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MOLYBDENUM-BASE ALLOY

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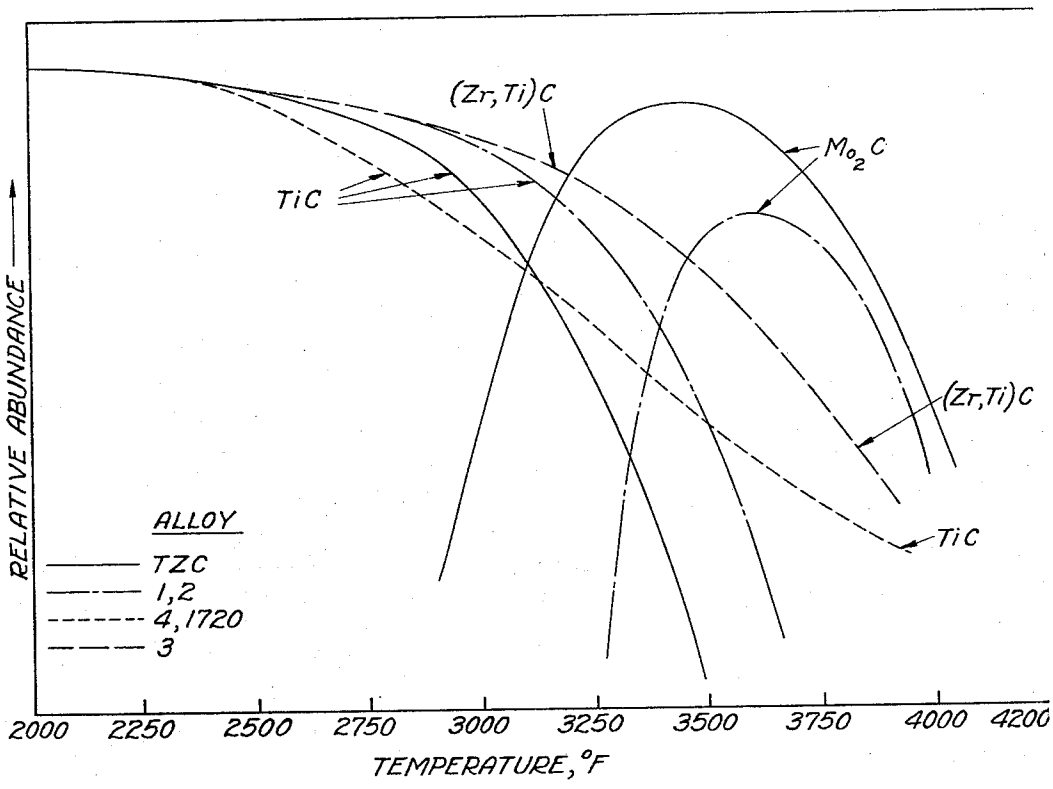

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MOLYBDENUM-BASE ALLOY

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This is a continuation-in-part of application Ser. No. 227,046, Chang, filed Sept. 28, 1962, now abandoned, and assigned to the assignee of the present invention.

This invention relates to molybdenum alloys and, more particularly, to molybdenum alloys having a combination of high temperature strength and low temperature ductility as a result of the alloying of molybdenum with judiciously selected amounts and proportions of the elements, titanium, zirconium and carbon.

Some of the advantages of alloying molybdenum with titanium and molybdenum with zirconium have been set forth in United States Patents 2,678,269 and 2,678,271, respectively. Furthermore, these two patents mention that carbon in very small quantities can be present. In addition with regard to carbon, United States Patent 2,947,624 indicates that certain advantages can be obtained from the use of carbon in molybdenum alloys in the range of 0.30 weight percent or higher.

In the modern design of molybdenum alloys the mechanisms of solid solution alloying and precipitation alloying have been extensively investigated. One of the molybdenum alloying systems on which much work has been done contains a minor but significant amount of titanium, a somewhat smaller amount of zirconium and some carbon. Several modifications in this alloy system have been investigated and some are presently being commercially exploited. However, in my persent investigations concerning the phase relationships and metallurgy of molybdenum alloys which can be precipitation hardened by combination of titanium-, zirconium- and molybdenum-carbides, I have found that such levels of titanium as have been advocated in the prior art are deleterious to both strength and ductility. Relatively small amounts of zirconium stabilize the precipitated titanium carbides and also form more stable complex carbides of zirconium and titanium. By appropriate small but critical adjustments of the levels of titanium, zirconium and carbon and the ratios of zirconium plus titanium to carbon, improvements over similar prior art molybdenum alloys have been obtained. However, many of the improvements have been in the direction of higher strength at elevated temperatures accompanied by lowered workability and ductility at room temperature and below.

