United States Patent [19]

Bates et al.

[54] **IRRADIATION SWELLING RESISTANT ALLOY FOR USE IN FAST NEUTRON REACTORS**

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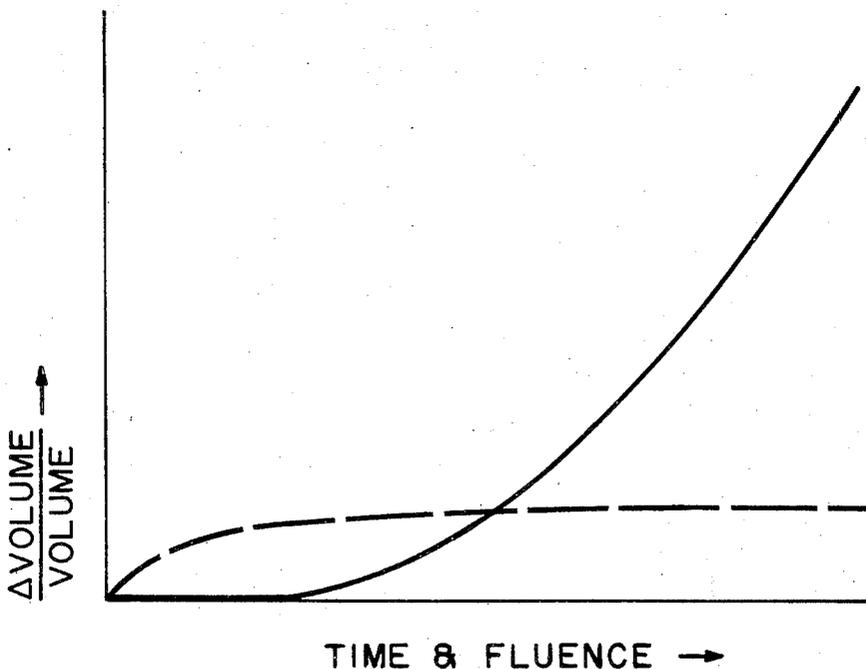3,563,728 2/1971 Allio .... 75/128 N

[57] **ABSTRACT**

A stainless steel alloy particularly suited for use in fast neutron reactors. It has high resistance to void information on irradiation by fast neutrons and excellent mechanical properties and is weldable. The basic composition in weight percent is, in addition to iron, chromium, 16.0 to 18.0; nickel, 11.0 to 14.0; molybdenum, 2.0 to 4.0; silicon, 1.1 to 2.0; manganese, 1.00 to 2.00; nitrogen, 0.04 to 0.06; carbon, 0.04 to 0.08; with certain limitation on other minor constituents.

