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METHOD FOR PROCESSING OF REFRACTORY METALS

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This invention relates to the reduction of refractory metals ingots to sheet form and, more particularly, to a method for converting refractory metal alloy ingots to a sheet form in which it can be further reduced by conventional methods.

The processing of high strength columbium base alloys from ingots to bar or sheet is complicated greatly by the relatively low resistance of these alloys to external oxidation and internal hardening by atmospheric gases. The selection of processing procedures such as protective atmospheres, working temperatures, heat treatment temperatures, and working reductions, are all critical in the production of an acceptable end product. The correct procedure for a particular alloy is not obvious to those skilled only in the general metallurgical art as evidenced by the lack of production of high strength columbium alloys.

It is the principal object of this invention to set forth specific procedures which have been discovered to allow successful production of high strength alloys heretofore considered unworkable.

A further object of this invention is to provide a method for converting cast refractory metal ingots into a form which can be further reduced by conventional methods.

It is another object to provide a practical method for converting arc cast refractory metals ingots to sheet form by a particular combination of extrusion and rolling steps coupled with significant heat treatment procedures.

These and other objects will be more apparent from the following detailed description which is not meant to limit the scope of the invention as defined in the appended claims.

Briefly, the method of this invention includes extruding an ingot into a substantially rectangular sheet bar at a temperature which enables a 2/1 to 6/1 reduction in thickness, heating to relieve stresses and to at least partially recrystallize the extruded sheet bar at a first heat treatment temperature, rolling to a total 50–70% reduction, heating to relieve stresses and to at least partially recrystallize the rolled material at a second heat treatment temperature, rolling to a total 50–70% reduction, heating to relieve stresses and to at least partially recrystallize the rolled structure at a third heat treatment temperature and then further reducing the thickness of the rolled sheet by conventional methods conducted at temperatures below about 900° C.

This invention will be better understood from the following illustrative examples which are not meant as limitations on the broad scope of the invention.

A 2½" diameter consumable electrode for a standard arc melting furnace was prepared from a columbium base alloy consisting essentially, in percent by weight, of .04–0.3C, 4–20Mo, 4–20W, 0.1–1.8Zr, with the balance essentially columbium. This material was vacuum cast into an ingot of 6" diameter.

In order to protect the ingot from atmospheric contamination such as from oxygen and nitrogen during heating and working, the ingot was jacketed or encased

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with molybdenum by conventional jacketing method so that the external dimensions of the jacketed ingot coincided with the extrusion press chamber of an extrusion machine. Other jackets or coatings can be used provided they have the same approximate strength and deformation characteristics as the refractory metals alloy being extruded. Otherwise, the jacket or coating will strip off during extrusion. A preferred thickness for a molybdenum jacket is about ⅛" wall thickness to provide protection during all of the processing above about 900° C.

After jacketing, the ingot is reduced in thickness by about 2/1 to 6/1 by extruding through a standard extrusion die into a rectangular sheet bar at a temperature of about 1500–1650° C. The lower 1500° C. extrusion temperature is merely a function of the force available in current equipment and can possibly be reduced through the use of stronger materials in the extrusion machine thus to enable the application of a greater force to an ingot which has not been heated as high as 1500° C. After extrusion the ingot is heated in a non-oxidizing atmosphere or a vacuum for about ½–1½ hours at a first heat treatment temperature of about 1350–1600° C. to relieve stresses from the extrusion operation and to at least partially recrystallize the extruded structure.

In the above described and the subsequently described heat treatments for the purpose of both stress relief as well as recrystallization, the time at temperature is more dependent on the rate of recrystallization than upon the relief of stresses because the stresses can be relieved in some cases in as little time as about 15 minutes at temperature. Higher heat treatment temperatures will require shorter time and lower temperatures will require longer times to relieve the stresses and to recrystallize the structure. The minimum practical heat treatment temperature would be that at which recrystallization occurs in a practical length of time. With the columbium base alloy mentioned above, it has been found that above about 1650° C. there is formed a coarse grained structure which can be detrimental to certain subsequent forming operations. In addition, the upper limit for the heat treatment temperature is that at which excessive grain growth and contamination occurs. In the alloy discussed, heat treatment temperature below about 1350° C. results in inadequate recrystallization.

