Argonne National Laboratory

SELECTION OF THE STRUCTURAL MATERIAL
FOR THE
FARET LIQUID-METAL SYSTEMS

by

L. R. Kelman and R. J. Dunworth

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Metallurgy Division

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INTRODUCTION

The combined high-temperature sodium-radiation environment proposed for the 15-year plant life of FARET* is an extrapolation beyond present experience and knowledge for available structural materials. Selecting the optimum material required close cooperation between the designers and those most knowledgeable in materials properties and technology. To that end, the following individuals were asked early in 1963 to serve on a FARET Materials Selection Committee:

T. L. Kettles (R.E.) - Chairman

N. Balai (R.E.) - Materials and Fabrication

L. R. Kelman (Met.) - Physical and Mechanical Properties

M. A. Pugacz (Met.) - Welding and Radiation Damage

S . Greenberg (Met.) - Corrosion

The first job of the Committee was to advise W. R. Simmons, FARET Project Manager, in the selection of a material for the core structure, primary vessel, and piping. The Committee first reviewed ground rules and pertinent FARET conditions with members of the Reactor Engineering Division to determine the materials requirements and probable problem areas. Through our discussions and reviews of the literature, we realized that most candidate materials did not meet the requirements.

In the course of our deliberations we consulted many materials experts from ANL, other research laboratories, and industry. Some of the well-known authorities in the high-temperature structural material field that were consulted included:

J. Chirigos
M. A. Cordovi
J. W. Freeman
Bettis Laboratory, Westinghouse
International Nickel Co., Inc.
University of Michigan

D. R. Johnson Bechtel Corp.

W. Leyda Babcock and Wilcox Research Center

R. A. Lula Allegheny Lundlum Steel Corp. J. J. Moran International Nickel Co., Inc.

^{*}Fast Reactor Test Facility

P. Shahinian Naval Research Lab.

E. N. Skinner International Nickel Co., Inc.

C. R. Sutton Nuclear Utility Services, Inc.

R. C. Werner MSA Research Corp.

High-temperature Materials Specialists from U. S. Steel Corp. High-temperature Materials Specialists from Huntington Alloy Products. INCO

We also arranged for a symposium on "Materials for Sodium-cooled Reactors," which was cosponsored by the AIME and the ANS and which was held at the 1963 Winter meeting of the ANS. We invited reactor engineers and metallurgists from all organizations that have designed, built, or operated sodium-cooled reactors. Thus we were able to collect in one volume (1) materials information that was widely scattered through the literature and some that was not yet reported. Most important to our immediate problem, the symposium permitted us to exchange views with knowledgeable and interested persons from other organizations, and especially those who are involved in materials problems similar to ours.

FARET REQUIREMENTS

The FARET vessel is intended to serve for 15 years as a safe container for engineering quality sodium at high temperatures while undergoing a total integrated fast-neutron irradiation of 10^{21} nvt. Failure of the vessel by brittle fracture is the most serious potential hazard. Therefore, the material selected must retain adequate ductility and impact resistance to resist the stresses and thermal shocks that the vessel must withstand. It is anticipated that the system will operate at $600\text{-}650^\circ\text{C*}$ for 10,000 hours, $550\text{-}600^\circ\text{C}$ for 40,000 hours, $300\text{-}550^\circ\text{C}$ for 40,000 hours, and $<300^\circ\text{C}$ for the remainder of its 15-year life.

Since there is to be no materials development or proof program, the material selected for FARET has to have a reasonably well-developed and adequate technology. Not only must it have adequate mechanical properties under FARET conditions, but the material must be readily available in the necessary sizes and shapes, as well as amenable to fabrication and welding into the final assembly. Ultimately, of course, it is the fabricated assembly that must satisfy FARET conditions.

MATERIALS CONSIDERED

A wide range of materials was examined, some of which looked very promising. However, most of them were developed too recently to satisfy

^{*}Throughout this report, the data in English units and °F have been converted to metric units and °C and rounded off.

the "existing technology" requirement. Others were eliminated because they did not have adequate properties.

Consideration of the long-time load-carrying ability at 650°C of candidate materials in Table I narrows the field to the austenitic chromium-nickel stainless steels and to the new superalloys. The low strength at 650°C of the ferritic steels and of the precipitation-hardenable stainless steels eliminates them from consideration for this application.

Table I

ALLOWABLE STRESSES AT 650°C FOR FERRITIC AND AUSTENITIC STEELS⁽²⁾

Type	Material	Grade	Stress (kg/mm²)
Ferritic	2.25 Cr, 1 Mo	P22	1.4
	5 Cr, 0.5 Mo	P5	1.1
	9 Cr, 1 Mo	P9	1.1
	13 Cr	410	0.7
	17 Cr	430	1.2
Austenitic	19 Cr, 10 Ni	304	3.2
	17 Cr, 12 Ni, 2.5 Mo	316	4.8
	18 Cr, 10 Ni, Ti	321	3.5
	18 Cr, 11 Ni, Nb	347	3.5

As can be seen from Table II, the relatively new superalloys are potentially far superior to the austenitic stainless steels in long-time, high-temperature strength. Superalloys high in cobalt were included in spite of the general belief that cobalt would cause radiation problems. D. Rossin (ANL) advised that the radioactivity contribution of the fast-neutron-induced isotope of cobalt having a 5.3-year half-life would be relatively insignificant compared with the 71- and 314-day half-life of like amounts of iron and nickel. (7) Most of these alloys were developed to solve the short-comings of the austenitic stainless steels for short-time, high-temperature applications and only recently have been considered for long-time use. Incoloy-800 is an example of a high nickel-chromium-iron alloy that was considered a promising candidate by the Committee. However, it has an inadequately developed technology and its compatibility with sodium is not well enough known. (8,9) It has recently been approved by the ASME Board of Codes and Standards for use under Sections I and VIII of the Code. (5)

Unfortunately, many of the superalloys are still laboratory curiosities, and none is commercially available in the desired sizes and shapes.

