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REFRACTORY METAL TUBE DRAWING

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The invention relates to a novel method for cold drawing shapes of refractory metals, more particularly for cold drawing fuel tubes of zirconium, zirconium alloys, tantalum alloys, nibium alloys, vanadium alloys, and titanium alloys to reduce their size for use in nuclear reactors.

Zirconium and its alloys are desirable as structural metals in nuclear reactors due to the low neutron absorption cross-section and favorable mechanical and corrosion characteristics. When used to contain the nuclear fuel, tubes and other shapes must be drawn to very close tolerances in order to carry out the exacting designs of a reactor, and the surfaces must be free from scratches, nicks, and other such defects. Contact with the high temperature water or alkali metals in reactors makes even a slight defect a starting place for corrosion, and the severe thermal and mechanical stresses operating along the line of weakness of a scratch may cause a tube to rupture and release the dangerously radioactive fission products of the fuel into the reactor coolant.

Conventional cold drawing methods have not proved to be satisfactory for drawing zirconium and zirconium alloy tubes. Ordinary steel can be cold drawn through a die with a hydrocarbon lubricant, but this is not feasible for zirconium which seizes in the die and either tears or breaks. Certain plastics such as those of the polyacrylic type, particularly of the methacrylic type, which have been successful lubricants for stainless steel cold drawing, give fairly good results with zirconium, but even these sometimes fail at times and seizing takes place. In any case it is necessary to renew the plastic coating before every pass through the die, and this requirement, of course, slows the process and adds to the cost.

Copper plating is another method of lubricating zirconium and zirconium base alloy tubes for cold drawing, but as in the case of polyacrylic plastics, or as they are more commonly called, acrylic plastics, it is good for only one pass, and even then is not perfectly reliable. Small areas of the copper plating frequently flake off just before entering the die, thus permitting seizing with its undesirable consequences already mentioned.

The cost of recoating before each pass is especially burdensome in the case of copper plating, not only because of the electrolytic deposition itself, but also because of the etching to remove the residual plating, and the rinsing and drying steps.

It is accordingly the object of the invention to provide an economical method for cold drawing tubes made of zirconium and other refractory metals.

It is a more particular object to provide a method for cold drawing tubes of zirconium and zirconium alloys which will not require a recoating with a lubricant before each pass through the die.

The foregoing objects have been attained by our discovery that if zirconium, zirconium alloy, or other refractory metal tubing is coated with a thin coating of a plastic with dispersed copper, such as an acrylic enamel containing a comparatively small amount of metallic copper pigment, it may then be cold drawn in reducing dies without recoating for six passes or more, and the finished tube or other shape will be of accurate size without objectional scratches, nicks or other defects.

This permits the process of working down the tube diameter by stages in successively smaller dies, beginning with commercial tubing and ending up with tubing meeting the specifications for nuclear reactor use, and requiring only a routine annealing to remove the strains of cold working.

Several theories have been advanced to explain why copper and plastic, which were good as lubricants for only one pass through a die by themselves, in combination, produce a lubricant of such unexpected staying power, but as none of the explanations have been proved, it would serve no purpose to set them forth here. Our invention is offered on the basis of our empirical findings, established through actual experimentation.

In practicing our invention any of the plastics now used as lubricants in metal cold drawing may be used, when a dispersion of metallic copper powder of suitable size is added. The size of the particles does not appear to be critical, so long as it is left within the range where a true pigment dispersion can be made in the sense that the term is used in the enamel and lacquer art. Likewise the proportions of the pigment to the resin, the solvent, and to the propellant are not critical, so long as a thin, continuous enamel or lacquer coating is produced by spraying, leaving sufficient copper to enhance the lubricating properties in the way named. We have found suitable, and prefer a bright copper spray enamel having the following percentages by weight:

Copper powder pigment	5.23
Acrylic resin	3.41
Aromatic hydrocarbon and chlorinated hydrocarbon solvents	51.36
Fluorinated hydrocarbon propellant	40.00

The lubricant is preferably sprayed on; brushing produces a coating of uneven thickness and an uneven draw results. Dipping under controlled conditions and electrostatic coating may also be used.

No special modification of conventional cold drawing procedures are necessary when our novel lubricant is used. Of course, in addition to the lubricant it is advisable, as a practical matter, to have a coolant liquid flowing over the tube as it enters the die to remove the large amount of heat generated by the deformation of the metal. Any known coolant may be used such as water, a soap solution in water, or one of the commercially available chlorinated hydrocarbon cold drawing coolants.

Our process has been successfully carried out on tubes of substantially pure zirconium and on the following alloys:

Zircaloy-2=0.05% C, 1.5% Sn, 0.1% Fe, 0.05% Cr, 0.25% Ni, all by weight, and balance Zr.
Zircaloy-3=0.05% C, 0.25% Sn, 0.25% Fe, 0.05% Cr, 0.05% Ni, all by weight, and balance Zr.
1 w/o (weight percent) W, balance Ta.
5 w/o Ti, 20 w/o Nb, balance Va.
1 w/o Zr, balance Nb.
10 w/o Tr, 3 w/o Ta, balance Va.
10 w/o Ti, 3 w/o Nb, balance Va.

Example

A tube of Zircaloy-2, 0.375 inch O.D. and 0.325 inch I.D., was degreased in trichloroethylene and sprayed with a bright copper aerosol enamel until a thin, uniform coating was produced. The enamel consisted essentially of 5.23 w/o copper powder pigment, 3.41 w/o polymethylmethacrylate resin, 12.84 w/o toluene, 38.52 w/o trichloroethylene and 40.00 w/o Freon. The tube was passed successively without removing the coating, through

cold drawing dies of the following diameters in inches: 0.360, 0.345, 0.330, 0.314, and 0.300. A chlorinated hydrocarbon coolant sold under the trade name of J 50 was used to cool the tube as it passed through the dies. The lubricant was then removed and the tube cleaned with trichloroethylene, and the residual copper removed by immersing the tube in a 50% nitric acid solution for one minute. The tube was then rinsed in water, dried and annealed. It was found to have a uniform outer diameter of 0.300 inch, uniform wall thickness, and to be free of surface nicks and scarring.

It will be understood that this invention is not to be limited to the details given herein, but that it may be modified within the scope of the appended claim.

What is claimed is:

In the method of cold drawing a refractory metal shape selected from the class consisting of zirconium, zirconium alloys, tantalum alloys, niobium alloys, vanadium alloys and titanium alloys, wherein the shape is coated with a lubricant and drawn through a die, the improvement consisting of coating the bare shape by means of a lubricant-propellant consisting essentially of 5.23 weight percent copper powder, 3.41 weight percent acrylic resin, 51.36 weight percent aromatic hydrocarbon and chlorinated hydrocarbon solvents, and 40.00 weight percent fluorinated hydrocarbon propellant.

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