Aug. 30, 1960 W. J. BUEHLER ET AL 2,950,526

ELEVATED TEMPERATURE WORKING OF METALS AND ALLOYS

Filed April 22, 1957

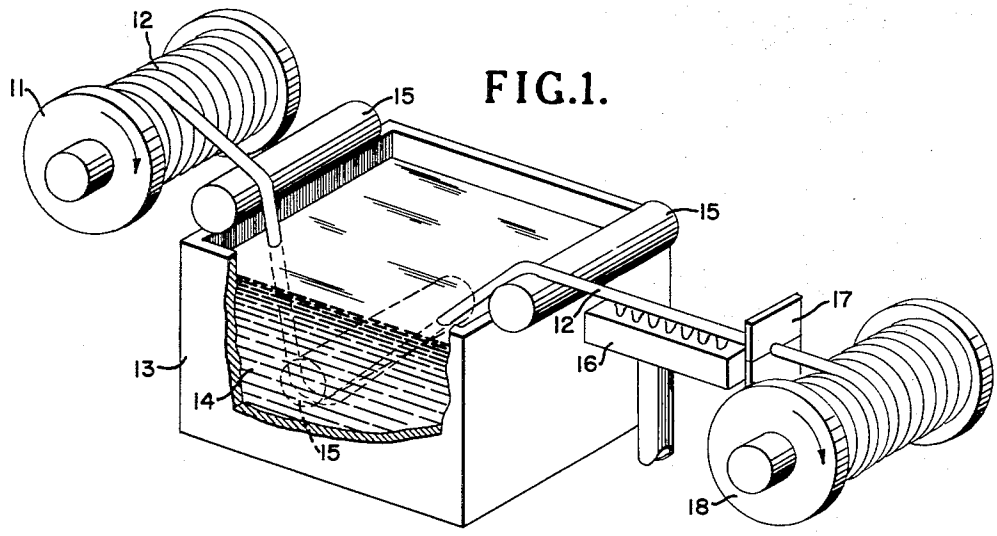



FIG.1.

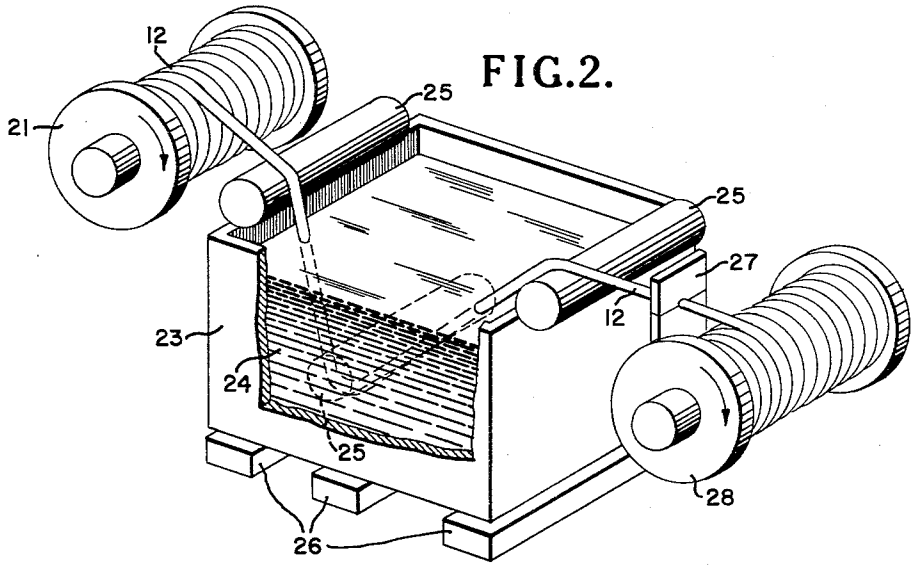



FIG.2.

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United States Patent Office 2,950,526
Patented Aug. 30, 1960



2,950,526

# ELEVATED TEMPERATURE WORKING OF METALS AND ALLOYS

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Filed Apr. 22, 1957, Ser. No. 654,429

14 Claims. (Cl. 29—424)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to improved processes for the warm working of high aluminum content iron base alloys.

More particularly the invention relates to an improved method of removing and preventing the formation of abrasive oxides on the surface of high aluminum content iron base alloys so as to permit the warm working of these alloys.