The stress relieved and recrystallized sheet bar is then reduced 50–70% total reduction by a first rolling operation after heating in a non-oxidizing atmosphere such as argon at a temperature of about 1200–1350° C. Although this rolling operation can be conducted at a temperature as low as about 1200° C., as a practical matter, below about 1250° C. a high scrap loss will occur. Rolling above about 1350° C. results in loss of the molybdenum protective jacket and contamination of the columbium by atmospheric gases. No compensating benefit is gained by the use of a higher temperature. Several passes through the roll dies are usually required in order to achieve the 50–70% reduction; however no stress relief annealing is required between passes for this degree of reduction. The material is merely heated to the rolling temperature and then passed through the rolls to give a percent reduction per pass of 10–25%.

After the first rolling operation, the material is again heated in a non-oxidizing atmosphere for about ½ to 1½ hours at a second heat treatment temperature of about 1350–1450° C. to again relieve stresses and to at least partially recrystallize the rolled material. Below

about 1350° C. grain growth occurs at an impractical rate and above about 1450° C. excessive grain growth results.

After this second heat treatment, the material is again reduced 50-70% total reduction by a second rolling operation after heating in a non-oxidizing atmosphere such as argon, this time at a temperature of about 1000-1150° C.

The material is then heat treated for the third time to again relieve stresses and to recrystallize the structure. This third heat treatment is conducted in a non-oxidizing atmosphere for about ½-1½ hours at about 1300-1400° C. for the same reasons as given above.

After this procedure, the material is now in a condition in which it can be further reduced to whatever extent is desired by the many well known conventional forming or rolling methods at temperatures at which no danger of contamination from atmospheric gases is present.

A specifically preferred method for processing a strong columbium base alloy known as F-48 alloy consisting, in percent by weight, of 0.08C, 5Mo, 15W, 1Zr with the balance essentially columbium was first to vacuum arc cast the alloy into a 6" diameter ingot, 16" long. In order to produce a 0.020-0.080" thick sheet, the ingot was first reduced 4/1 by extruding after heating at 1550° C. in argon to a 1¼" x 4" rectangular sheet bar. The sheet bar was then heated for one hour at about 1550° C. in argon to stress relief anneal and to recrystallize the extruded material. After this heat treatment, the sheet bar was rolled after heating in argon at 1350° C. in four passes, one pass per heat, the bar being reduced from 1.25" to 0.50" for about a 60% reduction. It was again heated for one hour, this time at 1370° C. in argon to stress relief anneal and recrystallize the rolled material.

The 0.50" thick sheet was further reduced to about 0.20" (about a 60% reduction) by rolling after heating in argon at 1100° C. in 5 passes, one pass per heat. Then it was heated at 1370° C. for one hour to relieve stresses and to recrystallize the rolled structure. The annealed and recrystallized 0.20" thick sheet material was then in a condition to be further reduced such as to 0.05" sheet by conventional rolling techniques.

One such conventional method satisfactorily used with this invention included first rolling the 0.20" sheet for a 50-70% reduction such as to 0.100" at 600-700° C. and preferably 675° C. The 0.100" sheet was then sand blasted and acid pickled to remove the molybdenum jacket. One pickling procedure which has been used and found practical was to place the sheet in a solution of, in parts by weight, 60HNO₃, 10HF (50% concentration) and 30H₂O until visible reaction stopped. Any high molybdenum concentration layer at the surface of the sheet was removed by immersion in a solution of, in parts by weight, 60H₂O, 20HNO₃ and 20HF (50% concentration) to remove 1 mil per side in about 20 minutes.

The pickled 0.100" thick sheet was then heat treated for an hour at 1150-1250° C. and preferably 1200° C. either in a high vacuum such as less than 1 micron pressure, or in argon with some standard protective coatings, in order to relieve stresses in the sheet due to rolling. No recrystallization of the sheet structure is necessary during this conventional processing. If protective coatings are to be removed, the above described sand blasting and pickling procedure can be repeated.

The annealed 0.100" thick sheet was then rolled to 0.050" at 650-675° C. after which it was cleaned of scale and annealed as described above.

