United States Patent

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[73] Assignee **The United States of America as represented by the United States Atomic Energy Commission**

[54] **PROCESS FOR PRODUCING DISPERSION-HARDENED SUPERALLOYS BY INTERNAL OXIDATION**
3 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** **75/213,** 75/224, 75/225, 29/182.5
[51] **Int. Cl.** **B22f 1/00**
[50] **Field of Search** 75/206, 208, 211, 213, 224

[56] **References Cited**

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ABSTRACT: Iron-, nickel-, and cobalt-base alloys containing chromium in an amount sufficient to provide excellent scaling resistance to high temperature are made pervious to controlled quantities of oxygen by alloying with an appropriate amount of a metal selected from thorium, yttrium, or one of the rare earth (4*f*) metals to form a lamellar eutectic structure. Powders of these alloys are roasted in air to pick up oxygen, then cold compacted and sintered to consolidate the mass while at the same time allowing diffusion of oxygen to form a uniform and ultrafine dispersion of stable oxide particles. Subsequent hot mechanical working shapes and further consolidates the alloy while improving the distribution of metal oxide particles.

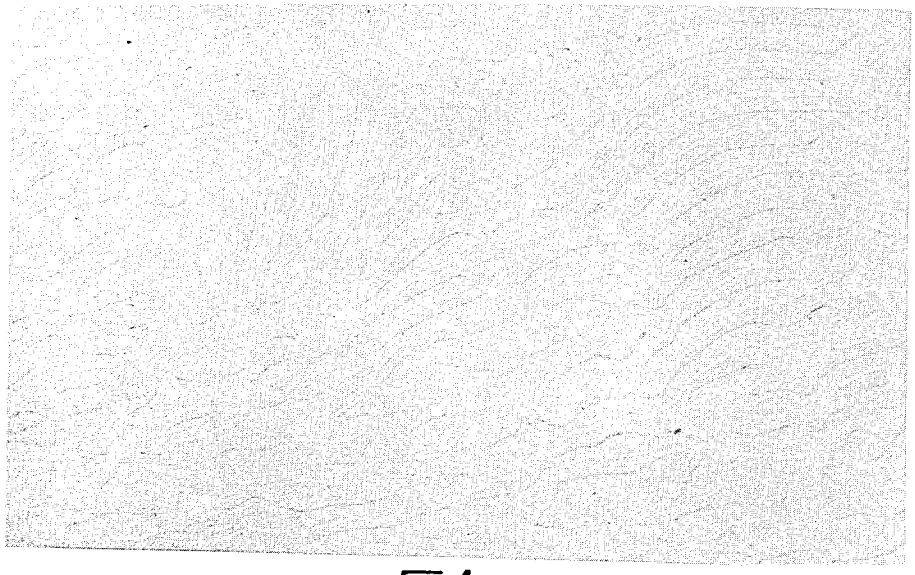


Fig. 1 a

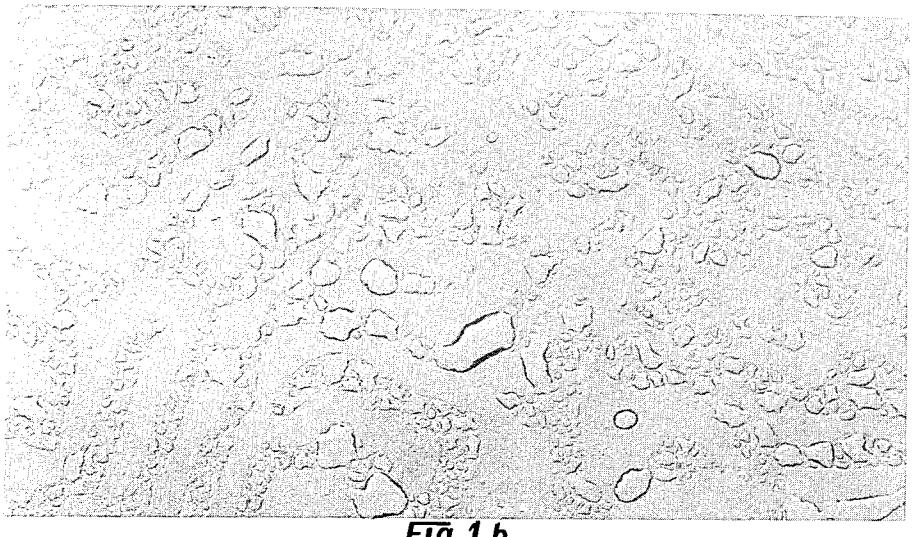


Fig. 1 b

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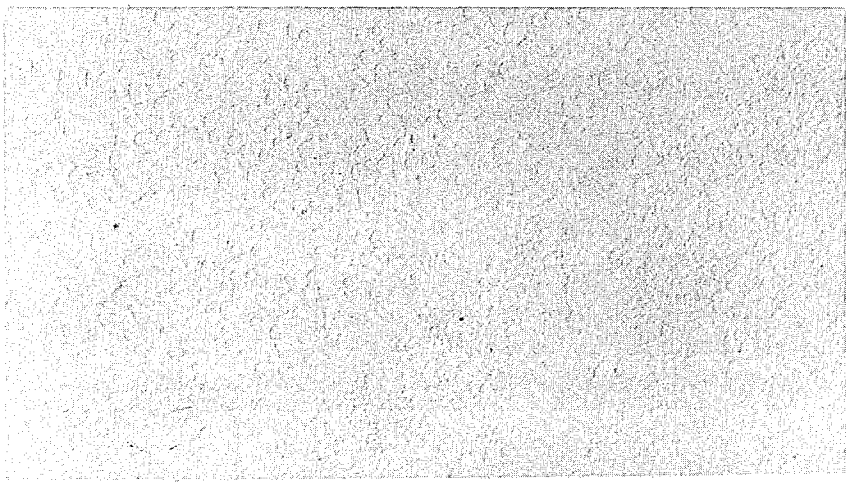


Fig. 2

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PROCESS FOR PRODUCING DISPERSION-HARDENED SUPERALLOYS BY INTERNAL OXIDATION

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

The present invention relates to dispersion-hardened superalloys and more particularly to a process for producing dispersion hardening in alloys classified as heat resisting by an internal oxidation technique.

With the advent of higher performing turbojet engines and various nuclear propulsion devices for space exploration, need has arisen for loading-carrying materials capable of operation in oxidizing atmospheres at temperatures of the order of 1,100° C. Because of the difficulty of developing scaling resistance in refractory metals, the family of nickel-and cobalt-base materials known as superalloys has been intensively investigated for filling this need. A 2,000 ° F. temperature requirement, however, is some 300 degrees higher than the maximum useful in-service temperature designated for these alloys. Strong incentive, therefore, exists for developing hard particle dispersion strengthening in these materials.