2 Claims, 8 Drawing Figures

TIME & FLUENCE →

Fig. 2

Fig. 1

Fig. 4

WEIGHT % SILICON

VOID NUMBER DENSITY, CM^{-3}

Fig. 3

WEIGHT % SILICON

% DENSITY DECREASE
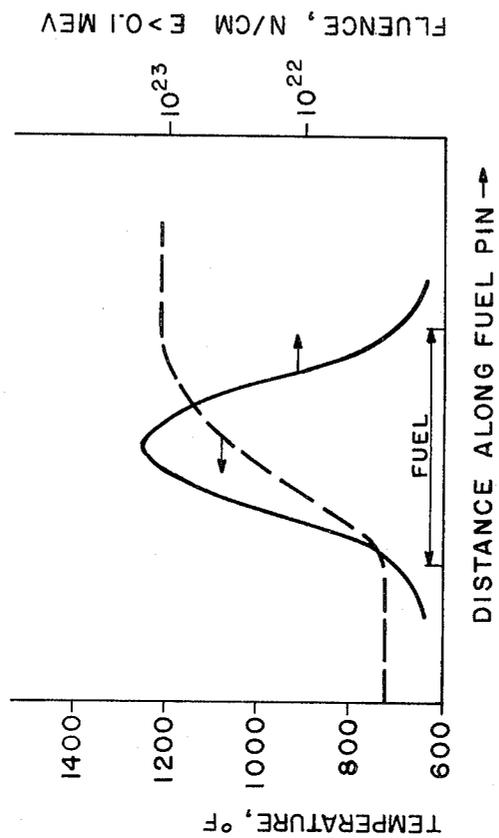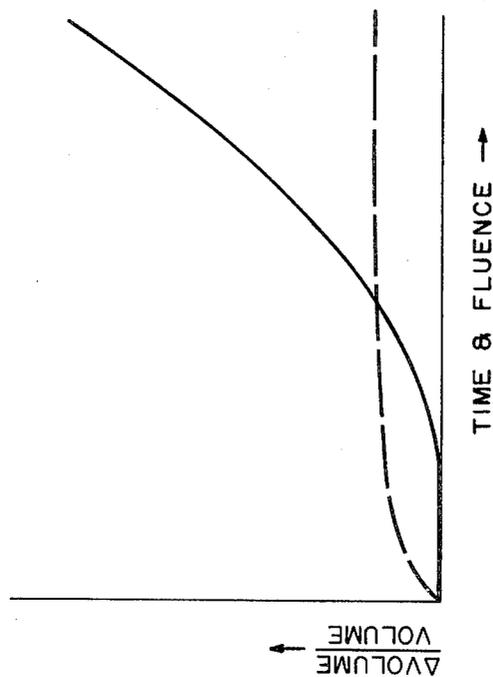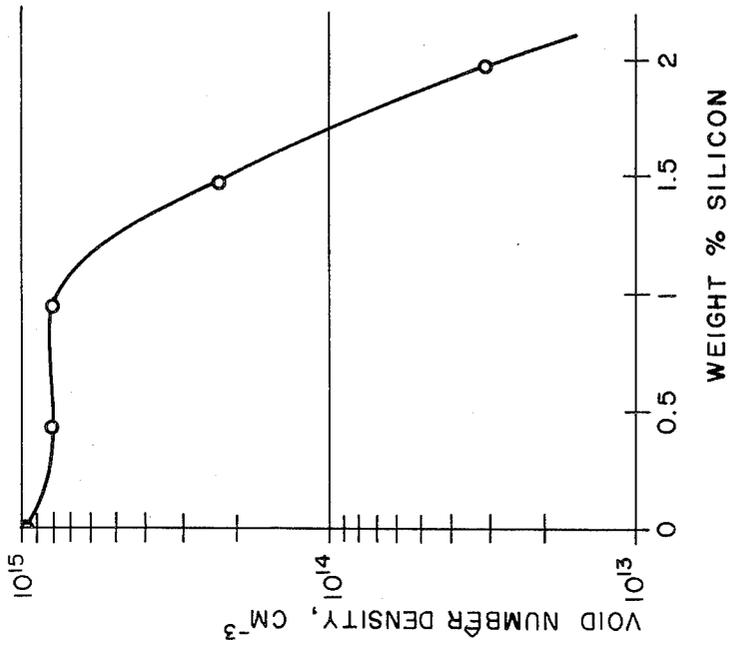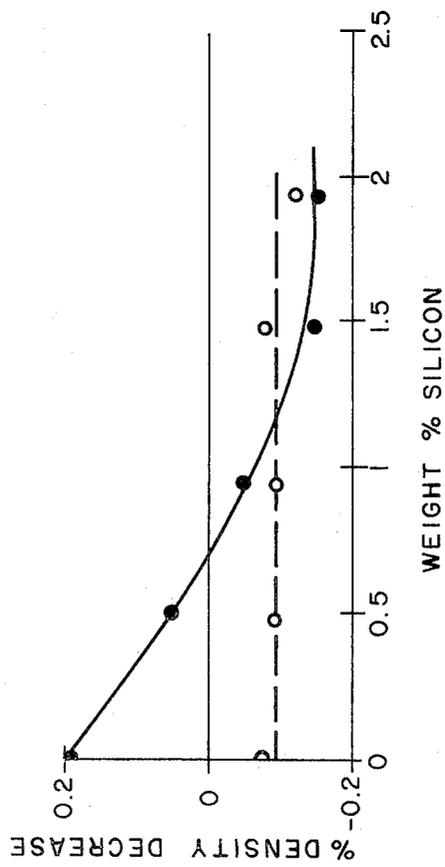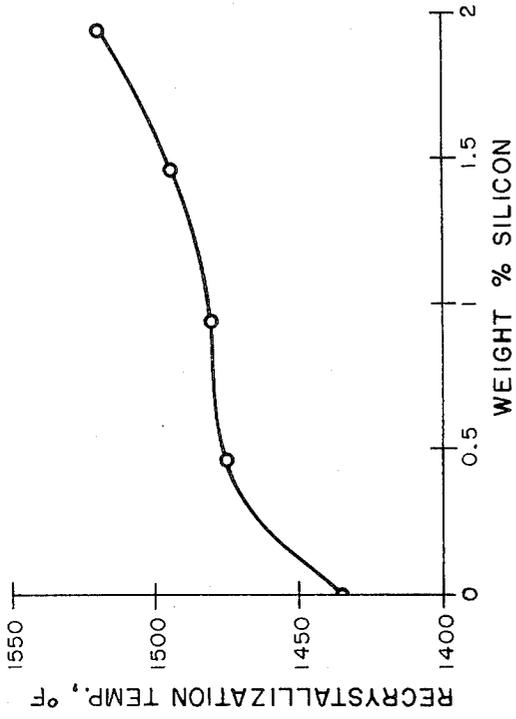
Fig. 6