Furthermore, many of the previously known alloys in the molybdenum-titanium-zirconium-carbon system contain significant amounts of Mo_2C. Interactions between Mo_2C and other precipitating phases are generally undesirable. Massive deposits of Mo_2C often are formed as a molten ingot freezes, and the carbon is not readily redistributed through the martix on decomposition of the Mo_2C to other precipitates during aging. Also, unstable lower temperature precipitates that convert to Mo_2C at moderate temperatures do not provide the desired strength levels. Preferential distribution of Mo_2C in the grain boundaries is quite deleterious to properties. Thus, molybdenum alloys that can be hardened by precipitation from solution in the absence of difficult-to-control interactions between different precipitated phases are greatly to be desired, and are not generally found among previously known alloys.

It is the desire of development metallurgists to produce alloys of unusual strength at high temperatures. However, it is important to the designers of highly

stressed articles, such as turbine buckets for gas turbine engines, that an alloy be ductile at lower temperatures to avoid brittle fractures during the starting of such apparatus. Furthermore, the designers of articles for use in flight apparatus prefer materials which have a high strength-to-density ratio so that lighter weight parts can be fabricated.

It is a principal object of the present invention to provide an improved molybdenum-base alloy having unusual high temperature strength up to about 3500° F. along with good room temperature ductility.

It is another object of this invention to provide a high strength molybdenum-base alloy having a high strength-to-density ratio.

Another object of the invention is to provide molybdenum-base alloys with optimum contents and proportions of titanium, zirconium and carbon such that they can be treated to develop desired properties at elevated temperatures and at room temperature and below.

Another object of the invention is to provide a precipitation-hardenable molybdenum-base alloy in which the formation of undesirable Mo_2C is avoided.

Still another object of the invention is to provide a precipitation-hardenable molybdenum-base alloy which is not deleteriously susceptible to aging during use at elevated temperatures.

These and other objects and advantages will be more readily recognized from the following detailed description, tables and examples which are representative of but are not intended to be limitations on the scope of the present invention.

The drawing is a graphic representation of the interrelations of carbide precipitates in various molybdenum-base alloys including the alloys of the present invention.

It has been found that molybdenum-base alloys containing judiciously selected concentrations and proportions of titanium, zirconium and carbon have properties unexpected from that which was previously known. The alloys of the present invention consist essentially of about, by weight, 1.25–2% Ti, 0.4–0.7% Zr, 0.05–0.2% C, the atomic ratio of (Ti+Zr)/C being from about 2:1 to about 6:1, with the balance Mo. Percentages given in this specification are by weight except where otherwise indicated.

In titanium and carbon-bearing dispersion-hardened molybdenum-base alloys, the major dispersion phase is titanium carbide. However, an excess of carbon with regard to the amount of titanium will allow the formation of massive Mo_2C which is not effective for strengthening in the manner of the finely dispersed titanium carbide. It has been recognized that a careful and judicious selection of amounts and proportions of the elements titanium, zirconium and carbon results in the formation of a (Ti, Zr) complex carbide.

The inclusion of too small an amount of titanium will not provide enough titanium carbide for strengthening and also will permit the formation of Mo_2C. Too high a titanium content will lower the alloy's melting point, form massive carbides, and increase the diffusion rate to the detriment of high temperature strength.

Zirconium in relatively small quantities stabilizes the titanium carbide phase. But zirconium within the range of the present invention forms a complex zirconium-titanium carbide which is more stable than titanium carbide.

The function of carbon in the alloy of the present invention is that it is necessary for carbide dispersion. A critical amount of carbon must be present with the range of titanium and zirconium in order to form a fine dispersion of the complex titanium-zirconium carbide. If there is too large an amount of carbon or two low an amount of

titanium and zirconium, too much Mo_2C forms. This molybdenum carbide does not provide the strengthening effect of the complex titanium-zirconium carbide.

Even though the titanium-zirconium-carbide dispersoid is much harder than the molybdenum matrix, it also is desirable that the precipitated particles be of a size small enough that there be few if any dislocations in each particle, and so that dislocation movement in the particle is very limited if existent at all, thereby greatly increasing the effective hardness of the dispersed particles. A finer particle size also leads to smaller interparticle spacing, thereby improving the mechanical properties of the alloys.

