Status of Metallic Structural Materials for Molten Salt Reactors

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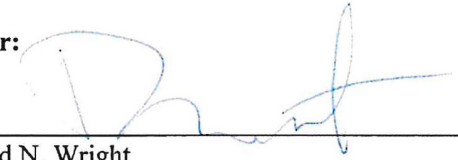
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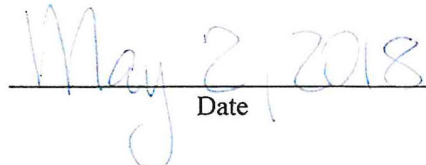
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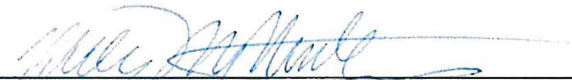
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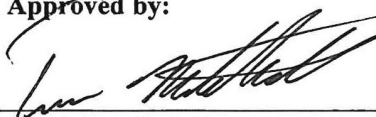
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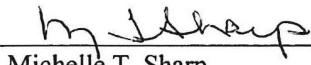
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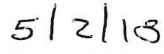
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ABSTRACT

In the US and around the world, significant interest surrounds development and deployment of nuclear systems using molten salts to transfer heat. Several configurations are being explored, including the use of fluoride salts either as the primary coolant of a reactor with solid fuel or with the fissile material dissolved in the salt. Molten Salt Reactors (MSRs) with fluoride salt typically have a thermal neutron spectrum. There are also fast-spectrum reactors that could use chloride salts to transfer heat.

As a result of operation of the Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Laboratory during the 1960s, a system with uranium fuel dissolved in a fluoride-salt medium is the most well-established technology. A nickel alloy with about 6%Cr and molybdenum as a solid solution strengthening agent was developed and deployed for all structural applications in this reactor. The alloy was commercialized as Hastelloy N. During these experiments and in post-decommissioning characterization of material behavior, it was determined that the most significant challenges for structural materials are embrittlement, from helium introduced by transmutation of Ni, and corrosion and grain boundary embrittlement from the fission product tellurium. The MSRE had an outlet temperature of approximately 650°C. The mechanical properties of Hastelloy N are not sufficient to support long-term operation of an MSR above this temperature.

Qualification of a material for use in the ASME Boiler and Pressure Vessel Code, Section III, "Rules for Construction of Nuclear Facility Components," Division 5, "High Temperature Reactors," will facilitate licensing with the Nuclear Regulatory Commission. Hastelloy N has not been qualified for use in nuclear construction, and significant additional characterization would be required for Code qualification. Given that this alloy is susceptible to He embrittlement and has limited high-temperature strength, it is not recommended that Code qualification be pursued. Instead, it is recommended that a systematic development program be initiated to develop new nickel alloys that contain a fine, stable dispersion of intermetallic particles to trap He at the interface between the matrix and particle and with increased solid solution strengthening from addition of refractory elements. Extensive screening of attractive alloy compositions for elevated temperature strength, microstructural stability, weldability, and resistance to He embrittlement (characterized using ion implantation) will lead to an alloy down-selection for commercialization and Code qualification.

CONTENTS

FIGURES

TABLES

ACRONYMS

ARE   Aircraft Reactor Experiment

ART   Advanced Reactor Technologies

MSR   Molten salt reactors

MSRE   Molten Salt Reactor Experiment

ORNL   Oak Ridge National Laboratory

Status of Metallic Structural Materials for Molten Salt Reactors

1. INTRODUCTION

Molten-salt-cooled or liquid-fueled nuclear reactors are currently under development across the world. This broad class of potential systems is noteworthy in part because development is being driven by the interests of a large number of commercial entities, many times in cooperation with government-sponsored agencies. Molten-salt reactors (MSRs) can have a neutron spectrum which is fast, epithermal, or thermal and, in some embodiments, can be breeder or burner systems. It is generally envisioned that an MSR will operate at low pressure, have a reactor outlet temperature well above light water reactor technologies (typically 700°C or above) and have one or more secondary loops to separate the primary salt from the balance of plant.[1] Both uranium and thorium fuel cycles are under investigation. The molten salt in the primary loop is typically either a fluoride or chloride, and the salt in the secondary loop can have different composition from that in the primary loop. A summary of the main characteristics of some of the reactors under commercial development is shown in Table 1.

Table 1. Characteristics of some of the MSR systems under development by commercial entities.

Company Name	Location	Reactor Name	Description of Design
Transatomic Power	Boston, USA	Waste-Annihilating Molten Salt Reactor (WAMSR)	ZrH-moderated SNF/LEU burner
Terrestrial Energy	Toronto, Canada	Integral Molten Salt Reactor (IMSR)	Graphite-moderated integral LEU burner
TerraPower	Washington, USA	Molten Chloride Fast Reactor (MCFR)	Chloride-based fast U-Pu cycle reactor
FLiBe Energy	Alabama, USA	Liquid Fluoride Thorium Reactor (LFTR)	Graphite-moderated two-fluid Th breeder
ThorCon Power	Florida, USA	ThorCon	Graphite-moderated Th+LEU burner, deployed by ship
Elysium Industries	Boston, USA	Molten Chloride Salt Fast Reactor (MCSFR)	Fast spectrum, chloride salt based liquid fuel
Copenhagen Atomics	Copenhagen, Denmark	Copenhagen Atomic Waste Burner	Graphite-moderated Pu+MA+Th burner
Seaborg Technologies	Copenhagen, Denmark	Seaborg Technologies Wasteburner (SWaB)	Graphite-moderated Pu+MA+Th burner
Moltex Energy	London, UK	Stable Salt Reactor (SSR)	Chloride-fueled Pu breeder, internal fluoride salt cooling
IFK Berlin	Berlin, Germany	Dual Fluide Reactor (DFR)	Chloride or metallic-fueled Pu breeder internal lead cooling
Thorium Tech Solutions	Tokyo, Japan	FUJI, miniFUJI	Graphite-moderated single-fluid Thorium breeder

With the wide range of MSR systems under consideration suitable structural alloys are difficult to determine. The critical issues that must be considered include high-temperature strength, stability of microstructure, and properties for long-time thermal and environmental exposure, irradiation damage, fission product induced grain boundary embrittlement and status of standardization and codification. In this report, the available and proposed structural alloys will be assessed compared to these critical issues, and a path forward to provide suitable materials for construction of MSR systems in the required time frame will be presented.