Fig. 7

Fig. 5a

Fig. 5b

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IRRADIATION SWELLING RESISTANT ALLOY FOR USE IN FAST NEUTRON REACTORS

CONTRACTUAL ORIGIN OF THE INVENTION

This invention was made in the course of or under a 5 contract with the United States Atomic Energy Commission.

BACKGROUND OF THE INVENTION

The core structures of nuclear reactors impose se- 10 vere material problems because of the high temperatures, mechanical stresses, exposure to flowing coolants, and as a unique problem, neutron irradiation. A class of materials that has found wide acceptance is that of the stainless steels. They have been used both 15 for the structural components and for the fuel tubes. The latter are long tubes of small, typically ¼ to ¾ inch diameter and one to a few hundredths inch in thickness. They are filled with the nuclear fuel, usually uranium dioxide, plutonium dioxide or a mixture of the 20 two. They are located closely adjacent to each other and are surrounded by the coolant.

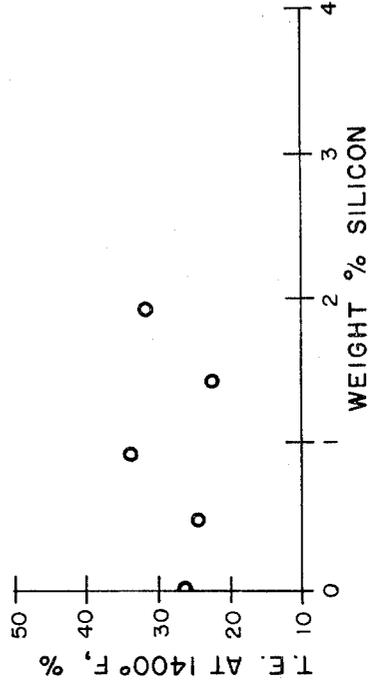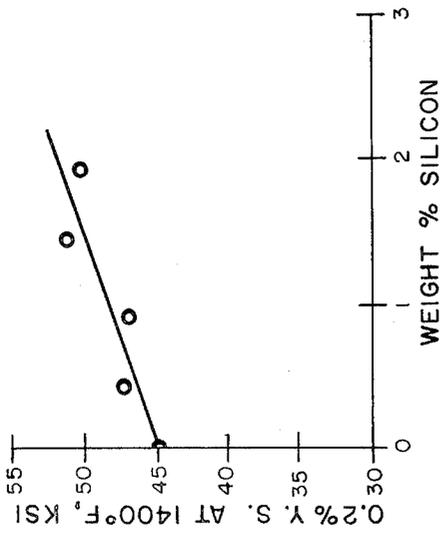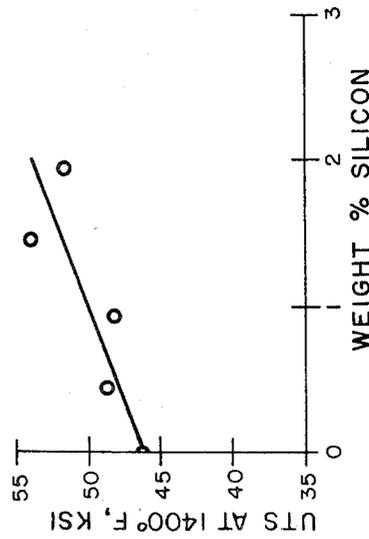In "thermal" or "slow neutron" reactors, the coolant is usually water, although in some cases carbon dioxide or helium is used. The radiation causes dissociation of 25 the water into hydrogen and oxygen. The austenitic stainless steels, particularly AISI types 304 and 316 have excellent resistance to corrosion under these conditions. In fast neutron reactors the coolant is usually molten sodium, which is very corrosive to ferritic 30 steels. The austenitic stainless steels show excellent resistance to corrosion by sodium. They also have excellent high temperature mechanical properties.

However, these steels exhibit swelling problems under irradiation by fast neutrons, i.e., those having en- 35 ergies of at least 0.1 Mev. [million electron volts]. Even in a thermal reactor certain components, particularly the fuel tubes, are subjected to irradiation to some extent by fast neutrons. In a fast neutron reactor the swelling problem is much greater, since the fast neu- 40 trons predominate throughout the reactor core. Whereas in a thermal reactor materials may be subject to a fluence (integrated flux) of 10^{21} fast neutrons per square centimeter, fast power reactors, which are usually cooled by molten sodium, are expected to subject 45 some of the materials to fast fluences of at least 1.5 × 10^{23} n/cm^2 and perhaps 10^{24} n/cm^2 at temperatures in the range of 600° F to 1,500° F. Volume increases in excess of 10% have already been observed in an existing fast neutron reactor, the EBR-II near Idaho Falls, 50 Idaho. Swelling of this magnitude is unacceptable for power reactors.

In fast reactors, as currently built and designed, the core is formed of hexagonal ducts which are closed packed. Some of these ducts enclose assemblies of fuel 55 elements, while in others there are control rods containing neutron absorbers. Swelling in the ducts is particularly troublesome because gradients in swelling give rise to large amounts of bending and distortion.

At present, AISI 316 is the preferred material for the 60 fuel tubes and the ducts, since it exhibits less swelling than AISI 304, the other stainless steel commonly used in nuclear reactors, apparently due to its molybdenum content of 2.0 to 3.0 percent by weight. Nevertheless, 65 as indicated above, the problem persists.

Various thermal and mechanical treatments have been proposed to remedy the situation, but have not

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been completely successful. For example, prior cold work AISI 304 and 316 stainless steel decreases swelling but the cold work is inherently unstable at high temperatures, a situation which is thought to be aggravated by neutron irradiation. If the cold work is recovered during irradiation, the swelling may actually become enhanced relative to that of the same steel in the annealed state.

Electron microscope studies have shown that there are at least two mechanisms involved in swelling-precipitation and void formation. The latter is considered the more serious since it appears that it may go on without limit on continued exposure, while precipitation has a finite limit. This is shown qualititatively in FIG. 1 where the solid line shows typical swelling behavior of metal due to precipitation (broken line) and that due to void formation produced by neutron irradiation (solid line). It is therefore very important to produce material which will have a minimum void formation.

