

April 27, 1971

H. E. MCCOY, JR

3,576,622

NICKEL-BASE ALLOY

Filed May 29, 1968

3 Sheets-Sheet 1

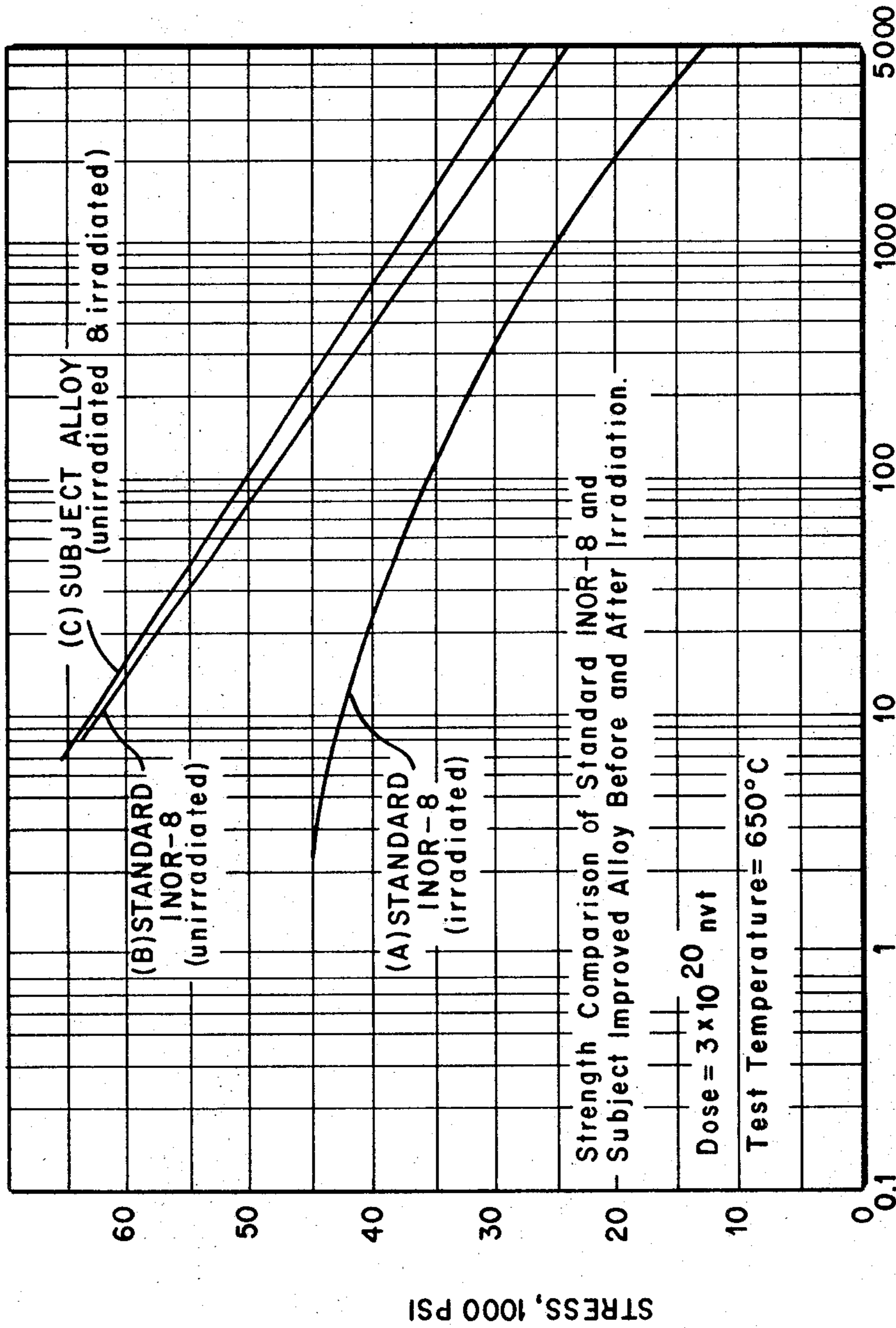


Fig. 1

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3 Sheets-Sheet 2

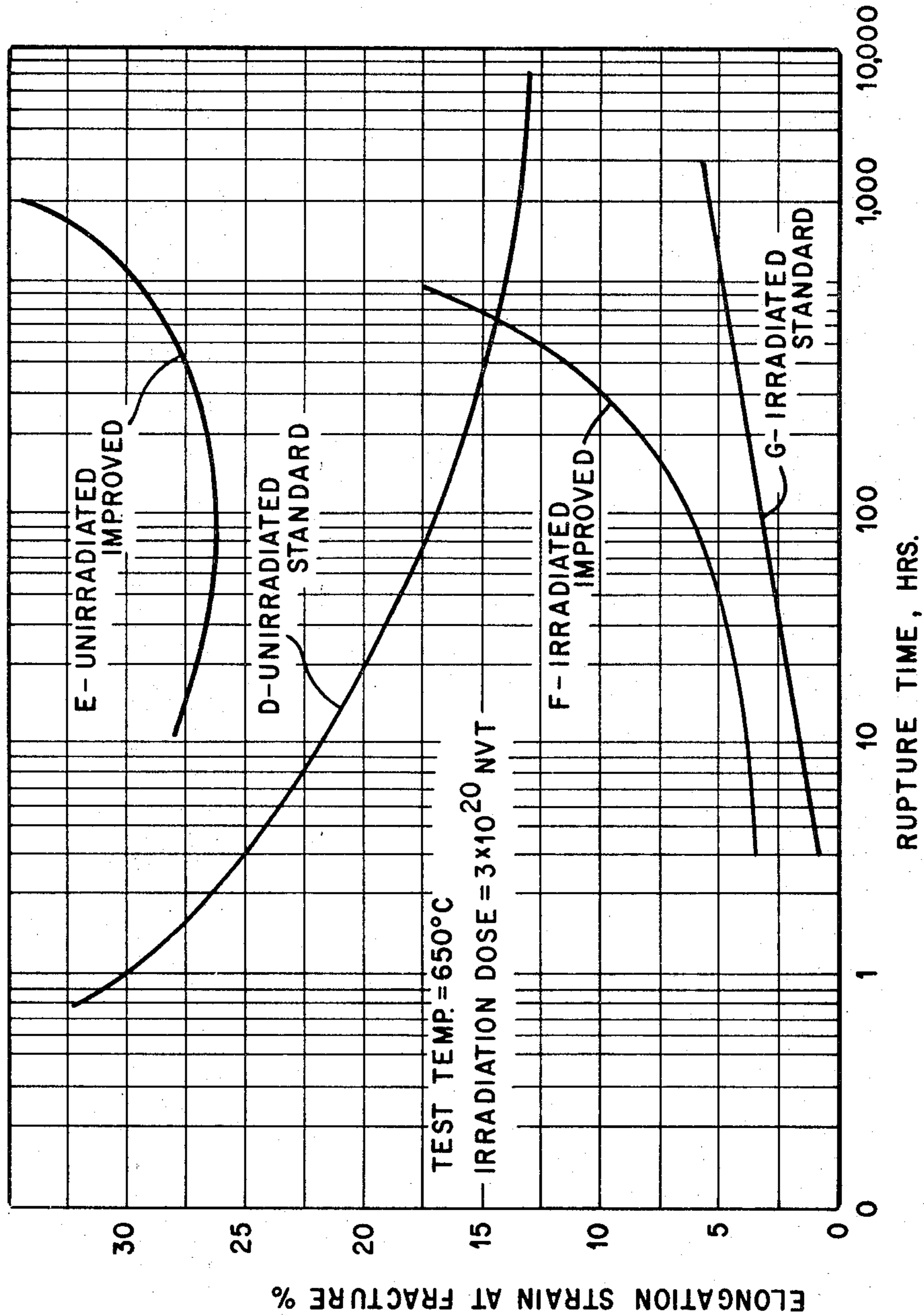


Fig. 2

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3 Sheets-Sheet 3

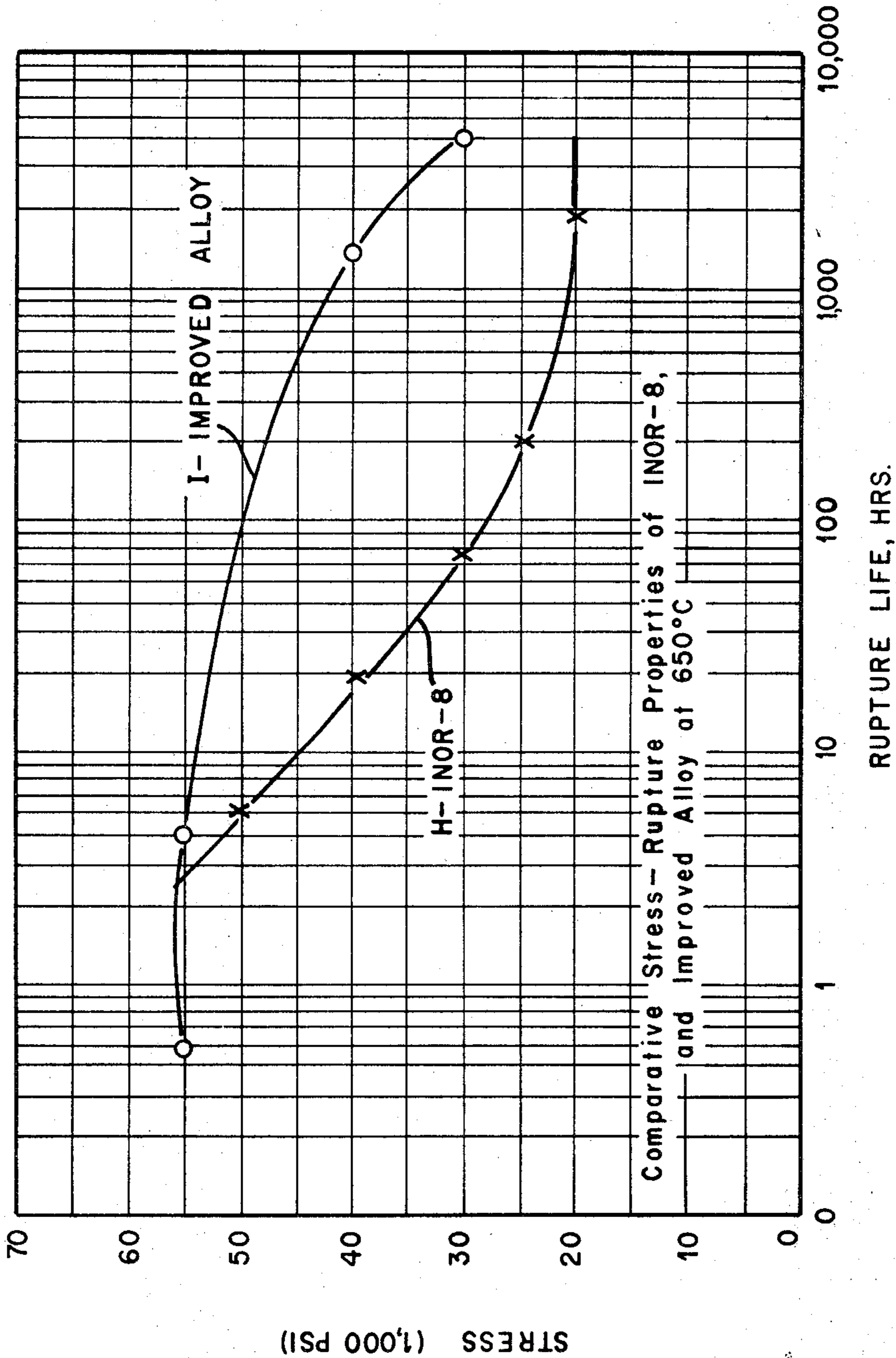


Fig. 3

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3,576,622

NICKEL-BASE ALLOY

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U.S. Cl. 75-171

1 Claim

ABSTRACT OF THE DISCLOSURE

An improved nickel-base alloy which contains as essential alloying ingredients 11-13 weight percent molybdenum, 6-8 weight percent chromium, 0.02 to 0.5 weight percent carbon, up to 1.0 weight percent of a boride forming element selected from titanium, zirconium, and hafnium, up to 4 weight percent of at least one strengthening agent consisting of tungsten, tantalum, vanadium, and niobium, and the balance nickel.

BACKGROUND OF THE INVENTION

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

The present invention relates to an improved nickel-base alloy. More particularly, it relates to an improvement in the nickel-base alloy known as INOR-8 or Hastelloy-N, the composition of which is described in U.S. Pat. No. 2,921,850 as comprising 15-22 weight percent molybdenum, 6-8 weight percent chromium, 0.02-0.5 weight percent carbon, and the balance nickel. This alloy was developed to meet a specific need for a material with sufficient high temperature strength that would also resist corrosive attack by molten fluoride salt mixtures. As such it was intended to serve as a fuel carrier and coolant in molten salt reactors of the kind under development by the U.S. Atomic Energy Commission at Oak Ridge, Tenn.

