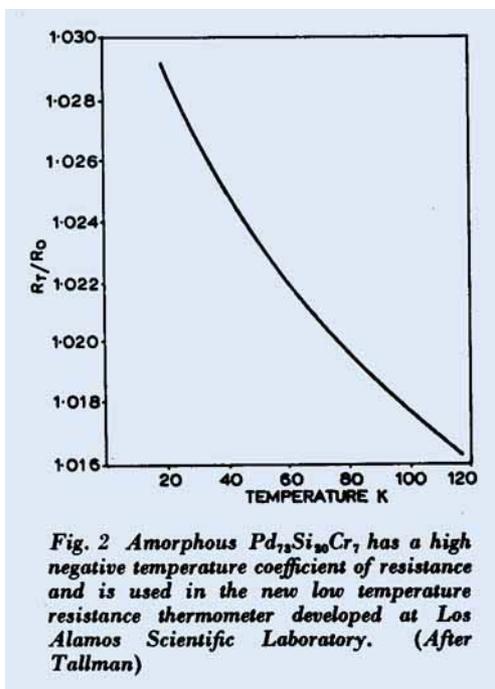
The resistance temperature curve of the $Pd_{80}Si_{20}$ amorphous alloy is contrasted with that of the crystalline material in Fig. 1. When slowly heated a strong exothermic reaction occurs at about $400^{\circ}C$ and the amorphous metal reverts to the crystalline state. The heat evolved, about 1000 cal/mole, compares with the latent heat of solidification of this alloy. Although $Pd_{80}Si_{20}$ retains its amorphous state for at least 15,000 hours at $250^{\circ}C$, its use as a resistance thermometer

material is not very feasible because of the very low temperature coefficient of resistance.

Palladium-Silicon-Chromium Alloys

The new resistance thermometer developed at the Los Alamos Scientific Laboratory uses an amorphous $Pd_{73}Si_{20}Cr_7$ alloy which has a high negative temperature coefficient of resistance even at very low temperatures. As shown by the curve on Fig. 2, the resistance ratio of the alloy decreases from 1.028 at 20 K to 1.016 at 120 K, and temperatures in the range 1.2 to 20 K can be readily monitored.

The remarkable effect of chromium on the electrical characteristics of these amorphous palladium-silicon alloys has been interpreted by Tallman in terms of the Kondo effect, which in crystalline materials manifests itself as a small low-temperature resistivity perturbation caused by the presence of very small concentrations of magnetic impurities in a non-magnetic matrix. This anomaly appears to be magnified considerably in an amorphous matrix, which discourages strong magnetic coupling between the chromium atoms, and allows them, by virtue of their individual magnetic moments, to scatter the conduction electrons very effectively. As



the temperature falls, these individual magnetic moments become less randomised, thus causing more scattering and accounting, therefore, for the strong negative temperature coefficient of the amorphous alloy.

Applications

The amorphous palladium-silicon-chromium alloy can be cold rolled into foil and cut into resistance elements by conventional press-tool techniques. The preparation of thin foil resistance thermometers which can be bonded on to substrates of very low thermal capacity is, therefore, fairly straightforward. Such elements, it is reported, have a high electrical stability even after prolonged cycling between 1 and 600 K.

Although unsuitable for resistance thermometers, the amorphous binary palladium-silicon alloy might possibly be used for making radiation-tolerant strain gauges or balance resistances in circuits subjected to intense radiation. In such applications its low-temperature coefficient of resistance would be of considerable value.

The whole subject of amorphous metal alloys is now of considerable theoretical and practical interest and it is becoming very apparent that quenched noble metal eutectic alloys provide the bridge between the crystalline and vitreous state which has so long been required. Since the pioneer experiments of Duwez in 1960 more than 200 technical papers have been published on this rapidly expanding subject and a recent bibliographical review (9) deserves very close attention.

The true nature of the amorphous state was considered in considerable detail during the Autumn Meetings of the Metallurgical Society of A.I.M.E. and of the A.S.M. held in October 1971, and two recent papers by Polk (10) and Turnbull (11) propose structural models for these metallic glasses that help to explain their visco-elastic behaviour. This can be simulated realistically by a geometrical structure based on random hard sphere packing. The large polyhedral voids inherent in such a structure (12) are conveniently occupied by metalloids atoms, thus explaining why approximately 20 atomic per cent of silicon or germanium, when added to palladium or rhodium, successfully stabilises the glassy condition.

A. S. D.

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