PREPARING MOLTEN ALUMINUM - COPPER EUTECTIC ALLOY

STIRRING

PERMITTING THE MOLTEN MATERIAL TO SOLIDIFY

FORMING ARTICLES SUCH AS WELDING FILLER RODS

FIG. 1

FIG. 2
The present invention relates to improvement of properties of metals by way of unique internal reinforcement effects of minute particles, and, in one particular aspect, to novel and improved composite metallurgical products in which a host metal alloy, such as aluminum, is used internally reinforced by uniformly distributing throughout the host minute filament, for example, of refractory materials, such as silicon carbide of the order of hundreds of microns down to a few microns or less in diameter.

It is of course a commonplace objective for the metallurgist to pursue improvement of the physical properties, economics, and convenience in processing of metals, and the mainstream of efforts along such lines has been in the direction of alloying. However, it has also been known that certain beneficial effects can be realized through inclusions of materials which are not involved in true alloying actions and which may instead serve such simple mechanical functions as filling, gross structural reinforcement, and imparting abrasive qualities or the like. Further, there have been significant advances in powder metallurgy, involving compacted and/or sintered particles of various types which together form coherent masses having characteristics which are advantageous for special purposes.

By way of distinction, the present teachings are concerned with internally-reinforced metals which may be cast directly from a melt, using generally conventional elementary techniques and uncomplicated low-cost equipment, to form complex configurations having a high degree of structural integrity and precise dimensions, and to form billets or the like lending themselves to extensive mechanical working into a variety of shapes without serious weakening. The resulting products thereby exhibit certain characteristics of homogeneous material, although in fact they comprise metal alloy in which minute particles of higher-melting-point materials are automatically distributed substantially uniformly, essentially along the grain boundaries as the melt solidifies. In the case of aluminum products, for example, it is well known that a commonly-used alloy with about 4.5% copper is rather lightly susceptible to hot tearing and cracking, does not well resist high temperatures, and does not lend itself to high-quality welding. In accordance with this invention, the unique addition of slightly less than about 0.30%, by weight, of acicular refractory (e.g., silicon carbide) particles, which are about 0.5 mil long and only a few microns in diameter, significantly improves all of these characteristics.

Accordingly, it is one of the objects of the present invention to provide unique composite metals of substantially homogeneous character in which relatively minor amounts of minute substantially-refractory particles impart improved structural strength and resistance to deleterious effects of high temperatures.

Still further, it is an object to provide novel and improved cast aluminum alloys in which substantially refractory minute particles of entrapped materials impede grain boundary sliding and dislocation cross-slip to enhance elongation, workability, and hot-tearing characteristics, and to improve performances at relatively high temperatures, and to increase weld strengths.

By way of a summary account of practice of this invention in one of its aspects, a quantity of molten aluminum-copper alloy (such as a popular one including 4.5% by weight of copper) is poured and de-gassed using conventional techniques and equipment, and to this melt is added a batch of silicon carbide and/or alumina fibers. These particles are of the order of a few microns or so in diameter and may have random lengths of up to about one mil, and are preferably wrapped together as a package within aluminum foil and then pre-heated to avoid large thermal differences when the package is plunged deeply into the molten alloy. The fibers may constitute about 0.30% by weight of the entire melt. Preferably, a mechanical stirring is then performed, as an aid to substantially uniform dispersal of the wetted fibers throughout the melt. Thereafter, the molten material is permitted to cool and solidify, as in a mold after casting. The resulting composite material is found to resist hot tearing, cracking under high elongations and working, and high temperatures such as those of welding, and, although apparently substantially homogeneous, evidences a localizing of the added fibers at the sites of grain boundaries.

The term refractory as used herein means capable of enduring or resisting high temperature. More particularly, this means that the fibers or microfilaments are not fusible at the temperature of molten base metal. Although the features and aspects of this invention which are considered to be novel are set forth in the appended claims, further details as to preferred practices of the invention, as well as the further objects and advantages thereof, may be readily comprehended through reference to the following description taken in connection with the accompanying drawings, wherein:

FIGURE 1 presents a block diagram of steps involved in one preferred practice of the present teachings for producing improved composite materials; FIGURE 2 is an 800× enlargement of the microstructure of an improved aluminum-copper alloy including about 0.08% of aluminum nitride-oxide crystals; FIGURE 3 is an 800× enlargement of the microstructure of an improved aluminum-copper alloy as cast in a machined graphite mold and exhibiting aluminum oxide fibers of about 10–30 microns diameter at the grain boundaries; FIGURE 4 is an 800× enlargement of the microstructure of an improved aluminum-copper alloy solutionized one hour at 900° F. and water-quenched, exhibiting aluminum oxide fibers of about 10–30 microns diameter at prior grain boundaries; FIGURE 5 is an 800× enlargement of the microstructure of the fusion zone of an improved aluminum-copper alloy parent stock AC welded using a filler rod of the same composition and including silicon carbide fibers of about 3 microns diameter; FIGURE 6 is an 800× enlargement of the microstructure of an improved aluminum-copper alloy as cast in a machined graphite mold and including about 0.06% of silicon carbide fibers of about 3 microns diameter; FIGURE 7 is another 800× enlargement of the microstructure of an improved aluminum-copper alloy as cast...
3,492,119