High aluminum content iron base alloys having an aluminum content between 12–18% have been found useful because of their desirable magnetic properties and their resistance to oxidation at high temperatures. This resistance to oxidation is primarily due to the coating of oxides, principally aluminum oxide, which forms on the surface of the alloy when exposed to air particularly at high temperatures. This oxide coating, while highly desirable for some purposes, is highly abrasive and interferes with the fabrication of the alloys. This is particularly true in those types of operations such as wire drawing, extruding, straightening extruded shapes by post drawing, etc. wherein the alloy must be forced through a sliding friction reducer. As these operations must be performed at relatively high temperatures the oxide coatings form rapidly and these operations are made extremely difficult if not impossible. For this reason, prior to this invention, wire has never been successfully drawn from rods of iron base alloys having an aluminum content much more than 12%.

In accordance with the present invention these troublesome oxide coatings are removed and prevented from forming during the warm working of these high aluminum content iron base alloys by treating the surface of the alloys with a preselected halide salt. This permits these alloys to be worked at elevated temperatures without the difficulties previously experienced due to the presence of the abrasive oxides.

It is therefore an object of the present invention to provide an improved method of warm working high aluminum content iron base alloys.

Another object is to provide a method of removing and preventing the formation of refractory, highly abrasive oxides on the surface of high aluminum content iron base alloys during warm working operations.

A further object is to provide an improved method of working high aluminum content iron base alloys at elevated temperatures.

Other objects and the attendant advantages of the invention will become apparent to those skilled in the art as the disclosure is more completely described in the following detailed description relating to the accompanying drawing in which:

Fig. 1 is a diagrammatic view in perspective and partly broken away, of one embodiment of apparatus suitable for use with the instant invention; and



Fig. 2 is a diagrammatic view in perspective and partly broken away of another embodiment of apparatus suitable for use with the instant invention.

Referring now to the drawing, there is shown in Fig. 1 thereof, a rotatable drum **11** having a length of wire **12** wound thereabout. Wire **12** extends from drum **11** into container **13** which contains a copius supply of solution **14** of a halide salt, the wire being guided by three guides **15** arranged on opposite sides and within the container, respectively. Wire **12** is immersed in solution **14** by passing around the guides **15** and receives a coating of the solution while the wire is immersed therein. When wire **12** emerges from container **13**, it passes over heater **16** where the solvent of the coating evaporates leaving a coating of halide salt which is then rendered molten as the wire is heated to its warm working temperature. Wire **12** then passes through die or sliding friction reducer **17** and is wound about drum **18** which has power means, not shown, connected thereto to cause it to turn in the direction indicated by the arrow and just fast enough for the wire to be heated to its proper working temperature by heater **16** prior to being drawn through the reducer **17**.

There is shown in Fig. 2 a drum **21**, free to rotate in the direction of the arrow and having a length of wire **12** wound thereabout. Wire **12** extends from drum **11** into container **23** which is filled with liquid **24** of a molten halide salt, being guided by guides **25** in a manner similar to the arrangement of Fig. 1. Heaters **26** arranged beneath container **23**, heat the halide salt to the warm working temperature of the wire which receives a coating of the molten halide salt as it passes through container **23** and, upon emerging in a heated state, passes through reducer **27** and is wound about drum **28** which has power means, not shown, connected thereto to cause the drum to rotate in the direction of the arrow and just fast enough to allow wire **22** to be heated to its proper working temperature in the molten halide bath. Any well known means, not shown, are preferably employed to facilitate the wire being wrapped about drum **18** or **28**, as the case may be, in layer fashion and to maintain the wire in heating relation to heater **16**, Fig. 1, at all times.

Because of the criticality of the supply of certain elements such as nickel chromium and cobalt in the field of metallurgy, in recent years increasing emphasis has been placed upon the development and improvement of silicon-iron and aluminum-iron alloys which do not include these critical elements. These alloys have not been widely used, however, because of the extreme difficulty in fabrication due to their inherent hard and brittle characteristics. With the recent development of iron-aluminum alloys in the range of 12–18 percent aluminum, there has been increasing interest in developing methods of working these alloys.

One particular iron-base group of alloys which possesses excellent heat and oxidation-resistance and stress rupture strength as well as attractive magnetic properties is the ternary system of iron-aluminum-molybdenum called "Thermenol." This alloy is described in the United States Patent No. 2,768,915 which was issued to applicants on October 30, 1956. This high temperature and oxidation resistant material has been found useful in compressor blades for jet engines, in skins for supersonic missiles and aircraft, in airframe components, in automotive engine parts, in hot rolls, and in furnace parts. Thermenol wire has been found to be useful as resistance wire in heating elements having long life at high temperatures.

Another alloy having good magnetic properties is "Alfernol" an alloy of iron and aluminum containing from 10–17% aluminum. This type of iron-aluminum alloy is treated at length in a publication of the U.S. Naval

Ordnance Laboratory dated April 9, 1953, and designated NavOrd Report 2819. Besides their desirable magnetic properties these alloys have such desirable properties as high strength, high temperature oxidation resistance, high electrical resistance, low thermal conductivity and corrosion resistance. It is useful in transformer laminations, in shielding, in tape recorder playback and record heads and in transducer and ultrasonic applications.

