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METHODS FOR HEAT-TREATING MOLYBDENUM-BASE ALLOYS

John L. Ham, Dearborn, Frederick P. Bens and Alvin J. Herzig, Detroit, and George A. Timmons, Ferndale, Mich., assignors to Climax Molybdenum Company, New York, N. Y., a corporation of Delaware

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This invention relates to refractory metal alloys and more particularly to cast, heat-treatable alloys containing molybdenum and beryllium and to a method of heat treating the same; and the present application is a continuation-in-part of applicants' copending application, Serial No. 218,527, filed March 30, 1951, now abandoned.

The alloys of the present invention are especially useful in applications of the type which require a material to retain its high hardness, strength or resistance to creep at elevated temperatures. Applications of this type include points for piercing seamless steel tubing, electrodes for heating molten glass, die-casting dies for brass and other metals, etc.

An American Society for Metals publication, preprint No. 33 of 1949, by Kessler, and Hansen, reports on experiments with molybdenum-chromium alloys, a few of which contained between .1% and .2% beryllium and no carbon. The report does not mention any forging tests on beryllium-containing alloys and it indicates that while some increase in hardness resulted from beryllium additions, no precipitation or age hardness was obtained.

The principal objects of this invention are to provide cast molybdenum-base alloys which are capable of being worked at elevated temperatures; to provide cast molybdenum-base beryllium-containing alloys which are capable of being worked or machined into the desired shape and form and thereafter hardened materially by heat-treatment; to provide a method for heat-treating such alloys that will markedly increase their hardness; and, in general, to provide improved molybdenum-base alloys which are characterized by high temperature properties superior to those of heretofore known materials.

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.

It has now been found that certain molybdenum-base alloys containing beryllium are age or precipitation hardened when subjected to the hereinafter described heat-treatment, and that improved high temperature properties are induced by such heat-treatment and are retained at elevated temperatures even after prolonged periods of time. Such heat-treatable alloys may

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be cast, annealed, then fabricated into the desired shape and thereafter hardened by the heat-treatment. This invention is also concerned with molybdenum-base alloys containing beryllium which are subject to heat-treatment in accordance with this invention but which are not capable of being worked by forging, rolling, pressing, swaging, drawing, etc. Such unworked alloys are useful in the as-cast form after heat-treatment, and in some applications may be used without heat-treatment.

If the alloy is to be worked at elevated temperatures, it may contain up to a maximum of .25% beryllium. It has not been possible to hot-work alloys containing more than .25% beryllium. However, larger quantities of beryllium may be present if no working is required.

Cast molybdenum-base alloys containing small quantities of oxygen cannot be worked at elevated temperatures if molybdenum oxide is segregated at the grain boundaries of the cast alloy since that oxide materially reduces intergranular cohesion. Small quantities of carbon or aluminum appear to overcome this defect when the amount of oxygen is limited. Similarly, it is found that in the presence of beryllium within the limits contemplated by the present invention, alloys capable of being worked at elevated temperatures are obtained even though no carbon or aluminum is present. While the reasons for this phenomenon are not fully understood, it is believed that oxides of beryllium replace those of molybdenum, and that the beryllium oxides are less detrimental. In any event, alloys containing from .001 to .25% beryllium and not more than .05% oxygen can be worked at elevated temperatures to a beneficial degree if the beryllium is present in an amount at least sufficient to react with all the oxygen to form beryllium oxide.

Although not essential, it is preferred that the molybdenum-beryllium alloys of the present invention also contain small quantities of carbon and/or aluminum. These elements, aside from the beneficial effect upon the forging characteristics, have the effect of increasing the strength of a sintered rod formed of the powder materials employed in the alloy and thus facilitate the practice of forming a casting by using such a sintered rod as a consumable electrode in an arc furnace. Moreover, carbon in amounts of about .02% or more makes it possible to employ lower temperatures in the heat-treatment hereinafter described. Thus, cast alloys of the present invention which are capable of being worked at

elevated temperatures may contain carbon within the range of zero to .25% or aluminum in the range of .003% to 2.5%. However, when the alloy is to be worked at elevated temperatures, it is preferred that the carbon not exceed .06% or that the aluminum not exceed .4%. If both carbon and aluminum are present it is desirable to further restrict the maximum carbon content as the aluminum increases toward .4%; the preferred alloy contains not more than .02% carbon.