The merits and characteristics of dispersion-hardened metals are well documented. Oxide dispersion-strengthened alloys show outstanding high-temperature mechanical properties and thermal stability when certain structural conditions are met. These conditions include: (1) the size of dispersant particles should be small (<0.05 micron) and uniformly and closely spaced less than about 0.5 micron; (2) the dispersed phase should be hard; (3) the interfacial energy of the particle-matrix interface should be low; (4) the solubility and diffusivity of the particle's constituent elements should be low; and (5) the free energy of formation of the dispersed phase should be high.

Whereas a number of processes have been used to obtain fine dispersions of oxides, a most promising one, especially from the standpoint of microstructural requirements, is that of internal oxidation. The process basically consists of selectively oxidizing one component of a solid-solution alloy by diffusing in oxygen to form a stable-oxide precipitate. Best results are achieved when using more noble metals, e.g., Au, Cu, or Ni, as the solvent and strong oxide formers as the solute. In addition to the feature of desirable fine and uniform dispersion, materials processed by this method have low dispersoid-to-matrix interfacial energy and generally have shown marked resistance to particle coalescence. Some of the better examples of elevated temperature property improvement through dispersion hardening have resulted from this technique.

Prior to this invention the internal oxidation technique had not been effective in alloys which contain chromium and/or aluminum in sufficient amounts to make them oxidation resistant. Oxidation-resistant concentrations of chromium and/or aluminum form protective scales and oxygen no longer diffuses in to form precipitates. Thus, materials of great industrial importance have not benefited by this technique. Attempts to overcome this limitation by internally oxidizing chromium-lean alloys and subsequently diffusing in chromium for oxidation resistance have not been practicable. Attempts by other investigators to internally oxidize materials already alloyed for oxidation by using oxidizing atmospheres of very low oxygen partial pressure also were unsuccessful.