2.   MSR EXPERIENCE

The first molten salt reactor, the Aircraft Reactor Experiment (ARE) operated in 1954 at Oak Ridge National Laboratory (ORNL) with a fuel salt mixture of NaF, ZrF_4 and UF_4. These experiments were intended to establish the feasibility of molten-salt fuels based on the ideas that salts are among the most stable chemical compounds, have reasonably good heat-transfer properties, are not damaged by radiation, do not react violently with air or moisture, and have high solubility for uranium. The reactor operated successfully for 9 days with a reactor outlet temperature up to 860°C.

Construction of a test reactor called the Molten Salt Reactor Experiment (MSRE) began in 1962 using ^7LiF-BeF_2ZrF_4-UF_4 fuel salt. The plant began operation in 1966. In 1968, all uranium was extracted and replaced with ^{233}U, the fissile nuclide of the thorium cycle. The maximum power of this reactor was approximately 8,000 kW, and the outlet temperature was about 650°C. A very large number of ORNL reports that detail design, operation, and performance of the reactor have been made available in searchable databases.[2] An overview schematic of the MSRE is shown in Figure 1, and details of the piping and major components is shown in Figure 2.

2.1   Fuel-salt Development

To be successful, the reactor needed a fuel salt that absorbed very few neutrons, dissolved uranium and thorium, was thermally stable, and was chemically compatible with structural materials. Fluorides are attractive in part because the high reactivity of fluorine traps most fission-reaction products. However, UF_4 has a very high melting temperature (1035°C). Mixed with BeF_2, the melting temperature became practical for the MSRE, but viscosity was too high. Mixing in some LiF reduced viscosity; this composition is now commonly called Flibe. The initial fuel salt composition was ^7LiF-BeF_2-ZrF_4-$^{235}UF_4$ (65-29.1-5.0-0.9 mole%). The secondary salt was LiF-BeF_2 (66–34 mole%). After 1968, the uranium was changed to ^{233}U.
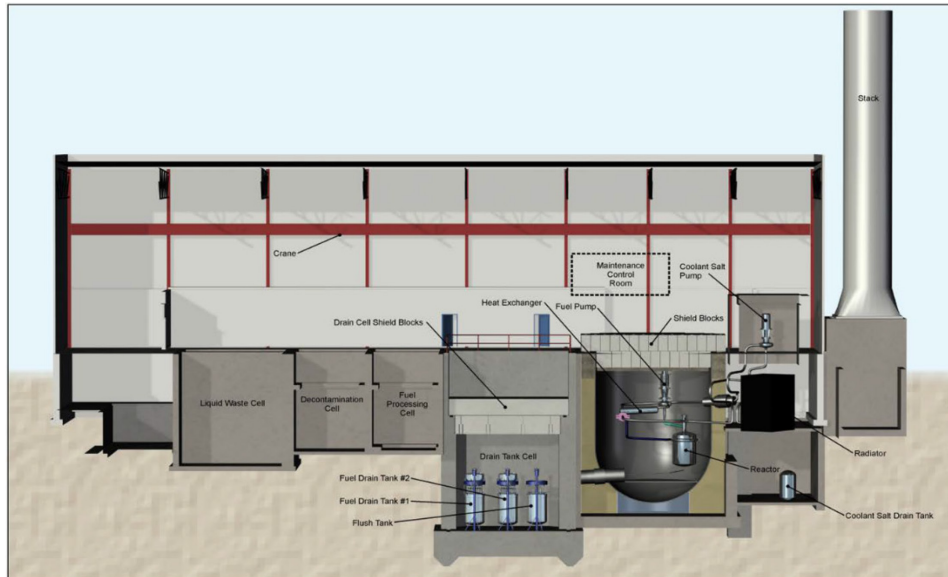
Figure 1. Schematic overview of the MSRE.
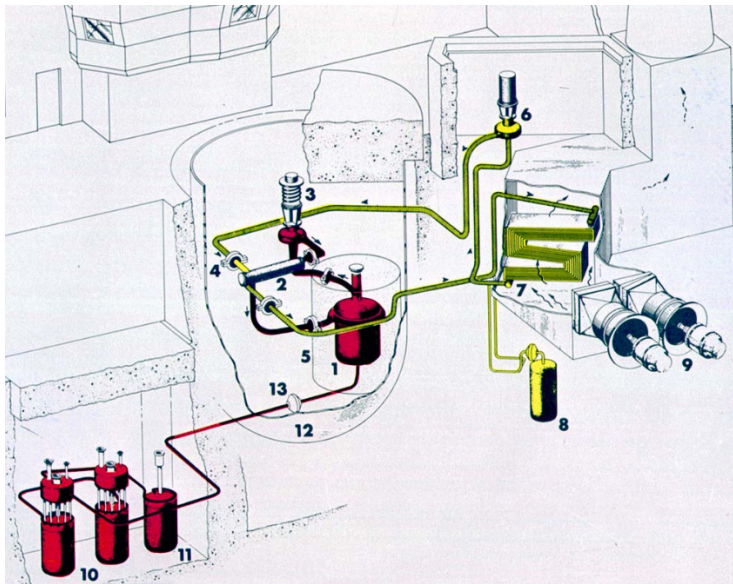
Figure 2. MSRE plant diagram: (1) Reactor vessel, (2) heat exchanger, (3) fuel pump, (4) freeze flange, (5) thermal shield, (6) coolant pump, (7) radiator, (8) coolant drain tank, (9) fans, (10) fuel drain tanks, (11) flush tank, (12) containment vessel, (13) freeze valve. Also note control area in upper left and chimney, upper right.

2.2 Alloy Development

ARE used Inconel 600 piping for salt containment and a BeO moderator. When the MSRE was under development, it was determined that graphite would provide a suitable moderator and was adequately resistant to corrosion. Experiments showed that Inconel 600 corroded to a depth of about 0.25mm in 1,000 hours when exposed to circulating salt at 816°C (1500°F). A significant alloy-development program was undertaken. A series of INOR alloys was investigated. (It is thought that the alloys were named for one of the developers, Hank Inouye as IN-Oak Ridge alloys).[3] Compositions of the alloys that were investigated are shown in Table 2.

Table 2. Compositions of nickel based alloys (weight %) that were investigated for use in the MSRE.

Alloy	Mo	Cr	Fe	Ti	Al	Nb	W
INOR-1	30						
INOR-2	16	5					
INOR-3	16			1.5	1		
INOR-4	16			1.5	2		
INOR-5	15					2	2
INOR-6	16	5		1.5	1		

Table 2. (continued).