In all cases, workability improves with reductions in the oxygen content, and the maximum permissible quantity in an alloy that is to be worked at elevated temperatures is about .05%. It has not been found practical, in the production of large cast ingots of molybdenum-base alloys, to reduce the oxygen content below about .001%.

Molybdenum-base alloys containing aluminum and no beryllium are disclosed and claimed in applicants' copending application, Serial No. 250,202, filed October 6, 1951, on "Molybdenum-Tungsten-Aluminum Alloys."

Molybdenum-beryllium alloys are susceptible to age or precipitation hardening. Beryllium has limited solubility in molybdenum in the solid state; the solubility of beryllium increases with increasing temperature. To gain the full hardening from the heat-treatment, it is necessary that a certain minimum quantity of beryllium be present. To preserve workability, it is desirable to employ the lowest beryllium content which will provide the desired hardening effect from the heat-treatment.

Since a part of the beryllium in any given molybdenum-base alloy may be combined with some of the oxygen present to form beryllium oxide and in that case would be ineffective as a hardening agent, the total amount of beryllium to produce a given hardening effect varies with the amount of oxygen in the final alloy. In alloys containing minimum oxygen, i. e., in the order of .001% oxygen, as little as .03% beryllium will produce a significant increase in the as-cast hardness as well as a significant amount of age or precipitation hardness. When the oxygen content is at its maximum permissible value of .05%, approximately .08% beryllium will be required to produce an equivalent effect. Quantities below .03% are insufficient to provide significant hardening on heat-treating and quantities above .25% render the material incapable of being worked to a beneficial degree. Where the alloy is to be used in the unworked condition, the beryllium content may be increased to a maximum of about 7%.

Age hardness is induced in these alloys by holding them at an elevated temperature for a period sufficient to increase the amount of beryllium in solution, quenching the alloy, reheating it to a suitable temperature, and holding it at the latter temperature for a period of time. The temperature from which the alloy is quenched is hereinafter referred to as the solution temperature, and the temperature to which the alloy is raised after quenching is referred to as the aging temperature.

Both time and temperature affect the amount of beryllium which goes into solution. The solution rate increases rapidly with increases in temperature and, therefore, in order to avoid prolonged heating, it is preferred to use the highest practical solution temperatures. In addition, the total amount of beryllium has an effect on the solution rate, larger quantities increasing the rate. Therefore, lower temperatures and shorter solution periods may be employed with larger quantities of beryllium. In addition, it is found that the carbon content has an important effect on the solution temperature, low carbon alloys requiring higher solution temperatures than higher carbon alloys, all other things being equal. The maximum amount of beryllium which will go into solid solution with molybdenum containing carbon between .02% and .06% at any temperature is about .05% and, consequently, larger quantities of beryllium are employed primarily to reduce the solution temperature or the holding time or both.

In applying the above principles to practical needs, it is found that where it is possible to produce low oxygen alloys, as little as .03% beryllium will effect a small but significant amount of age or precipitation hardness. However, it is necessary to use very high solution temperatures or hold the alloy at its solution temperature for a prolonged period. The preferred solution temperature for such an alloy would be about 3800° F., with a holding period in the order of four to six hours. With this treatment, the age hardness will be increased if at least .02% carbon is present. As the oxygen content increases from its practical minimum of .001%, the amount of beryllium should be increased, the added beryllium being at least that required to combine with the increased oxygen to form beryllium oxide.

Age hardness is obtained only if the minimum beryllium content increases from .03% to .08% as the oxygen content increases from .001% to its maximum of .05%. In view of the desirability of reducing the solution temperature and time, it is preferred to employ beryllium in a minimum amount which increases from .05% to .1% as the oxygen content increases from .001% to its maximum of .05%; a high degree of precipitation hardening may be obtained with such minimum amounts of beryllium. It is also preferred that not more than .15% beryllium be employed in alloys which are to be hot-worked.