Relative to titanium-zirconium complex carbide precipitates in alloys of the invention, molybdenum carbide generally precipitates in the form of massive, sometimes feathery particles which serve little useful purpose in strengthening the alloy or in making it ductile. Although molybdenum carbide serves a purpose in some related alloys as an intermediate phase for the purpose of promoting controlled aging reactions, it is not generally desirable as a constituent of a final alloy in condition for application. Moreover, residual molybdenum carbide left after controlled heat treatment in processing can cause deleterious "on-the-job" aging and embrittling of such alloys by conversion to other carbides at elevated temperature during application, particularly with the aid of strain-induced aging. Although for some applications it may be desirable to have an alloy that will age during use, it is also quite desirable to have alloys that will not age during use for other applications.

utilized in the formation of useful and controllable precipitates, and in which unwanted aging reactions can be avoided.

The following Table I is representative of the number of the alloys which were considered in the study of the alloy of the present invention.

TABLE I

Alloy	Weight Percent (Balance Mo)			Ti+Zr/C Atomic Ratio
	Ti	Zr	C	
TZC	1.0	0.1	0.14	1.8
1	1.8		0.13	3.5
2	1.7	0.1	0.13	3.2
3A	1.6	0.6	0.13	3.7
3B	1.28	0.6	0.08	5
4	6.0		0.09	6
1720	5.0		0.25	5
45	3.0	0.5	0.05	
6	3.0	0.4	0.32	
44	3.0	0.5	0.16	

Alloys 1, 2, 3A and 4 were made in 25 pound heats by melting in a vacuum arc furnace. The composition given for alloy TZC is one of several with which the name TZC has been used in the art. Alloys 1, 2, 3A and 4 were then extruded and swaged to a total of 93% reduction in area to ¼" bars. These bars were tested for strength and ductility after being stress relieved at 2100° F. for about one hour. The results of these tests, which were conducted in a vacuum at the temperatures shown, are given in Table II.

TABLE II.—TENSILE TEST RESULTS ON SWAGED ALLOYS

Alloy	Temp. (° F.)	U.T.S., ksi.	0.2% Y.S., ksi.	El. (percent in 1")	RA (percent)	Strength to Density Ratio (in.)
1	78	121.8	103.1	1	5	337,000
2	78	139.8	118.7	2	2	388,000
3A	78	162.3	129.0	13	51	450,000
4	78	106	90.6	1	1	310,000
1	500	108.5	89.5	15	56	302,000
2	500	115.6	99.0	18	64	321,000
3A	500	134.3	112	14	49	373,000
4	500	95.0	87.0	22	69	278,000
1	1,000	103.0	85.5	14	65	287,000
2	1,000	101.5	91.6	15	71	282,000
3A	1,000	119.0	93.2	11	61	331,000
4	1,000	88.7	66.6	21	74	259,000
1	1,500	92.5	79.0	17	69	258,000
2	1,500	97.5	87.8	13	75	270,000
3A	1,500	108.5	88.5	13	67	301,000
4	1,500	71.0	54.8	17	85	208,000
1	2,000	70.1	62.5	19	78	195,000
2	2,000	80.5	71.3	12	74	224,000
3A	2,000	92.9	72.1	12	67	258,000
4	2,000	54.8	48.8	17	85	160,000
1	2,500	47.2	42.7	22	83	131,000
2	2,500	61.5	54.0	16	80	171,000
3A	2,500	65.6	49.8	15	77	182,000
4	2,500	29.4	24.6	42	94	86,000
1	3,000	21.5	16.9	37	92	60,000
2	3,000	27.1	22.4	29	92	75,000
3A	3,000	31.3	25.5	29	88	87,000
4	3,000	10.7	8.5	88	97	31,300
1	3,500	12.1	8.7	34	87	33,700
2	3,500	18.0	14.5	48	94	50,000
3A	3,500	20.9	14.5	31	90	58,000
4	3,500	2.9	2.3	110	96	8,500

I have discovered that, in some of the alloys of the invention, not only are the mechanical properties greatly improved over those of prior art alloys, but also the formation of Mo_2C has been essentially completely avoided. The precipitated carbon is present in the form of (Ti, Zr)C. By the choice of appropriate combinations of composition and thermal and mechanical treatments, alloy bodies can be produced within the limits of the present invention in which the carbide present is efficiently

In Table II and subsequent tables, "U.T.S." means "Ultimate Tensile Strength," "0.2% Y.S." means "0.2% Yield Strength," "El" means "Elongation," "R.A." means "Reduction in Area" and "ksi." means "thousands of pounds per square inch." The densities of alloys 1, 2, 3A, 3B and 4 were respectively, in pounds per square inch: 0.359; 0.360; 0.360; and 3.342.