Alloy	Mo	Cr	Fe	Ti	Al	Nb	W
INOR-7	16	6			1	1	
INOR-8	16	6	5				
INOR-9	17		5			3	

    The alloy compositions were based on the free energy of Ni and Mo as among the least likely to form stable fluorides. Mo is also a potent solid solution strengthener. Cr forms stable fluorides and is preferentially removed by circulating salts at MSRE temperatures, however, some Cr is necessary for oxidation resistance.[3,4] The need for 5-7% Cr to maintain oxidation resistance is shown in Figure 3 where it can be seen that the oxidation rate drops sharply when the Cr content is in this range, depending on the temperature. All of the structural components for the MSRE were made from INOR-8.
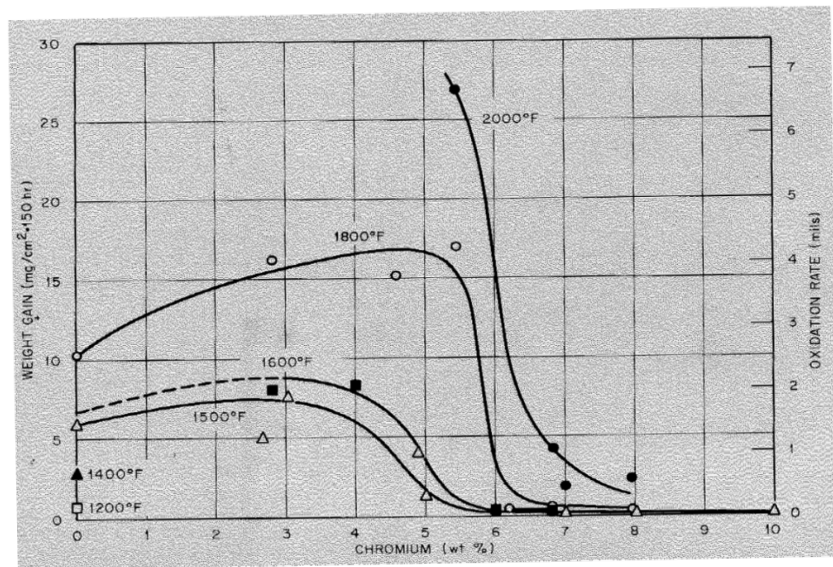
Figure 3. Oxidation rate of Ni alloys as a function of the Cr content for several temperatures.[4]

    An alloy with composition very close to INOR-8 was commercialized by Haynes as Hastelloy N, (UNS 10003).[5] The nominal composition of Hastelloy N is shown in Table 3. Almost 200,000 lb (90,000 kg) was produced commercially in a variety of shapes of material for the MSR. Requests for bids on component fabrication went to several companies in the nuclear fabrication industry, but all declined to submit bids because of lack of experience with the new material. Consequently, all major components were fabricated by the US Atomic Energy Commission facilities at Oak Ridge and Paducah, TN.[3]

Table 3. Nominal composition of Hastelloy N; compositions in weight %.

Nickel:	71 Balance
Chromium:	7
Molybdenum:	16
Iron:	4 max.
Silicon:	1 max.
Manganese:	0.8 max.
Vanadium:	0.5 max.
Carbon:	0.06
Cobalt:	0.2 max.
Copper:	0.35 max.
Tungsten:	0.5 max.
Aluminum + Titanium	0.5 max

The performance of INOR 8 was judged to be adequate during operation of the MSRE. Upon examination of some components after decommissioning of the reactor it was found that there was significant surface cracking.[6] In one of the very early applications of Auger electron spectroscopy, it was eventually determined that the cracking was associated with grain boundary embrittlement by the fission product tellurium.[7] A series of new alloy compositions based on INOR-8 with additions of niobium and titanium were examined using laboratory corrosion tests to mitigate cracking. These alloy additions were made with the assumption that those elements that form stable compounds with Te would be most beneficial.[8,9] It was found that Ti additions did not mitigate Te embrittlement and additions of Ti along with Nb would negate the beneficial effects of niobium. Based on these results there was a focus on Nb additions for mitigation of Te embrittlement. The influence of alloy composition on cracking probability is shown in the Table 4. The influence of Nb content specifically is shown in Figure 4.

Table 4. Cracking frequency of Hastelloy N variants[9].

Alloy	Exposure Time (hr)[a]	Salt Additive	Crack[b] Density (m^{-1})	Average Crack Depth (μm)	Density Times Depth
Standard	504	Cr_2Te_3	1.46×10^4	42.5	0.6205
2.6% Nb, 0.7% Ti	504	Cr_2Te_3	0.71	33.1	0.2350
Standard	499	Cr_2Te_4	1.38	50.4	0.6955
2.6% Nb, 0.7% Ti	499	Cr_2Te_4	0.97	24.3	0.2357
1.0% Nb, 1.0%Ti	244	Cr_2Te_4	1.02	37.4	0.3185
1.0% Nb	244	Cr_2Te_4	0.17	30.5	0.0519
7% Cr	500	Cr_2Te_4	0.47	35.6	0.1673
10% Cr	500	Cr_2Te_4	0.28	41.3	0.1156
12% Cr	503	Cr_2Te_4	0.71	43.7	0.3103
15% Cr	503	Cr_2Te_4	0.57	48.9	0.2787

a   All exposures were at 700°
b   Measured number of cracks per meter of length along edge of a polished cross section of specimen.
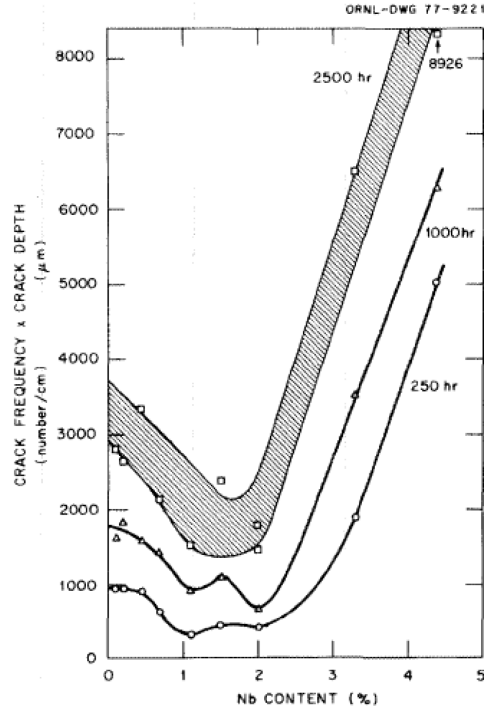
Figure 4. The influence of Nb content on cracking frequency in modified Hastelloy N.

