Tough Wear Resistant Alloys of Zirconium-Palladium-Ruthenium

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Most of the intermetallic compounds that crystallise in the atomically ordered body centred cubic configuration known as the B2-type structure are too brittle to permit bending or deformation without the risk of fracture. But there are a few compounds of this type that can be readily shaped and even drawn into wire. Notable among these is the B2-type compound NiTi (Nitinol) which is sufficiently ductile to be drawn into wire, and possesses some remarkable mechanical properties, such as its well-known "memory effect" (1) and its so-called "pseudoelastic" behaviour. The source of the unusual behaviour of this compound lies in a diffusionless (martensitic) phase transformation which normally occurs at or near room temperature when the compound is cooled, and importantly, can be induced by stress.

A martensitic transformation similar to that in NiTi occurs in the B2-type compound ZrPd, which is composed of elements from positions corresponding to those of titanium and nickel in the Periodic Table, except that they are from the second rather than the first long period. The compound ZrPd, unfortunately, transforms at 620°C and it is not notably ductile at room temperature. We were curious to see if ductility or some other interesting mechanical behaviour could be obtained in zirconium-palladium alloys simply by using ternary or quasi-binary additions to stabilise the high-temperature (austenitic) B2 structure at room temperature. Ruthenium was chosen as the third element since it combines with zirconium to form the compound ZrRu, of B2-type structure, which is stable from room temperature to its melting point. Furthermore, ruthenium atoms seemed likely to substitute freely for palladium atoms on the B2 lattice sites because of similarities in size and electronic structure.

Hardness measurements on a series of arc-melted alloys in the "cast" condition, see Figure 1, revealed a sharp minimum just prior to the onset of the martensitic transformation at room temperature (Figure 2). X-ray diffraction established that an extensive B2 solid solution exists from the composition ZrRu (x = 0) to approximately $Zr_{50}(Pd_{35}Ru_{15})$, (x = 0.7). A gradual but pronounced change from brittle to ductile behaviour was observed over this range, as the ratio of palladium to ruthenium atoms increased on the B2 lattice sites.

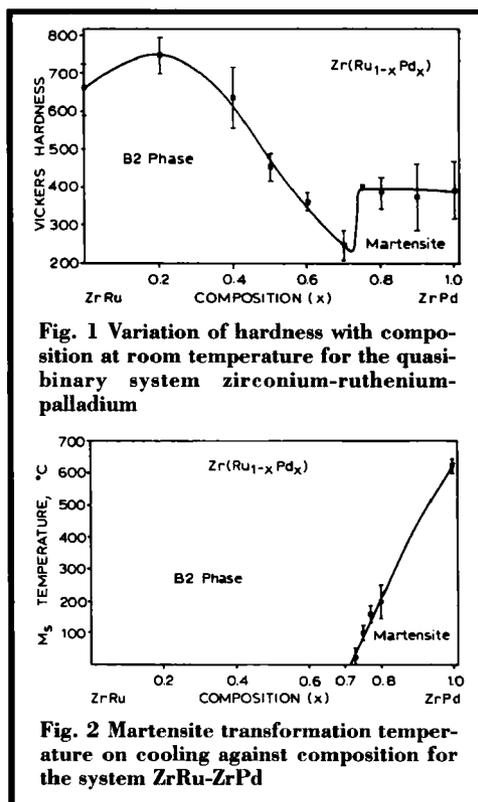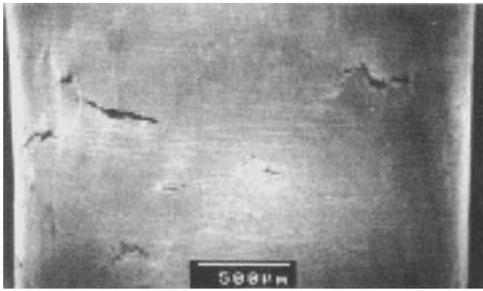A zone-melted $Zr_{50}(Pd_{35}Ru_{15})$ polycrystalline

