April 22, 1969 W. R. MARTIN ET AL 3,440,037
STAINLESS STEEL ALLOY EXHIBITING RESISTANCE TO EMBRITTLEMENT BY NEUTRON IRRADIATION
Filed Nov. 5, 1965

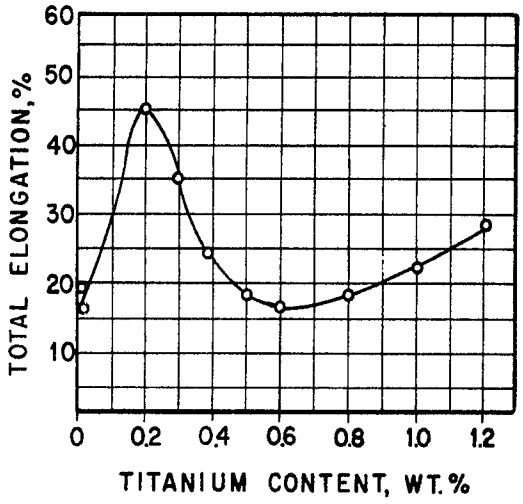


Fig. 1

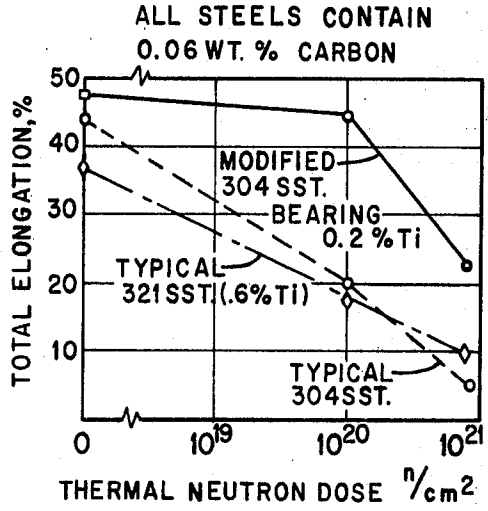
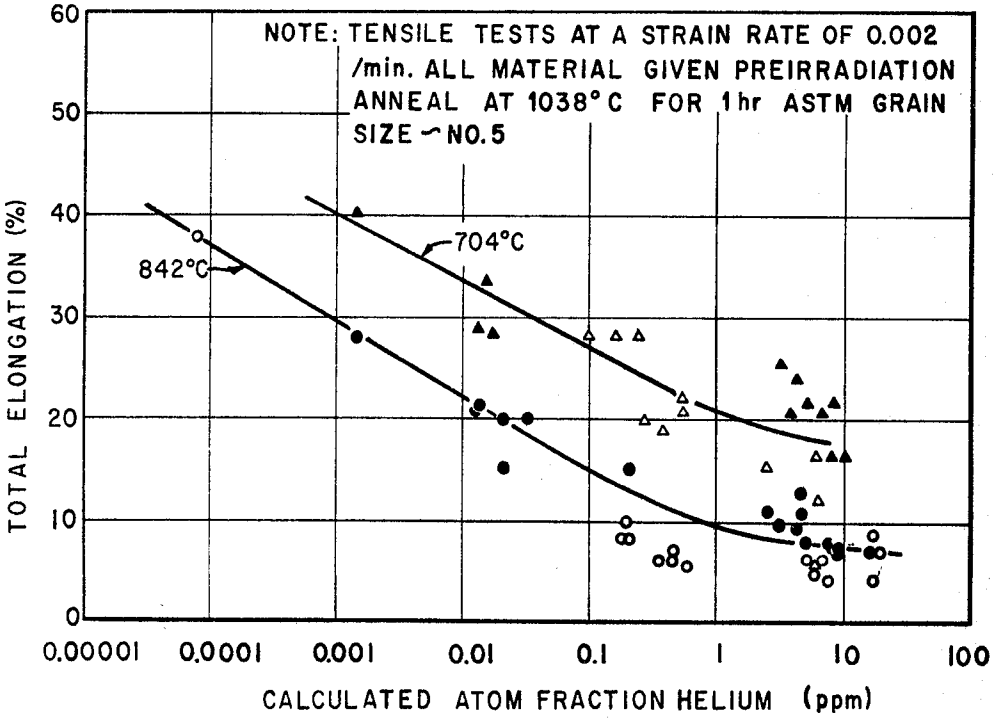


Fig. 2



TENSILE TESTED TYPE OF 304 SST.

842° C	704° C	
o	△	0.02 CARBON HEAT
o	▲	0.06 CARBON HEAT

Fig. 3

INVENTOR.
William R. Martin
James R. Weir
BY
Roland Q. Gadreaux
ATTORNEY.