For example, to obtain maximum hardness, an alloy containing .10% beryllium and .02% or more carbon is preferably held at a solution temperature of about 3350° F. for three to four hours and then quenched. An alloy containing .15% beryllium and about .02% or more carbon is preferably held at a solution temperature of about 3350° F. for about two to three hours. An alloy containing .15% beryllium and as little as .006% carbon is preferably held at a solution temperature of about 3800° F. for about two hours or 3600° F. for about six hours. If maximum hardness is not required, the holding period and solution temperature may be reduced.

In all cases, a solution temperature of at least 3200° F. is required to produce significant age or precipitation hardness. Higher solution temperatures than those specified above may be employed, but care should be taken to avoid holding the alloy at a temperature which will melt any substantial portion. The time for which the alloys of the present invention may be held at the solution temperature is limited only by the practical consideration that equilibrium is approached asymptotically with time. The solution heat-treatment should be carried out under substantially nonoxidizing conditions, i. e., in an atmosphere of inert gas, such as argon or helium, or of hydrogen or in a vacuum.

After the solution heat-treatment is complete, the alloy should be cooled at a rate sufficient to

retain a supersaturated solution of beryllium. This rate may be attained in pieces of about one-half inch controlling section by cooling in still air, and in larger sections by quenching in oil or water.

The alloy is next subjected to a temperature in the range of about 1600° F. to 2000° F. for a prolonged period of time. The time required depends primarily upon the temperature employed. For example, maximum hardness has been obtained by employing temperatures of 2000° F. for a time of only forty minutes with an alloy containing .15% beryllium, .033% carbon and the balance molybdenum. About six hours at 1750° F. is required to obtain maximum hardness with the identical composition. At 1500° F., substantially less than maximum age hardness was developed in sixty-six hours, although the hardness was still increasing at the end of that period. In general, the lower the aging temperature used, the greater the ease of control and the longer the time required to attain maximum hardness; but it will be apparent that the temperature and time selected will depend upon considerations of practical convenience and the particular requirements of the application. To produce any significant age hardening it is necessary to hold the alloy at least fifteen minutes at 2000° F. or three hours at 1600° F., the time increasing as the holding temperature decreases from 2000° F. to 1600° F. The preferred aging temperature is in the neighborhood of 1800° F., at which temperature maximum age hardness may be produced in from two to eight hours. During aging the alloy should be protected against oxidation by means such as an inert atmosphere, a hydrogen atmosphere, a vacuum, or immersion in a molten salt bath.

The hardness developed in molybdenum-base alloys containing beryllium by the above-described heat-treatment is decidedly higher than that obtained in any hitherto known, forgeable molybdenum-base alloys. Thus, in general, the hardness which may be achieved exceed 500 V. P. N. (Vickers Pyramid Numeral) if beryllium is present in amounts of .05% or more.

If desired, instead of quenching to room temperature and then reheating, the alloy may be cooled fairly rapidly from the solution temperature to the aging temperature and then aged. For this purpose, the alloy may be quenched in a molten metal or molten salt bath to a temperature at or below the aging temperature.

As set forth in the application of Norman L. Deuble, Serial No. 234,465, filed June 29, 1951, an oxidation resistant coating may be formed on molybdenum-base alloys by dipping them in a molten bath of aluminum containing from 5% to 50% silicon. Thus, a bath, at a temperature between 1350° F. and 2000° F., may be employed as a quenching bath in the heat-treatment of the present invention and the resulting quenched alloy may then be aged in an oxidizing atmosphere. The preferred practice is to use an aluminum quenching bath containing from 10% to 15% silicon at a temperature of 1350° F. to 1600° F. and then age the alloy at about 1800° F. The use of a quenching bath of molten metal which will form an oxidation resistant coating may be applied with advantage to any molybdenum-base alloy that is capable of developing age hardness.

Tungsten and molybdenum form a continuous series of solid solutions. The addition of tungsten to molybdenum causes a mild increase in the elevated temperature hardness and reduces the capacity of the alloy to be worked at elevated temperatures. Molybdenum-beryllium-tungsten alloys which are capable of being worked at elevated temperatures and of developing age hardness may be obtained if, as the tungsten percentage approaches a maximum of about 50%, the amount of berylium is proportionately reduced from its maximum of .25% toward its minimum of .03%. It is preferred to use no tungsten or to maintain the tungsten content below about 10%.