By comparison, the strength of alloy 3A at temperatures from about room temperature (78° F.) to 3500° F.

is unusually high and unexpectedly better than other alloys tested.

Alloy 3B was produced by consumable arc melting in a vacuum furnace to a 31-pound ingot. The ingot was extruded at 3500° F. to sheet bar at an extrusion ratio of 4 to 1. The resulting bar, 1.93 inches wide by 0.94 inch thick, was bisected along the plane of thickness and rolled to 0.05 inch thick sheet. The rolling procedure consisted of 50% reduction in thickness at 2750° F. at 10% per pass, 50% at 2500° F. at 10% per pass, and final reduction to 0.05 inch thick at 2200° F. at 10% per pass. The heating was done in a hydrogen furnace, with the material being soaked at temperature for 5 to 10 minutes between passes. High-quality sheet was produced with a material recovery of greater than 90%. The results indicated that the alloy is quite fabricable. With appropriate adjustments in techniques, the melting difficulties should be readily overcome.

Bend tests were preformed on the sheet at room temperature in both the stress-relieved condition (2100° F./1 hour) and the recrystallized condition (3000° F./1 hour). In the stressed-relieved condition the alloy sustained a full bend around less than a 1T radius (T equals thickness of the sheet), while the recrystallization treatment only raised the radius for full bend to 2T, indicating no significant embrittlement on recrystallization.

Tensile tests were performed on 0.05 inch thick sheet of alloy 3B as stress-relieved at 2200° F. for one hour and as-recrystallized at 3200° F. for one hour. The results are presented in Table III below. "SR" indicates the stress-relieved condition and "RX" indicates the recrystallized condition. The specimens had 0.5 inch long gauge lengths, ⅛ inch wide. The major surfaces were as-pickled in the rolled condition, and the tests were performed on an Instron machine at a nominal strain rate of 0.05 per minute. Elevated temperature testing was done in a vacuum of about 10^{-5} torr.

TABLE III.—TENSILE PROPERTIES OF SHEET ALLOY 3B

Test Temp., ° F.	Condition	Tensile Strength, ksi.	Tensile/Density Ratio, in.×10^{-3}	0.2% Yield Strength, ksi.	Elongation, Percent
78	SR	145.0	400	125.0	18.6
	SR	142.1	394	122.5	18
	RX	96.9		83.4	8.3
500	SR	117.7	327	100.0	12.7
	RX	67.6		40.0	27.5
1,000	SR	123.0	342	98.7	12
1,500	SR	102.7	284	94.7	9
2,000	SR	87.2	242	75.6	8.4
	RX	71.1		35.4	14.7
2,500	SR	63.1	175	44.8	14.5
	RX	51.2		30.6	24.5
3,000	SR	28.6	80	21.7	33.1
	RX	18.4		14.1	44.5
3,500	SR	14.3	40	10.5	79
	RX	15.2	42	6.0	69

The tensile data on the alloy 3B sheet compare very favorably with those on the alloy 3A swaged material shown in Table II for the following reasons:

First, as in the swaged condition of alloy 3A, the 0.05-in. sheet material possesses an excellent combination of high-temperature strength and low-temperature ductility which appears far superior to that of any other molybdenum sheet alloy reported in the literature. The high-temperature strength is illustrated by the tensile strength of 28,600 and 14,300 p.s.i. at 3000° and 3500° F., respectively, corresponding to a tensile strength to density ratio of 80,000 and 40,000 inches at the respective temperatures. This remarkable high-temperature strength is accompanied by room-temperature tensile elongation of almost 20% (probably corresponds to a 10–15% elongation in a 1-in. gage length) which agrees well with the bend test results. Second, the literature is full of examples which show much lower strength in sheet form than in bar or plate form. The sheet alloy 3B material is shown to have strength and ductility properties very similar to those of the strongest swaged alloy 3A condition up to 3000° F. Above the latter temperature, the swaged material becomes superior mainly because of its higher recrystallization temperature of 3500° F., as compared with 3000° F. or 3200° F. for the sheet material. In this connection, it may be noted that the titanium and carbon contents in alloy 3B are 1.28% and 0.08%, respectively, which are lower than the 1.6% and 0.13% present in alloy 3A. The excellent properties of the sheet material, in spite of the possibly adverse chemical differences, further accentuate the importance of processing and heat treatment in controlling microstructure and properties.