Fig. 1 Variation of hardness with composition at room temperature for the quasi-binary system zirconium-ruthenium-palladium

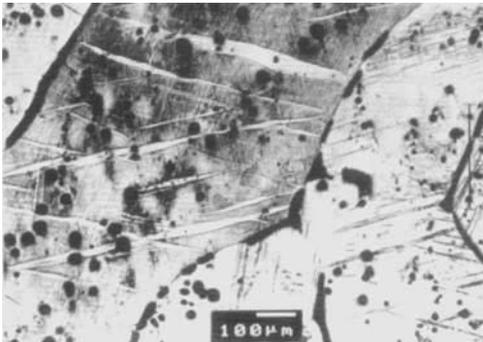
Fig. 2 Martensite transformation temperature on cooling against composition for the system ZrRu-ZrPd
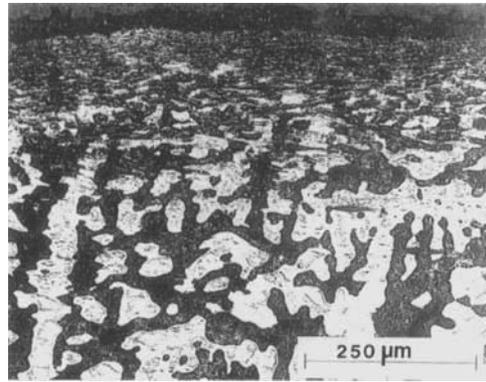
Fig. 3. SEM photograph of cracks in a fractured test bar of the cast alloy $Zr_{50}Pd_{35}Ru_{15}$

Fig. 5 Fibrous surface layer produced by machining the alloy $Zr_{50}Pd_{37.5}Ru_{12.5}$. Light areas are B2 solid solution of zirconium, palladium and ruthenium. Dark, palladium-rich interdendritic regions are composed of fine martensite formed on cooling after casting

bar, was tested in tension in the "as-melted" condition. It melted at 1760°C, but apparently not congruently, and there was considerable dendritic segregation. An elastic modulus of 74.9 GPa and a yield stress of 262.3 MPa were measured. The stress-strain curve showed some erratic behaviour, just after the onset of plastic flow, but the stress continued to increase until fracture occurred at 475.2 MPa. A total elongation of 6.6 per cent was observed (2, 3).

The fractured specimen, see Figure 3, had a number of transverse cracks along the axis of the sample which apparently had formed prior to fracture, but were somehow stabilised until one of them propagated elsewhere in the sample at a significantly higher stress. Light microscopy, see Figure 4, revealed that platelets had formed in the plastically deformed regions of the sample, but they were not present in the less-highly stressed regions more remote from the fracture. Electron microscopy revealed that

Fig. 4. Photomicrograph of a stressed region of the alloy $Zr_{50}Pd_{35}Ru_{15}$ showing twin bands and grain boundaries. The black areas are etch pits
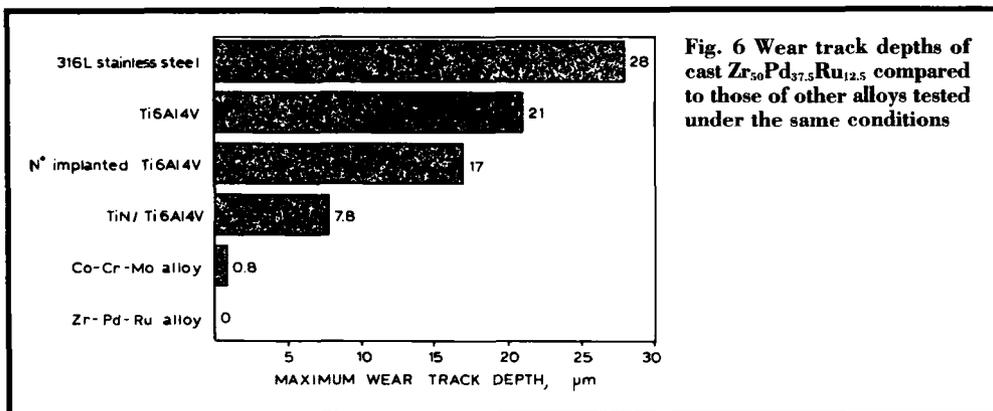
the platelets were mechanical twins of the {114} type. Dislocations of the <100> type also were observed (2, 3).

