

UNITED STATES PATENT OFFICE

2,679,466

SURFACE DECARBURIZATION OF CARBON-CONTAINING ALLOYS

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No Drawing. Application April 16, 1952,
Serial No. 282,678

4 Claims. (Cl. 148—13.1)

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This invention relates to a method for reducing the carbon content of the surface portions of articles composed of carbon-containing alloys.

Carbon is an important constituent in many alloys and must be present to provide certain desired properties pertaining to strength in such alloys. Under some conditions, however, the presence of carbon in the proportions necessary for the attainment of such properties is somewhat deleterious to other equally desirable properties pertaining to ductility. These latter properties are of greater import in the surface layers in certain instances, and in such cases it has been proposed that the surface portions of articles composed of carbon-containing alloys be decarburized.

A specific example of a class of alloys in which carbon is an essential constituent is the group of "high temperature alloys" that has been developed for use in jet engines, gas turbines and like devices where high temperature operation is encountered. Broadly, such alloys are iron-base, nickel-base or cobalt-base materials containing about 10% to 30% chromium, up to about 15% of molybdenum or tungsten or both, up to about 8% in the aggregate of columbium or tantalum, or titanium or combinations thereof, up to 1% boron and up to 1% carbon. For conciseness the method of this invention will be described with particular reference to its effects on this broad class of materials but its usefulness is not limited to treatment of such materials.

Articles composed of these high temperature alloys have the property of withstanding great stress at high temperature; generally the higher the carbon content the greater is the strength of these articles. However, in circumstances where repetitive heating, loading and cooling cycles are encountered, service life is often disappointingly short. It has been discovered that in such cases failure is caused or hastened by poor resistance to thermal shock; it has also been discovered that surface-decarburization of such articles improves their resistance to failure by thermal shock. Therefore surface-decarburization of articles composed of these alloys is desirable.

The conventional way of decarburizing the surface portions of metal articles is to heat such articles in a hydrogen atmosphere. While satisfactory decarburization is thus attained, the treatment must be conducted at quite high temperatures, and in the case of highly alloyed materials of relatively low melting point incipient fusion, or "burning" may occur, adversely affecting the mechanical properties of the arti-

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cles. In the case of higher melting alloys, the high temperatures required for treatment often cause changes in the microstructure of the alloys, also adversely affecting the mechanical properties of the articles. The high temperature alloys in particular are subject to such damage.

This invention comprises a method of lowering the carbon content of at least the surface portions of carbon-containing alloy articles by subjecting such articles to the action of a gaseous mixture of hydrogen and hydrogen chloride at elevated temperature. With hydrogen chloride present, effective decarburization may be carried out at temperatures considerably below those required when hydrogen alone is used. More specifically, in accordance with the invention an article to be surface-decarburized is treated with a gaseous mixture of hydrogen and hydrogen chloride containing 3% to 15% hydrogen chloride while being maintained at a temperature upwards of about 1050° C. for a period of time sufficient to effect the desired decarburization. Ordinarily it is desirable to use the lowest possible temperature even though at such temperature a longer treatment may be required. For instance, in the case of high temperature alloys of the broad class referred to above, decarburization may be accomplished by treatment for less than one hour at temperatures of 1250° to 1300° C., whereas at 1100° C., treatment for four hours may be required. Nevertheless the lower-temperature treatment will ordinarily be more desirable both from the standpoint of equipment required and effect on the properties of the material treated.

In practicing the method of the invention the articles to be treated are heated in a furnace in which the atmosphere can be controlled, and dry hydrogen containing hydrogen chloride is introduced. A convenient way to introduce hydrogen chloride into the hydrogen is to pass the gas through concentrated hydrochloric acid, and then dry the mixture but the hydrogen chloride may be introduced in other ways or may be formed in situ by introduction of chlorine or a chlorine compound which will react with the hydrogen.