Table IV compares alloys 3A and 3B with some other titanium-zirconium-carbon-molybdenum alloys. The data on alloy 3B are from sheet specimens, those on the other alloys are from swaged specimens.

TABLE IV

Alloy	Temp. (° F.)	U.T.S., ksi.	El. percent in 1 inch	Strength to Density Ratio (inches)
3A	3,000	31.3	29	87,000
3B	3,000	28.6	33.1	
45	3,000	10.8	128	
6	3,000	10.9	110	
44	3,000	14.4	76	41,000

The data of Tables II and III show that alloys of the invention have an unexpected and unusual combination of high strength at low as well as at high temperatures along with good low temperature ductility not found in closely similar alloys. It has been found that a preferred range in which alloys of the invention are included consists essentially of, by weight, 1.25–2% titanium, 0.4–0.7% zirconium, 0.08–0.2% carbon, with the atomic ratio of (Ti+Zr)/C being from about 3:1 to about 5:1, with the balance molybdenum. The higher titanium bearing alloys as represented by alloys 4, 45, 6, 44 and 1720 were very much weaker and had a much lower strength-to-density ratio than do the alloys of the present invention. This is true even for alloy 44 which has the same general zirconium and carbon content as the alloy of the present invention but with a higher titanium content. Referring to Table IV, for example, it is seen that alloy 44 has less than half the strength of alloy 3A at 3000° F. with a change of less than about 1.5% titanium.

Alloy TZC has too low a content of alloying additions and too low a ratio of titanium plus zirconium to carbon to possess the desired properties. Specifically, the ratio leads to the formation of Mo_2C which is difficult to control and the undesirable characteristics of which have been discussed above. The higher titanium content alloys without zirconium, alloys 4 and 1720, had such high ratios of titanium to carbon that it was quite difficult to produce a fine dispersion of precipitate. These alloys have relatively low recrystallization temperatures and unattractive strength properties.

Similarly, alloys 4 and 45 having lower carbon and alloy 6 having higher carbon content are substantially weaker than the alloy of the present invention. Alloys 1 and 4 show dramatically the effect of the absence of zirconium in the presence of titanium and carbon, and in particular with regard to alloy 4, the effect of high titanium and low carbon in the absence of zirconium.

Although the presently claimed compositions may appear superficially to be similar to those of prior art, they are in fact critically different as shown in part by a particular kind of susceptibility of alloys of the invention to alterations in their mechanical properties through ther-

mal and mechanical treatments. This susceptibility or capability is, in itself, a valuable property. It is present in alloys within the composition limits stated in the specification and the claims, and having the specified ratios between the Group IV–A metals (zirconium and titanium) and carbon. These ratios as claimed establish a critical relationship between the Group IV–A metals and carbon which determines the type and morphology of carbides which will be precipitated with various types of heat treatments. The claimed ratios are all above a threshold ratio which is the maximum which would generally allow precipitation of Mo_2C. Therefore, as stated above, all the carbides precipitated in alloys of the invention are carbides of the Group IV–A metals. Previously known alloys in the molybdenum-titanium-zirconium-carbon system which do not meet the ratio or proportion limits in addition to the composition limits produce alloys that are different in kind from those of the present invention. For example, an alloy having a zirconium plus titanium to carbon ratio substantially less than 2:1 would contain deleterious amounts of Mo_2C in various heat treated and worked conditions. Furthermore, the present invention is directed toward alloys having a carbon content low enough in relation to the zirconium and titanium contents to substantially avoid the presence of Mo_2C, as distinguished from alloys that could be considered to be high carbon content alloys. When properly treated, as discussed herein or as described in patent application Serial No. 227,046, Chang, filed Sept. 28, 1962, and in other manners as well, alloys of the invention are capable of forming precipitates of complex carbides in a fine, evenly dispersed, non-oriented condition, thereby permitting substantial ductility at room temperature and greatly enhancing the high temperature strength.