The swelling behavior of metal under neutron irradiation is a function both of the fluence and of operating temperature. This results in a rather complex relationship. In a reactor the coolant ordinarily enters at one end of the fuel elements, flows along them and exits at the other end. The temperature is therefore lowest at one end of the fuel rods and highest at the other end. On the other hand, the neutron flux, and therefore the total fluence received by the material, follows the well-known "cosine law" with the maximum at the midpoint of the fuel rod.

The expected conditions for a typical liquid metal cooled fast breeder reactor are shown approximately in FIG. 2. The solid curve shows the expected fluence along the reactor axis and the dotted curve shows the mid-wall cladding temperature under full power operating conditions. For this particular reactor, it is expected that the most severe swelling will occur at a temperature of about 900° to 1,100°.

It is therefore desirable and an object of this invention to provide an alloy with improved resistance to void formation in fast reactor environments.

SUMMARY OF THE INVENTION

Our invention involves an alloy which exhibits, as compared to AISI 304 and 316 stainless steels, reduced void formation even in the annealed condition, improved high temperature yield strength and ultimate tensile strength to withstand the high stresses generated in LMFBR (liquid metal cooled fast breeder reactor) components, and improved cold work stability. It has fabrication characteristics (i.e., forgeability, weldability) comparable to AISI 304 and 316 stainless steels.

Basically the new steel is an AISI 316 steel modified to have a specific range of silicon content considerably greater than that of the usual AISI 316 steel. Since type 316 differs from type 304 in having a higher molybdenum content, the new steel differs from AISI 304 in having both higher molybdenum and higher silicon contents. Preferably, the molybdenum content is somewhat higher than the usual 316 steel. The new steel contains specific quantities of carbon and manganese falling within the AISI 316 range, which are necessary to restrain void formation, yet not produce undue hardening. It also contains specific quantities of nitrogen to give the proper mechanical properties while limiting

the effects of neutron irradiation. Limits are placed on other minor constituents.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing qualitatively the relationship of swelling and fluence due to different swelling mechanisms.

FIG. 2 is a graph showing typical operating temperatures and fluence at different points in a fast reactor core.

FIG. 3 is a graph showing change in density on neutron irradiation of basically AISI 316 stainless steels containing varying amounts of silicon.

FIG. 4 is a semi-logarithmic graph showing the number of voids per cubic centimeter produced by neutron irradiation of basically AISI 316 stainless steels containing varying amounts of silicon.

FIGS. 5a and 5b are graphs showing the high temperature yield strengths and ultimate strengths respectively of basically AISI 316 stainless steels containing varying amounts of silicon.

FIG. 6 is a graph showing the recrystallization temperatures of cold worked basically AISI 316 stainless steels containing varying amounts of silicon.

FIG. 7 is a graph showing high temperature ductilities of basically AISI 316 stainless steels containing various amounts of silicon.

DESCRIPTION OF THE PREFERRED EMBODIMENT

While we do not wish to be bound by theory, we believe the mechanism by which the higher silicon content reduces void formation to be as follows. One must first consider the basic cause of void formation under irradiation. During irradiation, atoms are knocked out of their normal position in crystalline structure of the metal by incident neutrons. When an atom is displaced from the crystal structure, two types of defects are formed: The vacancy, which consists of the vacant crystal lattice site (a hole), and the interstitial, or displaced atom, which lies between normal lattice sites. Irradiation produces equal amounts of these defects. Over the temperature range that void formation occurs, both vacancies and interstitials are mobile and randomly migrate throughout the metal until they are annihilated by recombining with one another or condense upon structural features such as voids or dislocations.

