June 1, 1971 J. CHORNE 3,582,480

HEAT TREATING PROCESS FOR IMPROVING HIGH TEMPERATURE DUCTILITY OF ELECTRODEPOSITED NI AND NI ALLOYS

Filed June 2, 1969

FIG. 1

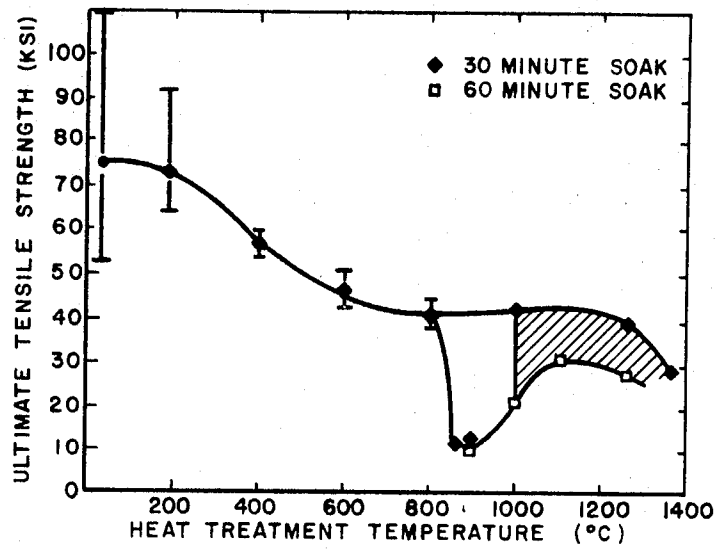


FIG. 2

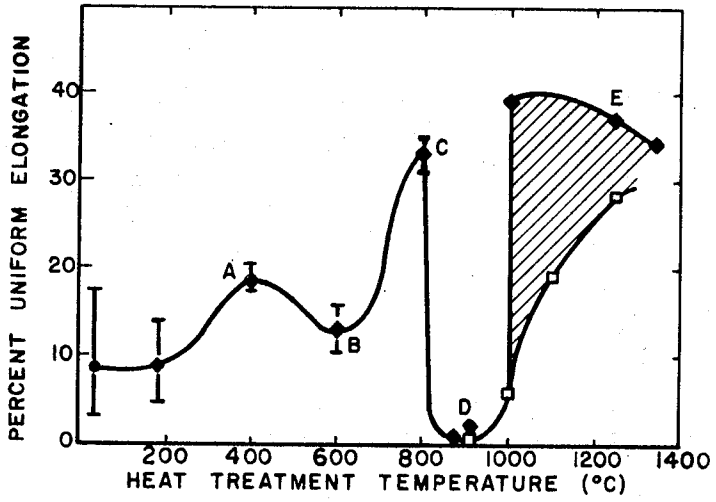
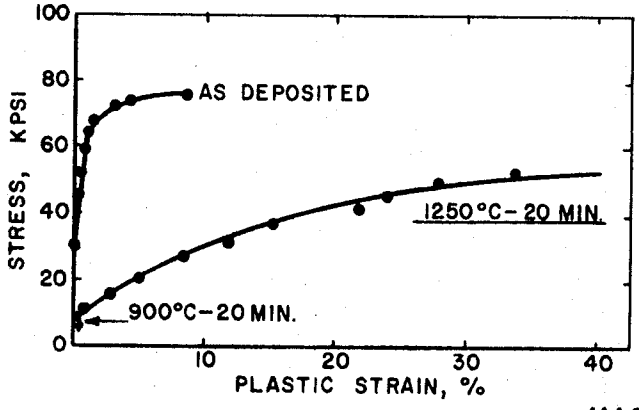


FIG. 3



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United States Patent Office 3,582,480 Patented June 1, 1971

3,582,480

HEAT TREATING PROCESS FOR IMPROVING HIGH TEMPERATURE DUCTILITY OF ELECTRODEPOSITED NI AND NI ALLOYS

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Filed June 2, 1969, Ser. No. 829,215
Int. Cl. C23b 5/52
U.S. Cl. 204—37R 3 Claims

ABSTRACT OF THE DISCLOSURE

A heat treating process for eliminating high temperature embrittlement intrinsic to electroplated nickel. The treatment is carried out in a vacuum for periods of twenty hours or more and at temperatures between 1000°–1250° C.

CROSS REFERENCE TO RELATED APPLICATIONS

The process in this application is closely related to an application Ser. No. 804,593 filed Mar. 5, 1969 for Nickel Electrodeposition Process for Improving High Temperature Ductility in the name of Charles A. Bruch.

STATEMENT OF GOVERNMENT INTEREST

The invention 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.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the heat treatment of electroplated products (electrodeposited Nickel or Nickel-Manganese alloys) at temperatures between 1000°–1250° C. in vacuo (10^{-5} torr) for periods of twenty hours or more.

Description of the prior art

A process, known as the Barrett Sulfamate Nickel Plating Bath and described in U.S. Pat. 2,318,592 to Martin E. Cunery, is used to deposit nickel or nickel alloy. It consists of an electrolyte containing a sulfamate which may be used in either an acid or an alkaline bath. An example bath would be made if sulfamic acid and nickel carbonate. However, using this process in detail, the results are not completely satisfactory to produce a product for use at high temperatures. There is an embrittlement in the nickel coating which renders the product insufficiently ductile for the desired use.