Another zone-refined polycrystalline bar of composition $Zr_{50}Pd_{37.5}Ru_{12.5}$ was tested in tension in the as-melted condition. Again, there was considerable dendritic segregation and this time the interdendritic regions contained large amounts of fine athermal martensite, of a CrB-type structure. The dendrite cores were composed of the austenitic B2-type solid solution.

A test bar of this alloy strongly resisted being cut in a lathe using an ordinary carbide cutting tool. The hardness of an uncut surface, however, was only about 250 khn; well within the normal range for machinable alloys. Light microscopy of a machined surface of this alloy, see Figure 5, revealed a thin, fibrous surface layer which consisted of a fine mixture of twins, martensite crystals and untransformed austenite (B2 phase). This layer was not present on uncut surfaces of the same alloy. It was suspected, therefore, that the twins and at least part of the martensite had been stress-induced by the action of the cutting tool. Grinding the surface did not produce a surface layer of this type and we were able to prepare test bars by grinding.

Wear testing of the alloy was performed according to a test protocol developed by a

316L stainless steel — 28
Ti6Al4V — 21
N* implanted Ti6Al4V — 17
TiN / Ti6Al4V — 7.8
Co-Cr-Mo alloy — 0.8
Zr-Pd-Ru alloy — 0

5   10   15   20   25   30
MAXIMUM WEAR TRACK DEPTH, μm

Fig. 6 Wear track depths of cast $Zr_{50}Pd_{37.5}Ru_{12.5}$ compared to those of other alloys tested under the same conditions

manufacturer of medical implants whereby the metal was placed in sliding contact with a poly-methyl methacrylate pin (4). Wear profiles of the zirconium-palladium-ruthenium alloy after 10^6 cycles, when compared, under the same test conditions, to those of alloys currently in use in such implants, revealed no net volume loss due to wear, whereas there is measurable wear for the other materials, see Figure 6. The slightly negative wear rate of the zirconium-palladium-ruthenium alloy may be due to the formation of ZrO_2. Similar results were obtained when the test was extended to 5×10^6 cycles (4).

Corrosion testing, by anodic polarisation methods at room temperature (5), gave the break-down potential of the zirconium-palladium-ruthenium alloy as 1.0 volts vs. saturated calomel electrode, which can be compared with 0.44 V for a commercial cobalt-chromium-molybdenum alloy and 2.4 V for a Ti6Al4V alloy. Further corrosion tests, wear tests, and tests of biocompatibility are now in progress. None of the elements present are known to produce toxic reactions in living tissues.

Measurements of thermal expansion with temperature showed that the athermal marten-sitic transformation in the zirconium-palladium-ruthenium alloys has a large hysteresis (~200°C) on heating and cooling. This large hysteretic behaviour suggests that the zirconium-palladium-ruthenium martensite is non-thermoelastic, in marked contrast to the thermoelastic martensite formed in the titanium-nickel system.

No evidence of the "memory effect" found in Nitinol alloys was found in the zirconium-palladium-ruthenium alloy.

In addition to the possible application of these alloys in medical implant devices, such as hip prostheses, it may be useful as an industrial coating for bearing surfaces and mechanical joints (6). Coating methods remain to be developed, however, and the effect of a variety of thermomechanical treatments on the mechanical properties must be explored before commercial products can be designed.

Acknowledgements

References

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