Swelling is presently thought to occur because interstitials have a slightly increased tendency, over that of vacancies, to condense on dislocations, leaving an excess of vacancies to condense at voids. The net process of interstitials condensing at dislocations and vacancies condensing at voids results in increased void volume or swelling. At temperatures slightly below the void formation temperature range, the interstitials are highly mobile whereas vacancies are not. At these temperatures, the vacancy concentration tends to become very high because vacancies are being created at a much faster rate than they can migrate and subsequently condense on microstructural features. Although the interstitials can still freely migrate, their most probable fate is recombination with one of the stationary vacancies because of the high vacancy concentration. The recombination event annihilates both the vacancy and the interstitial and therefore removes the possibility of these defects contributing to the void formation process. It

follows that swelling or void formation can be reduced by promoting recombination in this steel over a wide temperature range by forming a strong chemical (electronic) bond with vacancies. In the bonded or trapped state, the vacancy is immobile and will remain trapped until recombination with an interstitial. This frees the silicon atom to trap yet another vacancy and repeat the process.

Other impurities may tend to have the same influence on void formation, but silicon is believed to be the most potent because of the following criteria that it meets: (1) It exhibits a high degree of chemical interaction (compound formation) with the principle constituents in the steel; (2) it has a high solubility limit in the steel which allows it to be atomistically dispersed in the matrix; (3) it is a substitutional impurity (occupies normal lattice site when in solution) and therefore has a very low mobility; and (4) its concentration range in the alloy is sufficiently low that the electronic bonding state around the impurity is drastically different from the electronic configuration around the majority of lattice sites (i.e., the electronic state in the immediate vicinity of a lattice site is occupied by silicon is vastly different from the electronic state in the vicinity of a lattice site occupied by a chromium, iron, or nickel atom).

As was mentioned above, it is necessary that the steel contain specific proportions of molybdenum, manganese, and carbon in order to possess thet desired resistance to void formation although these proportions may overlap or fall within the normal limits of AISI 316 stainless steel. It should also contain limited amounts of nitrogen to give the proper mechanical property for nuclear use. Too much nitrogen is undesirable; however, because the neutron reaction with nitrogen involves the emission of alpha radiation which is damaging to the metal.

The amounts of cobalt and boron should be kept as low as possible since both are neutron poisons which reduce the performance of the reactor and the neutron reaction with cobalt produces cobalt-60 which emits hard gamma radiation and has a long half life, making it difficult to handle the equipment after it has been used in the reactor.

Copper, phosphorus and sulfur are limited because of their adverse effects on mechanical properties.

The ranges of compositions of the alloys constituting this invention are listed in Table I.

TABLE I

Element	Weight Percent
Chromium	16.0 to 18.0
Nickel	11.0 to 14.0
Molybdenum	2.0 to 4.0
Silicon	1.1 to 2.0
Manganese	1.00 to 2.00
Carbon	0.04 to 0.08
Nitrogen	0.04 to 0.06
Phosphorus	0.00 to 0.03
Sulfur	0.00 to 0.03
Cobalt	0.00 to 0.05
Copper	0.00 to 0.01
Boron	0.00 to 0.001
Iron	Balance

Preferably the above constituents are further limited as shown in Table II.

TABLE II

Element	Weight Percent
Chromium	17.0 to 18.0
Nickel	12.0 to 14.0
Molybdenum	2.3 to 3.5
Silicon	1.5 to 2.0
Manganese	1.00 to 2.00
Carbon	0.04 to 0.06
Nitrogen	0.04 to 0.06
Phosphorus	0.00 to 0.02
Sulfur	0.00 to 0.01
Cobalt	0.00 to 0.05
Copper	0.00 to 0.01
Boron	0.00 to 0.001
Iron	Balance

EXAMPLE

A series of samples were made up by varying the amount of silicon in a steel having otherwise the composition of an AISI 316 stainless steel to give zero, 0.5, 1.0, 1.5, and 2 percent. The other constituents fell within the preferred range given in Table II.