SUMMARY OF THE INVENTION

The scope of the inventive concept herein disclosed refers to, in one aspect, a process which converts materials which are normally oxidation or heat resistant to a condition which accommodates the diffusion of a controlled quantity of oxygen within their interior to result in a precipitated, finely dispersed, and stable-oxide phase. By this internal oxidation process, materials are formed comprised of a hard-particle oxide phase suitable dispersed in a heat-resistant metal matrix. This is made possible by modifying appropriate alloy compositions which in themselves are quite heat resistant and, consequently, nonconductive to internal oxidation, by adding a eutectic-forming concentration of at least one element selected from thorium, yttrium, and the 4*f* rare earth metals having an atomic number in the range 58–71, inclusive.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 consists of replica electron micrographs at 7,500 magnification of arc-melted and cast heat-resistant nickle-base alloy modified with yttrium (a) before internal oxidation and (b) after internal oxidation and precipitation of the oxide phase and illustrates the kind of changes in microstructure which result form the oxidation step of this general process.

FIG. 2 is a replica electron micrograph at 15,000 magnification of an extruded rod (transverse section) of an internally oxidized modified nickel-chromium alloy resulting from the procedure as described in example I.

We have found that modified nickle-base alloys containing from50 to 80 weight percent nickel and from 10 to 20 weight percent chromium, iron-base alloys containing up to 84 weight percent iron and 11.5 to 22 weight percent chromium, and cobalt-base alloys containing 20 to 25 weight percent chromium are amenable to the internal oxidation process of our invention to produce a stable, internally oxidized, induced, dispersed phase. In addition, these nickel iron, and cobalt base alloys, when allowed with moderate amounts of molybdenum and/or tungsten, are also amenable to this form of oxide dispersion hardening. Unmodified alloys, on the other hand, have shown no evidence of internal oxidation under oxidizing conditions.

When a melt of any of these alloys is appropriately modified by the addition of thorium, yttrium, or one of the rare earth metals, an essentially two-phase lamellar or modified eutectic structure is formed. This eutectic is comprised of a hexagonal $M_{17}X_2$, modifier containing intermetallic and a solid-solution terminal phase. The M of the intermetallic consists of iron, nickel, or cobalt, depending on the base composition of the alloy, and the X is the thorium, yttrium, rare earth metal. The chromium which is added to high-temperature alloys for conferring oxidation resistance partitions to the matrix or terminal phase of the eutectic. Tungsten and molybdenum, generally present in superalloys as strengtheners, also reside in the terminal phase. The intermetallic phase thus is largely void of chromium, tungsten, and molybdenum and exists as a continuous or semicontinuous constituent in an alloy-rich, heat-resistant, matrix phase. Most significant to this invention, oxygen diffuses at elevated temperatures with great facility within the intermetallic phase and combines with the modifying additive to form a fine precipitate of stable oxide particles. As a consequence, the intermetallic changes in composition and may undergo a structural transformation. Thereupon, chromium and the other alloying elements diffuse in and around the precipitate from the surrounding terminal phase constituent.

The characteristics of the dispersion structure produced by the inward diffusion of oxygen are illustrated for an arc-melted and cast nickel-base alloy containing 7 atomic percent yttrium alloy in FIG. 1*b*. The microstructure of this alloy in the cast state showed a completely lamellar structure (FIG. 1*a*) indicating that the alloy was at the eutectic composition as is the case when pure nickel is alloyed with 7 atomic percent yttrium. The depth of internal oxidation observed in this alloy after 2 hours at 1200° F. was approximately 0.005 inch. Penetration is also substantial at 900° C. and more than ample for the treatment of alloys in power form.

A property most important to the elevated-temperature mechanical properties of dispersion-hardened materials, that of thermal stability of the precipitated particles, is most outstanding for these materials. Whereas the intermetallic phases from which the stable oxide particles form generally coarsen at relatively low temperatures (around 900 ° C.), the oxide precipitates resist coalescence to 1250° C. and higher.

DETAILED DESCRIPTION

In order to practice this invention an alloy composition is formulated in such a way as to produce the desired lamellar eutectic structure. To assure in the final microstructure a low interparticle spacing of the oxide precipitate, important to high-temperature strength, a means for refining the eutectic structure over and above that obtainable by casting or shotting of the liquid metal is needed. The finer the eutectic structure, the finer will be the oxide precipitated from it.

This refining of the eutectic structure can be accomplished by a special process known in the trade as splat-cooling. In one variation of this process, molten material is poured, as a fine stream, under a protective atmosphere into the path of a horizontal inert gas jet where the liquid metal is atomized and simultaneously jetisoned at high velocity against a rotating quenching disc. This supercools the molten particles from the liquid state and thereby refines the eutectic structure. Powder particles prepared by this process vary in form from star-shaped splashings to ski-shaped ones, depending upon the alloy being treated. They are flat and vary in length from one-sixteenth to one-half inch or higher. The powder in this form is not generally suitable for carrying out usual powder metallurgy operations and needs to be ground into particles of equiaxed shape. The splat powder, therefore, is granulated by ball-milling for several hours in a suitable ball-mill using a hydrocarbon such as petroleum ether or hexane as a lubricant. The ground powder is freed of the lubricant by evaporating it off and then sieved to a −100 +325 mesh size. In this form, the powder handles well and is easily dispensed and compacted.