3 in a machined graphite mold and including about 0.06% of silicon carbide fibers of about 3 microns diameter; and FIGURE 8 is an 800× enlargement of the microstructure of an improved aluminum-copper alloy solutionized one hour at 990° F. and water-quenched, exhibiting silicon carbide fibers of about 3 microns diameter which comprise about 0.06% of the composite material.

In the preparation of a light-weight aluminum-copper "eutectic" alloy, such as one including about 4.5% by weight of copper and which will on solidification exhibit tendencies for grain growth to occur with liquid eutectic of the constituents present at the same time, a de-gassed quantity of the molten alloy is produced (FIGURE 1) in the usual way with conventional equipment. In addition, a relatively small quantity (example: 0.06 to 0.30% by weight of the total) of minute reinforcement particles having higher melting temperatures than that of the molten alloy (example: substantially refractory material) is also prepared. For purposes of the present invention, these particles are desirably elongated or acicular, and have the appearance of fibers or whiskers, although they are only of exceeding small transverse cross-section (typically, 3 to 30 microns across) and may have random lengths of only about 0.5 to 1 mil. Particles such as aluminum oxide (Al₂O₃), and silicon carbide (SiC), and aluminum nitride-oxygen crystals, which are readily wetted by the alloy, are highly satisfactory, and may be used singly or in combination. The production of these particles may be realized in accordance with known techniques. Preferably, the batch of reinforcement particles is packaged within a thin foil wrapper, such as an aluminum foil which is compatible with the alloy under discussion and which will melt away shortly after being immersed in the molten alloy, and the entire package is heated to prevent too large a thermal gradient from appearing when it is next plunged deeply into the molten alloy with the aid of a suitable tool. A stirring operation follows, with the object of dispersing the wetted particles rather uniformly throughout the melt, although this need not be a particularly thorough procedure if the particles are readily wetted by the alloy and if they do not tend to group and settle or float. Particles which are not likely to be wet easily may first be pre-coated with another material which promotes such wetting with whatever alloy is being processed.

Once the reinforcement particles have been introduced into the molten alloy, it is permitted to cool and solidify at a normal rate, preferably as a casting in a mold into which it has been poured (such as a machined graphite mold for the aluminum-copper alloy under discussion). The solidified composite material may then be rolled, swaged, extruded, wrought and formed into desired shapes with significantly improved characteristics attributable to the presence of the reinforcement particles primarily at the sites of grain boundaries. In addition, the aforementioned aluminum-copper alloy with reinforcement particles may be shaped into welding filler rods and used in welding aluminum parts, with or without such reinforcement particles in them, to produce high-strength crack-free weldments. Importantly, moldings of complex configurations are significantly improved in that the risks of encountering the usual hot tearing at corners are greatly reduced.

The altered properties of the alloy including the minute particles are remarkable in view of the small percentages of particles involved and because of the apparent absence of any alloying effects or gross mechanical-locking effects (such as would be expected with substantial amounts of large fibers or material akin to steel wool). The particles do not merely serve as filler, to augment the volume of the resulting product, but, instead tend to be, and are small enough to be, localized substantially uniformly along grain boundaries, where they evidently impede grain boundary sliding and dislocation cross-slip. It is theorized that once the fine particles have been introduced into the melt, and the molten material commences solidification upon gradual cooling, grains of the alloy tend to grow while other amounts of the alloy having lower eutectic solidification temperatures are present between the growing grains. This accords with known eutectic characteristics for alloys which do not have a predetermined proportion of constituents promoting a single lower most eutectic temperature for solidification of the alloy. The fine particles are apparently automatically forced into the grain-boundary regions where liquid phases of the alloy are present during the solidification process, being rejected by the growing grains, until, upon solidification of the entire mass, they are trapped in place at the grain boundary regions. Beneficial effects are promoted at high temperatures at which the alloy alone would be relatively weak structurally. Rolling of the improved aluminum-4.5% copper alloy, with the silicon carbide and with the aluminum oxide particles from a thickness of about 0.75 inch to about 0.025 inch produced a smooth sheet free from defects, while the same alloy without the particles developed cracks and was irregular in appearance after rolling to the same extent. The same grain-boundary-reinforced material, especially with silicon carbide exhibits highly improved as-cast properties, being very advantageously free of hot tears. Welding filler rods including the particles and used in AC arc welding of ¾ inch aluminum sheet produced crack-free welds, with tensile-test failures occurring in the material adjacent the welds rather than in the weld itself, whereas like welding with the usual filler material (a filler metal commonly known in the trade as "4043") resulted in failures in the weld. Re-melting may be performed other than in the course of welding, with the resulting products also exhibiting improved properties, such that the composite materials may be prepared as ingots or the like for subsequent re-melting and molding or other processes.