In addition, there are very little pertinent long-time test data^(10,11) and practically no service history or developed technology to permit their selection for FARET.

Table II

ESTIMATED ALLOWABLE STRESSES AT 650°C

FOR SUPER STRENGTH ALLOYS

I.	Fe-Cr-Ni-Mo Alloys	Stress (kg/mm^2)
	19-9 DL	4(3)
	15-15 N	8(3)
	17-14 Cu-Mo	8(3)
	16-25-6	7(3)
	A286	8(4)
	Incoloy-800	₅ (5)
II.	Fe-Cr-Ni-Co Alloys	
	N155	7(3) 10 ⁽³⁾
	S590	10(3)
III.	Nickel Base Alloys	
77	Inconel	4(5)
	Inconel X	16(3)
	Inconel 102	13(5)
	Hastelloy X	8(6)
	René 41	17(6)
IV.	Cobalt Base Alloys	
	HS25	13(3)
	HS31	8(3)
	S816	10(3)

AUSTENITIC STAINLESS STEELS

A stainless steel with nominally 18% chromium and 8% nickel was originally developed for corrosion resistance about 55 years ago and first saw high-temperature service in 1928 in the petrochemical industries. (12) Since then, modifications of 18-8 containing titanium (Type 321), niobium (Type 347), and molybdenum (Type 316) have been developed. A large body of service-experience and laboratory creep-test data has been developed in the last 35 years as the result of extensive heat-resistance applications of these steels in the power and processing industries. The ASME Boiler and Pressure Vessel Code approves their use to 815°C.(2) The extensive

industrial use of 18-8 type stainless steels has resulted in a very well-developed technology. This steel can be obtained readily through normal channels in a wide variety of shapes and sizes with reasonable assurance that specifications and delivery schedules will be met.

Composition and Microstructural Stability (2,13)

The 18-8 type austenitic stainless steels are iron-chromiumnickel alloys with AISI- and ASTM-recognized compositions as shown in Table III. They are metastable solid-solution alloys with a facecentered-cubic gamma structure (austenite) at low temperatures that has been retained by quenching from high temperatures. These steels therefore have a tendency to transform to more stable ferrite and/or sigma phases on reheating to intermediate temperatures. Reheating can also result in precipitation of carbides and other compounds that tend to accumulate at grain boundaries. The rates of these reactions are a function of time at temperature and result in varying degrees of precipitation strengthening and embrittlement. Radiation, stress, and external environment are also known to influence the rate of these reactions. Unfortunately, there is no quantitative information on reaction rates and their influence on pertinent properties in the temperature range of interest in FARET. It is necessary to reheat to over 1000°C to transform back to austenite and to redissolve precipitated compounds.

Table III

COMPOSITION RANGES FOR SOME 300-SERIES
AUSTENITIC STAINLESS STEELS(14)

	Nominal Composition (w/o)					
AISI Type	C (max)	Mn (max)	Si (max)	Cr	Ni	Other
304	0.08	2.00	1,00	18 to 20	8 to 12	
316	0.08	2.00	1.00	16 to 18	10 to 14	2 to 3 Mo
321	0.08	2.00	1.00	17 to 19	9 to 12	$Ti = 5 \times C$
347	0.08	2.00	1.00	17 to 19	9 to 13	$Nb = 10 \times C$

The composition of the austenitic stainless steels is balanced so that the austenite formers have a dominant effect in solid solution over the ferrite formers. Precipitation from solution can upset this balance and increase the tendency for the austenite to transform.

The chief role of nickel in these alloys is to stabilize the austenite. Other important austenite promoters are carbon, nitrogen, and manganese. Carbon and nitrogen are about 30 times as potent as nickel, and manganese is about half as potent.

Chromium's chief role is to increase corrosion resistance. Chromium, silicon, molybdenum, niobium, titanium, aluminum, and phosphorus are ferrite formers.

In the 425-870°C range, chromium-carbide precipitates in the grain boundaries of the 300-series steels, and the resulting local depletion of chromium makes these alloys sensitive to intergranular corrosion. The Types 321 and 347 stainless steels were developed to maintain corrosion resistance by tying up the carbon as titanium and niobium carbides, thus protecting against precipitation of chromium carbide.

One way to minimize carbide precipitation is to lower the carbon content of the alloy. But carbon is an extremely potent strengthener; some carbon must be kept or the alloy will be too weak for use in FARET. This disadvantage of lower carbon may be partially offset, however, by the control of residual elements as will be discussed later in this report.

The sigma phase is a brittle compound usually consisting, in unbalanced austenitic steels, of almost equal amounts of iron and chromium. It can drastically reduce ductility and notch toughness at room temperature. Sigma forms slowly in the 565-925°C range in the ferritic portions of austenitic alloys and to a much lesser degree in austenite itself. Therefore ferrite formers, particularly molybdenum, niobium, and titanium, promote sigma formation. (2) Stress at elevated temperatures is also believed to promote sigma formation. Because of its slow development, there is little evidence that sigma forms on heat treatment; it is a long-time service problem. Sigma can be redissolved by heating above 925°C.

In general, the creep and creep-rupture strength of the 300-series steels increases and the rupture-ductility decreases with increasing grain size. Therefore a compromise between strength and ductility depends to some degree on the specified grain size. The magnitude of the grain size effect varies with composition; for example, grain size has less effect on the strength of 304 and 316, than on 321 and 347, stainless steels. Factors that control grain size, such as heat treatment and composition, may simultaneously achieve a second effect, masking that of grain size. An example is a high-temperature heat treatment to achieve coarse grains for added high-temperature strength, a treatment that by also increasing the solubility for carbides and nitrides effects an even greater increase in strength.