In addition to Te embrittlement, it was recognized during the alloy development program that irradiation embrittlement in the form of He bubbles on grain boundaries would be a problem for Ni-based alloys. In Ni alloys, a two-step process forms He from transmutation resulting from thermal neutrons:

^{58}Ni + $n \rightarrow$ ^{59}Ni

^{59}Ni + $n \rightarrow$ ^{4}He + ^{56}Fe.
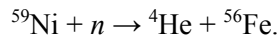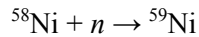
Additions of carbide forming elements Nb, Ti, Zr and Hf were explored.[8] Experiments were carried out by irradiating small samples of alloys with varying elemental additions followed by post-irradiation creep testing. It was found that Zr and Hf were effective in forming desirable carbide structures; however, these elements resulted in poor weldability, and alloys with these compositions were dropped. Additions of Ti were found to be very beneficial for suppressing He embrittlement by trapping He at the precipitate interface and preventing its migration to grain boundaries. The Ti modified alloy was developed extensively; 100 kilogram size heats, twenty 22–45 kg heats and two large commercial scale heats (3,600 and 4,500 kg) were eventually produced and characterized. Very late in this development program it was found that Ti additions did not mitigate Te embrittlement and additions of Ti along with Nb would negate the beneficial effects of niobium.

The influence of Ti on post-irradiation creep properties was found to be dependent on irradiation temperature. Experimental results are shown Figure 5 for the rupture life at 650°C as a function of irradiation temperature for alloys with varying Ti content. The overall conclusion of these studies was that Ti carbides were very effective in mitigating He embrittlement at 650°C, adequate at 704°C, and largely ineffective at 760°C.

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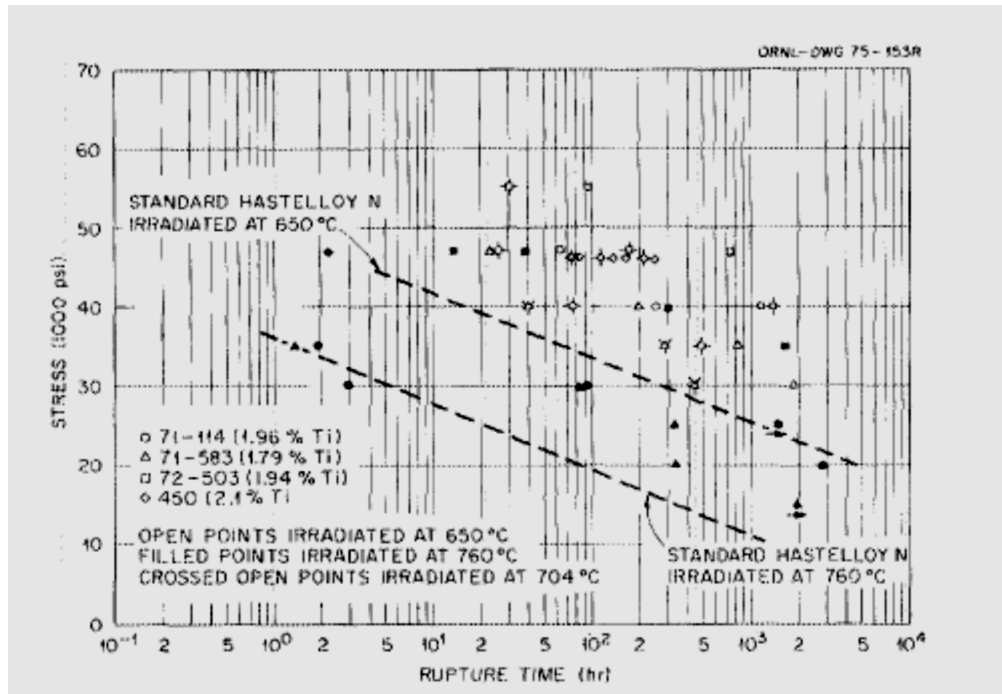
Figure 5. Comparison of creep rupture at 650ºC of Hastelloy N and alloys with Ti additions after neutron irradiation at different irradiation temperatures.

In addition to modifying the alloy chemistry, the possibility of a chemical change in the salt that could alter the extent of attack by tellurium was also considered. It has been suggested that since chromium-ion activity can be controlled, within a certain range, by the U(IV)/U(III) ratio, it might be possible to control tellurium activity by "complexing" reactions with chromium or other salt constituents, for example, as a telluride rather than as elemental tellurium by the reaction where M is Cr or some other metal:

$$2UF_3 + MF_2 + xTe \leftrightarrow MTe + 2UF_4$$

Data for cracking in Hastelloy N as a function of U(IV)/U(III) ratio are shown in Figure 6 for test coupons exposed for 260 hours at 700°C.[9] The figure shows a sharp reduction in cracking frequency when the U(IV)/U(III) ratio is below about 70, in this case through the addition of Be to the salt.

EXTENT OF TELLURIUM EMBRITTLEMENT OF HASTELLOY N
IS STRONGLY AFFECTED BY OXIDATION POTENTIAL OF SALT.
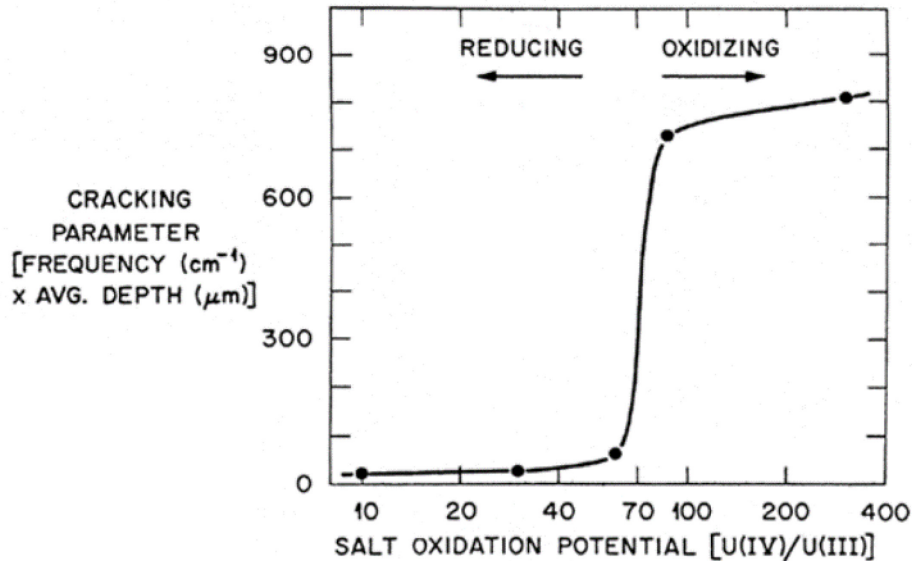
Figure 6. Frequency of Te cracking for Hastelloy N as a function of the fluoride-salt oxidizing potential.

