

Plastic Deformation and Fracture of Ruthenium Single Crystals

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At the present time ruthenium, with its hexagonal close packed lattice, does not find wide application in industry when compared with platinum and iridium, due to its poor workability and its unsatisfactory resistance to corrosion at elevated temperatures (1–3). However, its high melting point, 2250°C, and relatively low cost suggest that some ruthenium-based compounds might possibly be considered as high temperature materials for aerospace applications (4).

Ruthenium is of interest to materials science since it has a low value for the ratio of the lattice constants $c:a$ of 1.582 (1). In general hexagonal close packed metals obey an empirical rule, according to which structures with $c:a > \sqrt{(8/3)}$ display basal slip behaviour, while those with $c:a < \sqrt{(8/3)}$ show prismatic slip behaviour under deformation. The value of $c:a = \sqrt{(8/3)}$ is determined from geometric considerations of the atomic stacking in the hexagonal unit cell (5). The value for ruthenium lies between the $c:a$ ratio for titanium (1.587) and for beryllium (1.567) (1). Titanium is deformed at room temperature by prismatic slip while beryllium is deformed by means of basal slip, which is an exception to the empirical rule (5). Thus it would be very interesting to discover what is the main deformation mechanism in ruthenium single crystals at room temperature. This information may be helpful in specifying optimal regimes for processing ruthenium workpieces. Plastic deformation and fracture of ruthenium single crystals are considered here at room temperature.

Crystal Production

Large single crystals of ruthenium have been grown by electron beam melting at the Ekaterinburg Plant for Processing of Non-

Ferrous Metals, which is also the method for growing iridium crystals (6). They had sizes: 100 mm in length and 10 mm in diameter. The amounts of metallic impurities in compacted ruthenium workpieces for growing crystals and in the single crystals are given in the Table. X-ray analysis has shown that ruthenium crystals are grown along the c axis. Samples of single crystal ruthenium for use in mechanical tests have been cut from a large ruthenium crystal by means of spark erosion.

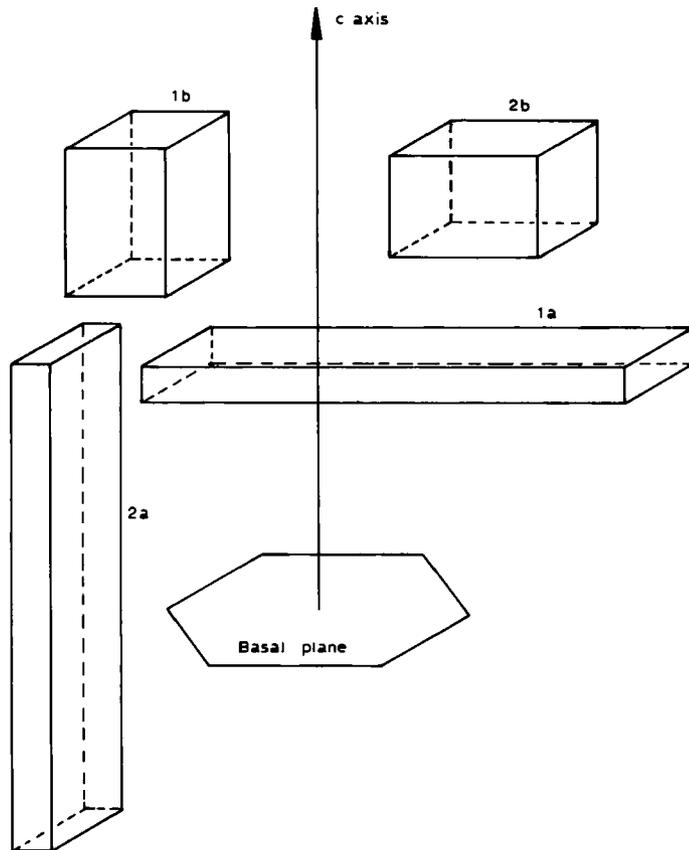
Crystals for tensile testing were parallelepipeds of size 10–15 × 2 × 0.5 mm, while crystals for compression were of size 3 × 2 × 2 mm. Mechanical tests were carried out at room temperature on Instron test machines; the traverse speed being 1 mm/min and hydraulic grips were used in tensile tests. Fracture surfaces of the crystals were examined by scanning electron microscopy.