Some of the samples were solution treated by aging for 1,000 hours at 600° C (1,112° F). Others were subjected to about 20% cold work by drawing. Samples of each composition, with each type treatment were then exposed to neutron flux in the core of the EBR-II reactor to a total fluence of 2.0×10^{22} n/cm², considering those neutrons having energies of 0.1 Mev. or greater, at a temperature of 760° F. Densities were measured by immersion weighing before and after irradiation and the decrease in density, a measure of swelling, determined and plotted. Results are shown in FIG. 3, where the solid curve shows the results for the solution treated material and the broken line shows the results for the cold worked material. Electron micrographs were made and the number of voids per cubic centimeter were determined. Results are given in FIG. 4.

It will be noted from FIG. 3 that an increase in silicon content caused a progressive decrease in swelling of the solution-treated metal which actually became a densification at the higher silicon contents. The plot of the void density in FIG. 4 shows a very rapid decrease in the number of voids as the silicon content is increased above about 1.1%

Other samples of the same compositions were subjected to the same irradiation at a temperature of 1,110° F. Complete results are not available at this time but qualitatively somewhat different results appear than at 760° F. At this temperature and fluence, the samples showed a slight increase in swelling as the amount of silicon was increased above about 0.75%. However, the number of voids per cubic centimeter appears, from inspection of the photomicrographs, to decrease in a manner similar to that shown in FIG. 4.

In this connection, attention is called to the discussion of FIG. 1 given above. It appears that at 1,100° F and the fluence employed, conditions correspond to those in the left hand portion of the graph. At increasing fluence, such as would be attained in a fast power reactor, the effects on void formation given in FIG. 4 would become the governing factor.

A silicon content of about 1.1% to 2.0% therefore produces a dramatic improvement. There is nothing to indicate that, in this respect, further increase in silicon concentration would be disadvantageous. However, too high a silicon content has adverse effects on weld-

ability and certain other properties. We therefore limit the silicon content to 2.0%.

The recrystallization temperatures of the cold worked material of different silicon contents were determined by measuring the hardness at room temperature, heating various samples to various temperatures, and again measuring the hardness at room temperature. After heating to some temperature, there will be a sudden drop in hardness. This is taken as the recrystallization temperature.

The recrystallization temperatures for different silicon contents are plotted in FIG. 6. It will be noted that whereas up to about 1% silicon (the usual upper limit of AISI 316 steel) there was a "leveling off" of the recrystallization temperature with increasing silicon content, our range shows a marked increase. This is desirable since it means that the steel retains its cold worked properties despite heating in the reactor and should avoid the phenomenon, mentioned above, of swelling being enhanced after heating.

The high temperature ductilities were determined by measuring the tensile elongation at 1,400° F. Results are plotted in FIG. 7. The data results are too scattered to definitely indicate a trend, but there appears to be no adverse effect from increased silicon content.

Still other samples which had received the 20% cold work were subjected to tensile tests at 1,400° F and the 0.2% yield strength and ultimate strength determined. The results are plotted in FIGS. 5a and 5b, FIG. 5a showing the yield strength and FIG. 5b the ultimate strength in "kilopounds" per square inch. Note that increasing the silicon content increases both the yield point and the ultimate strength.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stainless steel alloy resistant to void formation under irradiation by fast neutrons consisting essentially of the following:

Element	Weight Percent
Chromium	16.0 to 18.0
Nickel	11.0 to 14.0
Molybdenum	2.0 to 4.0
Silicon	1.1 to 2.0
Manganese	1.00 to 2.00
Carbon	0.04 to 0.08
Nitrogen	0.04 to 0.06
Phosphorus	0.00 to 0.03
Sulfur	0.00 to 0.03
Cobalt	0.00 to 0.05
Copper	0.00 to 0.01
Boron	0.00 to 0.001
Iron	Balance

2. An alloy as defined in claim 1 and further limited as follows:

Element	Weight Percent
Chromium	17.0 to 18.0
Nickel	12.0 to 14.0
Molybdenum	2.3 to 3.5
Silicon	1.5 to 2.0
Carbon	0.04 to 0.06
Phosphorus	0.00 to 0.02
Sulfur	0.00 to 0.01

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