Welding

The properites of the fabricated and welded assembly are our final interest. The 300-series steels are the most readily welded of the stainless-steel group. The usual concern for sensitization in the areas near

the weld that reach 425-870°C, the carbide precipitation range, is not so important in the FARET application as in applications where corrosive liquids are handled. There are, however, problems associated with the solution of compounds in the heat-affected zone, the large contractions resulting from the high expansion coefficient (50% greater than for ordinary steels), and hot cracking due to a grain-boundary weakness near the melting temperature.(14) The practice of using a carefully selected, unbalanced weld metal to produce from 3 to 10% ferrite helps to solve the welding hot-shortness problem.(14) However, it is necessary to stay below about 3 or 4% ferrite to avoid the formation of appreciable amounts of the undesirable brittle sigma phase in high-temperature service.(15,16)

Austenitic Stainless Steels Other Than Types 304 and 316 SS

Type 347 stainless steel has been used with fair success for many years for main-steam-pipe service up to about $600^{\circ}\text{C.}^{(3)}$ However, sporadic cracking at welded joints, both during fabrication and early in service, has been a continuous problem. In recent years, Type 347 stainless steel has developed a notorious reputation in service. (3,17,18,19) It also exhibits a very low ductility in long-time rupture tests; in the $600\text{-}700^{\circ}\text{C}$ range, elongations of only 1-3% are common. (20)

An industry-wide task force extensively studied this problem and carried out a research program at the University of Michigan. (19) They recommended that Type 347 be avoided for heavy-section pressure parts for high-temperature power piping.

Service experience with Type 321 is about the same as with Type 347. Type 321 is also an extremely dirty steel full of nonmetallic inclusions. We found no published evidence in recent years that anyone is specifying it for high-temperature service.

Other austenitic stainless steels offered no advantages over Types 304 and 316 stainless steel. The high-chromium alloys, like Types 309 and 310, are susceptible to sigma formation. (21,22)

TYPES 304 AND 316 STAINLESS STEEL

Of all the materials considered, the austenitic stainless steels Types 304 and 316 came closest to satisfying FARET conditions and selection requirements. Therefore, it was necessary to examine them closely to determine which of these two has the best combination of technology and properties to permit a selection between them.

Studies and Service Experience of Types 304 and 316

While there are no long-time service behavior data under FARET conditions for Types 304 and 316 stainless steel, there are several service applications that are pertinent. Also, several applications similar to FARET's have been proposed. However, we must examine closely the ground rules for these applications and proposals to avoid being misled.

The petrochemical and the chemical-processing industries have used both Types 304 and 316 stainless steels extensively at 650°C, often under very corrosive conditions. However, their ground rules usually permit scheduled shutdowns for inspection and maintenance. A vessel failure can be corrected without the radiation problems of FARET. Since they can accept the probability of occasional failures, they can be somewhat arbitrary in their selection of design stresses. They might also be less concerned about brittle failure, and, therefore, they might be willing to sacrifice some ductility in favor of strength.

The steam-power industry is currently involved in a large-scale experiment in which Type 316 stainless steel is used for main steam piping at 650°C - $4~\text{kg/mm}^2$ service. (3,17,23) The Eddystone No. 1 plant of the Philadelphia Electric Company is the largest installation of austenitic steel for a single turbine unit in the world. The plant cannot be justified on the basis of current economics. It is an extrapolation in temperature, pressure, and size of steam-generating unit with a view toward the future.

Selection of a 17 Cr-13 Ni-2.5 Mo steel (within the Type 316 composition range) with a 16 Cr-8 Ni-2 Mo welding electrode for the Eddystone application was made after a comprehensive study of available materials including the superalloys. Superalloys were eliminated from consideration for lack of adequate property information and relevant manufacturing, fabrication, and service histories. The selection of 316 over 347 was based on an assessment of service history and a comparative metallurgical laboratory evaluation of weldability, heat-treatment, and high-temperature stability. The final selection had to be made long before much of the laboratory data were available. The research program was supposed to reveal materials or fabrication problems early enough to permit reconsideration of their material selection or their procedures. Recently published information indicates that Type 316 is working satisfactorily. (23)

The ground rules of Eddystone differ completely from those for FARET. The use of Type 316 stainless steel for this application is recognized as an experiment and is so treated. A careful schedule of inspection and removal or repair of cracks is used at relatively frequent intervals. For example, numerous small cracks developed on an inner cylinder and were detected by close inspection. (23)

Types 304 and 316 stainless steels have been used to at least 540°C in many sodium reactors, sodium loops, and in many laboratory experiments. The SRE, Hallam, Fermi, and EBR-II reactors all used Type 304 stainless steel for this purpose. A steel similar to Type 316 stainless steel is being used for the Rapsodie vessel. The proposed SEFOR and FCR reactors, where the maximum design temperature is 590°C (and higher for short-time transient tests in SEFOR), specify either Type 304 or 316 for their sodium system components, with economics to be the deciding factor. (24)

In the four recent 1000-MWe liquid-metal fast breeder reactor studies, Allis-Chalmers and Combustion Engineering selected Type 316 and General Electric and Westinghouse selected Type 304 stainless steel for their vessels, which are designed for 430 to 540°C sodium service. (25,26,27,28)

Large sodium test facilities in this country at MSAR, (29) GE-APED, (24) and LASL(30) and numerous smaller facilities at many laboratories have operated for years using Types 304 and 316 stainless steel to temperatures of 650°C and higher.

Properties of Types 304 and 316 Stainless Steel

The properties of the austenitic stainless steels are summarized in several handbooks. (31,32,33) Only those properties immediately pertinent to our problem will be considered here.

