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HIGH TEMPERATURE COLUMBIUM BASE ALLOYS

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This invention relates to novel columbium base alloys and to a method for making such alloys, and more particularly to new and improved columbium base alloys and to a method for making such alloys that possess both superior stress-rupture strength at high temperatures and a satisfactory low-temperature ductility that gives to them a range of utility that they were previously denied.

The principal limitation in gas turbine technology today is the maximum turbine inlet temperature. The maximum turbine inlet temperature is in turn set by the temperature that the turbine vanes and blades are able to withstand without danger of failure. Formerly, the best available high-temperature alloys were nickel and cobalt base superalloys, but critical structural components, such as turbine vanes and blades constructed from such alloys are limited to maximum operating temperatures of between 1600 and 1900° F.

Among the technically most important physical qualities of columbium as an alloy base are its high melting temperature (4380° F.) and its low neutron-capture cross-section. Columbium is, therefore, potentially useful for fast aircraft and space flight vehicles and in nuclear reactors.

For many years it has been generally known that the high temperature strength properties of metals are closely related to their melting points. Thus, metals having high melting points also tend to have high temperature strength potentials.

The need for structural materials for service at temperatures in excess of those obtainable with present materials of construction has stimulated interest in the refractory metals, particularly chromium, columbium, molybdenum, and tungsten. Until about 1957, molybdenum was considered the chief prospect for such usage. However, at the high temperature service conditions needed, molybdenum oxidizes at a catastrophic rate, principally because molybdenum oxide is volatile at elevated temperatures. Due to the very great problems encountered in attempts to coat molybdenum and problems in fabricating molybdenum, interest has recently shifted to columbium as an alloy base for high temperature service.

Columbium is inherently a soft, ductile, readily fabricable material. Although its melting temperature is about 4380° F., pure columbium becomes too weak for structural use at temperatures above 1200° F. Columbium is also a very reactive metal in that it dissolves large quantities of oxygen, and probably nitrogen, on exposure to atmospheres containing even small amounts of these elements at modest temperatures.

Although columbium suffers from oxidation, its oxide does not volatilize, and it is thus potentially possible to localize oxygen attack on columbium by coating the metal. Further advantages offered by columbium base alloys as compared with molybdenum base alloys are that columbium alloys are relatively more ductile and workable at low temperatures and columbium has a lower density than molybdenum.

Until recent years, estimated ore reserves of columbium were so small that there was only a mild interest in columbium base alloys. However, with the discovery

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of substantial ore bodies the potential availability of columbium has become so great that scarcity is no longer a restriction on its use.

The strength and oxidation resistance of pure columbium can be vastly improved by the addition of alloying elements. Unfortunately, a number of the best solid solution strengthening elements for alloying with columbium, such as tungsten and molybdenum, adversely affect its room-temperature ductility and fabricability.

It is uniquely demonstrated by this invention that processes well known to the state of the art for manufacture of refractory metals and their alloys to effect substantial improvement in low-temperature ductility, are limited relative to the improvement in low-temperature ductility compatible with retention of high-temperature structural stability and strength normally inherent in these metals and their alloys. This invention, then, pertains to processing methods that achieve an optimum balance between improved low-temperature ductility and retained stability of high-temperature strength inherent in, specifically, columbium alloys.

It is, therefore, a primary object of this invention to provide novel and improved columbium base alloys that possess both superior stress-rupture strength at high temperatures up to at least 2500° F. and that also have some useful ductility or improved ductility at low temperature.

It is another object of this invention to provide a process for making new and improved columbium base alloys of superior stress-rupture strength that lowers the brittle-to-ductile transition temperature of the alloys sufficiently to give them improved ductility, including in most cases at least some useful room-temperature ductility, without any detrimental effect on their stress-rupture strength.

A further object of this invention is to provide new and improved columbium base alloys and a process for making them that achieves alloys of superior stress-rupture strength at temperatures up to at least about 2500° F. without sacrificing their ductility at room-temperature.

Additional objects and advantages of the invention will be set forth in part in the description that follows, and in part will be obvious from the description, or may be learned by practice of the invention, the objects and advantages being realized and attained by means of the compositions and combinations particularly pointed out in the appended claims.

It has been found that the objects of this invention may be realized with a columbium base alloy containing tungsten and/or molybdenum in solid solution in amounts sufficient to significantly improve its stress-rupture strength at high temperatures, by heating the alloy, preferably after initial fabrication or breakdown and an intermediate annealing treatment have been completed, to a temperature in the range of from about 1800° to about 2800° F., and then subjecting the alloy in a specimen of a given thickness, while at such elevated temperature, to deformation forces so as to effect a final fabrication or plastic deformation of the alloy whereby the cross-sectional area of the alloy is substantially reduced. Columbium base alloys treated in the manner just described have been found to possess both satisfactory stress-rupture strength at high temperatures and a low-temperature ductility.

