AEC-NASA TECH BRIEF

Oxide Film on Metal Substrate Reduced to Form Metal-Oxide—Metal Layer Structure

The problem:

To form an electrically conductive layer of zirconium on a zirconium-oxide film residing on a zirconium substrate.

The solution:

Reduce the oxide in a sodium–calcium solution at an elevated temperature so the reduced metal remains on the oxide surface as an adherent layer.

How it's done:

A zirconium alloy sample containing 1% copper by weight and 1% iron by weight is preoxidized to form a surface oxide layer. The surface of the oxide is reduced by exposure to liquid sodium saturated with calcium (94% sodium by weight and 6% calcium by weight) at a temperature near 600°C. A 20-hour exposure period is typical for a sample having an oxide thickness of about 10 microns. The reduction takes place in an argon-filled 100-ml autoclave. The oxidized zirconium sample is suspended by a stainless steel wire from the top plug of the autoclave. The autoclave is then sealed, inverted, and heated to the process temperature. At the end of exposure, the vessel is turned upright and allowed to cool. The sample is then withdrawn and cleaned in water.

The reduction process produces an adherent layer of zirconium on the outer surface of the oxide. This resultant adherent metallic layer is typically several microns thick and displays substantial electrical conductivity between test probes contacting the surface. The reduced layer is characteristically very hard, implying a high residual oxygen content. The layer is readily etched away on brief exposure to nitric–hydrofluoric acid solution, producing loss of conductivity between surface probes.

Notes:

1. The reduced metal layer appears to form a barrier that inhibits further reaction at the initially rapid rate.
2. The outer layer was found to be electrically shorted to the substrate metal, due probably to isolated cracks present in the oxide prior to reduction. If undesirable, such cracked areas might be sectioned out after reduction. Alternatively, use of thinner oxide films would minimize the occurrence of cracks. However, electrical leakage through the bulk oxide should be reduced by a thick insulating layer. Limitation of time and/or temperature during reduction, oxygen enrichment of the underlying metal surface, or substrate alloying to inhibit oxygen diffusion should also improve the insulating character of the oxide in the final layer structure.
3. The process does not depend on the particular alloy described. Surface reduction of unalloyed zirconium samples bearing corrosion films has also been accomplished by the technique described. Further, substrate materials other than zirconium might be susceptible to the technique, since the reduction of zirconium oxide is relatively difficult.
4. This method of metal-oxide–metal layer formation or the oxidation-back reduction approach may find application in the manufacture of integrated circuitry and similar thin-layer devices and structures.

(continued overleaf)

5. Inquiries concerning this innovation may be directed to:

   Office of Industrial Cooperation
   Argonne National Laboratory
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   Reference: B67-10187

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Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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