A satisfactory range of the alloy of this invention consists essentially of, by weight, 1.5–2% Ti, 0.4–0.7% Zr, 0.1–0.2 C with the balance Mo. These composition limits, of course, establish a range of ratios of (Ti+Zr)/C. The two extreme limits of this range on an atomic basis are about 2.13:1 and about 5.94:1. In like manner, the ratio of (Ti+Zr)/C inherent in the composition of alloy 3A is about 3.70:1, and in alloy 3B about 5:1.

In order to enable a better understanding of the criticality of the amounts and proportions of alloying additions in the alloys of the invention, consideration will now be given to various types of carbide precipitation reactions in molybdenum-base alloys containing various amounts and proportions of titanium, zirconium and carbon. The drawing integrates the information discussed below and should be referred to for perspective and for comparison of the characteristics of the various alloys. The addition of titanium in Mo-C alloys first results in the appearance of TiC at low temperatures, with Mo_2C remaining as the high-temperature equilibrium carbide. In the TZC alloy which had a (Ti+Zr)/C ratio of 1.8, the stability ranges were characterized by complete TiC dissolution at 3500° F. and persistance of Mo_2C down to about 3000° F. The effect of further increase in Ti is seen to raise the equilibrium solution temperature of TiC, while restricting the stability range of Mo_2C. Thus, in alloys 1 and 2 which contain 1.6–1.8% titanium with (Ti+Zr)/C ratios of 3.2–3.5, the TiC phase did not completely dissolve until about 3750° F., while the Mo_2C was no longer stable below 3300° F. This effect of titanium continues until a concentration is reached which eliminates the Mo_2C phase completely, as in the case of alloys 4 and 1720. It is interesting to note that while a substantial amount of Mo_2C remained stable in alloy 1 which had a Ti/C ratio of 3.5, none existed in alloy 1720 which had a Ti/C ratio of 5. The threshold Ti/C ratio for eliminating the Mo_2C phase thus appears to lie at about 4.5 in the Mo-Ti-C system.

Compared with titanium, zirconium proved to be much more potent in stabilizing the monocarbide at the expense of Mo_2C. The difference, indeed, appears to be greater than indicated by the free energy of formation of the respective bulk carbides. This is shown first by the similar stability ranges found in alloy 1 (Ti/C=3.5) and alloy 2 (Ti+Zr/C=3.2) and more clearly, by a comparison between alloys 1 and 3A. Although the latter two alloys did not differ appreciably in the values of the (Ti+Zr)/C ratio (3.5 vs. 3.7), the presence of 0.6% zirconium in alloy 3A was sufficient to eliminate Mo_2C which was a predominant high-temperature carbide in alloy 1. Furthermore, although the atomic concentration of titanium in alloy 3 (about 3.2%) was some five times that of zirconium, the monocarbide was found to be zirconium-rich, as evidenced by the large lattice parameter and the strong zirconium emission intensities. These results indicate that the threshold Zr/C ratio in the Mo-Zr-C system is considerably below the Ti/C ratio in the Mo-Ti-C system. More recent data indicate the threshold Zr/C ratio to be below 2.5, as compared with the Ti/C threshold ratio of 4.5 in the Mo-Ti-C system.

In alloys of the invention, the zirconium limits claimed, particularly the lower limit of 0.4%, are critical to the properties, structure, and characteristics of the alloys. Below 0.4%, and generally outside of the composition range of 0.4–0.7%, zirconium does not give the desired aging kinetics for the formation and growth of the complex carbides, and does not give the desired stability and morphology to the precipitates. Moreover, insufficient amounts of zirconium will not insure against the presence of deleterious amounts of Mo_2C, the undesirable characteristics of which have been discussed above.

As compared to alloy 2, alloy 3A represents an interesting case by virtue of its moderately higher (Ti+Zr)/C ratio and zirconium content. These two characteristics influence the carbide nucleation in such a favorable manner that the alloy develops a fine and extensive dispersion both by partial precipitation on cooling and upon working or aging. Thus, the carbide is utilized more effectively in alloy 3A than in alloys 1 or 2, as it is not tied up in large clusters of decomposed Mo_2C sometimes seen in the worked or aged conditions of the latter two alloys.