As used in this application the terms "initial fabrication" or "breakdown" are used in their conventional sense and mean the first fabrication to which an ingot is subjected after casting. An object of this "initial fabrication" is to reduce the thickness of the ingot to a more manageable dimension (generally from 33 to 80% reduction in thickness or cross-sectional area) preparatory to final fabrication. Initial fabrication of high temperature columbium alloys will usually be accomplished at a temperature of from about 1800° F. to about 3000° F.

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Also as used in this application, the term "intermediate process annealing" means the intermediate annealing heat treatment to which the alloy specimen is subjected after initial fabrication and before final fabrication. Unless otherwise indicated in this application, the process annealing step is conducted at a high enough temperature (2200°–3000° F.) and for a long enough time (1 hour) to effectuate substantially complete recrystallization or recovery of the alloy specimen thereby substantially eradicating any work hardening introduced during initial fabrication.

The columbium base alloys treated in accordance with this invention are those which have tungsten and/or molybdenum incorporated therein to improve their stress-rupture strength at elevated temperatures. When tungsten and molybdenum are added to columbium for improving its stress rupture-strength tungsten is generally added in an amount from 5 to 35% by weight, and preferably 20 to 30% by weight for significantly improved stress rupture-strength at temperatures of 2200° F. or above, while molybdenum is generally added in amount from 5 to 25% by weight, and preferably 10 to 20% by weight for significantly improved stress rupture-strength at temperatures of 2200° F. or above. Of course, when both tungsten and molybdenum are incorporated for this purpose, the amount of each employed may be lower than that indicated above, and in a preferred form of alloy the ratio of tungsten to molybdenum in percentage by weight is about three to one. Then, too, the columbium base alloys treated in accordance with this invention may contain amounts of other metals that may be normally added to columbium base alloys for improving the properties thereof such, for example, as tantalum in an amount from 0.5 to 40% by weight, and preferably 20 to 40% by weight, and the alloys may also contain either with or without tantalum an element from the group consisting of zirconium, hafnium, vanadium, and beryllium, in amounts of from 0.2 to 5% by weight each, but the total of such added elements in the alloys should not be more than 10% by weight.

The invention is particularly advantageous with respect to columbium base alloys having relatively high amounts of tungsten, e.g., over 20% by weight, or molybdenum e.g., over 10% by weight, or combined additions of these elements, e.g., over 10% expressed in terms of atomic concentration. Such alloys because of the inclusion of high amounts of tungsten and/or molybdenum exhibit very superior stress-rupture strength at elevated temperatures up to at least 2500° F. But, when made by conventional melting and casting techniques, such as an induction furnace or arc melting furnace using either consumable or non-consumable electrodes and not improved upon as provided by this invention, these alloys may be too brittle at room temperature to make them useful in such a primary application as turbine vanes or blades in a jet engine.

Quite surprisingly, however, when alloys of the type just described are treated in accordance with the present invention, such alloys possess not only outstanding stress-rupture strength at high temperatures but also a satisfactory low temperature ductility.

Examples of typical alloys which may be treated in accordance with this invention are now given, the parts being expressed as percentages by weight:

<i>Alloy 1</i>	
Columbium	75
Tungsten	20
Molybdenum	5

<i>Alloy 2</i>	
Columbium	57.6
Tantalum	20
Tungsten	18
Molybdenum	4.4

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<i>Alloy 3</i>	
Columbium	80
Tungsten	15
Molybdenum	5
<i>Alloy 4</i>	
Columbium	60
Tantalum	20
Tungsten	20
<i>Alloy 5</i>	
Columbium	75
Tungsten	25
<i>Alloy 6</i>	
Columbium	60
Tantalum	20
Tungsten	15
Molybdenum	5
<i>Alloy 7</i>	
Columbium	62.5
Tantalum	20
Tungsten	10
Molybdenum	7.5
<i>Alloy 8</i>	
Columbium	70
Tungsten	30
<i>Alloy 9</i>	
Columbium	77.5
Tungsten	15
Molybdenum	7.5
<i>Alloy 10</i>	
Columbium	40
Tantalum	40
Tungsten	20
<i>Alloy 11</i>	
Columbium	55
Tantalum	20
Tungsten	15
Molybdenum	10
<i>Alloy 12</i>	
Columbium	57.5
Tantalum	20
Tungsten	10
Molybdenum	12.5
<i>Alloy 13</i>	
Columbium	75
Tungsten	10
Molybdenum	15
<i>Alloy 14</i>	
Columbium	70
Tungsten	20
Molybdenum	10
<i>Alloy 15</i>	
Columbium	57
Tantalum	20
Tungsten	15
Molybdenum	5
Vanadium	3
<i>Alloy 16</i>	
Columbium	72.5
Tungsten	25
Molybdenum	2.5
<i>Alloy 17</i>	
Columbium	90
Molybdenum	10
<i>Alloy 18</i>	
Columbium	87.5
Molybdenum	12.5