United States Patent Office 3,440,037 Patented Apr. 22, 1969

3,440,037

STAINLESS STEEL ALLOY EXHIBITING RESISTANCE TO EMBRITTLEMENT BY NEUTRON IRRADIATION

William R. Martin and James R. Weir, Oak Ridge, Tenn., assignors to the United States of America as represented by the United States Atomic Energy Commission

Filed Nov. 5, 1965, Ser. No. 506,914
Int. Cl. C22c 39/22; G21c 13/08
U.S. Cl. 75—128 1 Claim

ABSTRACT OF THE DISCLOSURE

This invention relates to a structural alloy material for service in a neutron environment wherein the improvement comprises a boride-forming element incorporated in said alloy in an amount which forms a homogeneous dispersion of boride within the metal matrix of said alloy, thereby reducing the migration of said boron to the grain boundaries, said alloy consisting essentially of 17–20% chromium, 8–11% nickel, a small proportion of carbon, 0.1–0.25% titanium, incidental amounts of boron-10, and the balance substantially all iron.

This invention described herein was made in the course of, or under, a contract with the U.S. Atomic Energy Commission.

This invention relates generally to alloys and more particularly to an alloy which exhibits marked resistance to embrittlement by high temperature-high neutron exposure. These compositions are especially adapted for use at elevated temperatures in nuclear reactors.

Stainless steels, owing to their good corrosion resistance and suitable mechanical properties, have found widespread usage as construction materials. While the stainless steels are quite suitable in a wide variety of circumstances, there are a number of difficulties encountered when used in particular applications, such as for example as structural and/or cladding materials for nuclear reactors. As is known, the mechanical properties of many structural materials, including the stainless steels, may be deleteriously affected by irradiation at elevated temperatures in a nuclear reactor. One such radiation-damage problem is the tendency for embrittlement to occur in these materials, resulting in poor ductility and strain fatigue properties.

Recent work indicates that the effect of irradiation on the ductility of structural stainless steels differs significantly depending upon whether the irradiation and deformation test are carried out at temperatures above or below about 600° C. The low ductility observed for stainless steels tested below 600° C. is a result of irradiation damage related to atomic displacements. This type of damage affects the deformation process, but not the fracture process. On the other hand, the low ductility observed for stainless steels tested above 600° C. is believed to be a result of irradiation damage related to processes other than atomic displacements. This elevated temperature damage is one which appears to affect only the fracture process in the metal. While the radiation damage that effects the low-temperature properties can be removed by post-irradiation heat treatment at elevated temperatures, post-irradiation annealing does not remove the damage that causes low ductility at elevated temperatures. Additionally, this irradiation embrittlement at elevated temperatures has been found to be common to most alloys and is not specific to one given class of alloys. Hence, even stainless steels containing stabilizers such as titanium and niobium (types 321 and 347) have heretofore been found to experience this irradiation embrittlement. It is highly desirable to provide stainless steel alloys which

have improved ductile properties at high temperature under neutron irradiation.

It is therefore a primary object of this invention to provide a composition which retains its ductility after high temperature-high radiation exposure.

Another object is to provide an austenitic stainless steel having physical and mechanical properties which make it useful at elevated temperatures as a nuclear fuel cladding and/or structural material.

Still another object is to provide austenitic stainless steels of improved composition which resists high temperature embrittlement by neutron irradiation.

A still further object is to provide irradiation resistant austenitic stainless steels which can be readily welded.

Other objects of this invention will become apparent to those skilled in the art from the following description and claims when read in conjunction with the accompanying drawings of which:

FIG. 1 is a plot illustrating the effect of titanium concentration on post irradiation, elevated temperature ductility of 18–8 type stainless steels which were tested at tensile test temperature of 842° C. and a strain rate of 0.02% per minute.

FIG. 2 is a plot of the ductility of 18–178 type stainless steels at various levels of neutron exposure.

FIG. 3 is a plot demonstrating the correlation of helium content with short-time tensile ductility.

In accordance with the present invention there is provided an austenitic stainless steel composition comprising approximately 17–20% chromium, 8–11% nickel, a small proportion of carbon and from 0.1 to 0.25 titanium, the balance being substantially all iron. Applicant has found that small quantities within the range of from 0.1 to 0.25% by weight titanium markedly increase the post-irradiation ductility of the austenitic stainless steels. For example, the addition of only 0.2% titanium to type 304 stainless steel resulted in a post-irradiation ductility (neutron dose—1×10^{20} neutrons/cm.^{2}) of approximately 45% as compared to a post-irradiation ductility of about 20% for type 304 stainless steel without any titanium addition and about 18% for type 321 stainless steel which contained 0.6% titanium when tested at 842° C. at a strain rate of 0.2% per minute. Advantageously, these stainless steel alloys containing small quantities of titanium can be welded without the attendant problems encountered with stainless steels containing larger titanium concentrations such as type 321 stainless steel.