A brief review of the usefulness of existing mechanical property data is desirable before presentation of the data on Types 304 and 316 stainless steel. The high-temperature properties of the austenitic stainless steels are particularly influenced by their composition and their manufacturing and fabricating history. Variations in chemical composition and thermal variations during fabrication and heat treatment are practical manufacturing necessities that are allowed for in standard specification tolerances. This results in important variations in the grain size and the kind, size, composition, distribution, and orientation of microstructural constituents. A spread in the data can also be attributed to vibration problems and to problems in control and measurement of environment, temperature, and elongation. To add to this, only limited long-time hightemperature strength and ductility data are available because of the high cost of long-term creep and creep-rupture testing. Therefore, it is not surprising that these data are best represented by wide "scatter bands." There are numerous references to precautions in using any but the minimum values for a particular material and in resisting the temptation to extrapolate to longer times than the data justify. Finally, most of these data were obtained in environments different from that of FARET and so can be used only as first approximations for our purposes.

Strength and Ductility

The important mechanical properties are strength and ductility over a long time at high temperatures in an environment of stress, radiation, and sodium.

The ASME Boiler and Pressure Vessel Code lists allowable design stresses to 815°C for Types 304 and 316 stainless steels. (2) These values are based on the data obtained before 1952. (34) The extreme brevity of the tests (500 to 5000 hours) necessitated extrapolations to 100,000 hours, which the data did not justify. Recent long-time data based on currently commercial Type 304 stainless steel show that the Code values may be too low. One reason for this is that the large amounts of scrap required in the charge by modern steel-making practice introduces "tramp" (residual) elements, such as niobium, in amounts that can appreciably raise the high-temperature strength. (35) There is considerable pressure by most producers to increase the Code values. However, the high-temperature properties of Type 304 stainless steel can vary significantly within the AISI standard composition limits. Unless the composition is selected for strength, it is possible to obtain a low-strength Type 304 stainless steel. Table IV summarizes suggested allowable stress values based on the best current data. (36,37)

Table IV

SOME PROPOSED ALLOWABLE STRESS VALUES FOR
TYPES 304 SS, 316 SS, AND 347 SS

AISI	Temperature		Allowable S	tress Values ((kg/mm^2)
Туре	(°C)	(°F)	ASME Code ⁽²⁾	в & W ⁽³⁶⁾	Timkin(37)
304	593	1100	5	8	8
	650	1200	3	5	5
	704	1300	2	3	- 1
316	593	1100	7	9	9
	650	1200	5	6	5
	704	1300	3	3	-
347	593	1100	9		10
	650	1200	4	-	6
	704	1300	2	-	-

A pertinent study of the influence of chemical composition on the strength of low-carbon Type 304 stainless steel shows that niobium and boron in very small amounts are extremely potent in raising the creep-rupture strength. (35) The 100-hour rupture stress of Type 304L at 650°C was raised from 18 to 22 kg/mm 2 on increasing the niobium content

from 0.02 to 0.14%; the increase was almost linear with niobium content. Addition of a similar amount of niobium to a Type 304 stainless steel containing 0.05% carbon raised the 100-hour rupture stress from 22 to 27 kg/mm². Vanadium had a similar but considerably smaller influence on strength. Additions of only 0.007% boron raised the 100-hour rupture stress at 650°C of a 0.018% carbon Type 304L from 12 to 15 kg/mm². Boron has the additional benefit of improving the rupture ductility of Type 304L. The results of the short-time tests are pertinent to our problem if they are confirmed by long-time tests. The level of residual elements in Type 304 stainless steel should be controlled, and the carbon content should be kept on the low side to minimize carbide precipitation. The decrease in strength, because of lower carbon content, can be offset with a small increase in niobium.

The creep-rupture strength bands and average curves of Types 304, 316, 321, and 347, that have been given the "H" heat treatment for maximum heat resistance, $(^{38})$ are very much alike at 650 and 733°C. At 565°C, the stabilized steels are somewhat stronger than 304H. $(^{39})$ Heat treating for 10,000 hours at 650°C without stress increases slightly the creep-rupture strength of 304 and 316; the creep-rupture strength is decreased for similarly treated 321 and 347. $(^{40},^{41})$

The material selected for FARET must have adequate ductility to accommodate normal static and cyclic stresses and the sudden impact of thermal shocks that could cause catastrophic brittle failure of the vessel and piping.

Austenitic stainless steels have excellent room-temperature ductility, a property common to most face-centered-cubic metals. However, these steels work harden easily and rapidly lose their ductility when plastically deformed at low temperatures. A recrystallizing heat treatment of over 1000°C is necessary to restore their ductility once they have been work hardened. Also, although the ductility of most metals increases with increasing temperature, the reverse is true for this group; their ductility decreases with temperature and, most important, their ductility is often drastically lowered on exposure for long times at FARET temperatures; within this temperature range, the longer the time and the higher the temperature, the greater the loss in ductility. This can be attributed to the metallurgical instabilities discussed earlier - transformation to the sigma phase and the formation at grain boundaries of precipitates such as carbides (sensitization) and nitrides. Type 304 stainless steel is embrittled by carbide precipitation; the lower the carbon content, the less sensitive it is to carbide precipitation. There are some indications that sigma can form within the regular 304 composition range (40,42) but this can be avoided by controlling composition. On the other hand, Type 316 stainless steel is sensitive to both carbide precipitation and sigma formation. (43)

The short-time tensile elongation of both Types 304 and 316 stainless steel decreases from about 60% at room temperature to about 35% at $650^{\circ}\text{C.}(34,37,41)$ Similarly, the impact strength of several 300-series stainless steels was about 20% lower at 650°C than at room temperature. (44)

Long-time exposure to high temperatures lowers the room-temperature ductility of both Types 304 and 316 stainless steel. Heating for 10,000 hours at 650°C lowered the short-time tensile elongation by 35% for Type 316 as opposed to 13% for Type 304. $^{\rm (41)}$ In another series of tests under these conditions, the decreases in elongation of Types 304 and 316 stainless steel were almost identical. $^{\rm (44)}$ For these conditions, room-temperature impact strengths were lowered to about one-fourth their original value for Type 316, as opposed to one-half for Type 304. $^{\rm (41,45)}$