Certain of the physical properties of a conventional aluminum-4.5% copper alloy, designated as the Control, are compared with those of the same alloy including fibers of reinforcement materials in the tabulations which follow.

(A) Properties As-Cast in Machined Graphite Molds

(B) Properties in Solutionized Condition (90° F. for 1 Hour, Water Quenched)

(C) Properties in Aged Condition (300° F. for 3 Hours)
The alumina fibers used in these evaluations were of diameters about 10–30 microns, in random lengths (example: about 1 mil), and the silicon carbide fibers were of diameters about 3 microns, in random lengths (example: about 0.5 mil). The Rockwell hardness scale was that for a \( \frac{1}{4} \) inch diameter ball and a 60 kg. load.

Aluminum alloy sheets (aluminum-copper alloy of the type designated in trade as "4032") of dimensions 6 x 6 x \( \frac{3}{4} \) inch were manually heliarc-welded with (1) the aforementioned type "4043" filler rods; (2) filler rods of aluminum-4.5% copper including 0.1% Al\(_2\)O\(_3\) whiskers (about 10–30 microns diameter); and (3) filler rods of aluminum-4.5% copper including 0.1% SiC whiskers (about 3 microns diameters). Item (2) and (3) were first cast as \( \frac{9}{16} \) inch diameter bars and then rolled to \( \frac{3}{8} \) inch thickness for use as the filler rods. Wells made with the latter filler rods were crack free, while those produced with a similarly-made filler rod of aluminum-4.5% copper developed cracks during welding (probably because of the high short tendency of the alloy). The fiber-containing alloy has a reduced but tearing tendency, which was found to be the case for both casting and welding. Finished welds made with filler rods (1)–(3) were machine flat, and samples were cut transverse to the weld zone and notched at the edges of the welds; results of the ultimate notch tensile strength were as follows:

**Filler Rod:** Ultimate tensile strength, KSI

(1) "4043" .............................................. 25.5
(2) Al-4.5 Cu-0.1% SiC .................................. 29.1
(3) Al-4.5 Cu-0.1% Al\(_2\)O\(_3\) .............................. 29.0

In addition to edge-notched samples, unnotched standard machined bars taken transverse to the weld were tested with results as follows:

<table>
<thead>
<tr>
<th>Filler Rod</th>
<th>Yield, p.s.i.</th>
<th>Tensile Strength, p.s.i.</th>
<th>Elongation, %</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) &quot;4043&quot;</td>
<td>15,369</td>
<td>28,500</td>
<td>3.1</td>
<td>Weld</td>
</tr>
<tr>
<td>(2) Al-4.5 Cu-0.1% SiC</td>
<td>15,710</td>
<td>28,979</td>
<td>4.4</td>
<td>Fault</td>
</tr>
<tr>
<td>(3) Al-4.5 Cu-0.1% Al(_2)O(_3)</td>
<td>15,769</td>
<td>28,481</td>
<td>4.6</td>
<td>Base Metal</td>
</tr>
<tr>
<td>(4) Al-4.5 Cu-0.1% SiC</td>
<td>16,499</td>
<td>33,700</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>(5) Al-4.5 Cu-0.1% Al(_2)O(_3)</td>
<td>15,739</td>
<td>21,144</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>(6) Al-4.5 Cu-0.1% SiC</td>
<td>15,379</td>
<td>30,289</td>
<td>10.9</td>
<td></td>
</tr>
</tbody>
</table>

These data indicate that the welds made with the composite fiber-containing alloy were stronger than the adjacent metal merely affected by the heat of welding. Radiographic examinations of the welds made with the fiber-containing material confirmed that they were free of cracks.