The mechanical behaviour of single crystal samples with two orientations has been studied under both tensile and compression tests. The first orientation was favourable for basal slip and thus unsuitable for prismatic slip, while the second orientation was favourable for

Element	Scrap	Single crystal
Platinum	100	10
Iridium	800	140*
Rhodium	900	1
Palladium	–	1
Silver		1
Iron	\$	90*

\$ content of non-noble metals is approximately 300 ppm
* impurity has been estimated after analysis

Fig. 1 The crystal geometry of ruthenium single crystal specimens for tensile and compressive tests. Favourable orientation for basal slip (unfavourable for prismatic slip): 1a tensile axis is normal to c axis; 1b compression axis is parallel to c axis. Favourable orientation for prismatic slip (unfavourable for basal slip): 2a tensile axis is parallel to c axis; 2b compression axis is normal to c axis



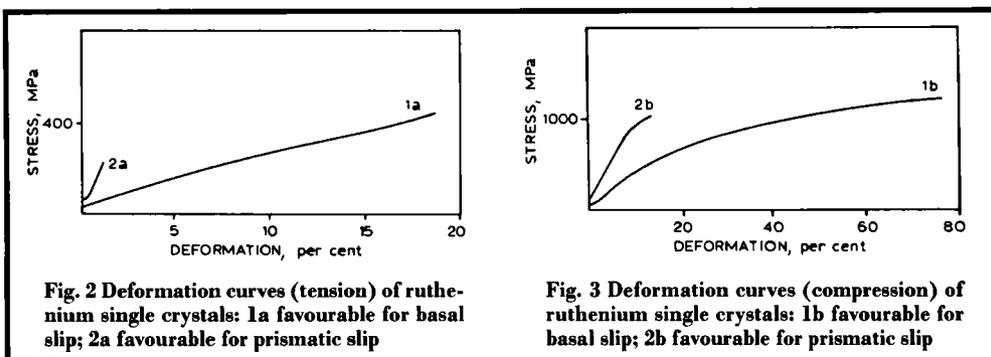
prismatic slip and unsuitable for basal slip. The crystal geometry of the samples is shown in Figure 1.

Results and Discussion

Deformation curves of tensile testing and compression for single crystal ruthenium samples are given in Figures 2 and 3, respectively. It is clear that crystals under tension, with orientation favourable for prismatic slip, fail without any preliminary plastic deformation. However, for crystals of orientation favourable to basal slip the deformation prior to failure can reach 20 per cent. In both cases, the fracture mode of the ruthenium crystals was attested as cleavage or brittle transcrystalline fracture, see Figure 4, and the morphology of the ruthenium crystal fracture surfaces resembled the mor-

phology of the fracture surfaces of iridium single crystals (7). Crystal geometry analysis shows that the fracture surface of these ruthenium crystals is macroscopically parallel to one of pyramidal planes.

Similar behaviour takes place during compression. Samples of ruthenium crystals with orientation favourable for basal slip can be deformed by up to 80 per cent of their original size. It should be noted that a number of small cracks appeared on their surfaces under loading, but this did not lead to single crystals being separated. Crystal samples with an orientation favourable for prismatic slip changed the direction of their compression after the application of load: they began to crack and fold, after which the crystals were deformed in the direction favourable for basal slip. Their fracture mode



was also attested as cleavage or brittle transcrystalline fracture.

The results obtained may be briefly summarised as follows. Ruthenium crystals with an orientation favourable for basal slip are deformed quite well under both tensile and compression tests, while the plasticity of single crystals having an unsuitable orientation for basal slip is poor. When doing this, “plastic” ruthenium samples fail by cleavage under tension and crack under compression. In addition, it should be pointed out that the “re-orientation” of the crystals from unsuitable to favourable for basal slip direction of compression, takes place during compression tests.

Similar mechanical behaviour can be observed in single crystals of hexagonal close packed metals, such as zinc, which are deformed by basal slip and cleave under tension. Therefore, these findings provide a basis for stating that at room temperature the main deformation mode in ruthenium single crystals is by basal slip*. However, some insignificant contributions to their plasticity may be brought about by alternative deformation mechanisms, such as mechanical twinning and both prismatic and pyramidal slip. Consequently, ruthenium is the next metal to beryllium in the Periodic Table with hexagonal close packed structure and a low c:a ratio, which is deformed by basal slip.

* By contrast in Ref. 8 it was stated that deformation of ruthenium occurs through slip along the planes of a prism, and the following arguments were presented: a low c:a ratio in ruthenium and observations of slip bands on the surfaces of compressed ruthenium single crystals.

This fact, contrasted with the above discussed empirical rule, will be the subject of further work.