As indicated above, in carrying out the process of this invention, the columbium base alloy is heated to a temperature from about 1800° to about 2800° F., preferably, but not necessarily, after an initial fabrication or break-down and intermediate annealing have been completed, and then the alloy of given cross-sectional area is subjected to deformation forces to effect plastic deformation whereby a substantial reduction in cross-sectional area is effectuated. Excellent results have been achieved where the reduction in cross-sectional area is in an amount of about at least 1/3 of the initial cross-sectional area (e.g., 33% to 98% reduction). Also, it has been found desirable to effect a greater reduction in cross-sectional area at lower temperatures. Thus, for example, when the temperature is about 1800° F. for good results, the plastic deformation step should provide a reduction of from about 60 to 90 percent. Best results concerning improved low temperature ductility compatible with structural stability and resistance to recrystallization for the alloys created by the method of this invention are obtained if a temperature of from about 2000° to 2600° F. and a plastic deformation or reduction of from about 60 to 95 percent are used. Generally, with the alloys of this invention, a temperature of about 2400° F. and a reduction of from about 60 to 95 percent provide the most preferred parameters and condition or stabilize the metallurgical structure and give the alloys superior properties of ductility at low temperature commensurate with stable strength characteristics during subsequent high-temperature fabrications or service.

When the alloys of this invention are treated by the process of this invention, their brittle-to-ductile transition temperature is significantly lowered and they thereby achieve superior low-temperature ductility. The alloys created by this process may thus attain an important range of utility previously denied to them, and be given a usefulness they could not achieve before, because in the past their relative brittleness at low-temperatures (e.g., room temperature) has prevented their use for many applications.

The columbium base alloys treated in accordance with this invention have good low-temperature ductility. A convenient measure of low-temperature ductility is the 4T ductile-to-brittle transition temperature, defined as the minimum temperature at which an alloy strip can be bent without cracking or fracture through an angle of 105 degrees with an included radius of curvature equal to four times the strip thickness. As will be evident from the discussion which appears below, the alloys treated in accordance with this invention show good low-temperature ductility when judged by the 4T ductile-to-brittle transition temperature criterion described above.

Unalloyed columbium exhibits a 4T transition temperature of about -320° F. Additions of tungsten and/or molybdenum increase the transition temperature as shown in Table 1 (below). The data of this application are seen to agree well with the tensile transition data reported by Begley and Bechtold, despite probable structural differences. It has been established that the spread between the 4T bend transition temperature and the minimum temperature at which the alloys retain useful tensile ductility is about 200° F. (tensile transition is lower) for alloys strengthened with molybdenum and about 300° F. (tensile transition is lower) with alloys strengthened primarily with tungsten, i.e., alloys containings twice as much tungsten on a weight percent basis as molybdenum, or more. As is taught in our copending application, Serial No. 65,962, filed October 31, 1960, now abandoned, Table 1 also shows the beneficial effect of the presence of tantalum in decreasing the transition temperature at a given tungsten and molybdenum strengthening level, or, conversely, in allowing a greater strengthener level (tungsten and molybdenum) for a given transition temperature. However, as shown by the results of Table 1, in alloys having a rather high amount of tungsten and

molybdenum, the resulting alloys do not have desirable low transition temperatures despite the fact that tantalum does serve to decrease the transition temperature of the alloys. It is desirable therefore to provide the process of this invention for reducing the transition temperature of alloys containing tungsten and molybdenum in significant amounts even though such alloys may contain tantalum which serves to reduce the transition temperature to some extent, while still retaining the superior high temperature strength inherent in such alloys.

TABLE 1.—EFFECT OF TUNGSTEN AND/OR MOLYBDENUM CONTENT ON 4T TRANSITION TEMPERATURE OF COLUMBIUM BASE ALLOYS

Tungsten Plus Molybdenum Content, Atomic percent	10 Percent Tensile Reduction in Area (Approx. range), ° F. ^a	4T Bend Transition Temperature, ° F. ^b	
		Tantalum-Free Alloys	Alloys Containing 20 Weight Percent Tantalum
0.....	-320.....	-320.....	-400.....
5.....	-200 to -15.....	-70.....	-140.....
10.....	50 to 390.....	200.....	130.....
12.....	250 to 570.....	290.....	220.....
14.....		380.....	310.....
16.....		460.....	400.....
18.....		530.....	480.....
20.....		590.....	