Considerable developments have been made in methods of working these high aluminum content iron base alloys. However, attempts to extrude or draw into wire alloys containing 14% or more of aluminum have been heretofore unsuccessful. A hard oxide coating, principally aluminum oxide, forms on the surface of the alloy when the alloy is heated in air to the rather high temperatures necessary for the warm working of the alloys. Such oxide coatings, while desirable in that they inhibit further loss of surface material by oxidation are tightly adherent, quite abrasive and make some forms of working quite difficult if not impossible.

In fabrication or shaping processes by which the alloys are worked deformed or otherwise changed in size and shape, the instrumentality or tool bears on the surface of the alloy and a coating of the oxide thus is transferred to the tool. This contamination of the tool surface often materially effects the quality of the article produced in that the surface of the article is often marred by imperfections or roughened. In those operations wherein the alloy is forced through a sliding friction reducer or die as in extruding, drawing, straightening extruded shapes by post drawing operations, etc. these oxide coatings cause excessive friction and galling between the die and the alloy causing the extruded or drawn material to break. For this reason alloys containing over 12 percent aluminum have not been successfully drawn into wire.

Recently the method of working these difficult-to-work high aluminum content alloys at warm temperatures has received much attention. By warm working the alloy is worked at a temperature at which it is suitably malleable and yet a "cold worked" structure is induced. To induce this "cold worked" structure the alloy must possess a recrystallization temperature safely above the upper limit of the warm working temperature range. In these warm working operations it is sometimes necessary to heat the alloy to a rather high temperature particularly in the case of Alfenol, Thermenol and Si-Fe alloys. However, without a practical method of removing and inhibiting the formation of the oxides on the surface of the alloys no satisfactory method of warm working these alloys has been found and drawing or extruding them has been exceedingly difficult if not impossible.

The tightly adhering abrasive oxides that are most frequently encountered in the warm working of metals or alloys thereof are aluminum oxide, $Al_2O_3$, silicon dioxide, $SiO_2$, titanium dioxide, $TiO_2$, chromium oxide, $Cr_2O_3$ and to a lesser extent the oxides of Mn, Co, Pd, Ce, Cu, Zn, Hf and Cd. In the warm working of Alfenol and Thermenol the oxide most frequently encountered is aluminum oxide.

In accordance with the improved process of the invention the alloy which is to be worked is treated with a preselected halide salt. When the oxide coating on the surface of the alloy is brought into contact with the halide ion at the proper temperature a reaction will occur yielding a new halide salt composed of the metal ion of the oxide and the halogen ion of the halide salt. The following is an equation representing a typical reaction between an oxide coating and a halide salt:

$$\underset{\text{(abrasive oxide)}}{Al_2O_3} + \underset{\text{(halide)}}{KBF_4} \xrightarrow{\text{heat}} AlF_3 + \text{Metal Borate}$$

Any halide salt, i.e. any salt which is stable at the working temperatue and yields one or more halide-ions namely $F^-$, $Cl^-$, $Br^-$, $I^-$, may be employed in the method of this invention. The halide ions readily react with the metal oxides in question and removing them from the surface of the alloys.

To be useful with a particular alloy however the halide salt must have a melting temperature lower than the warm working temperature of the alloy. The halide salt should also be non-toxic in all physical states and should be easily removed from the surface of the alloy when desired. The halide should also, if possible, be relatively inexpensive and possess properties so that it can act as a die lubricant. The following halide salts have been found to possess these desirable characteristic:

(*a*) $Na_3AlF_6$ (cryolite)
(*b*) $KBF_4$ (potassium fluoborate)
(*c*) $CaF_2$ (calcium fluoride, fluorspar)
(*d*) $NaBF_4$ (sodium fluoborate)
(*e*) $K_2TiF_6 \cdot H_2O$ (potassium fluotitanate)

The chemical effectiveness of the halide salts is enhanced by the presence of boron or carbon. Examples (*b*) and (*d*) above each have boron in the compound. Carbon may be added to the salt in the form of fine graphite. This not only makes the chemical reaction more effective in removing the abrasive oxide coating but also aids the lubrication of the alloy when drawn through a friction die.

The following example is given by way of illustration and should not be considered as limiting the invention in any manner.