Although this invention has been described in connection with specific examples, one skilled in the art of metallurgy, heat treatment and metals manufacture will recognize the modifications and variations of which this invention is capable, particularly in relation to the physical characteristics of the refractory metals alloys being processed.

What is claimed is:

1. A method for processing a refractory metals ingot comprising the steps: coating the ingot with a material having the strength and deformation characteristics of the ingot material; heating the coated ingot to 1500-1650° C. and then extruding the heated ingot into a substantially rectangular sheet bar; heating the sheet bar at 1350-1600° C. to relieve stresses and to at least partially recrystallize the material of the sheet bar; heating the sheet bar at 1200-1350° C. and then rolling the heated sheet bar; heating the rolled sheet at 1350-1450° C. to relieve stresses and to at least partially recrystallize the rolled sheet; heating the rolled sheet at 1000-1150° C. and then further rolling the heated sheet; heating the further rolled sheet at 1300-1400° C. to relieve stresses and to at least partially recrystallize the further rolled sheet; and then further working the rolled sheet at temperatures at which no danger of contamination from atmospheric gases is present.

2. A method for processing a refractory metals ingot comprising the steps of: coating the ingot with a material having the strength and deformation characteristics of the ingot material; heating the coated ingot to 1500-1650° C. and then extruding the heated ingot into a substantially rectangular sheet bar; heating the sheet bar for ½-1½ hours at 1350-1600° C. to relieve stresses and to at least partially recrystallize the material of the sheet bar; heating the sheet bar at 1200-1350° C. and then rolling the heated sheet bar for a 50-70% reduction; heating the rolled sheet for ½-1½ hours at 1350-1450° C. to relieve stresses and to at least partially recrystallize the rolled sheet; heating the rolled sheet at 1000-1150° C. and then further rolling the heated sheet for a 50-70% reduction; heating the further rolled sheet for ½-1½ hours at 1300-1400° C. to relieve stresses and to at least partially recrystallize the further rolled sheet; and then further working the rolled sheet at temperatures at which no danger of contamination from atmospheric gases is present.

3. A method for processing a columbium base alloy ingot consisting essentially, in percent by weight, of 0.04-0.3C, 4-20Mo, 4-20W, 0.1-1.8Zr, with the balance essentially columbium comprising the steps of: coating the ingot with a material having the strength and deformation characteristics of the ingot material; heating the coated ingot to about 1550° C. in a non-oxidizing atmosphere and then extruding the heated ingot into a substantially rectangular sheet bar; heating the sheet bar for about 1 hour at about 1550° C. in a non-oxidizing atmosphere to relieve stresses and to at least partially recrystallize the material of the sheet bar; heating the sheet bar at about 1350° C. in a non-oxidizing atmosphere and then rolling the heated sheet bar for about a 60% reduction; heating the rolled sheet for about 1 hour at about 1370° C. in a non-oxidizing atmosphere to relieve stresses and to at least partially recrystallize the rolled sheet; heating the rolled sheet at about 1100° C. and then further rolling the heated rolled sheet for about a 60% reduction; heating the further rolled sheet for about 1 hour at about 1370° C. in a non-oxidizing atmosphere to relieve stresses and to at least partially recrystallize the further rolled sheet; and then further working the rolled sheet at a temperature below 900° C.

4. A method for processing a columbium alloy ingot comprising the steps of: coating the ingot with a material having the strength and deformation characteristics of the columbium alloy ingot; heating the coated ingot to 1500-1650° C. and then extruding the heated ingot into a substantially rectangular sheet bar; heating the sheet bar at a first temperature sufficient to relieve stresses and to at least partially recrystallize the sheet bar; heating the sheet bar at a second temperature lower than said first temperature and then rolling the heated sheet

bar into a sheet; heating the rolled sheet at a third temperature higher than said second temperature to relieve stresses and to at least partially recrystallize the rolled sheet; heating the rolled sheet at a fourth temperature lower than said third temperature and then further rolling the heated sheet; heating the further rolled sheet at a fifth temperature higher than said fourth temperature and sufficient to relieve stresses and to at least partially recrystallize the further rolled sheet; and then further

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working the rolled sheet at temperatures at which no danger of contamination from atmospheric gases is present.

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