Although it has been shown that INOR-8 has suitable properties for long-time use at high temperatures, a deterioration of these properties occurs in a high neutron field. Specifically, it has been found that the alloy is susceptible to a form of high temperature irradiation damage that reduces its creep rupture life. One form of irradiation damage has been attributed to nuclear transmutation involving helium formation, principally from the n, α reaction with boron-10. It has been postulated that the helium collects at the grain boundaries and promotes intergranular cracks. This type of irradiation damage has been found to be general for iron- and nickel- base alloys. The addition of small amounts of titanium, zirconium, or hafnium up to about 1.0 weight percent has been found to reduce this form of irradiation damage significantly. Alloy modification of the basic INOR-8 composition designed to alleviate the helium embrittlement problem is the subject matter of U.S. patent application S.N. 603,085 of common assignee. Although additions of titanium, zirconium, and hafnium have resulted in improvement, high temperature test data continue to evidence degradation of creep rupture and high temperature ductility. The reduction in those properties has been found to be particularly evident in welds made from the alloy where cracking along the line of the weld presents a serious problem. Weld integrity is, of course, essential to the development of the alloy as a nuclear reactor structural material.

In the original concept of the basic INOR-8 alloy, a molybdenum concentration range of 16-18 weight percent was selected principally because it yielded a desirable solution strengthened phase. Subsequent high temperature strength and ductility studies have now shown that both the basic INOR-8 composition and the additives made to

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it to accommodate intergranular cracking due to helium formation continue to show embrittlement under reactor service conditions.

SUMMARY OF THE INVENTION

The present inventive concept is based on the recognition of the cause and provides a means for reducing the effect of the embrittlement which has been noted even after modifications have been employed to deal with embrittlement due to helium formation. The cause of the persisting embrittling effect is related to the formation of a secondary, precipitated phase which has been identified by microprobe analysis as a M_6C type precipitate where M, in weight percent, represents approximately 55 Mo, 31 Ni, 5 Cr, 5 Si, 4 Fe, and a residuum of other metals and non-metals.

The present invention provides a modification of the basic INOR-8 alloy as disclosed in U.S. Pat. No. 2,921,850 and modified in U.S. patent application S.N. 603,085 by varying the molybdenum concentration in an amount sufficient to effectively reduce or eliminate formation of the M_6C type precipitate as a secondary phase. Specifically, the present invention resides in a nickel-base alloy containing as essential alloying ingredients, in weight percent, 11-13 percent Mo, 6-8 percent Cr, 0.02-0.5 percent carbon, an amount of boride forming element selected from Ti, Zr, and Hf sufficient to convert incidental amounts of boron to a boride of said selected element, from 0 up to 4 percent of a strengthening agent selected from W, Ta, V, and Nb, the balance being nickel.

BRIEF DESCRIPTION OF THE DRAWINGS

The effect of the alloy modification proposed by this invention will be more clearly understood by reference to the accompanying drawings in which:

FIG. 1 shows curves relating strength in creep in a plot of stress vs. rupture time of alloys within the scope of the invention in the unirradiated and irradiated states;

FIG. 2 shows ductility curves in terms of elongation at fracture as a function of rupture time in the irradiated and unirradiated states;

FIG. 3 shows curves of stress vs. rupture time of welds made from alloys within the scope of the invention.

FIGS. 1-3 also include strength and ductility curves of alloys falling outside the scope of the invention which serve as a basis for comparison. Reference in detail to the data shown in these drawings will be made in the ensuing description.

BRIEF DESCRIPTION OF A REPRESENTATIVE EMBODIMENT

For the sake of illustration, the invention will be described in comparative terms using as a standard alloy the "standard INOR-8 alloy" as disclosed in U.S. Pat. No. 2,921,850 and in U.S. patent application S.N. 603,085 as a basis for comparison against a representative improved alloy of this invention. The compositions of the standard and the representative alloys are given in Table I below.

TABLE I

Composition of representative improved alloy, wt. percent	
Ni	Bal.
Mo	12.0
Cr	7.18
Fe	.034
Mn	.29
Ti	.49
C	.015
Si	.015
Al	.02
Zr	0.01

Composition of standard INOR-8 alloy, wt. percent

Ni	Bal.
Mo	16.3
Cr	6.2
Fe	3.3
Mn	.67
Ti	<.01
C	.054
Si	.58
Al	.02
Zr	<.01

Several heats from each alloy composition were made up and tensile specimens were subjected to short-term tensile testing at temperatures ranging from room temperature (25° C.) up to 800° C. The results are summarized in Table II below. The strength and tensile values as given in Table II represent an average of several tests using several heats. The higher and lower values bracket the range of values obtained under the stated conditions.