Age hardness is obtained by the above treatment when beryllium is present in molybdenum-base alloys as long as, in a given alloy, molybdenum is present in an amount exceeding the amount of tungsten present, if any, and the total of the molybdenum and tungsten constitutes at least 70% of the alloy. Other elements may also be present. Thus, certain hereinafter-listed transition elements produce advantageous effects when added to the molybdenum-berryllium alloys which are capable of being age hardened by the process of the present invention. However, to produce an alloy which can also be worked at elevated temperatures to a beneficial degree, the amounts of tungsten, other transition elements, aluminum and berryllium must be limited; the preferred alloys contain at least 85% molybdenum. Thus, even in pure binary alloys of molybdenum, the following advantageous transition elements should not be present in amounts exceeding the following percentages of the alloy is to be worked at elevated temperatures:

	Percent
Titanium	14.0
Vanadium	7.0
Chromium	2.0
Iron	1.3
Cobalt	.9
Nickel	.4
Columbium	10.0
Tantalum	9.0
Zirconium	2.0

Beryllium in amounts in excess of about .03% and up to a maximum of about .25% and aluminum in amounts in excess of .4% and up to a maximum of 2.5% have an effect on workability similar to that of the above transition elements. They all produce a proportionate increase in solution hardness at 1600° F. as their quantities increase toward their maximums. The maximum amounts given for aluminum and each of the transition elements other than tungsten correspond roughly to those quantities of each element which, when added alone to molybdenum, will produce a hardness at 1600° F. of 200 V. P. N. in an annealed casting. Beryllium alone in the amount of .25% has the same effect. It has not been possible with normal working techniques to achieve a worthwhile percentage of recovery from the working of molybdenum-base alloys having hot hardnesses above that value, but a beneficial working at temperatures substantially above 1600° F. may be performed on the alloys of the present invention, provided the hardness at 1600° F. does not exceed about 200 V. P. N. in an annealed casting. The effects of all the above-mentioned metals, including tungsten, are additive and, therefore, when any two are present, the maximum permissible amount of one should be proportionately reduced from the stated maximum given above to the extent that the other metal approaches its stated maximum if the alloy is to have the capacity of being worked at elevated temperature to a beneficial

degree. Still further reductions on the same basis must be made if more than two are present, and in all cases less than these maximums gives the best results.

For the purpose of obtaining maximum hardness and strength at elevated temperatures in molybdenum-base alloys which contain beryllium and which are well adapted to hot-working, the preferred alloying transition elements are titanium, columbium, vanadium, zirconium and tantalum. Molybdenum-base alloys characterized primarily by the beneficial effects of these elements, respectively, are more fully disclosed and claimed in applicants' copending applications filed concurrently herewith, as follows: Serial No. 250,204, "Molybdenum-Titanium Alloys"; Serial No. 250,207, "Molybdenum-Columbium Alloys"; Serial No. 250,203, "Molybdenum-Vanadium Alloys"; Serial No. 250,206, "Molybdenum-Zirconium Alloys"; Serial No. 250,205, "Molybdenum-Tantalum Alloys."

Therefore, the expression molybdenum-base alloy as used in the following claims, means unless otherwise specified that the alloy is at least 70% molybdenum or molybdenum and tungsten with the molybdenum exceeding the tungsten, but other elements may be present in amounts which do not materially impair the age-hardening characteristics of molybdenum-beryllium alloys.

Aluminum in amounts above .4% and the above transition elements, other than tungsten, when present will usually reduce the temperature at which a liquid phase appears and, consequently, may necessitate the use of somewhat lower solution temperatures which approach 3200° F. as a minimum. The maximum safe temperature can be determined readily by trial.