While applicant does not wish to be bound by any rigid theory, it is thought that the low ductility resulting from this high temperature irradiation embrittlement is caused by helium gas generated by (n,α) reactions. It is theorized that ^{10}B, which is typically found in stainless steels in the 1-to-10 parts/10^6 range, undergoes an (n,α) reaction to produce helium gas. Previous experiments have shown that boron segregates to grain boundaries in the solid state of austenitic stainless steels. Thus the concentration of helium generated by the thermal neutron reaction with ^{10}B at the grain boundary can be several orders of magnitude greater than the average value. A correlation of helium content with short-time tensile ductilities, which is typical for most structural materials, is given in FIG. 3 and demonstrates that as the deformation temperature is increased the amount of helium needed to initiate the embrittling process decreases. Thus, it is believed that the helium concentration at the grain boundary is sufficient to cause irradiation embrittlement of these steels at elevated temperatures. Additionally, helium gas may be generated by (n,α) reactions with other elements such as iron, nickel, nitrogen, and others; and fast neutrons with the quantity produced being significant for normal engineering alloys irradiated to a dose level above 1×10^{21} neutrons/cm.^{2}.

With respect to the improved ductility of the irradiated alloys, it is believed that the titanium forms stable complex metal borides dispersed homogeneously within the matrix and beneficially provides a helium sing or depository in the precipitate-matrix interface. By this mechanism the helium, which is believed to be only deleterious when concentrated at the grain boundaries, is tied up within the grains and is not able to migrate to the grain boundary, thereby greatly reducing the helium per unit length of the grain boundary. Titanium boride is beleived to be highly stable and not subject to aging effects which could redistribute the boron to the grain boundary.

It should be apparent from the foregoing discussion that in contradistinction to prior art belief that irradiation embrittlement, as for example in those alloys stabilized with niobium and titanium in concentrations generally set at from 4 to 8 times the minimum carbon content, is caused by the redistribution of carbides at the grain boundary, the present invention is based on helium generated from thermal (n,α) and fast (n,α) reactions as being the primary cause of irradiation embrittlement. Accordingly, only small quantities of titanium, which is sufficient to react with the boron present and form stable bromide compounds, is required to successfully carry out the practice of this invention. While it appears that only enough titanium need be present to react with the boron present one would think that the stabilized stainless steels, as for example type 321, which contains a considerable excess of that titanium found critical in this invention, should afford similar improvements in post-irradation ductility. However, when applicant tested type 321 containing 0.6% titanium, the post-irradiation ductility as shown in FIG. 2 was less than half of that of type 304 modified with 0.2% titanium. This result is not understandable, except insofar as demonstrating that as shown in FIG. 1 a critical range of titanium concentration between 0.1 to 0.25% titanium by weight is required to obtain the hereinbefore mentioned improved post-irradiation ductility of the austenitic stainless steels.

In practice, the present invention can be carried out by the addition of small amounts of titanium to low carbon stainless steels such as the 18–8 class of stainless steels. In any event the titanium concentration should be within the range of from 0.1% to 0.25% by weight, preferably being abuot 0.2% by weight. It should be apparent here that the actual procedures and techniques for incorporating the hereinbefore mentioned titanium concentration, in a particular type steel, forms no part of this invention; it being deemed well within the skill of the art to carry out

these manipulations in accordance with the teaching herein detailed. Moreover, the final fabrication of the herein described improved alloys into finished products, likewise, form no part of this invention.

In carrying out the practice of this invention, it is preferred that the stainless steel alloys be given a high temperature pre-irradiation anneal. For this temperatures between 926° C. to 1100° C. are preferred for the 18–8 type stainless steels.

While the invention has been generally described as applicable to low-carbon stainless steels (<0.08%) of the 18–8 type alloys for example, the foregoing is intended as illustrative only and is not to be taken as limiting the scope of the invention to those particular type stainless steels. Thus, while it appears that the low carbon stainless steels appear to offer slightly better improved ductile properties, it is intended that the scope of the invention be construed to include higher carbon content steels.

What is claimed is:

1. A structural alloy material for service in a neutron environment wherein the improvements comprises a boide-forming element incorporated in said alloy in an amount which forms a homogeneous dispersion of boride within the metal matrix of said alloy, thereby reducing the migration of said boron to the grain boundaries, said alloy consisting essentially of 17–20% chromium, 8–11% nickel, carbon less than .08, 0.1–0.25% titanium, small amounts of boron substantially present as a boride with incidental amounts of boron-10, and the balance substantially all iron.

References Cited

UNITED STATES PATENTS

3,258,370	6/1966	Floreen	75—128 X
3,199,978	8/1965	Brown	75—128.4
3,301,668	1/1967	Cope	75—128.4
3,303,023	2/1967	Dulis	75—128.4
3,306,736	2/1967	Rundell	75—128.4

OTHER REFERENCES

"New Age-Hardening Stainless Steel Provides" by T. C. DuMond from "Materials & Methods" pp. 432 and 433 February 1946, copy 75/128.

"Steel Products Manual," "Stainless & Heat Resisting Steels," February 1949, Published American Iron & Steel Institute, p. 9, copy 75/128.

HYLAND BIZOT, *Primary Examiner.*