Illustrative of the invention, samples of an alloy commonly used for fabrication into articles for use at elevated temperature were treated. The alloy contained 17.5% to 19.5% chromium; 14% to 15% tungsten; 9% to 11% nickel; 2% maximum iron; 0.01% to 0.05% boron; 0.35% to 0.45% carbon; remainder cobalt. The samples were placed in a furnace and heated, different

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samples being held at different temperatures in different tests, and, while hot, were subjected to the action of a gaseous mixture of hydrogen and hydrogen chloride. This mixture was prepared by passing commercially pure hydrogen through concentrated hydrochloric acid and then passing the gas through concentrated sulfuric acid to dry it. The average dry hydrogen chloride content of the mixture obtained in this way was about 6%.

By experiments conducted as just described it was found that effective decarburization (i. e. the production of a substantially carbonless skin to a depth of 0.01") was attained at temperatures as low as 1100° C., whereas the lowest temperature at which a comparable degree of decarburization was attained using hydrogen alone was in the temperature range 1225° to 1250° C.

The effectiveness of this degree of decarburization on high temperature alloys has been demonstrated by tests which have shown that surface-decarburized articles possess much greater resistance to thermal shock than do otherwise similar but untreated articles. For instance, specimens of the alloy composition described above were subjected to the thermal shock test described in Technical Note 2037, published February 1950 by the National Advisory Committee for Aeronautics. In this test a wedge-shaped specimen $\frac{1}{8}$ inch thick at the thin edge is heated to 950° C. and quenched in a rack which holds the thin edge in contact with water. After quenching, oxide is removed and the specimen examined for cracks. The test is continued in a cyclic manner, and when a crack has progressed across the full thickness of the quenched edge, the specimen is considered to have failed. A specimen which had been decarburized in accordance with the method of this invention by treatment at 1150° C. for four hours underwent 173 cycles of this test before failure. Another specimen treated by the method of the invention at 1100° C. for four hours underwent 75 cycles before failure. Three untreated specimens failed after 6, 7 and 7 cycles respectively.

An important advantage that the method of this invention has over prior methods of effecting surface-decarburization is that lower temperatures may be used. This is particularly important in the treatment of highly alloyed materials which have relatively low melting points. Further, as already indicated, the lower heat treating temperatures are advantageous in that they cause less modification of the microstructure of the alloys than do higher temperatures, as well as from the standpoint of equipment and fuel costs.

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While the invention has been discussed with particular reference to its utility in the treatment of high temperature alloys, it is equally useful for the surface decarburization of any carbon-containing alloys.

Related subject matter is disclosed and claimed in the application of F. S. Badger, Serial No. 282,677, filed April 16, 1952.

What is claimed is:

1. A method of lowering the carbon content of at least the surface portions of an article composed of a carbon-containing alloy which method comprises heating such article for a period of time sufficient to produce a relatively thin skin of substantially carbonless metal at a temperature upwards of 1050° C. and subjecting such heated article to the action of a hydrogen-hydrogen chloride atmosphere containing between 3% and 15% hydrogen chloride.
2. A method of lowering the carbon content of at least the surface portions of an article composed of a carbon-containing alloy which method comprises heating such article at a temperature of 1050° C. to 1300° C. for a period of time sufficient to produce a relatively thin skin of substantially carbonless metal while subjecting such heated article to the action of a hydrogen-hydrogen chloride atmosphere containing between 3% and 15% hydrogen chloride.
3. A method of lowering the carbon content of at least the surface portions of an article composed of a carbon-containing alloy which method comprises heating such article at a temperature of 1050° C. to 1300° C. and subjecting such heated article to the action of an atmosphere composed of hydrogen and hydrogen chloride containing about 3% to 15% hydrogen chloride, and continuing such treatment until a substantially carbon-free skin at least about 0.01 inch thick is produced on such article.
4. A method of improving the resistance of a carbon-containing metal article to thermal shock failure which method comprises heating such article to a temperature of 1050° C. to 1300° C. for a period of time sufficient to produce a relatively thin skin of substantially carbonless metal, and subjecting such heated article to the action of a hydrogen-hydrogen chloride atmosphere containing between 3% and 15% hydrogen chloride, thus lowering the carbon content of the surface portions of such article.

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