

# UNITED STATES PATENT OFFICE

2,678,272

## MOLYBDENUM-COLUMBIUM ALLOYS

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No Drawing. Application October 6, 1951,  
Serial No. 250,207

13 Claims. (Cl. 75-176)

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The present invention relates to alloys of molybdenum and columbium which are capable of being worked at elevated temperatures by forging, pressing, rolling, extrusion and other similar methods. This invention is also concerned with molybdenum-columbium alloys containing minor quantities of other elements and to such alloys in which a part of the molybdenum has been replaced by tungsten. Such alloys are useful, in general, in applications which require high strength and hardness at elevated temperatures and more specifically in such applications as electrodes for heating molten glass, die-casting dies for brass and other metals, etc. This application is a continuation-in-part of Applicants' copending application, Serial No. 218,523, filed March 30, 1951, now abandoned.

It is one of the objects of the present invention to provide improved molybdenum-base alloys which are capable of being worked at elevated temperatures.

A further object of this invention is to provide molybdenum-base alloys which are superior to molybdenum in strength and hardness both at room and elevated temperatures.

A still further object of the invention is to provide molybdenum-base alloys which retain at elevated temperatures, hardening induced by working at elevated temperatures and in which the carbide phase is dispersed by the addition of the alloying element.

A further object is to provide cast molybdenum-base alloys having the above advantages.

The terms "cast" and "casting" as used in this specification are intended to designate the product resulting from the melting of metal and solidifying the same in a mold, whether or not the metal has been subjected to subsequent working or machining. The term "casting" is also used to designate any process or method which involves melting metal and solidifying the same in a mold.

In accordance with this invention, molybdenum alloys having the above-mentioned properties are produced when columbium is used as an alloying element. While such alloys may be produced by pressing and sintering metal powders; the preferred alloys of the present invention are produced by casting since it has not been found practical to produce pieces of large cross section by pressing and sintering. Cast alloys of molybdenum and columbium are capable of being worked at elevated temperatures only when the alloy contains limited amounts of oxygen and columbium.

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It has previously been established that the presence of minute amounts of oxygen in a casting of molybdenum or a molybdenum-base alloy seriously impairs or destroys the capacity of the casting to be worked at elevated temperatures if the oxygen is segregated at the grain boundaries in the form of certain metallic oxides. The detrimental oxide is visible on microscopic examination of intergranular fractures and is believed to consist largely of  $\text{MoO}_2$ . However, the oxides of certain other metals, if present, are also detrimental. In any event, when examined microscopically, castings which can be worked at elevated temperatures have no visible oxide segregations at the grain boundaries which are similar to the manifestations of  $\text{MoO}_2$ . Cast molybdenum containing less than about .001% oxygen can be worked at elevated temperatures but it is very difficult in the production of cast ingots of molybdenum and its alloys to reduce the oxygen content of the metal to such a low value.

As set forth in Frederick P. Bens et al., Patent No. 2,580,273, the detrimental oxide segregation is not found in molybdenum castings containing not more than .005% oxygen if small amounts of carbon are present. Such castings can be worked at elevated temperatures.

It is now found that the detrimental oxides may also be eliminated by incorporating in the casting certain metals which have a stronger affinity for oxygen than does molybdenum and form oxides which either do not segregate at the grain boundaries or, if segregated at the boundaries, provide greater intergranular cohesion than does the oxide of molybdenum. Aluminum and beryllium have been found to fulfill these requirements, and forgeable castings of molybdenum and molybdenum-base alloys containing up to a maximum of .05% oxygen have been produced by incorporating small quantities of aluminum or beryllium or both in the casting. Carbon may also be present, if desired, and small quantities of carbon or aluminum are particularly beneficial in molybdenum-base alloys containing beryllium.

The effect of oxygen on the molybdenum-columbium alloy castings of the present invention is similar to its effect in other molybdenum-base alloy castings, and consequently it is necessary to eliminate segregations of molybdenum oxide at the grain boundaries if the casting is to be worked at elevated temperatures. This is preferably done by incorporating carbon, aluminum or beryllium in the alloy, either singly or in com-