Before oxidizing the powder it is important to make sure that all fines are removed since extremely small pieces of the material develop into undesirable all-oxide particles during the subsequent oxidation step and are manifested as oxide clinkers in the final microstructure. This can give adverse effects in the final material by acting as stress risers to promote cracking or acting in other ways to open up voids during extended deformation.

After the powder preparation steps, oxygen in the appropriate amount is imparted to the material for purposes of internal oxidation and then the powder is cold pressed into compacts, sintered, and finally sealed in billets for hot extruding to bar or sheet form. The oxidation operation may be done by production-type techniques using rotary kilns with atmospheres of selected concentrations of oxygen. It can also be done simply by roasting the powders in air at 500° C. to 600° C. while spread over the top surface of an alumina brick. The intent is to associate the correct amount of oxygen with the powder and then subsequently diffuse it into the interior of the grains to form the desired dispersion of precipitated oxide particles when conducting the subsequent pellet sintering operation. Accordingly, during heating to the sintering temperature, compacts were soaked at about 900° C. for 1 to 2 hours in an inert atmosphere (argon or vacuum) allow internal oxidation to proceed before consummating the sintering, which was usually done at 1,500° C. to 1,100° C.

As mentioned earlier, internally oxidation alloys in the powder form ordinarily present problems by forming continuous oxide films over the powder grains which interfere with subsequent sintering and metal working of the alloys. This is not the case here. The oxide films are actually eliminated from the powder granules during the latter stages of the internal oxidation while the pressed pellets are being soaked at the intermediate temperatures and then later heated for the sintering. In other words, the powders are capable of self-cleaning which occurs by driving the oxygen in the form of surface oxide into the interior of the powder grains as an incident to sintering.

For the purposes of this invention, the most stable oxide form when using thorium as the alloy modifier may be considered to be ThO_2 and for yttrium and the rare earths, M_2O_3, where M is the metal. In selecting the suitable concentration of oxygen for conducting the internal oxidation, we arbitrarily chose a level which corresponded to 90 percent of the amount needed to completely oxidize the modifying additive to its most stable oxide form; that is, to MO_2 or M_2O_3, as the case may be.

Cold pressing is done in steel dies at a pressure of around 33 tons per square inch. The sintering operations can be conducted in argon or vacuum and in either case produce strong, good quality compacts with metallic gray surfaces. When sintering at 1,050° C. to 1,100° C., as was done here, compacts shrank only a moderate amount leaving the major consolidation for the hot extrusion step. The compacts are finally incorporated in billets made of appropriate superalloys and extruded to a reduction ratio of 4/1 to 9/1 at a temperature of 1,050° C. to 1,100° C. Further metal working can be done by hot swagging or forging as desires.

To summarize, when oxygen is incorporated in powders of the modified alloys at the indicated levels by roasting in air and subsequently sintered, an oxide precipitate of submicroscopic size forms which, on subsequent working of the powder to form wrought shapes is responsible for high elevated-temperature strength at exceptionally high temperatures. In addition, specified material so treated exhibits unusually high oxidation resistance, displaying a thin, tenacious surface oxide scale.

The following examples illustrate exemplary embodiments of the invention.

EXAMPLE I

This example describes the preparation of an improved nickel-chromium alloy having outstanding strength of oxidation resistance at high temperatures, i.e., at temperatures in the range 1,000° C. to 1,200° C. The original composition consisted of a binary nickel-base alloy containing 20 weight percent chromium, a heat-resisting alloy commonly referred to as Nichrome. Thorium metal in an amount of 21 weight percent, a concentration appropriate to forming a nickel-chromium-thorium eutectic, was added to the alloy and the resultant ternary material was induction melted and prepared as a plated powder in the following way. After induction melting within a chamber back-filled with argon, the molten alloy was atomized by bottom-pouring from the crucible as a thin stream of liquid metal into the path of a horizontal jet of argon. The jet dispersed the molten metal as tiny droplets and impinged them at high velocity against a 3½-foot-diameter, chromium-plated, copper quenching disc rotated at 900 revolutions per minute. Powder formed by splashing against the wheel, referred to as splat, was collected and the fines (particles missing the wheel) removed by sieving through a 100-mesh screen. Crusty conglomerates of powder formed by particles sticking against the atomizing chamber were removed from the splat. The splat was then ball-milled for 4 hours in an argon-filled, hermetically sealed mill using petroleum ether as the lubricant. The powder was sized to −100 +325 mesh by sieving and then roasted in air at 500° C. for 3 hours to associate 2.48 weight percent oxygen with the alloy. The oxidized powder was then compacted in a die at 33 tons per inch and heated for 2 hours at 900° C. before sintering in argon at 1,075° C. for 3 hours. The sintered compacts were incorporated in a nickel-base alloy, evacuated and sealed, and then extruded at a reduction ratio of 4/1 at 1,050° C. The extruded product, along with unmodified Nichrome, was machined into suitable metallurgical specimens for tensile testing. In addition, specimens were heated to 1,095° C. in air for 100 hours along with samples of Nichrome in order to test for oxidation resistance. A comparison of the tensile properties at 1,095° C. between the modified alloy and the original nickel-chromium alloy is presented in the table.