3.   COOLANT AND SECONDARY SALT CONSIDERATIONS

The MSRE addressed many of the issues associated with fuel salt by developing an initial fuel-salt composition that was ^{7}LiF-BeF$_2$-ZrF$_4$-^{235}UF$_4$ (65-29.1-5-0.9 mole%). Lithium present in the fuel salt must be purified to the ^{7}Li isotope; ^{6}Li captures neutrons to produce tritium. As noted in the MSRE alloy development discussion, Be is added to the salt to lower the melting point and to control, in part, the redox potential and suppress Te embrittlement.

In the secondary circuit, it is common to see salts that do not use lithium, for cost reasons. ZrF$_4$-NaF-KF, ZrF$_4$-KF, NaF-BeF$_2$ eutectic mixes are often mentioned, as well as LiF-NaF-KF (FLiNaK). Salts near these compositions are also under consideration for molten-salt-cooled reactors that use a solid fuel, e.g., TRISO particles, and only use salt as the primary coolant.

For fast-spectrum reactors, chloride salts are under consideration. The actinide trichlorides form solutions with lower melting points and have higher solubility for actinides. Thus, these salts can contain significant amounts of transuranic elements. While NaCl has good nuclear, chemical, and physical properties, its high melting point means it needs to be blended with MgCl$_2$ or CaCl$_2$, the former being preferred in eutectic, and allowing the addition of actinide trichlorides. The major isotope of chlorine, ^{35}Cl, gives rise to ^{36}Cl as an activation product, so ^{37}Cl is preferable in a reactor.

4.   IRRADIATION EFFECTS

The important variables in understanding potential irradiation effects are the irradiation temperature (a surrogate for defect mobility) and the neutron spectrum (fast or thermal neutrons). For low homologous temperatures, the primary effects of fast neutron irradiation are hardening and embrittlement. These effects are not likely to be important for Ni-based MSR structural materials because of high outlet temperatures. At intermediate temperatures, it is possible that cavity swelling and irradiation creep will become significant at fluences above about 30dpa.

Figure 7 below shows swelling of Nimonic PE-16, a Ni-Cr-Mo alloy, for two levels of fast neutron irradiation.[10] It can be seen from the figure that the peak swelling regime is at temperatures below the anticipated outlet temperature of an MSR (650°C).
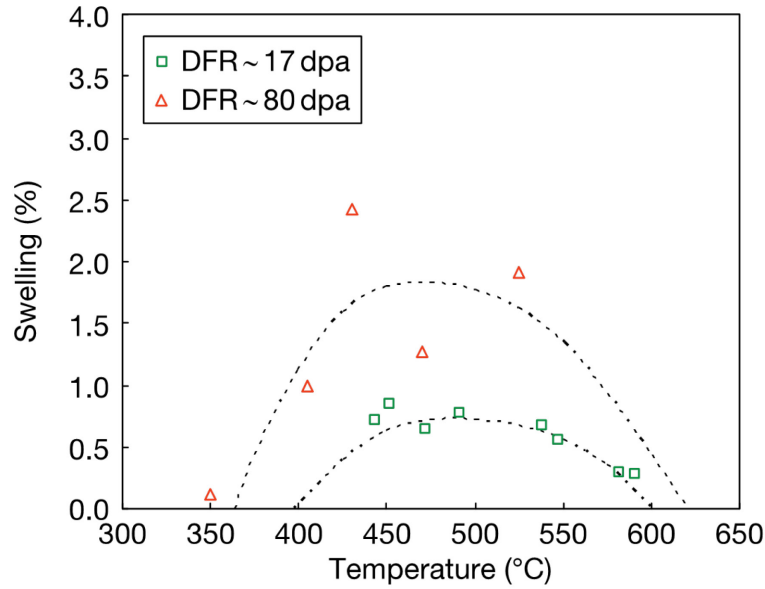
Figure 7. Swelling of a Ni-Cr-Mo alloy as a function of temperature for two different damage levels.

As noted above regarding the MSRE experience, for Ni alloys, the most significant irradiation effect was from formation of He bubbles on grain boundaries at high homologous temperatures. It was initially thought that He was formed from transmutation of trace levels of boron in the alloy resulting from capture of thermal neutrons by the reaction:

$^{10}B + n \rightarrow He + {^7}Li$.
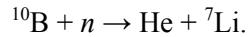
It was later determined that He embrittlement is from the two-step process, forming He from transmutation resulting from thermal neutrons:

$^{58}Ni + n \rightarrow {^{59}}Ni$

$^{59}Ni + n \rightarrow {^4}He + {^{56}}Fe$.
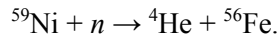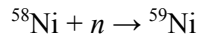
This is a significant result because one might expect He formation from boron transmutation to stop when the small quantities of the element in structural alloys were used up; however, transmutation of Ni is essentially continuous over the lifetime of the component. Figure 8 is a bright-field transmission electron micrograph of PE-16 containing 10 atomic ppm of He from ion implantation after aging for 60 hours at 750°C.[11]
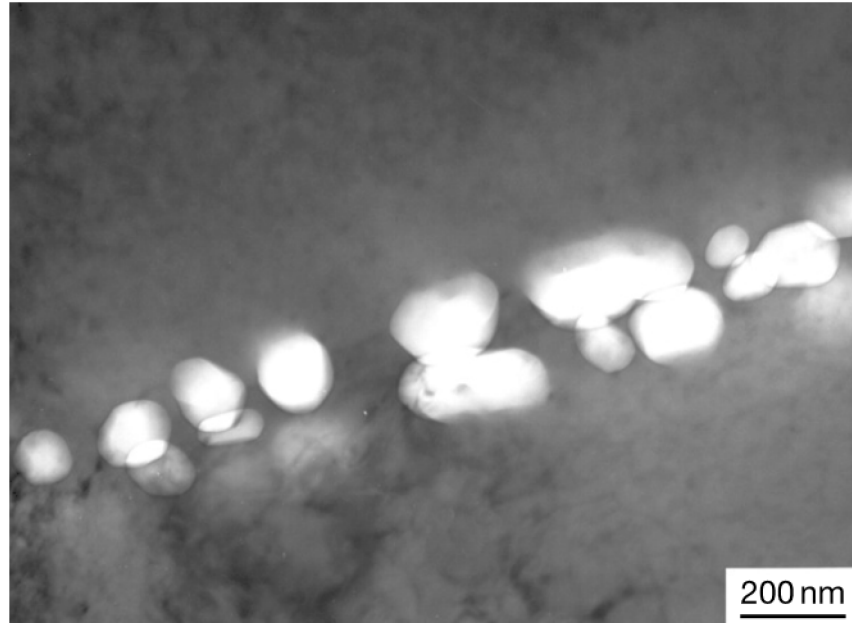
Figure 8. Grain boundary He cavities in PE-16 after 10 atomic ppm He implantation, aging at 750°C for 60h, and tensile testing at 650°C