From lattice parameter studies, it is apparent that essentially all the zirconium addition in alloy 3A is consumed in the (Zr, Ti)C phase, thereby indicating that the amount of zirconium dissolved in the molybdenum matrix is so small as to make insignificant any possible solution strengthening. This means that, theoretically, properties of the alloy of the invention can be varied extensively by heat treatment to give optimum desired properties for either working or application of the alloys. Such a theoretical conclusion coincides with the very favorable results actually obtained with an alloy of the invention, discussed above. X-ray diffraction showed almost exclusively a zirconium-rich (Zr, Ti)C with a lattic parameter of about 4.628 angstrom units.

As shown in Table V, the room temperature ductility of alloy 2 can be improved, though with a slight sacrifice of strength at room temperature, through the use of Heat Treatment B. However, through the use of such heat treatment, there is an improvement in high temperature strength as well, although alloy 3A within the preferred range of this invention is unexpectedly improved with all heat treatments shown. As used in Table V Heat Treatments A, B and C, following extrusion at 3500°–3650° F., are as follows:

Heat Treatment A: As-extruded material swaged 93% at 2500° F.–2100° F.; stress-relieved at 2100° F. for one hour in hydrogen.

Heat Treatment B: As-extruded material aged at 2500° F. for 50 hours before swaging 93% and stress-relieved as in Heat Treatment A.

Heat Treatment C: As-extruded material swaged 88% at 2500° F.–2100° F.; stress-relieved at 2200° F. for one hour in hydrogen.

TABLE V

Alloy	Temp. (° F.)	Heat Treatment	U.T.S. (ksi.)	0.2% Y.S. (ksi.)	El. (percent in 1")	R.A. (percent)	Strength to Density Ratio (inches)
2	78	A	139.8	118.7	2	2	388,000
2	78	B	133.2	111.0	18	41	370,000
2	78	C	125.0	107.0	1	3	348,000
3A	78	A	162.3	129.0	13	51	450,000
3A	78	B	148.0	120.0	23	53	411,000
3A	78	C	149.5	117.5	12	13	415,000
2	3,000	A	27.1	22.4	29	93	75,000
2	3,000	B	28.3	25.5	36	96	78,500
3A	3,000	A	31.3	25.5	29	88	87,000
3A	3,000	B	30.7	26.6	35	88	85,200

One-hour vacuum annealing at various temperatures was found to lead to recrystallization in alloy 3B at temperatures between 3000° and 3250° F. depending on variations in heat treatment before the rolling process. Material which was given a vacuum anneal of 3200° F. for one hour prior to rolling recrystallized at about 3000° F. after rolling, while the material that was rolled directly from the extruded condition recrystallized at about 3250° F. Although the recrystallized grain size was slightly larger in the directly rolled material, neither material underwent substantial grain growth in one hour at temperatures below 3750° F.

The heat treatment and processing of the alloys of this invention involve control of the interplay between dispersion hardening and strain hardening and can be applied to usefully vary the properties of alloys of the invention.

Thus, the present invention involves a dispersion-hardened molybdenum-base alloy of unusual characteristics in an unexpectedly critical range of compositions and proportions in order to control the amount, type and distribution of complex carbides formed.

Although this invention has been described in connection with specific examples, those skilled in the arts of metallurgy and heat treatment will recognize the variations and modifications of which the present invention is capable without varying from its scope.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. An improved molybdenum-base alloy consisting essentially of about, by weight, 1.25–2% titanium, 0.4–0.7% zirconium, 0.05–0.2% carbon, the atomic ratio of titanium plus zirconium to carbon being from about 2:1 to about 6:1, with the balance molybdenum.

2. An improved molybdenum-base alloy consisting essentially of about, by weight, 1.25–2% titanium, 0.4–0.7% zirconium, 0.08–0.2% carbon, the atomic ratio of titanium plus zirconium to carbon being from about 3:1 to about 5:1, with the balance molybdenum.

3. An improved molybdenum-base alloy consisting essentially of about, by weight, 1.6% titanium, 0.6% zirconium, 0.13% carbon, the atomic ratio of titanium plus zirconium to carbon being about 3.7:1, with the balance molybdenum.

4. An improved molybdenum-base alloy consisting essentially of about, by weight, 1.28% titanium, 0.58% zirconium, 0.08% carbon, the atomic ratio of titanium plus zirconium to carbon being about 5:1, with the balance molybdenum.

5. The alloy of claim **1**, wherein the precipitating phase is essentially all a complex carbide of zirconium and titanium.

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