SUMARY OF THE INVENTION

The invention relates to a heat treating process to be used on nickel or nickel-manganese alloy electroplated composites. Previous processes have left the composites embrittled at elevated temperatures. The heat treatment of the invention is carried out in a vacuum at temperatures between 1000°–1200° C. and for extended periods up to twenty-two hours.

The objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the heat treatment temperature in ° C. plotted against the ultimate tensile strength;

FIG. 2 is a graph showing the heat treatment temperature plotted against the percent of uniform elongation; and

FIG. 3 is a graph showing the Stress Plastic Strain Curves (at room temperature) to Limit of Uniform Elongation.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In attempting to eliminate the embrittlement found in composites which had been treated to electrobaths of either nickel or nickel-manganese alloys a careful examination was made of microphotographs at the edges of breakage.

In order to gain a better understanding of the source of weakness in this series of composites, the fractures of the composites were studied intensively. Studies of the micro-photographs revealed that fracture tended to occur along the matrix grain boundary. These composites were Ni-Al_2O_3 whisker composites which were plated with nickel-manganese alloys.

Preliminary experiments on the characterization of the matrix material suggested that the electroplated nickel was being embrittled by the pressure bonding process. Subsequent experiments indicated that weakening of the unreinforced matrix was primarily time/temperature depedent and independent of the pressing pressures and die materials used.

A study of the room temperature strength and elongation of the unreinforced electrodeposited nickel heat treated to simulate pressure bonding produced the results shown in FIGS. 1 and 2, which shows the tensile strength and elongation as a function of heat treatment temperature and soak time. As can be seen from the graphs, the ultimate strength decreased gradually with 30 minute heat treatments up to 800° C. These strength decreases were accompanied by gradual increases in elongation to 400° C., a gradual decrease to 60° C., and again a gradual increase to 800° C. At temperatures between 800° C. and 1000° C. a sharp reduction in both elongation and strength is observed; at even higher temperatures (1100° C. to 1350° C.), the ductility (elongation) and tensile strength were equal to the values observed at around 800° C. heat treatments.

Stress-Strain curves typical of as-deposited specimens and of specimens heated to 900° C. (brittle temperature range) and to 1250° C. for twenty minutes are shown in FIG. 3. These curves illustrate the drastic changes in tensile properties which occur as a result of heating the electrodeposited nickel to various temperature ranges. An observation made during this study of the fractures was that many of the specimens which were heated to temperatures above or below the brittle zone (800°–1000° C.) exhibited brittle fracture even though the specimens underwent significant uniform elongation. The evidence of this was: that the fractures occurred perpendicular to the tensile axis rather than at an angle which would be normal for flat ductile tensile specimens having a high width-to-thickness ratio; that there were negligible differences between the uniform and the total elongation on the recorded load-deflection curve, and that there was little evidence of localized deformation (necking) near the fracture.

The presence of a "hot brittleness" temperature range, which is frequently observed for nickel and nickel alloys is usually associated with the presence of low melting phases located at grain boundaries. Grain boundary embrittlement by a segregated nickel sulfide phase is perhaps the most commonly observed mechanism of embrittlement. It is generally postulated that the sulfide phase is precipitated early in the recrystallization stage and is carried along in the grain boundary with further grain growth. At higher annealing temperatures, it is believed that the sulfide diffuses into the nickel matrix, thereby restoring ductility. Since many of the organic compounds contained in nickel plating baths contain sulfur, it is highly

probable that the deposits produced from these plating solutions also contain sulfur impurities.

The foregoing experiments and results showed that the electrodeposited nickel was subject to embrittlement by heat treatment in the temperature range of 800° C. to 1000° C. and indicated that the source of embrittlement could be sulfur or sulfur compounds at the grain boundaries.

As a result of further studies it was determined that the embrittling grain boundary phase is not sulfur as no phases other than nickel could be detected using X-ray fluorescense, X-ray diffraction, electron micro-probe and microscopic techniques.

Further microstructural studies revealed that the embrittling grain boundary phase could be completely eliminated by a high temperature treatment. It is conjectured that the grain boundary phase is redissolved by the matrix or eliminated by decomposition and evaporation during the heat treatment (at the desired temperature range) in vacuum. Additional experiments were undertaken to determine if this remedial heat treatment is non-reversible and effective and to establish the minimum time required to eliminate embrittlement.

Further experiment proved:

That after 24 hours of heat treatment at 1250° C., the nickel was not embrittled by subsequent heating at 900° C. for times up to 450 minutes;

That after one hour at 1250° C. the nickel was not embrittled by subsequent heating at 900° C. for times up to 20 minutes;

That twenty minutes at 1250° C. was inadequate to prevent embrittlement of the nickel by a subsequent heat treatment of 5 minutes at 900° C.

A one hour treatment at 1250° C. reduced the amount of grain boundary precipitate but did not eliminate it completely.

Further experiment proved:

That heat treatment carried out in a vacuum at temperatures between 1000° C. and 1250° C. for periods of twenty hours or more completely eliminated the boundary phase from the matrix and resulted in greatly improved composite tensile strengths.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings.

What is claimed is:

1. A process for improving high temperature ductility of electrodeposited nickel alloy composites consisting of:

coating a substrate with nickel by an electroplating process to form a coated composite; and

heating the coated composite in vacuum to a temperature between 1000° C. and 1250° C. for a period of not less than 1 hour.

2. A process according to claim **1** wherein the time of heating is not less than twenty hours.

3. A process according to claim **1** wherein the nickel coating is a nickel alloy coating.

References Cited

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