^a R. T. Begley and J. H. Bechtold, "Effect of Alloying on the Mechanical Properties of Niobium," Journal of Less Common Metals, Vol. 3, No. 1, February, 1961, Pages 1-12. Tested in recrystallized condition.

^b Data of this application based on material annealed for 1/2 hour at 2,200° F. after working.

In accordance with this invention, a method of fabricating columbium base alloys containing significant amounts of tungsten and/or molybdenum is achieved in which the 4T bend transition temperatures of such alloys can be reduced by at least 200° F. and thereby imparting to the alloys some ductility at room temperature.

The following examples illustrate warm-working a columbium base alloy in accordance with the teachings of this invention. For the purpose of illustration, the specific alloys which are warm-worked in accordance with this invention are Alloy 1 and Alloy 2, described above in detail. For convenience sake, the composition of these alloys will be repeated, being expressed both in terms of percent by weight and atomic percent.

ALLOY 1

	Weight Percent	Atomic Percent
Columbium.....	75	83.4
Tungsten.....	20	11.2
Molybdenum.....	5	5.4

ALLOY 2

	Weight Percent	Atomic Percent
Columbium.....	57.6	30.6
Tantalum.....	20	12.8
Tungsten.....	18	11.3
Molybdenum.....	4.4	5.3

Thus, each alloy or example contains precisely 16.6 atomic percent combined tungsten plus molybdenum, and the ratios of tungsten atoms to molybdenum atoms in both alloys are nearly identical. In other words, the only appreciable difference between these alloys is the inclusion of 12.8 atomic percent tantalum in Alloy 2. From Table 1, the 4T bend transition temperatures for these alloys would be expected to be about as follows:

	° F.
Alloy 1	480
Alloy 2	420

A desired 4T bend transition temperature of about 300° F. or less in these alloys would permit the retention of useful tensile ductility at room temperature.

The expected 100 hour stress-rupture strength of both alloys is between 20,000 and 22,000 p.s.i. at 2200° F. Both alloys are thus classified as superior high-temperature stress-rupture strength alloys. These alloys were selected as examples from a very broad group of alloys which exhibited good high-temperature stress-rupture strength. Among the other alloys that could have been optionally selected for use as examples, on the basis of demonstrated good high-temperature stress-rupture strength, and for which improved low-temperature ductility commensurate with stability of high temperature strength can be achieved by the method of this invention are Alloys 3-18, described above in detail.

In preparing Alloys 1 and 2, elemental charges for these alloys were melted 13 times (one charge of Alloy 2 was melted 15 times) for homogenization and shaping to nominal $2\frac{1}{2} \times \frac{3}{4} \times \frac{7}{16}$ -inch oval ingots. Non-consumable, tungsten-electrode arc melting was conducted under $\frac{1}{3}$ atmosphere of high-purity helium. Homogeneity of the ingots was assured by the melter's observation and by radiography. The cast hardness of each ingot was measured.

Fabrication variables studied included the following:

(I) Initial fabrication temperature

- (a) 1800° F.
- (b) 2400° F.
- (c) 3000° F.

(II) Process annealing temperature

- (a) 2200° F. (stress relief)
- (b) 2600° F. (partial recrystallization)
- (c) 3000° F. (full recrystallization)

(III) Final fabrication temperature

- (a) 1800° F.
- (b) 2400° F.
- (c) 3000° F.

(IV) Final fabrication reduction

- (a) 33 percent
- (b) 65 percent
- (c) 90 percent

For initial fabrications conducted at 1800° F., ingots were machined to nominal $2\frac{1}{4} \times \frac{5}{8} \times \frac{7}{16}$ -inch size, sheathed in thin molybdenum sheet, and then inserted into cavities in steel "picture-frame" yokes. Steel cover plates were welded to the yokes forming air-tight seals. Prior to rolling, the packs were evacuated at 1800° F. to vacuums of about 10^{-4} mm. of mercury, and then sealed by forge-welding of the evacuation stems. For 2400° F. fabrication, similar prerolling procedures were followed. Alternative procedures for 2400° F. fabrication were to encapsulate the ingots in molybdenum yoke-cover plate assemblies, and weld-seal the assemblies under argon. When this alternative procedure was used, the initial 3 to 5 rolling passes were accomplished at temperatures higher than 2400° F. (nominally 2900° F.), but the majority of the initial, or breakdown rolling was accomplished at 2400° F. Procedures for 3000° F. initial fabrication were the same as the alternative (Mo-pack) 2400° F. procedures, except, of course, that all rolling was accomplished at 3000° F. All rolling was accomplished using nominal 10-percent-per-pass reductions, the packs being reheated after each pass. The total reduction accomplished during breakdown rolling for individual specimens was predetermined by the over-all experimental design, and varied from 41 to 77 percent.