The effects of He on mechanical properties are more pronounced after exposure at higher temperatures. This can be seen for Hastelloy N in Figure 5. The influence of reducing the strain rate of mechanical testing is seen in Figure 9 for PE-16 containing varying levels of He from ion implantation.[12] Reducing the strain rate from that typical of tensile testing to one order of magnitude less dramatically decreases uniform elongation. It can also be seen in the figure that the influence of He concentration on reduced ductility for slow strain-rate testing essentially saturates at a He concentration of as little as 1 atomic ppm. The reduction in total elongation in austenitic stainless steel tested after neutron irradiation to a He content of approximately 0.5 and 7 atomic ppm on going from tensile to creep strain rates is shown in Figure 10.[13]
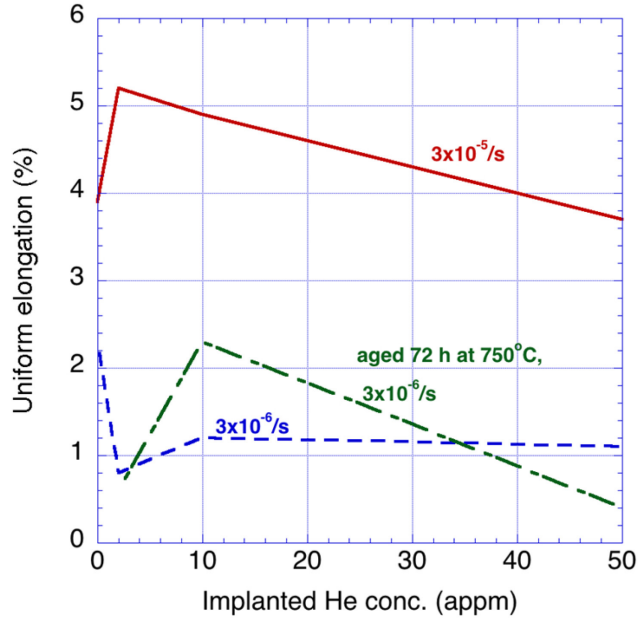
Figure 9. Influence of tensile strain rate for Ni-Cr-Mo alloy containing varying levels of He from ion implantation.
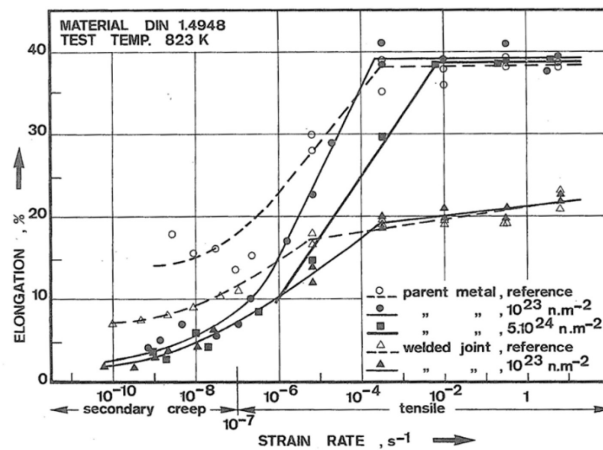
Figure 10. Reduction in elongation for stainless steel containing 0.5 and 7 atomic ppm of He from neutron irradiations of 10^{23} and 5×10^{24} n/m^2, respectively) as a function of strain rate.

Embrittlement by He bubbles on grain boundaries is intrinsic to Ni alloys when exposed to thermal neutrons. A common strategy to mitigate this embrittlement is to provide a large number trapping sites for helium to prevent migration to grain boundaries by methods such as cold working or by a dispersion of fine incoherent precipitates. The efficacy of these strategies can be limited by microstructural instability at high temperature. Alloying of Hastelloy N became ineffective above about 700°C. This was attributed to coarsening of the titanium carbides at the higher temperature, which eventually allowed He migration to the grain boundaries.

5.   ASME CODE QUALIFICATION

The ASME Boiler and Pressure Vessel Code has rules that govern the construction of vessels, storage tanks, piping, pumps, valves, supports, core support structures for use in high-temperature reactor systems, and their supporting systems. These are contained in ASME Section III, "Rules for Construction

of Nuclear Facility Components," Division 5, "High Temperature Reactors." The term construction is used here to mean materials, design, fabrication, installation, examination, testing, overpressure protection, inspection, and certification. High-temperature reactors include the MSRs. Design procedures and material properties not contained in Division 5 may be required to ensure the integrity or continued satisfactory function of the component during the specified service life. The rules do not provide methods to evaluate deterioration that may occur in service as a result of corrosion, mass-transfer phenomena, radiation effects, or other metallurgical instabilities. It is the responsibility of the owner/operator to demonstrate to the Nuclear Regulatory Commission that these effects are properly accounted for in the design of the component.

There are currently only five materials approved for use in Division 5: 2¼Cr-1Mo and 9Cr-1Mo steels, Type 304 and Type 316 stainless steel and Alloy 800H. The materials are qualified for a maximum use temperature and time. New materials can be qualified either within the body of Division 5 or by a code case. The material characteristics which must be determined to qualify a material or Division 5 are contained in Appendix HBB-Y to Division 5 and are shown in Table 5. Note that some of these data are required for a minimum of three different commercial heats of the alloy and in all of the product forms for which code qualification is requested. Testing to determine these data is performed in air and over the temperature range from ambient to the requested upper temperature limit.

Table 5. Requirements for material property characteristics to incorporate a new material in ASME Section III, Division 5.

Required testing to introduce a new structural material into Section III, Division 5, or a Division 5 Code Case	
• HBB-Y-2100 Requirement For Time-independent Data • HBB-Y-2110 Data Requirement for Tensile Reduction Factors for Aging • HBB-Y-2200 Requirement for Time-Dependent Data • HBB-Y-2300 Data Requirement for Weldments • HBB-Y-3100 Data Requirement for Isochronous Stress-Strain Curves • HBB-Y-3200 Data Requirement for Relaxation Strength • HBB-Y-3300 Data Requirement for Creep-Fatigue • HBB-Y-3400 Data Requirement for Creep-Fatigue of Weldments	• HBB-Y-3500 Data Requirement for Cyclic Stress-Strain Curves • HBB-Y-3600 Data Requirement for Inelastic Constitutive Model • HBB-Y-3700 Data requirement for Huddleston multiaxial failure criterion • HBB-Y-3800 Data Requirement for Time-Temperature Limits for External Pressure Charts • HBB-Y-4100 Data Requirement for Cold Forming Limits • Validation of Elastic-Perfectly Plastic (EPP) Simplified Design Methods for the new alloy

Haynes International has qualified Hastelloy N in the ASME Code for use in Section VIII, "Design Rules for Unfired Vessels," Division 1, up to 704°C and, Division 2, up to 427°C. Specification in the ASME Code include: SB 434 for sheet, plate, and strip; SB 573 for billet, rod, and bar; and SB 366 for fittings.[5] There have been several reviews of the data that were used for code qualification to Section VIII. They include the tensile properties, relatively short-time creep-rupture data, and some creep curves.[13,14] To qualify this material for Division 5 would require considerably more testing, including long-time aging and creep rupture of base metal in the requested product forms and weldments, as well as creep-fatigue characterization. This alloy is not currently qualified for construction on nuclear components in ASME Section III, Division 5. Modification of Hastelloy N with Ti or Nb additions would

result in essentially a new alloy for which the Hastelloy N data would not be applicable as part of code qualification.