The improved elevated-temperature strength in the modified alloy is self-evident from the table of tensile strengths. The internally oxidized product also had an improved oxidation resistance as well as improved strength at elevated temperature. For example, the unmodified nickel-chromium binary alloy, when heated for 100 hours at 1,095° C., experienced a weight gain of 0.24 mg./cm.², whereas the

TABLE

Tensile Properties of Extruded Internally Oxidized Modified Nichrome Alloy at 1095° C.[a]

Alloy	Yield Strength (psi)	Ultimate Tensile Strength (psi)	Elongation (%)
Internally oxidized Nichrome-Thorium [b]	12,040	13,179	1.47
Nichrome Standard [c]	6,779	7,895	22

[a] Heated by induction in air.

[b] Chemically analyzed 63.7% Ni, 15.33% Cr, 20.2% Th, and 2.48% oxygen. Fabricated by internally oxidizing ground splat powder 3 hours at 500° C., cold pressing, sintering at 1075° C., and extruding at 4/1 reduction ratio at 1050° C.

[c] Nominally 80% Ni and 20% Cr. Arc melted and cast in copper mold, and extruded at 4/1 reduction ratio at 905° C.

modified alloy strengthened by internal oxidation experienced a weight gain of only 0.06 mg./cm.²—an improvement in oxidation resistance by a factor of 4. More important, the scale formed on the internally oxidized alloy was very thin and extremely tenacious, whereas the scale on the unmodified Nichrome spalled off easily with thermal cycling.

EXAMPLE II

A cobalt-base alloy containing 28 weight percent chromium, 3 weight percent nickel, and 6 percent molybdenum (known under the trademark Vitallium) was modified by adding 7 atomic percent thorium and prepared as splat powder generally as described in example I. The ball-milled powder was heat treated in air at 600° C. for 2 hours to yield a powder containing 2.42 weight percent oxygen. The oxidized powder was consolidated, sintered at 1,100° C., and extruded at 1,050° C. at a reduction ratio of 4/1. This material responded well to the fabrication steps and displayed a fine dispersion structure. Specimens of this material were examined for oxidation resistance in air at 1,095° C. for 100 hours and compared with their unmodified counterpart, Vitallium. An excellent oxidation resistance in comparison to the unmodified alloy was noted. Under these conditions, the unmodified alloy experienced a weight gain of 0.79 mg./cm.², whereas the modified alloy had a weight gain of only 0.14 gm./cm²—a reduction in oxidative scaling by a factor of nearly 8. The scale formed on the internally oxidized alloy was thinner and much more tenacious than that formed on the unmodified alloy.

What is claimed is:

1. A method for dispersion hardening iron-, nickel-, or cobalt-base alloys containing at least 10 weight percent chromium which comprises:
   a. adding a eutectic-forming concentration of a metal selected from Th, Y, or a 4*f* metal having an atomic number from 58 to 71 to said alloy;
   b. forming a melt of the resultant alloy;
   c. atomizing the melt to produce a powder containing a fine lamellar eutectic structure;
   d. roasting the powder to impart oxygen required to form stable oxides of the selected metal;
   e. compacting the oxidized powder;
   f. heating the compact below the sintering temperature to precipitate an oxide phase; and
   g. sintering the compact in an inert atmosphere.

2. The method according to claim 1 in which the liquid metal is atomized by splat-cooling.

3. The method of claim 1 in which the powder resulting from atomization of the melt contains an $M_{17}X_2$-eutectic phase in which M is selected from the group consisting of iron, nickel, or cobalt and X is selected from the group consisting of thorium, yttrium, or a 4*f* metal having an atomic number from 58 to 71.

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