The following specific examples are given by way of illustration to show molybdenum-beryllium alloys which have compositions within the above-specified ranges and to which the heat-treatment of this invention is applicable:

Example 1

	Per cent
Berryllium	.15
Carbon	.033
Molybdenum	balance

Example 2

	Per cent
Beryllium	.05
Carbon	.042
Tungsten	10
Molybdenum	balance

Example 3

	Per cent
Beryllium	6.5
Carbon	.05
Molybdenum	balance

Example 4

	Per cent
Beryllium	.04
Aluminum	.08
Molybdenum	balance

Example 5

	Per cent
Beryllium	.05
Aluminum	.10
Carbon	.01
Molybdenum	balance

Example 6

	Per cent
Beryllium	.09
Tungsten	5
Carbon	.04
Molybdenum	balance

Example 7

	Per cent
Beryllium	.137
Carbon	.027
Aluminum	.130
Molybdenum	balance

Example 8

	Per cent
Beryllium	.137
Carbon	.006
Aluminum	.156
Molybdenum	balance

The effect of heat-treatment on the alloys of this invention may be illustrated by the first example given above. That alloy, having a hardness of 230 V. P. N. in the annealed casting, was raised to a temperature of 3600° F. and oil quenched after being maintained at that temperature for two hours. The hardness after quenching was 430 V. P. N. After heating at 1750° F. for seven hours, the room temperature hardness of the alloy was increased to 680 V. P. N. A second sample of the same composition, subjected to the first two steps of the heat-treatment, was then heated at 2000° F. for forty minutes and attained a hardness of 675 V. P. N. A third sample of identical composition, after quenching from 3600° F., was heated at 1500° F. for sixty-six hours and a hardness of 520 V. P. N. was reached.

This heat-treatment also improves the hot-hardness of the alloy. The hot-hardness, as well as room temperature hardness, is retained by the alloy for substantial periods of time on exposure to elevated temperatures. The alloy of Example 1, after being fully hardened, had a hardness of 680 V. P. N. at room temperature and a hardness of 520 V. P. N. at 1600° F. Its hardness was fully retained after long exposure at 1500° F. and showed very little reduction after fifty-eight hours of exposure at 1750° F.

Although the hardness induced by heat-treating is retained for a long period at 1600° F., the induced age hardness may be removed by heating to a temperature between 2200° F. and 3000° F. and furnace cooling. This characteristic of molybdenum-base alloys containing beryllium above .03% is particularly beneficial in the respect that the hardness of the alloy may be reduced to facilitate fabrication operations and thereafter increased to meet service requirements.

Cast molybdenum-beryllium alloys may be produced in accordance with the following process: (1) mixing molybdenum, beryllium and any other desired elements in the form of powders, in the desired proportions; (2) pressing the mixture into successive pellets to form a continuous rod; (3) sintering the rod to impart sufficient strength to the same to render it self-supporting; and (4) arc-melting the sintered rod as a consumable electrode in an inert atmosphere and collecting the metal directly in a water-cooled copper mold.

In this process, the starting materials used are commercially pure molybdenum powder, preferably containing not more than about .05% oxygen, and commercially available beryllium pow-

der. Metals in the form of small chips or granules may comprise part of the charge.

The powder charge is fed into an extrusion die positioned beneath the ram of a reciprocating press wherein successive pellets or layers of the powder material are pressed continuously on top of preceding pellets to form a continuous rod of pressed metal powder. Adequate compaction of the pellets is obtained by using pressures of 10,000 p. s. i. to 20,000 p. s. i., with 14,000 p. s. i. normally being adequate. Pressing, sintering and arc-melting are preferably performed within the same container in an inert atmosphere such as argon or helium.

Sufficient strength to make the pressed metal rod self-supporting is imparted by sintering the rod at a temperature of 2400° F. to 2900° F. for approximately a quarter of a minute to several minutes. In some cases, difficulty has been encountered in making a molybdenum-beryllium rod which was self-supporting in the absence of carbon and/or aluminum. The explanation for this phenomenon is unknown but, when the difficulty is encountered, it may be remedied by incorporating in the powder metal mixture .01% or more carbon or .01% or more aluminum. Sintering may be accomplished by any desired method of heating. Electrical resistance heating has been employed successfully.

The sintered rod is then used as a consumable electrode in an inert atmosphere arc furnace. Melting is started by striking an arc between the rod and a starting electrode comprising a pile of chips of the same or similar alloy placed on a disc of molybdenum at the bottom of the casting mold. A water-cooled copper mold has been successfully used for receiving the molten molybdenum alloy without contaminating the alloy with copper. Molten alloy striking the water-cooled copper mold quickly solidifies, forming a protective coating on the surface of the mold. Thereafter, the liquid alloy becomes the lower electrode and the upper, consumable electrode is mechanically fed toward the lower, liquid electrode to maintain continuous melting with the proper arc spacing.