Enlargements (800\( \times \)) of etched surfaces of composite aluminum-copper alloys appear in FIGURES 2 through 5, the alloy in each instance including the currently-popular 4.5% by weight of copper, and Keller's etch being used in preparing the surfaces for examination. In FIGURE 2, the aluminum nitride-oxyde crystals, 9, are evident in substantially uniform dispersals at the grain-boundary "eutectic" regions, 10, between various dendrite-studded crystals or grains 11. Solutionizing and aging have reduced the prominence of the grain boundary regions. The 10–30 micron diameter aluminum oxide fibers 12 in FIGURE 4 are highly elongated while nevertheless being oriented essentially within the boundary regions 13 where the high-copper-content eutectic was the last to solidify between the high-aluminum-content dendritic grains 14. Solutionizing of the weld at 990° F., and water-quenching, reduced prominence of the boundaries but left the aluminum-oxide particles 12 at the sites 13 of prior boundary junctions. In FIGURE 5, silicon carbide fibers 15, of about 3 microns diameter appear at the grain boundaries 16 of a fusion zone where the composite filler rod was used to weld (manual TIG AC welding) a similar stock of material. The fibers have reappeared at the boundaries between the high-aluminum-content masses 17 in about the same relative concentration as they occurred in the rod and stock before welding. Similar silicon carbide fibers 15 are shown in the boundaries 16 between grains 17 of a like alloy, as cast in a machined graphite mold, in FIGURES 6 and 7. The FIGURE 8 illustration is of a like alloy also with the substantially 3 micron diameter silicon carbide fibers, 15', after being solutionized one hour at 990° F. and water-quenched. The boundary sites 16' between grain masses 17' are reduced in size because of the solutionizing.

Practice of these teachings need not be restricted to the materials specified, provided the reinforcement particles are of appropriate sizes and refractoriness in relation to the host metal involved, and provided they can be wet sufficiently. In general, a length-to-diameter ratio of between about 100–2,000 is desired for these particles, which may typically run about 3 to 30 microns in approximate transverse dimensions, or "diameters." Thence all such particles currently, from the standpoint of cost, are the aforementioned alumina, silicon carbide, and aluminum nitride-oxide, which also have the other desirable properties referred to hereinabove. However, other less commonly available particles, such as those of graphite, magnetite oxide, and refractory or ceramic materials, have properties which make them attractive and suitable for welding techniques (on iron particles, for example) may be referred to in improving wettability and preventing undesirable alloying or other deteriorations of the particles in appropriate instances. Similarly, the host alloys need not be restricted to the aluminum-copper alloy which has been discussed and illustrated in detail for purposes of setting forth the currently preferred embodiments and expressions of these teachings. For example, an alloy of aluminum and 10% by weight of silicon is found to produce the same type of grain-boundary orientations of all of the same fibers (namely, alumina, silicon carbide, and aluminum nitride-oxide). Although "eutectic" and grain-growth actions have been alluded to in venturing an explanation for the unique phenomena which appear to be involved, it should also be recognized that other metallurgical explanations involving the growth of solid masses with surrounding liquid phase material speak of dendrite formations, as in the case of nickel-copper alloys, and that the "boundaries" in such a case can serve as sites for entrainment of the reinforcement particles. Orientations of grain boundaries in preferred directions, as by so-called "planar freezing" techniques, will have the effect of giving preferred directional orientations of the fibers trapped there, also.

Although specific practices have been described, and preferred embodiments and materials have been discussed, it should be understood that various modifications, substitutions, and additions may be effected by those skilled in the art without departure from these teachings, and it is aimed in the appended claims to embrace such variations as fall within the true spirit and scope of this invention.

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

1. A particle-reinforced metallic composite material comprising an aluminum base alloy matrix containing between six hundredths of a percent and three-tenths of a percent by weight, based on the metal matrix weight, of discrete high-strength refractory microfilaments being wettable by said base alloy metal in its molten state and having a diameter less than 900 microns wherein, during solidification, said material exhibits minute substantially solid-phase matrix alloy particles dispersed by boundaries of substantially liquid-phase alloy and said microfilaments being distributed substantially uniformly throughout the said liquid-phase alloy and primarily throughout said boundary regions.
2. A particle-reinforced metallic composite material as set forth in claim 1 wherein said microfilaments are of dimensions small enough to be entrapped substantially within said boundaries.

3. A particle-reinforced metallic composite material as set forth in claim 1 wherein said microfilaments have ratios of length-to-transverse cross-sectional dimensions of the order of between about 100 and 2,000 and have transverse cross-sectional dimensions of the order of between about 3 and 30 microns.

4. A particle-reinforced metallic composite material as set forth in claim 1 wherein said alloy consists essentially of aluminum and copper, wherein said microfilaments are from the group consisting of alumina, silicon carbide, and aluminum nitride-oxide.

5. A particle-reinforced metallic composite material as set forth in claim 4 wherein said alloy consists essentially of aluminum and about 4.5% by weight of copper.

6. The metallic material of claim 1 in the form of a welding filler rod for the welding of aluminum containing metal, said rod consisting essentially of aluminum and copper.

7. A welding filler rod of claim 6 wherein said alloy consists essentially of aluminum and a relatively small percent by weight of copper.

References Cited
UNITED STATES PATENTS
10 3,098,723  7/1963  Micks  --------------  29—183.5
2,793,849  5/1957  Imich  --------------  75—138 X
3,037,857  6/1962  Conant  --------------  75—138

L. DEWAYNE RUTLEDGE, Primary Examiner
J. E. LEGRU, Assistant Examiner

U.S. Cl. X.R.

29—183.5; 75—148