6.   CANDIDATE MSR ALLOYS

The properties of Hastelloy N (UNS 10003) were investigated for the MSRE program. ASTM standards are available for a number of product forms of this alloy, and some specifications have been incorporated in the ASME Boiler and Pressure Vessel Code. Specifications for the latter include: SB 434 for sheet, plate and strip; SB 573 for billet, rod and bar; and SB 366 for fittings.[5] There is no evidence that the new materials described below have established standards or significant data to support code qualification.

A number of alloys designed to ameliorate some of the issues identified by the MSRE have been investigated. A partial list of these alloys is given in Table 6.[15] All of the alloys in the table have Cr content in the range of 5–8 wt%. GH3535 is intended to be a Chinese domestic version of Hastelloy N. Extensive characterization of the alloy has been carried out by the Shanghai Institute of Applied Physics and the Australian Nuclear Science and Technology Organization. The Czech alloy MONICR appears to be very closely related to Hastelloy N chemically. Studies of this alloy that have been reported are largely limited to investigation of the relationship of processing on the microstructure.[16-18]

The French alloy, EM-721 has significant addition of tungsten as a solid-solution strengthening agent to address the limited high-temperature strength of Hastelloy N. Very little information is available on this alloy; however, it has been reported that its elevated-temperature ductility is limited compared to the other variants of Hastelloy N. One of the Russian alloys, HN80MTW, also has a notable addition of tungsten. It is not clear how much recent activity has occurred in characterizing the family of Russian alloys. Much of the work that has been reported is associated with characterizing the resistance to cracking resulting from Te embrittlement.[19]

Table 6. Chemistry of alloys that have been investigated for MSR structural applications.

Element	Hastelloy N US	Hastelloy NM US	HN80M-VI Russia	HN80MTY Russia	HN80MTW Russia	MONICR Czech Rep	GH3535 China	EM-721 France
Ni	base	base	82	82	77	base	base	68.8
Cr	7.52	7.3	7.61	6.81	7	6.85	6.88	5.7
Mo	16.28	13.6	12.2	13.2	10	15.8	15.9	0.07
Ti	0.26	0.5—2.0	0.001	0.93	1.7	0.026		0.13
Fe	3.97	< 0.1	0.28	0.15		2.27	4.1	0.05
Mn	0.52	0.14	0.22	0.013		0.037	0.49	0.086
Nb	-	-	1.48	0.01		< 0.01	0.01	-
Si	0.5	< 0.01	0.040	0.040		0.13	1.01	0.065
Al	0.26	-	0.038	1.12		0.02	0.88	0.08
W	0.06	-	0.21	0.072	6	0.16		25.2

A series of four alloys was developed by ORNL and patented.[20-23] Compositions of these alloys, specified in the patents, is given in Table 7. These alloys were developed using relatively short-term Laboratory Directed Research and Development funding, and the amount of characterization that was possible was limited to tensile and relatively short-time rupture testing. Resistance to corrosion by MSR salts and radiation-effects studies remain to be completed.

Thermodynamic simulations of the equilibrium phases in these alloys were completed and reported in the patents. The alloy described in patent 9,435,011 is solid solution strengthened with 1–2.25 wt.% M_6C. Alloy 9,540,714 is a solid solution with the addition of γ' (3–17.6 wt.%) strengthening and 1–2 wt.% M_6C. The primary strengthening in Alloy 9,683,279 is from carbides: 1.9–16.14 wt.% M_6C and 1.9–16.14 wt.% $M_{23}C_6$.

Alloy 9,683,280 has primary strengthening from carbides (1–8 wt.% M_6C, up to 3.5 wt.% MC) with the addition of intermetallic precipitates (up to 3 wt.% Ni_5M). The total volume fraction of precipitates is in the range 4.0–10 wt.%.

Table 7. Composition of alloys recently developed at ORNL for MSR applications.

Patent #	Ni	Cr	Mo	W	Al	Ti	Ta	Re	Ru	Fe	Hf	Nb	Mn	Co	C	N	B
9,435,011	bal	6.0–7.5	11–19.5	0.01–9	0–0.15	–	0.03–4.5	0–1	0–1	–	–	–	0.5–0.85	–	0.03–0.08	0.0005–0.005	0–0.001
9,540,714	bal	6.3–7.2	9–12.5	0.2–0.6	0.5–2	0.75–3.5	0–6	–	–	0–5	–	0.01–0.25	0.7–0.8	–	0.02–0.04	0.0001–0.002	0–0.001
9,683,279	bal	6–8.5	5.5–13.5	0.4–7.5	0.05–0.3	1–2	0–0.01	–	–	–	–	0–1	0.7–0.85	–	0.08–0.5	–	–
9,683,280	bal	6–8.5	5.5–13.5	0.4–7.5	0.05–0.3	1–2	1–5	–	–	–	1–3	1–4	0.7–0.85	Up to 0.1	0.08–0.5	–	–

7. ANALYSIS OF CURRENT STATE OF ALLOY DEVELOPMENT AND PROPOSED PATH FORWARD

The material challenges for molten salt reactors generally fall into categories of irradiation effects, corrosion, and elevated temperature strength. Given that there are at least two classes of MSRs that are under consideration, liquid-fueled and liquid-cooled, and at least two families of salt under consideration (fluoride and chloride), a single alloy is not likely to meet all of the requirements for potential designs. For fluoride systems it is possible to rank the material challenges—from most severe to less severe—as He embrittlement, high-temperature strength, and corrosion and embrittlement. For chloride systems, there is little or no experience, so it is more difficult to assess the significance of challenges from irradiation effects and corrosion.