Following initial fabrication, alloy specimens were removed from the packs, quality-graded (E=excellent, i.e., no visible flaws; VG=very good, i.e., barely detectable flaws; G=good, i.e., fine surface, edge, or end cracks; F=fair, i.e., moderate surface, edge, or end cracks or checks), conditioned by pickling or grinding, and cutting as required for further processing. Their hardnesses were then measured. The specimens were then annealed in vacuums of about 10^{-4} mm. of mercury for 1 hour at the desired temperatures (2200° F., 2600° F., or 3000° F.).

In preparation for final fabrication, the alloy specimens were re-encapsulated as described previously, using steel pack assemblies for 1800° F. and 2400° F. final fabrication, and molybdenum assemblies for 3000° F. final fabrication, as required. During assembly of the steel packs for final fabrication, additional inner covers of molybdenum sheet separated the steel covers from the alloys, to better distribute the normal rolling stresses during final fabrication. Final rolling was accomplished utilizing 10 percent reductions in each pass, the assemblies being reheated after each pass. Total final reductions, predetermined by experimental design, varied from 33 to 89 percent. Final nominal thickness of all alloy specimens was 30 mils.

Subsequent to final fabrication, strip specimens of the alloys were recovered from the rolling assemblies and quality graded. They were cleaned by pickling and grinding as required, and were then given a uniform stress-relief annealing treatment at 2200° F. in vacuum on the order of 10^{-4} mm. of mercury for $\frac{1}{2}$ hour. (The likelihood of this anneal producing partial recrystallization of more-severely-worked specimens was acknowledged, and considered in evaluation of results.) From the fabricated and annealed alloy strips, multiple bend test specimens, nominally 1 inch long $\times$ $\frac{1}{4}$ inch wide, were cut. These specimens were polished with 240-grit abrasive on the compression side and 600-grit abrasive on the tension side, with all residual scratches aligned perpendicular to the axis of bending. All specimens were carefully inspected after polishing, and those containing flaws were discarded. Where the amount of material allowed, stress-rupture-test specimens were prepared.

Progressive closed-die bend tests were conducted on the selected specimens for each alloy in each condition of fabrication at a series of temperatures designed to encompass the temperature at which a 4T failure would occur, insofar as the material available would allow. From these bend tests, the 4T bend transition temperature for each condition of fabrication was obtained.

Special fabrication data and a summary of the results of bend testing are presented in Table 2. In accordance with the invention, interaction between the process variables is important, and must be taken into account. To aid in this understanding, the following definitions are offered:

Fabrication temperature:

- 1800° F.—severe, i.e., the expected degree of retained work hardening is greatest.
- 2400° F.—moderate (intermediate retained work hardening).
- 3000° F.—slight (least retained work hardening).

Process annealing temperature:

- 2200° F.—stress relief.
- 2600° F.—partial recrystallization (except perhaps for 3000° fabricated examples, where only stress relief may have been achieved).
- 3000° F.—recrystallized.

Reduction during fabrication:

- 33-41 percent (nominal 33 percent)—mild (work hardening).
- 62-76 percent (nominal 65 percent)—appreciable (work hardening).
- 85-89 percent (nominal 90 percent)—heavy (work hardening).

TABLE 2.—FABRICATION AND BEND TEST RESULTS

Example ^a	Hardness, VHN	Initial Fabrication				Process Anneal Temp., ° F.	Final Fabrication			4T Bend Transition Temperature, ° F.	
		Temp., ° F.	Red'n., pct.	Quality	Hardness, VHN		Temp., ° F.	Red'n., pct.	Quality	Individual	Avg. for Condition
A1	270	1,800	70	VG	288	2,600	1,800	66	G	280	275
A2	265	1,800	71	G	292	2,600	1,800	64	G	270	
B1	270	1,800	70	VG	288	2,600	2,400	69	G	340	270
B2	265	1,800	71	G	292	2,600	2,400	71	G	200	
C1	270	1,800	70	VG	288	3,000	1,800	65	VG	365	300
C2	265	1,800	71	G	292	3,000	1,800	66	G	230	
D1	270	1,800	70	VG	288	3,000	2,400	71	E	235	220
D2	265	1,800	71	G	292	3,000	2,400	69	G	220	
E1	258	b 2,400	79	G	278	2,200	1,800	d 64	F	430	490
E2	258	b 2,400	79	G	282	2,200	1,800	d 64	F	550	
F1	258	b 2,400	79	G	278	2,200	2,400	d 69	F	270	235
F2	258	b 2,400	79	G	282	2,200	2,400	d 70	F	200	
G1	258	b 2,400	79	G	278	2,600	1,800	65	G	210	305
G2	258	b 2,400	79	G	282	2,600	1,800	64	G	400	
H1	258	b 2,400	79	G	278	2,600	2,400	70	VG	310	255
H2	258	b 2,400	79	G	282	2,600	2,400	70	G	210	
J1	258	2,400	41	F	278	e 2,600	1,800	33	G	475	480
J2	270	2,400	41	F	284	e 2,600	1,800	33	F	485	
K1	258	2,400	41	F	278	2,600	1,800	89	F	220	220
K2	270	2,400	41	F	284	2,600	1,800	85	F	175	
L1	282	3,000	77	E	324	2,600	1,800	d 62	G	635	530
L2	265	3,000	78	E	296	2,600	1,800	d 63	VG	455	
M1	282	3,000	77	E	324	2,600	2,400	d 74	E	235	260
M2	265	3,000	78	E	296	2,600	2,400	d 76	E	220	
N1	282	3,000	77	E	324	3,000	3,000	69	E	380	390
N2	265	3,000	78	E	296	3,000	3,000	69	E	400	