Extensive creep studies of Type 316 stainless steel show that the creep rate decreases as the time of test increases to long-time periods. (46) This change in creep rate has been attributed to metallurgical instability of the alloy. The creep rate of Type 304 stainless steel is, however, essentially constant in shorter tests (about 2000 hours). (37)

In general, creep-rupture elongation decreases with increasing time of test, indicating changes in the metallurgical structure. Reported test results are very erratic, frequently showing deterioration in ductility in a relatively short time. (34) However, it is common for the ductility of the sigma-forming steels to deteriorate badly in tests of long duration, whereas they maintain their ductility in shorter time tests. For example, a 316H steel with 66% elongation after 54 hours maintained its ductility for over 1000 hours but had only a 9.5% elongation in a 10,000-hour test. (37) In France, similar results are reported for Type 316. (15) In Great Britain, elongation values in excess of 10% are reported for many rupture tests on Type 316, some longer than 10,000 hours. (20)

The results of tube burst tests at 815°C indicate superiority at high temperatures and for long times of both Type 304 and Type 316 over the other austenitic steels and many of the super-strength alloys. (44)

Radiation Environment

Currently there is speculation that neutron irradiation may permanently damage the ductility of the austenitic stainless steels at FARET temperatures. The experimental evidence is meager, (47,48,49,50) but the implications to high-temperature reactors justify an all-out effort to verify and, if true, to understand the problem so that we can either solve it or learn how to live with it. Unfortunately, meaningful studies take a long time and are costly and difficult.

The austenitic stainless steels have performed very satisfactorily in reactor vessel applications to date. A major factor has been that these steels keep their excellent ductility in moderate-temperature radiation environments to which they have been exposed. They do not have a ductile-brittle transition temperature and, therefore, do not have the problem of raising this transition by radiation, as in the case of ferritic steels or carbon steels. (51,52)

The prevalent notion that radiation damage is reversible is based on low-temperature irradiation with subsequent annealing. There is some evidence that even this kind of damage is not completely reversible. (47)

Transmutations to foreign atoms that may accumulate at grain boundaries have been suggested by many investigators as a possible explanation of permanent radiation damage. For example, the shortening of the creep-rupture life of Inconel containing 0.001-0.005 w/o boron was attributed to the formation of helium gas by transmutation. (53) However, one recent study has tentatively attributed the irreversible changes induced in austenitic steels by high-temperature irradiation to precipitation on dislocation lines. (54)

Fast-neutron irradiation accelerates diffusion reactions, provided the temperature is high enough to permit mobility. It is not clear to what degree this will enhance the diffusion-controlled carbide precipitation and sigma transformation in austenitic steels at FARET temperatures. It has been pointed out that at high temperatures the number of thermally produced vacancies is large compared with those produced by radiation. (55) Therefore, high-temperature irradiation should have no appreciable effect on such diffusion-controlled processes as precipitation. Yet precipitation-hardening alloys like Inconel-X and A-286 suffered a gross loss in creeprupture properties when tested at and above 538°C after irradiation at that temperature. (10,11)

The effect of irradiation temperature to 704°C on the postirradiation tensile properties of Types $304\,\mathrm{and}\,347$ stainless steel is being studied at ORNL. $^{(50)}$ Some loss in ductility that was not recovered by high-temperature heat treatment has been observed and was attributed to thermal neutrons.

Sodium Environment

Austenitic stainless steels were favored for the main structural material of the first reactors cooled by NaK or sodium. Since then, the preference has shifted from Type 347 stainless steel in EBR-I to Types 316 and 304 in subsequent reactors and large test loops. The change to these compositions was a logical one based on experience and advantages in

high-temperature mechanical properties, fabricability, and economics, rather than on any differences in the effect of sodium on the various compositions of austenitic stainless steels.

Several problem areas will require close attention if this application is to succeed. These problem areas have been recognized by many investigators. (56) In FARET these areas will be aggravated by higher temperatures; but the results of thorough studies indicate that, with reasonable care, several materials, including the austenitic stainless steels, can be used in sodium at $650^{\circ}\text{C}.(24,25,26,27,28)$

One problem area is the influence sodium might have on the ductility and strength of the steel. The mechanism of embrittlement involves reactions that have been experienced under some conditions; for example, intergranular attack or reactions, as with carbon, to form a brittle surface layer in which cracks might start. Intergranular attack of Type 347 stainless steel has been observed in sodium containing 200 ppm oxygen, (57) but not in sodium of the purity normally used in reactors. This should not be a problem in FARET since oxygen will be kept at a low level to avoid excessive mass transfer of iron through a Na₂O mechanism. (56)

Several extensive investigations have demonstrated that austenitic steels are an excellent sink for carbon. (58,59,60,61) In fact, Type 304 stainless steel can be used as a very effective carbon trap. (62,63) Because of the difference in carbon activities, there is a transfer to austenitic steels from ferritic steels in the same system. (29) Of course, many other potential sources of carbon can be minimized by careful design and clean construction practices. (64,65)

MSAR has reported on the fatigue, tensile, creep, and creep-rupture strength and ductility of Type 316 stainless steel tested in dynamic sodium, air, and helium environments at 650°C. (29) According to the report, the fatigue life and creep-rupture properties in sodium are as good as, or better than, they are in air. The reported creep rates in sodium are consistently somewhat higher than in air, but the minimum creep rate of 1% in 10,000 hours is within a 15% spread for the two environments. The experimenters plan further tests to determine the effects of sodium containing various contaminants such as oxygen, carbon, and nitrogen. Highly stressed specimens that had undergone deformation are reported to carburize much more readily than do undeformed, unstressed specimens.