If the alloy is to be worked at elevated temperatures, it is necessary to avoid the introduction of significant quantities of oxygen as a contaminant in the inert atmosphere. The inert atmosphere may be purified by passing it through a commercial drying tower before introduction into the casting container. It may be recirculated and re-used after passing over a bed of titanium metal maintained at approximately 1500° F. and a bed of magnesium metal maintained at approximately 1100° F. Because of the relatively high volatility of beryllium and/or aluminum at the arc temperature, it has been found advantageous to maintain the pressure of the inert atmosphere within the casting container at substantially atmospheric pressure or slightly above—for example, up to about 15.5 pounds per square inch. In operation, the casting container is first evacuated and then filled with the inert gas, and thereafter a positive pressure of gas is maintained in the casting container at a pressure of atmospheric or slightly above. When carbon is used, the partial pressure of carbon monoxide in the melting chamber is preferably kept below about 100 microns. In some cases, this may require circulation of the purified inert gas through the chamber.

One suitable form of apparatus for use in forming, sintering and melting the powder rod is disclosed in the copending application of Edgar K. Leavenworth, Serial No. 787,797, filed November 24, 1947, now Patent 2,651,952.

It has not been possible to hot-work alloys containing beryllium in excess of .25%, but such alloys have highly desirable properties when used in an unworked state. Thus, molybdenum-base alloys containing beryllium in amounts up to 7% not only may be given the above-described age hardness by heat-treatment, but exhibit high as-cast hardness and a fine grain structure. Moreover, the alloys of higher beryllium content have a relatively low melting point and, therefore, may be produced by melting the constituents in a zirconium oxide crucible in a furnace containing an inert atmosphere. This is particularly true of molybdenum-beryllium alloys containing from 6% to 7% beryllium, which become entirely molten at temperatures in the range of 3400° F. to 3600° F.

It is known that beryllium in certain forms is highly toxic to humans. The toxic hazards, if any, involved in the production, heat-treating and forging of alloys of the present invention have not been determined but, pending further information, caution has been exercised, particularly during forging operations, to avoid inhaling fumes from the heated metal.

All of the proportions given are percentages by weight in the final alloy.

What is claimed is:

1. A process for hardening a molybdenum-base alloy containing not more than .05% oxygen and from .03% to 7% beryllium, the minimum beryllium increasing from .03% to .08% as the oxygen content increases from .001% to .05%, which comprises holding the alloy at a temperature of at least 3200° F. for at least one hour, quenching the alloy, and thereafter age hardening the alloy at a temperature between 1600° F. and 2000° F.

2. A process as defined in claim 1 for hardening a molybdenum-base alloy containing at least 85% molybdenum, from .03% to .25% beryllium and not more than .05% oxygen, the minimum beryllium increasing from .03% to .08% as the oxygen content increases from .001% to .05%.

3. A process as defined in claim 1 for hardening a molybdenum-base alloy containing at least 85% molybdenum, from .05% to .15% beryllium and not more than .05% oxygen, the minimum beryllium increasing from .05% to .10% as the oxygen content increases from .001% to .05%.

4. A process for hardening a molybdenum-base alloy containing not more than .05% oxygen and from .03% to 7% beryllium, the minimum beryllium increasing from .03% to .08% as the oxygen content increases from .001% to .05%, which comprises holding the alloy at a temperature of at least 3200° F. for at least one hour, quenching the alloy in a molten bath of an aluminum-silicon alloy, said bath being at a temperature between 1350° F. and 1600° F., and thereafter age hardening the alloy at a temperature between 1600° F. and 2000° F.

5. A process as defined in claim 4 for hardening a molybdenum-base alloy containing at least 85% molybdenum, from .03% to .25% beryllium and not more than .05% oxygen, the minimum beryllium increasing from .03% to .08% as the oxygen content increases from .001% to .05%.

6. A process as defined in claim 2 for hardening a molybdenum-base alloy containing at least 85% molybdenum, from .05% to .10% beryllium and not more than .05% oxygen, the minimum beryl-

lium increasing from .05% to .10% as the oxygen increases from .001% to .05%.

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