^a 1=Cb-20W-5Mo Alloy; 2=Cb-20Ta-18W-4.4Mo Alloy.

^b Alternative procedure using Mo rolling assembly. Initial passes at 2,900° F.

^c Intermediate fabrication plus second 2,600° F. process anneal was required.

^d Process annealing would not be expected to effect any appreciable recrystallization, probably 95 percent effective reduction.

All examples of Table 2 were finally stress-relieved (½ hour at 2200° F.) prior to bend testing. In general and in accordance with the invention, the greater the degree of retained work hardening, the lower the 4T bend transition temperature. Examples of interaction of process variables are important in understanding the new and useful result of improved low-temperature ductility combined with retained structural stability and high-temperature stress-rupture strength achieved by this invention:

(1) The thermal history of Examples E1 and E2 shows moderate (2400° F.) initial fabrication, coupled with stress-relief (2200° F.) intermediate annealing and severe (1800° F.) final fabrication, all of which combined to effect a very heavy degree of over-all work hardening and an effective total reduction of about 95 percent. The alloys of these examples were thus unable to resist at least partial recrystallization or recovery during the final stress-relief anneal (2200° F.), and the expected beneficial effects of the very heavy degree of work hardening were partially lost as a result of the structural instability exhibited during the final annealing process. As shown in Table 2, examples E1 and E2 thus failed to achieve the desired low-temperature ductility or a 4T transition temperature of 300° F. or less, commensurate with adequate structural stability at high temperatures.

(2) By comparison with Examples E1 and E2, Examples F1 and F2, which were final-fabricated under moderate (2400° F.) thermal conditions, but were like Examples E1 and E2 in all other respects, were beneficially conditioned during final fabrication, and exhibited good structural stability, resisting recrystallization during the final stress-relief anneal. Much improved low-temperature ductility of the degree desired resulted (Table 2).

(3) Like Examples E1 and E2, Examples L1 and L2, with only slight (3000° F.) initial fabrication, were essentially only stress-relieved (2600° F.) by the intermediate anneal, and were then subjected to severe (1800° F.) final fabrication, all of which again combined to effect a very severe over-all fabrication (rather than the merely "appreciable" condition indicated) and consequent poor resistance to recrystallization structural instability during the final stress-relief treatment. The result was inferior low-temperature ductility (Table 2). In all examples, for comparable prior histories, final fabrication at 2400° F. resulted in better resistance to structural instability

during the thermal exposure of the final heat treatment and better average low-temperature ductility than did final fabrication at 1800° F. (Table 2). This is indicated below:

Examples		4T Bend Transition Temperature Increment of 2,400° F. Superiority over 1,800° F., ° F.
1,800° F.	2,400° F.	
A	vs. B	5
C	vs. D	80
E	vs. F	255
G	vs. H	50
L	vs. M	270
Over-all average		*132

*4T temperature=248° F. for 2,400° F.-fabricated examples vs. 380° F. for comparable 1,800° F.-fabricated examples.