Mass transfer studies at GE-APED⁽²⁴⁾ on Type 316 stainless steel show relatively low overall corrosion losses, on the order of 25 to 50 microns/year (1 to 2 mils/year) at 650°C. Other austenitic materials of similar nickel content should have equivalent corrosion rates. (25) In the series of iron-chromium-nickel alloys ranging from the 300 series through

the high-nickel superalloys, thermal-gradient mass transfer tends to increase with increasing nickel content. (8,9) Thus, Incoloy 800 may not be as suitable for a FARET-type application as Type 304 stainless steel.

While there is no service or laboratory experience under conditions that duplicate FARET's high-temperature sodium-radiation environment, the selection of Type 304 stainless steel is based on a reasonable amount of high-temperature sodium experience.

SUMMARY AND CONCLUSIONS

The conclusions that were reached by the FARET Materials Selection Committee regarding selection of a material for the components of the liquid-metal systems (especially the pressure vessel and piping) are summarized as follows:

- 1. The FARET conditions of 650°C sodium in an intense neutron environment are an extrapolation from our current knowledge, necessitating some element of risk and speculation in our selection of a material.
- $2. \hspace{0.1in} AISI \hspace{0.1in} Type \hspace{0.1in} 304 \hspace{0.1in} stainless \hspace{0.1in} steel \hspace{0.1in} comes \hspace{0.1in} closest \hspace{0.1in} to \hspace{0.1in} meeting \hspace{0.1in} FARET \hspace{0.1in} conditions \hspace{0.1in} and \hspace{0.1in} material \hspace{0.1in} selection \hspace{0.1in} requirements.$
 - (a) It has been used extensively in liquid sodium systems to 540°C, and there is some experience to 650°C. It has been used extensively in the petrochemical and the chemical processing industries to 650°C, but with a different environment (usually extremely corrosive and for shorter times) than anticipated in FARET.
 - (b) Type 304 stainless steel has been selected by other organizations for proposed applications similar to those in FARET.
 - (c) Allowable stresses and the basis for establishing allowable stress values for service temperatures of 650°C are available in the ASME Boiler and Pressure Vessel Code.
 - (d) Long-time data, based on currently commercial Type 304 stainless steel, show that the Code values may be too low. The Code values are based on unwarranted extrapolations from a relatively limited amount of old, short-time data. The 650°C creep strength of Type 304 stainless steel is similar to that of Type 316 stainless steel if the optimum composition of Type 304 is specified and verified.

- (e) Retention of some ductility and impact resistance over a long time under FARET conditions is necessary to avoid catastrophic brittle failure. The excellent low-temperature ductility of Type 304 stainless steel is somewhat degraded at FARET temperatures by carbide precipitation. Type 304 stainless steel gives no sigma problem if its composition is controlled. It retains a greater degree of ductility under these temperature conditions than do most other candidate materials.
- (f) No service experience or convincing experimental data exist on the effect of long exposure to neutron radiation of Type 304 stainless steel (or of any other candidate material) under FARET's conditions of stress and temperature. This is the area of greatest extrapolation in the selection of a structural material for FARET.
- (g) The selection of Type 304 stainless steel for FARET is based on a reasonable extrapolation from our existing knowledge of sodium compatibility and the effect of sodium on mechanical properties.
- (h) Type 304 stainless steel has a very well-developed technology. It can be obtained readily through normal channels in a wide variety of shapes and sizes with reasonable assurance that specifications and delivery schedules will be met.
- (i) There is a wealth of experience that indicates that Type 304 stainless steel is one of the most readily welded of the austenitic stainless steels.
- 3. Type 316 stainless steel was the second choice for the FARET application. It was considered less desirable than Type 304 stainless steel only because of its tendency to develop sigma phase on long-time exposure at FARET temperatures with resulting embrittlement. Neutron irradiation may accelerate sigma formation, especially if the material is under stress. Except for this, Type 316 comes as close as Type 304 stainless steel to satisfying FARET conditions and materials selection requirements.
- 4. Types 347 and 321 stainless steel and the high chromium austenitic stainless steels were eliminated from consideration because of welding problems, and because they are subject to embrittlement from sigma formation.
- 5. The superalloys were eliminated from consideration because none of them has an adequately developed technology and they have very limited service history.

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Type 304 stainless steel was selected as the main structural material in the FARET liquid metal system by W. R. Simmons, FARET Project Manager, and his staff on the advice of the FARET Materials Selection Committee referred to at the beginning of this report. We would like to acknowledge their efforts and especially the efforts of N. Balai. However, we take full responsibility for the information that we have reported. It is based on our review of the literature and consultation with numerous experts.