At the present time, the physical mechanisms of cleavage in single crystals of hexagonal close packed metals are unclear; they may be connected with both features of crystal structure and the influence of impurities. As a rule, cleavage fracture is observed in metals having basal slip as the main deformation mode (5). Usually, brittle fracture in crystals of these metals is connected with an insufficient quantity of slip planes in the lattice. In agreeing with these arguments it may be concluded that the inclination to cleavage fracture is an inherent property of rutheni-

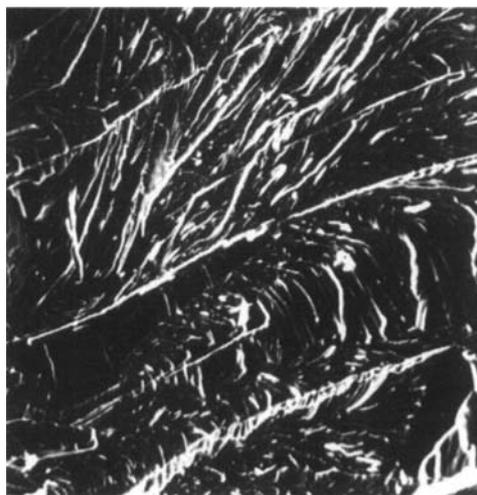


Fig. 4 SEM micrograph of the fracture surface of a ruthenium single crystal stretched at room temperature (orientation 1a). This fracture mode was confirmed as brittle transcrystalline fracture or cleavage

um single crystals. Indeed, experiments have shown that highly pure ruthenium single crystal workpieces crack during treatment at room

temperature. In so doing, the poor workability of polycrystalline ruthenium compacted from powder is caused by of different impurities.

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Extending the Life of Reactor Fuel Cladding Tubes

A number of factors determine the length of time that nuclear fuel rods can safely be left in pressurised water reactors, although it is generally accepted that the most important of these is waterside corrosion of the zirconium alloy cladding that contains the fuel. Over the past twenty years standard Zircaloy-4 tubes have performed satisfactorily in reactors throughout the world, but the economic and environmental constraints that determine the present day reactor operating parameters have changed somewhat, and now the fuel has to withstand more arduous working conditions for considerably longer times.

To ensure that fuel cladding materials are capable of meeting the requirements of reactor operators over the next decade a number of new zirconium alloys have already been developed. Now researchers in South Africa have reported the results of an investigation to establish if the oxidation resistance of Zircaloy-4 can be improved by alloying palladium into the surface layer ("Improvement in Oxidation Resistance of Zircaloy-4 by Surface Alloying with a Thin Layer of Palladium", G. A. Eloff, C. J. Greyling and P. E. Viljoen, *J. Nucl. Mater.*, 1993, 202, (3), 239-244).

A 2 μ m thick layer of palladium was electrodeposited onto the surface of test samples cut from standard fuel cladding tube material, which were then vacuum annealed at 950°C for various times to diffuse the palladium into the Zircaloy-4 before they were vacuum quenched to room temperature. Selected samples were then oxidised at 450°C, the rates of oxidation being monitored at intervals by determining the increases in weight of the samples.

The study showed that a substantial improvement in the short term oxidation resistance of

Zircaloy-4 was achieved when the electrodeposited palladium layer was diffused into the surface, by annealing for an optimum period of time. This resulted in a high concentration of intermetallic particles at the sub-grain boundaries of the α -Widmannstätten structured outer layer. It is suggested that this increases the plasticity of the oxide layer and permits a greater degree of deformation to take place before the onset of cracking occurs, from the outer surface of the oxide layer.

Platinum 1993 Interim Review

During 1993 it is estimated that consumer demand for platinum in the western world will grow by six per cent to 4.02 million ounces troy. Shipments of primary platinum are expected to grow to 4.21 million oz, so – despite a fall in Russian sales to a four-year low and reduced output from minor primary sources – a surplus of 190,000 oz will result. Demand for palladium amounting to 4.04 million oz will, however, exceed supplies by 100,000 oz. For rhodium, lower shipments and growing demand will leave the market virtually in balance. While a small increase in consumption of ruthenium is forecast, purchases of iridium are expected to be steady.

Supply and demand data, and a discussion of the many factors that determine the market for platinum metals, are presented and summarised in the latest issue of Johnson Matthey's twenty-four page illustrated publication "Platinum 1993 Interim Review".

Organisations requiring such information are invited to request a copy from: Alison Cowley, Johnson Matthey Precious Metals Division, New Garden House, 78 Hatton Garden, London EC1N 8JP, England; Fax 071-269 8389.