Although the amount of reduction for 2400° F.-reduced examples was generally slightly greater than for 1800° F.-reduced examples, these differences are not considered sufficient to explain the pronounced advantage. Also in accordance with the invention, the examples show that at a constant final fabrication temperature of 1800° F., an increase in the amount of reduction up to about 90 percent decreases the 4T bend transition temperature (Table 2), thus:

Examples	Nominal Percent Reduction	Average 4T Bend Transition Temperature, ° F.
J	33	480
A, C, G	65	293
K	90	200
E, L	95	510

Between 90 and 95 percent final reduction, the discontinuity is attributed to structural instability (recrystallization or recovery) during the final stress-relief treatment. This behavior is undesirable, not only from the degrading effects upon low-temperature ductility, but also from the inability of material in such a condition to retain its superior strength properties at high temperatures. After 2400° F. fabrication, data show that the detrimental

effects of possible slight instability are much less pronounced (Table 2), thus:

Examples	Nominal Percent Reduction	Average 4T Bend Transition Temperature, ° F.
B, D, H-----	65	238
F, M-----	95	248

In accordance with the invention and as disclosed in the foregoing examples (Table 2) the invention includes within its scope the following attributes:

(1) Breakdown fabrication temperatures and process annealing temperature in themselves are of little significance to the low-temperature ductility of stress-rupture resistant, solid-solution strengthened columbium base alloys.

(2) Final fabrication temperature is a process variable of major importance. Fabrication at temperatures of about 1800° F. (2000° F. and lower) may result in metallurgical structures that are oversensitive to recrystallization during subsequent fabrication (secondary) or service, although total reductions during fabrication of from 60 to 90 percent may be combined with a final fabrication temperature of 1800° F. to achieve a low-temperature ductility within the desired range. Fabrication at somewhat higher temperatures (2000° F. to 2600° or 2800° F.; and preferably at 2400° F., as shown in the examples) conditions or stabilizes the metallurgical structure of the alloy for superior properties during subsequent high-temperature fabrication or service yet still provides markedly improved low-temperature ductility. Still higher fabrication temperatures (greater than about 2600° or 2800° F., e.g., 3000° F. in the examples) tend to approach too closely the true-hot-working conditions (working at temperatures at which recrystallization occurs during the processing) for the alloys involved, making the achievement of desirable low-temperature ductility more difficult in practical application.

(3) The amount of reduction during final fabrication is highly significant. In the order of 33 percent working at 1800° F. is too little to achieve the desired benefits; reductions on the order of 65 percent at 1800° F. are markedly beneficial; reductions on the order of 85-90 percent at 1800° F. are even more superior; but these examples show that reductions on the order of 95 percent, with the majority (final) of the reduction being conducted at 1800° F., are too great to achieve optimum properties in this class of alloys when subsequent practical applications are considered. At final fabrication temperatures of 2400° F., the examples show that reductions in the order of both 65 percent and 95 percent (total) are superior. At 3000° F., it is doubtful that sufficient work hardening can be introduced in the alloys to effect the desired benefit to low-temperature ductility without recrystallization.

Stress-rupture tests on specimens from examples for which material was available were conducted. Specimens were wrapped in tantalum foil to prevent contamination and were tested in vacuums of better than 10⁻³ mm. of mercury at 2200° F. The results are presented below:

2200° F STRESS-RUPTURE TEST RESULTS

Example	Initial Stress, p.s.i.	Rupture Time, hours	Estimated 100-hour Rupture Strength, p.s.i
J1-----	30	>5	>20
K1-----	30	4	19
E2-----	30	7	20

These examples substantiate the expected good stress-rupture behavior inherent to the alloy compositions examined.

In accordance with this invention, the examples show that the low-temperature ductility of stress-rupture-resistant, solid solution strengthened columbium-base alloys can be markedly improved by the control of fabrication parameters as taught here. Specifically this invention embodies the following teachings.

(1) Intermediate final fabrication temperatures (in the range from about 2000° to 2800° F., the specific preferred temperature being dependent upon specific alloy composition and specific amount of reduction) provide superior low-temperature ductility and metallurgical stability to the alloys of this invention than do higher or lower fabrication temperatures.

(2) By increasing the degree of working at a given fabrication temperature the low-temperature ductility of the alloys can be significantly improved. However, at lower fabrication temperatures (e.g., 1800° F. in the examples) too high degrees of working result in structural instability which may degrade properties during high-temperature secondary fabrication or service.

In particular, this invention includes within its scope the concept of conducting fabrication at a temperature just insufficient to result in recrystallization (or recovery) during processing to thereby achieve both a low-temperature ductility, not readily attainable with higher-temperature fabrication, and a superior metallurgical stability compared with lower-temperature fabrication. This invention thus achieves stress-rupture-resistant solid-solution-strengthened columbium-base alloys having superior low-temperature ductility and thereby possessing a utility previously denied them. Although many of the alloys described in this application, when not subjected to the process of this invention, were too brittle to be useful for many applications at room temperature, several of the specimens after being treated by the process of this invention exhibited bend ductilities of less than 10 T at about room temperature.

From the foregoing description of this invention, it is apparent that the key parameters in achieving the new and useful result of this invention are the amount and temperature of final reduction imposed upon a prior recrystallized metallic structure. As used in this application, a recrystallized metallic structure is defined as a strain-free structure, i.e., one that has had all residual work hardening removed from it, and in this connotation, a "recrystallized metallic structure" includes the as-cast structure of the alloys of this invention.