REFERENCES

- Kelman, L. R., and S. Greenberg, ed., <u>Materials for Sodium-cooled Reactors</u>, Nuc. Met. Vol. IX, IMD Special Report Series No. 12, AIME (1963).
- 2. <u>ASME Boiler and Pressure Vessel Code</u>, Section VIII, ASME, New York, N. Y. (1962 ed.).
- Blumberg, H. S., Metallurgical Considerations of Main Steam Piping for High-temperature, High-pressure Service, Trans. ASME, 79, 1377-1397 (1957).
- 4. Simmons, W. F., and H. C. Cross, Report on the Elevated-temperature Properties of Selected Super-strength Alloys, S.T.P. No. 160, ASTM, Philadelphia, Pa., (1954).
- International Nickel Co., Inc., Manufacturer's Literature, New York, N. Y. (1964).
- Lyman, T., Metals Handbook, Properties and Selection of Metals,
 Vol. 1, 8th ed., ASM, Metals Park, Novelty, Ohio, pp. 513, 519 (1961).
- 7. Kettles, T. L., memo to W. R. Simmons re Second Meeting FARET Facility Materials Selection Committee, June 17, 1963.
- 8. Noble, J. S., Huntington Alloy Products Div., INCO, Huntington 17, W. Va., Letter to N. Balai, September 13, 1963.
- 9. Hoffman, E. E., and W. D. Manly, Comparison of Sodium, Lithium and Lead as Heat Transfer Media from a Corrosion Standpoint, Preprint 74, Nuc. Eng. and Science Cong., AIChE (Dec 1955).
- Robertshaw, F. C., et al., "Neutron Irradiation Effects in A-286, Hastelloy X, and Rene 41 Alloys," Symposium on Radiation Effect on Metals and Neutron Dosimetry, S.T.P. No. 341, 4th Pacific Area Nat. Meeting, Los Angeles, Calif., ASTM, Philadelphia, Pa., Oct. 2-3, 1962, pp. 372-409 (1963).
- 11. Collins, C. G., et al., Radiation Effects on the Stress Rupture Properties of Inconel X and A-286, APEX 676, General Electric ANP Dept., Cincinnati, Ohio (Dec 1961).
- 12. Krebs, T.M., and N. Soltys, "A Comparison of the Creep-Rupture Strength of Austenitic Steels of the 18-8 Series," Paper No. 34, <u>Joint International Conf.</u> on Creep, I.M.E., London, Eng., pp. 6-21 to 32 (1963).
- 13. Zapffe, C. A., Stainless Steel, ASM, Cleveland, Ohio (1949).
- Lyman, T., Metals Handbook, Properties and Selection of Metals,
 Vol. 1, 8th ed., ASM, Metals Park, Novelty, Ohio, pp. 408 and 426 (1961).

- Guegnaud, A., and C. Roques, "Selection and Application of an Austenitic Stainless Steel for the Fabrication of the Pressure Vessel for the Fast Reactor Rapsodie, "IMD Special Report Series No. 12, Nuclear Metallurgy, AIME, IX, 175 (1963).
- 16. Linnert, G. E., discussion to Ref. 3, p. 1395.
- 17. Caughey, R. H., and W. G. Benz, Jr., Material Selection and Fabrication, Main Steam Piping for Eddystone No. 1, 1200-F and 5000 PSI Service, J. of Eng. for Power, Trans. ASME, pp. 293-314 (Oct 1960).
- 18. Baker, R. A., and H. M. Soldan, "Service Experiences at 1050°F and 1100°F of Piping of Austenitic Steels," Paper No. 71, <u>Joint International Conf.</u> on Creep, I.M.E., London, Eng., pp. 4-85 to 4-94 (1963).
- 19. Cullen, T. M., and J. W. Freeman, Metallurgical Factors Influencing Hot Ductility of Austenitic Steel Steam Piping at Heat Affected Zone Temperatures During Welding, presented at National Power Conf., Baltimore, Md., Sept 1962, Trans. ASME (1963).
- Murray, J. D., and R. J. Truman, "The High Temperature Properties of Cr-Ni-Nb and Cr-Ni-Mo Austenitic Steels," Paper No. 61, <u>Joint International Conf. on Creep</u>, I.M.E., London, Eng., pp. 5-55 to 5-67 (1963).
- 21. Payson, P., and C. H. Savage, "Changes in Austenitic Cr-Ni Steels During Exposures at 1100 to 1700°F," Trans. ASM, 34, 404-452 (1947).
- Lena, A. J., and W. E. Curry, "The Effect of Cold Work and Recrystallization on the Formation of the Sigma Phase in Highly Stable Austenitic Stainless Steel," Trans. ASM, 47, 193-210 (1955).
- 23. Harlow, J. H., "Metallurgical Experience with the Eddystone 5000 lb/in.² 1200°F Unit No. 1," Paper No. 10, Joint International Conf. on Creep, I.M.E., London, Eng., pp. 5-55 to 5-67 (1963).
- 24. Lockhart, R. W., and G. Billuris, "Materials Selection Considerations for FCR and SEFOR," <u>IMD Special Report Series No. 12, Nuclear Metallurgy</u>, AIME, IX, 207-225 (1963).
- 25. McNelly, M. J., Liquid Metal Fast Breeder Reactor Design Study, GEAP-4418 (Jan 1964).
- Steck, R. B., Liquid Metal Fast Breeder Reactor Design Study, WCAP-3251-1 (Jan 1964).
- 27. Visner, S., Liquid Metal Fast Breeder Reactor Design Study, CEND-200 (Jan 1964).
- 28. Large Fast Reactor Design Study, ACNP-64503 (Jan 1964).
- 29. Andrews, R. C., Results of Physical Property Tests of 316 SS Specimens in 1200°F Sodium with Low Oxygen, MSAR Topical Report No. 2 to C.O.O., AEC (Mar 1964).

- 30. Bowers, H. I., and W. E. Ferguson, "Structural Materials in LASL Liquid Sodium Systems," IMD Special Report Series No. 12, Nuclear Metallurgy, AIME, IX, 227 (1963).
- 31. Lyman, T., ed., Metals Handbook, Properties and Selection of Metals, Vol. 1, 8th ed., ASM, Metals Park, Novelty, Ohio, pp. 408-431, 466-488 (1961).
- 32. Smith, K. F., "Stainless Steels," Reactor Handbook, Vol. 1, Interscience Publishers, Inc., New York, N.Y., pp. 563-589 (1960).
- 33. Smithells, C. J., Metals Reference Book, Vols. 1 and 2, Butterworths, Washington (1962).
- Simmons, W. F., and H. C. Cross, <u>The Elevated Temperature Properties</u> of Stainless Steels, ASTM, S.T.P. No. 124, Philadelphia, Pa. (1952).
- 35. Kozlik, R. A., "Developments in Alloys for High Temperature Service: Stainless Steels," Paper No. 3, 1961 INCO Power Conference, Estes Park, Colo.
- 36. Bolton, B. E., "New Stress Criteria for Designing Economical Higher Steam Temperature Boilers," Paper No. 53, <u>Joint International Conf. on</u> Creep, I.M.E., London, Eng., pp. 4-55 to 4-63 (1963).
- 37. Resume of High Temperature Investigations Conducted During 1957-59

