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Refractory metals Tungsten, Molybdenum and Tantalum *

The refractory metals tungsten, molybdenum and tantalum are employed in the electronic industry for the followin reasons:
The main reason is the good high temperature strength connected with the high melting point, the high purity, which can be attained in their industrial production, the low thermal expansion coefficient, important, for example, for sealin leads into glass or quartz, and in supports for semiconductor rectifiers, the good compatibility with a number of molten metals; in tantalum the possibility of producing by anodic oxidation very thin oxide layers with high dielectric constant and high electrical resistance as well as a very good chemical stability against electrolytes. The refractory metals tungsten, molybdenum and tantalum as well as their alloys and compound materials are still made for the most part by powdermetallurgical processes. Although the development of modern melting methods has made it possible in many cases to produce these metals by fusion methods, many materials used in electronics can only be made by powder metallurgy.

1. TECHNOLOGY

Metal powders, made by different methods and which must have a certain purity and physical properties such as particle shape, particle size, particle size distribution and flow behavior, in necessary, with addition of lubricants, alloying elements, dopants, thoria or other oxides, are pressed in steel dies or hydrostatically and sintered. The sintering is carried out preferably in a hydrogen atmosphere for molybdenum and tungsten, under high vacuum for tantalum. Originally, the high sintering temperatures required for Mo, W and Ta could be achieved only by direct resistance heating so that only rod could be sintered. With the development of the modern high temperature sintering furnaces, however, the more economical indirect sintering method has gained ground. It offers the additional advantage of being independent of the shape of the compacts and of permitting the sintering of large compacts. Depending on the pressure and the type of powder, the pressed compacts have porosities of 30 - 40% which are reduced to 2 - 8% by sintering. Further consolidation of

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the sintered compacts can be carried out by rolling, forging or swaging, to full density.

Almost theoretical density can also be attained by liquid phase sintering i.e., addition of a lower-melting phase which results in consolidation through solution and precipitation processes. Examples are the high-tungsten alloys W-Ni-Fe, W-Ni-Cu, W-Mo-Ni-Fe, the socalled heavy metals. In the porous refractory metals, where the porosity has a certain funcion, the lower limit is at 14 - 16% because below this porosity limit a large proportion of the pores is not interconnected. Examples are copper-infiltrated tungsten, porous tantalum electrodes. The upper porosity limit is usually determined by the required mechanical properties of the material.

During sintering, the compact is freed of undesired impurities; the sintering conditions must be such that particularly the impurities which are harmful in mechanical working and end use, are largely eliminated.

The properties primarily required by the electronic industry are achieved through the selection of the starting powders, additions, pressing and sintering conditions, subsequent working and thermal treatments; the practical experience with these materials then result in specifications for the different products, which must be adhered to within narrow limits.

2. THE MECHANICAL PROPERTIES OF TUNGSTEN, MOLYBDENUM AND TANTALUM

When the mechanical and chemical properties of the 3 refractory metals are considered, there is a basic difference between tantalum, on the one hand, and tungsten and molybdenum, on the other. This difference must be taken into account in the practical use of these metals.

1) The brittle-ductile transition temperature of tantalum is considerably below ambient; that of molybdenum is at -20 to 200-300°C, depending on structure, deformation history and thermal treatment; that of tungsten is 100-400°C. The upper values for Mo and W are situated in the recrystallization region.

2) Tantalum is conseguently worked only at room temperature; molybdenum, and. particularly, tungsten, and especially on bigger dimensions only at elevated temperature.

3) At elevated temperatures in air, oxide and nitride coatings form on tantalum which adhere tightly to the metal; part of the oxygen and nitrogen diffuses into the tantalum, making it harder and brittle.
Mo and W form oxide layers without dissolution of the oxygen and nitrogen in the base material. These oxide layers can be readily removed by pickling.

4) During fusion welding in a protective atmosphere or under vacuum, by different methods, a structure transformation naturally occurs in the fusion and weld zone and thus an alteration in the mechanical properties in these zones takes place. Whereas the ductility of tantalum is not affected in the

weld zone, Mo and W are embrittled, so that these metals can only be considered as conditionally weldable.