One of the important advantages of the invention is that its new and useful result is achieved by imposing a final reduction of the proper amount and temperature on a recrystallized or strain-free structure and that a strain-free state in the alloy specimen being processed may be introduced at any time during the processing by the use of a recrystallizing annealing treatment. The invention, however, provides great flexibility in the manner in which the final reduction parameters are imposed on the alloys. The important thing is the total amount and temperature of final reduction imposed on the alloy commencing from a strain-free or recrystallized base structure. In some instances, it may be desirable to impose the desired amount and temperature of final reduction in one step. In other instances, it may be desirable to break down the imposition of the desired amount of final reduction into two, three, or more steps.

As discussed in detail above, the final reduction imposed is partially dependent upon interaction between the process variables. Where the alloy specimen has a prior history of severe work hardening (e.g., initial fabrication at 1800° F.), it is more susceptible to recrystallization and is capable of being recrystallized at lower annealing temperatures (or subsequent fabrication or service temperatures) than where the alloy has been subjected to moderate work hardening (e.g., fabrication at 2400° F.). And the interaction of these process variables must be kept in mind in achieving the result of the invention though

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imposition of final reduction parameters. Although the recrystallization temperature of various alloy specimens may vary depending upon the prior history of the specimens (e.g., a severely work hardened specimen will have a lower recrystallization temperature than a moderately work hardened specimen), the new and useful result of the invention is obtained in each instance by warm-working of the alloy specimen, or working at a temperature slightly below the recrystallization temperature, to effect the desired final reduction.

It is important to note that as defined in this application, "reduction" means reduction in cross-sectional area of the alloy specimen. The new and useful result of this invention can be achieved by use of any of the known methods of reduction employed in fabrication of alloys similar to the alloys of this invention. In practicing the invention it does not matter whether the reduction is cross-sectional area is achieved by strip rolling, sheet rolling, tensile straining, forging, extrusion, wire drawing, or any other method of fabrication, so long as the desired amount of reduction in cross-sectional area is achieved.

This invention in its broader aspects is not limited to the specific alloys and processes shown and described, but also includes within the scope of the accompanying claims any departures made from such alloys and processes that do not depart from the principles of the invention and that do not sacrifice its chief advantages.

What is claimed is:

1. In a process for fabricating a high-temperature strength columbium-base alloy consisting essentially of columbium as the principal component and an additive selected from the group consisting of tungsten, molybdenum and mixtures thereof in an amount of from 5 to 35% by weight of the alloy with the total molybdenum content not exceeding 25% by weight of the alloy, the improvement that comprises the step of subjecting the alloy from a strain-free state to a reduction of at least 33% at a temperature of from 1800 to 2800° F., said reduction being sufficient to impart to the alloy a 4T-bend transition temperature not in excess of about 300° F., said 4T-bend transition temperature being defined as the minimum temperature at which an alloy strip can be bent without cracking or fracture through an angle of 105°

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with an included radius of curvature equal to four times the strip thickness, whereby substantial work hardening is introduced into the alloy, said step comprising the final reduction step on said alloy, and thereafter maintaining the alloy free from substantial recrystallization.

2. The invention as defined in claim 2, in which the alloy is subjected to a reduction of from 60 to 90% at a temperature of about 1800° F.

3. The invention as defined in claim 1, in which the alloy is subjected to a reduction of from 60 to 95% at a temperature of from 2000 to 2800° F.

4. The invention as defined in claim 1, in which the alloy is subjected to a reduction of from 60 to 95% at a temperature of about 2400° F.

5. The invention as defined in claim 1, in which the alloy is subjected to a reduction of at least 33% at a temperature of from 2000 to 2800° F.

6. The process according to claim 1 wherein the additive is tungsten in an amount of from about 20 to 30% by weight.

7. The process according to claim 1 wherein the additive is molybdenum in an amount of from about 10% to 20% by weight.

8. The process according to claim 1 wherein the alloy also includes tantalum in an amount of from about 0.5% to 40% by weight.

9. The process according to claim 1 wherein the alloy also includes tantalum in an amount of from about 20% to 40% by weight.

10. The process according to claim 1 wherein the alloy also includes at least one element selected from the group consisting of zirconium, hafnium, vanadium, and beryllium, with a total of the added elements from this group not exceeding 10% by weight of the alloy.

References Cited by the Examiner

UNITED STATES PATENTS

2,907,654	10/1959	Thielemann	75—174
3,034,934	5/1962	Redden	148—11.5
3,046,109	7/1962	Lottridge	75—174

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