*Example I*

The problem was to draw wire from rods of Thermenol (16% Al, 3.3% Mo, remainder Fe). Cast 1" diameter rods were swaged at temperatures of 950°–1050° C. (1742°–1922° F.) down to about 3/16" in diameter. Conventional methods of wire drawing were tried and found completely unsatisfactory. Since Thermenol, rolled at about 575° C. is characterized by the formation of a more highly fibered structure with improved toughness and ductility than is obtainable at lower temperatures, it was desired to draw the rods at that temperature. When heated, however, the rods formed an oxide coating principally aluminum oxide, which was found to be tightly adhering and highly abrasive. When these oxide coated rods were drawn warm (about 575° C.) they caught in the die and were broken. Various die lubricants were tried with little or no success and considerable galling occurred between the rod and die. These difficulties were overcome by placing the 3/16" rods in a bath of molten potassium fluoborate ($KBF_4$) heating the rods to about 600° C. (1112° F.) in the bath and drawing on a bull block with a 0.010" reduction per pass. At a diameter of about 0.1" the reduction per pass was reduced to 0.005". At approximately 0.040", once sufficient fibering had been induced in the wire, drawing could be conducted at room temperature and the wire was drawn cold using conventional oil and oil-graphites lubricants. From about 0.020" to 0.004" the wire was drawn by hand using reductions of 0.001". The potassium fluoborate was found to remove the oxide coating from the rods and eliminated the problem due to the abrasive oxides. It was also found useful in serving as a heating medium as well. It was found to be non-toxic and soluble in water being easily removed from the rods or wire after use.

The halide salt utilized in accordance with the invention may be applied to the surface of the alloy in any desired manner provided the halide ion is made available to react with the oxide prior to the rods passing into the die. For instance the halide salt may be incorporated into a solution with a liquid which vaporizes as the rods are heated leaving a dry coating of the salt on the surface of the rods which is subsequently reduced to the molten state as the rods are heated to the warm working temperature.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. The method of removing abrasive refractory oxides from the surface of a high aluminum content iron base alloy and preventing the formation of said oxides on said alloy during the warm working thereof at a temperature below the recrystallization temperature of the alloy comprising treating the surface of said alloy with a molten halide the nature of which is such that when in a molten state it reacts with the oxides formed on the surface of said alloy, said halide having a melting point substantially below the warm working temperature of the alloy, and treating the alloy with water after the warm working thereof sufficiently to dissolve the water soluble material adhering thereto.

2. The method of claim 1 in which the halide is potassium fluoborate.

3. The method of removing abrasive refractory oxides from the surface of an iron base alloy having an aluminum content between 14–18% and preventing the formation of said oxides on the surface of said alloy during the warm working thereof comprising treating the surface of said alloy with a halide the nature of which is such that when in the molten state it reacts with the said oxides and heating said alloy to a temperature above the melting point of said halide but below the recrystallization temperature of the alloy.

4. The method of claim 3 in which the halide is potassium fluoborate.

5. In the method of shaping an iron base alloy having an aluminum content between 14–18% in which rods of said alloy are forced through a sliding friction reducer, the steps of treating the said rods with a halide of such a nature that when in a molten state it reacts with the oxides formed on the surface of the rods, heating the treated rods to substantially 575° C. and forcing said heated rods through said reducer.

6. The method of claim 5 in which the halide is potassium fluoborate.

7. In the method of shaping a high aluminum content iron base alloy in which rods of said alloy are forced through a sliding friction reducer, the steps of heating said rods at a temperature below the recrystallization temperature of the alloy in a bath of molten halide salt of such a nature that it reacts with the oxides on the surface of said rods, forcing the heated rods through the said reducer and subsequently treating the rods with water sufficiently to dissolve the water soluble material adhering thereto.



8. In the method of shaping an iron base alloy having an aluminum content between 14–18% in which rods of said alloy are forced through a sliding friction reducer, the steps of heating said rods to substantially 575° C. in a bath of molten halide salt which reacts with oxides formed on the surface of said rods, and forcing said heated rods through said reducer.

9. The method of claim 8 in which the halide is potassium fluoborate.

10. In a method of shaping a high aluminum content iron base alloy in which rods of said alloy are forced through a sliding friction reducer, the steps of treating the said rods with a halide which reacts with the oxides formed on the surface of said rods, heating the treated rods to a temperature above the melting point of the halide and below the recrystallization temperature of the alloy, forcing the rods through the said reducer and subsequently treating the rods with water sufficiently to dissolve the water soluble material adhering thereto.

11. The method of claim 10 in which the halide has a melting point below the warm working temperature of the alloy.

12. The method of claim 10 in which the halide is of such a nature as to have substantially no reaction with the said alloy.

13. The method of claim 10 in which the halide is potassium fluoborate.

14. The method of claim 10 in which the temperature to which the said rods are heated is above the melting point of said halide but below the recrystallization temperature of said alloy.

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