5) Tungsten and molybdenum in the wrought form exhibit, depending on the degree of working, an anisotropy of the mechanical properties; for example, in sheet, the strength at right angles to the rolling direction is less; cleavage in sheet or rod can occur during stamping or bending, for example. Tantalum does not exhibit this behavior.

6) Tantalum can be used at elevated temperature only in high vacuum or in a noble gas atmosphere because it reacts with hydrogen (embrittlement) whereas tungsten and molybdenum can be used under vacuum, in noble gases, hydrogen, nitrogen or hydrogen/nitrogen mixtures.

2.1. Tungsten

Tungsten is the metallic material of choice for high temperature applications and is employed in the electronic industry in the form of wire, ribbon, sheet and different shaped parts. For directly heated hot cathodes, the use of tungsten is based on the high working temperature, the good electron emission, and the good degassing properties; the electron emission can be increased, other conditions being equal, by addition of thoria, with the addiotional bonus that this increases the recrystallization temperature and the creep strength.

An important application of tungsten is based on its low thermal expansion which is similar to that of certain glasses so that tungsten can be used for sealing leads into glass. An important condition for this application is complete freedom from cracks and a special grinding treatment. The low thermal expansion, combined with the good electrical and thermal condictuvity, permit the use of tungsten in the form of discs as supports for semiconductor rectifiers; the discs are usually gold-plated.

An important cathode material is porous tungsten infiltrated with Ba-Ca aluminate. Tungsten powder of a certain particle size is pressed into a compact and, depending on end use requirements, it is sintered to a defined porosity. The sintered porosity is usually 18-24%. Because porous tungsten is difficult to machine and the pores are closed by machining, it is infiltrated with copper or other auxiliary metal, machined and then the copper is dissolved out from the porous component with acid. The component is then infiltrated with the aluminates.
The infiltrated tungsten electrode in the transmitter tube is indirectly heated with a tungsten element.

The brittle/ductile transition of tungsten can be varied to some extent by working and annealing. Al alloying element which greatly reduces the transition temperature, is rhenium. A general use of this method is limited owing to the high price of rhenium.

2.2. Molybdenum

The refractory metal molybdenum is employed when the outstanding high temperature properties of tungsten are not required. It is cheaper than tungsten, easier to work, and to machine and the brittle/ductile transition is lower.

In electron tubes, molybdenum wire, rod, or sheet is used in the form of functional or structural parts. A large proportion of the molybdenum wrought products i used in high temperature furnaces as heating elements and heat. shields. It is also used in the same way as tungsten for glass and quartz sealing and for semiconductor supports.

The electronic industry uses molybdenum mainly in the form of pure molybdenum. Special grades are Mo/W alloys, alloys with small additions of iron group metals, e.g., Mo alloyed with 300 - 400 ppm cobalt, to increase the yield strength-tensile strength, thus improving the working range of Mo wire.

A doped molybdenum, which can only be made by powder metallurgy, the HT-molybdenum, has a higher recrystallization-temperature and gets after heating a structure, similar to that of NS-tungsten. The HT-molybdenum is Mo doped with potassium silicate; its recrystallization temperature is considerably higher than that of pure Mo and at high temperatures, it forms an overlapping fiber structure similar to NS-tungsten. Mo wire with this structure can withstand a much greater number of bendings than recrystallized pure Mo wire. These NS-properties are developed only after a sufficient degree of deformation.

The molybdenum alloys, such as TZM, which is an alloy of Mo with Ti, Zr and C, and which are widely used in other branches of engineering, have practically found no application in electronic so far.

2.3. Tantalum

About 80% of all tantalum used directly or indirectly in electronic is empioyed in form of electrolytic capactiors; mostly as porous Ta electrodes with tantalum wire sintered in and, to a lesser extent, tantalum foil capacitors with welded-on tantalum wire. 7 micron thick, smooth foil or thicker foil which has been chemically etched to enlarge the surface, are used. A very pure tantalum powder with certain particle shape and size distribution is used to make porous Ta electrodes; the powder is pressed at low pressure with addition of organic lubricant under high vacuum. The area ot the internal surface determines the capacitance; the degree of porosity and the pore size affect the loss factor.

Small quantities of tantalum are used in form of wire, sheet and shaped parts for transmitter tube grids. These applications are based on the ductitlity, weldability and gettering effect of the tantalum.