 and 1960-62. The Timkin Roller Bearing Company, Steel and Tube
 Division, Canton, Ohio.
- 38. Clark, C. L., Metals Under Extreme Conditions of Temperature and Stress, Metals Eng. Quart., ASM, 2 (3) 32 (Aug 1962).
- 39. Krebs, T. M., New Creep Rupture Data on Furnace Tubes, Hydrocarbon Processing and Petroleum Refiner, (Aug 1962) reprint from Tubular Products Division, Babcock and Wilcox Co., Beaver Falls, Pa.
- 40. Wilder, A. B., et al., High Temperature Stability of Tubular Products for Oil-Refinery Use, for presentation at the Petroleum Mechanical Engineering Conf., Paper No. 60-PAT-22, ASME (Sept 1960). Abstract in Mech. Eng. 83, 92 (Mar 1961).
- 41. Steels for Elevated Temperature Service, U. S. Steel Corp., Pittsburgh, Pa. (1961).
- 42. Lula, R. A., Allegheny Ludlum Steel Corp., Brackenridge, Pa., letter to J. F. Schumar, ANL (Feb 17, 1964).
- 43. Spoeder, C. E., Jr., and K. G. Brickner, "Modified Type 316 Stainless Steel with Low Tendency to Form Sigma," ASTM Symposium on Advances in the Technology of Stainless Steel at Atlantic City, N. J., in June 1963, ASTM, Philadelphia, Pa.
- 44. Clark, C. L., et al., Metallurgical Evaluation of Superheater Tube Alloys After 12 and 18 Months' Exposure to Steam at 1200, 1350, and 1500°F, Paper No. 61-Pwr-4, Trans. ASME, J. Eng. Power, Series A, 84, 252-238 (Table 1962).

- 45. Sticka, E. A., Structural Stability of Commercial Wrought Austenitic Steels for Power Plant Piping to 1450°F, paper presented at American Power Conf., March 31, 1960.
- 46. Jackowski, R., and J. W. Freeman, <u>Properties of Hydroforged Type</u>
 316 Steel Pipe at High Temperatures, (Dec 1961), report to U. S. Pipe
 and Foundry Co., Steel and Tube Div., Burlington, N. J.
- 47. Roberts, A. C., and D. R. Harris, Elevated Temperature Embrittlement Induced in a 20% Cr-25% Ni-Nb Stabilized Austenitic Steel by Irradiation with Thermal Neutrons, Nature, 200, 772 (Nov 23, 1963).
- 48. Hughes, A. N., and J. R. Caley, <u>The Effects of Neutron Irradiation at Elevated Temperatures on the Tensile Properties of Some Austenitic Stainless Steels</u>, J. of Nuc. Matls., <u>10</u> (1), 60-62 (1963).
- 49. Lowe, A. L., "Effects of Radiation on Two Low Alloy Steels at Elevated Temperatures," <u>ASTM-S.T.P. 341</u>, Symposium on Radiation <u>Effects</u>, <u>Oct 1962</u>, ASTM, Philadelphia, Pa., 199 to 211, (Jan 1963).
- 50. Martin, W. R., and J. R. Weir, Effect of Irradiation Temperature and Strain Rate on the Post Irradiation Tensile Properties of Stainless Steel, for presentation at Irradiation Effects on Reactor Structural Materials, San Antonio, Texas (Feb 11, 1964).
- 51. Shober, F. R., The Effect of Nuclear Radiation on Structural Metals, DMIC Report 166 (Sept 1961).
- 52. Lesser, D. O., Radiation Effects on Reactor Metals, Nucleonics, 18 (19), 68-73 (Sept 1960).
- 53. Berggren, R. G., et al., ORNL-2829 (1959).
- 54. Hardy, H. K., et al., Metallurgy of Fuels and Cans, AGR Symposium, London, Eng., 150 (Mar 13-14, 1963).
- 55. Billington, D. S., Relaxing Reliance on Emperical Data, Nucleonics, 18 (19), 64-67 (Sept 1960).
- 57. Brush, E. G., and R. F. Koenig, Evaluation of Ferritic Substitutes for the Austenitic Stainless Steels, I. Resistance to Attack by Sodium, KAPL-1103 (Apr 22, 1954).
- 58. Anderson, J. W., and G. V. Sneesby, <u>Carburization of Austenitic</u> Stainless Steel in Liquid Sodium, NAA-SR-5282 (Sept 1960).
- 59. Hayes, W. C., and O. C. Shepard, <u>Corrosion and Decarburization of the Ferritic Chromium-Molybdenum Steels in Sodium Coolant Systems, NAA-SR-2973 (Dec 1958).</u>

- 60. Hetzler, F. J., and R. S. Young, Sodium Mass Transfer: II. Screening Test Data and Analysis, GEAP-3726 (June 1962).
- 61. McKee, J. M., Sodium Corrosion as a Function of Time, presented at the Fifth Nuclear and Engineering Conference, Engineering Joint Council, Preprint V-1140 (1959).
- 62. Anderson, J. W., Removal of Carbon from Liquid Sodium Systems, NAA-SR-6386 (1961).
- 63. Hallam Nuclear Power Facility, Reactor Operations Analysis Program

 Semiannual Progress Report No. 1, Sept 1, 1962 through Feb 28, 1963,

 NAA-SR-8401 (July 1963).
- 64. Lockhart, R. W., et al., Sodium Mass Transfer: I. Test Loop Design, GEAP-3725 (June 1962).
- 65. Kovacic, E. C., et al., "Materials Problems and Selections in the Enrico Fermi Fast Breeder Reactor," IMD Special Report Series No. 12, Nuclear Metallurgy, AIME, IX (1963).

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