TABLE II.—COMPARATIVE TENSILE PROPERTIES¹

Temp., ° C.	Standard INOR-8 alloy				Representative improved alloy			
	Strength, K s.i. ²		Elongation, percent	Reduction in area, percent	Strength, K s.i. ²		Elongation, percent	Reduction in area, percent
	Yield	Tensile			Yield	Tensile		
25	45-56	120-122	55-61	58-63	37-40	106-109	73-75	64-72
200					32-34	99-101	75-78	58-62
427	33-41	106-111	58-69	51-60	29-31	95-98	75-79	60-80
500	31-45	100-106	58-64	48-64	26-28	89-91	82-83	57-59
550					28-30	92-94	75-77	52-54
600	31-40	98-101	58-67	50-52	24-26	82-86	74-74	51-53
650	32-39	80-95	33-59	32-48	23-25	72-76	43-51	30-40
760	28-35	62-67	31-38	29-32	22-25	60-67	31-33	21-25
800					23-24	52-59	27-30	22-24

¹ The strength and tensile values represent an average of several tests using several heats.

² K s.i. = thousand pounds/square inch.

From the results shown it will be seen that the improved alloy exhibits somewhat greater ductility, but at the cost of a loss in strength in comparison to the standard INOR-8 alloy (16 weight percent Mo). The loss in strength can be made up, however, by adding a solid solution strengthening concentration of at least one metal selected from W, Ta, V, or Nb. The strength in creep at 650° C. for the two alloys is shown in FIG. 2 for the irradiated and non-irradiated case. It is to be noted that the strength of the representative alloy of the subject invention (curve C) is unaffected by radiation, whereas there is considerable reduction in strength between the reference INOR-8 alloy in the irradiated (curve A) and non-irradiated (curve B) state.

A comparison of ductility in creep between the two alloys in the irradiated and unirradiated state at 650° C. is shown by the curves of FIG. 2. In the unirradiated state, the ductility of the improved alloy (curve E) is seen to increase with time at a given stress, while the ductility of the standard INOR-8 alloy (curve D) degrades with time. In the irradiated state, the ductility of the irradiated representative improved alloy (curve F) of the present invention is clearly superior to the irradiated standard alloy (curve G).

An examination of the microstructure of several nickel-base alloys within and outside the scope of the present invention shows that the alloys containing 14-16 weight percent Mo show the typical secondary M₆C phase segregated at the grain boundaries. On the other hand, alloys

containing the 10-12 weight percent Mo, which are typical of those within the scope of my invention, show no secondary precipitated phase and do not lose strength in creep after exposure to nuclear irradiation as do the alloys containing 16% Mo, i.e., alloys represented by the standard INOR-8 case.

The upper concentration of Mo in the alloy according to my invention should not exceed 13 weight percent in order to avoid the formation of the M₆C precipitated phase. Concentrations of Mo in the range 11-13 weight percent provide the optimum Mo concentration in terms of producing an alloy which (1) will not form the persistent M₆C brittle intergranular secondary phase, (2) will be corrosion resistant to molten fluoride compositions, (3) will make for maximum fabrication ease, and (4) will be weldable. While lower concentrations will be effective to eliminate the M₆C phase, it will also tend to reduce the other desirable criteria mentioned. Concentrations of iron may vary up to 6% by weight without affecting the advantages achieved by the essential alloying in-

Similarly, the use of minor amounts of such elements as manganese as a malleabilizing element or silicon as a deoxidizer is within the scope of this invention. The significance of the term "weldability" in the context of this invention is seen from the curves of FIG. 3 which compare the stress rupture properties at 650° C. of welds made with the Ti-modified INOR-8 alloy composition as disclosed in U.S. patent application S.N. 603,085 (curve H) with the stress rupture properties at 650° C. of welds made with the representative improved alloy within the scope of the present invention (curve I).

What is claimed is:

1. An improved nickel-base alloy consisting essentially of 11-13 weight percent molybdenum, 6-8 weight percent chromium, 0.02 to 0.5 weight percent carbon, an effective concentration of a boride forming element selected from the group consisting of titanium, zirconium, and hafnium sufficient to react with incidental quantities of boron in the alloy to form a boride of said element, up to 4 weight percent of at least one strengthening agent from the group consisting of tungsten, tantalum, vanadium, and niobium, and the balance nickel.

References Cited

UNITED STATES PATENTS

2,921,850 1/1960 Inouye et al. 75-171

RICHARD O. DEAN, Primary Examiner