Table 8 summarizes attributes (positive and negative) and potential limiting factors for most of the alloys that have been suggested for MSR applications, with an emphasis on liquid-fueled reactors. It might seem that Hastelloy N is the leading candidate for short-term application. There is operating experience with the material; it has established standards, and it has been produced at commercial scale. The bulk corrosion behavior up to approximately 700°C appears to be adequate for several years of operation and, with proper control of the redox chemistry of the salt, embrittlement from Te does not seem to be a serious issue. Hastelloy N is not currently qualified for construction of nuclear components in the ASME code; while there are existing data that would be helpful in code qualification, a great deal of additional testing and analysis would still be required. Even with Ti additions, this alloy is still severely embrittled by He bubbles at the grain boundary above about 700°C. As a solid-solution strengthened alloy Hastelloy N probably has good stability with respect to long-term metallurgical changes during operation; however, it does not have sufficient elevated temperature strength to support long-term service.

Table 8. Summary of attributes (positive and negative) and potential limiting factors for most of the alloys that have been suggested for MSR applications.

Alloy	Advantages	Disadvantages	Limiting Factor(s)	Comments
Type 316 stainless steel	Fully qualified in ASME Code Section III, Division 5; limited He embrittlement	Restricted to temperature on order of 700°C and only with good redox control	Corrosion resistance at higher temperatures Low allowable stresses for long time service	
Hastelloy N	Demonstrated in MSRE; commercial experience with production and fabrication. Extensive database of rupture properties	Limited to temperature of about 700°C by strength. Susceptibility to Te embrittlement. Poor oxidation resistance	He embrittlement; Te embrittlement if redox chemistry is not well controlled	Some product forms are commercially available from Haynes. Large heat produced. Under evaluation in China
Modified Hastelloy N composition	Ti modification showed reduced He embrittlement compared to N. Nb additions reduce embrittlement from Te	Limited experience with fabrication and scale-up. Little rupture data. Strength only marginally better compared to N at high temperature	He embrittlement for some variants; low high temperature strength	Some large heats have been produced and welding demonstrated

Table 8. (continued).

Alloy	Advantages	Disadvantages	Limiting Factor(s)	Comments
ORNL Advanced Alloys [20-23]	Various classes of alloys available for temperatures up to 850°C. All variants designed to have corrosion resistance comparable to Hastelloy N, but with much better creep resistance. Some variants also have higher strength compared to Hastelloy N. Some variants will have good resistance to He and Te embrittlement based upon experience with Modified Hastelloy N.	Limited experience with fabrication and scale-up. Limited rupture data from laboratory-scale heats	Alloy with best combination of properties need to be identified for each application One solution may not fit all needs. Solid solution strengthened alloys must be used where long term stability is an issue.	
Haynes 242 and 244 [24,25]	Precipitation strengthened alloys may mitigate He embrittlement. 242 is commercial product, and 244 is still in development; developed by alloy vendor with large amount of experience with melting and processing	Little or no experimental validation of corrosion resistance. Limited creep and rupture data.	Potential Te embrittlement if redox chemistry is not well controlled, needs to be evaluated. Maximum use temperature of 244 limited to 760°C. Stability of precipitates with respect to coarsening at times relevant to MSR not well known.	Capsule corrosion testing ongoing at ORNL.
HN80M variants	Family of alloys based on Hastelloy N. Some variants very resistant to Te embrittlement.	Little or no data on mechanical properties. Expected to have oxidation resistance similar to Hastelloy N.	He embrittlement; expected to have high-temperature strength comparable to Hastelloy N.	Resistance to Te induced cracking in these alloys appears to be major focus of development.
MONICR	Czech version of Hastelloy N.	Limited to temperature of about 700°C by strength. Susceptibility to Te embrittlement. Poor oxidation resistance	He embrittlement and Te embrittlement if redox chemistry is not well controlled.	Study of this alloy has focused on thermomechanical processing. Very little other information
EM-721	W additions are intended to improve creep resistance. Resistant to Te embrittlement if redox chemistry is well controlled.	Little property data reported. Limited ductility.	He embrittlement and Te embrittlement if redox chemistry is not well controlled.	Reports of material properties are very sparse. Not clear what scale has been produced
Alumina formers	Potential alternative strategy for corrosion resistance that might allow Cr content typical of commercial Ni alloys.	Little or no proof of concept.	Unknown.	This concept, if proven, could open a range of commercial alloys to MSR construction
ODS Alloys	Alternative strategy for improving creep and rupture resistance. Potential for reducing He embrittlement.	Little or no proof of concept in MSR chemistry.	Unknown.	This class of materials is historically expensive, hard to scale up, and difficult to weld

Apparently, preliminary discussions have begun with the Nuclear Regulatory Commission to modify the regulatory basis for licensing MSRs. It is not known how this approach will develop over the next several years. There is potential for use of a code-qualified structural material with corrosion-resistant cladding on the salt-facing surfaces. That approach is beyond the scope of this report. It should be noted that while there are projects underway within the US Department of Energy's Nuclear Energy University Program to explore this technology, assessment of the implications of clad components within the ASME code is in the very early stages.

It has also been suggested that some potential designs might allow for the reactor vessel to be changed out after a period on the order of four to seven years. If this is the case, perhaps Type 316 stainless steel may be adequate for at least first of a kind or technology demonstration reactors. This alloy is fully code-qualified for nuclear construction, there is substantial commercial experience with production and fabrication at the required scale, and helium embrittlement may be reduced with lower Ni content. It is likely that corrosion issues would restrict the operating temperature to less than 700°C using stainless steel components. However, the matching filler metal (16-8-2) for Type 316 stainless steel that has high creep rupture strength has only been qualified to 650C. Additional effort is required to increase the use temperature of this filler metal.

A new alloy or alloys might be developed, particularly for fluoride systems where the requirements are relatively well known. Such an alloy would be likely to have a dispersion of fine particles to trap He and prevent grain-boundary embrittlement. Experience with Hastelloy N with Ti additions suggests that particle coarsening is a limiting factor with carbides. The potential for developing a fine dispersion of intermetallics should be explored as an alternative. Increasing the contribution from solid solution strengthening by increasing additions of refractory elements is also an attractive alternative that should be further explored. While a particle dispersion may mitigate He embrittlement, this approach would likely negatively impact fabrication and welding.

The alloys that ORNL has developed and patented apparently use these strategies for improving material properties. These alloy compositions have been licensed by Haynes, International, which might facilitate commercialization and eventual code qualification. Limiting the development of alloys that have already been patented to a single vendor will, however, limit the interest of other potential alloy developers and vendors. One of the other major Ni alloy producers has expressed the view that they have little or no interest in developing alloys for what they view as an embryonic market in MSRs; however, they do have interest in what they view as a larger potential market for molten salt thermal energy storage (particularly in Europe).

If developing a new alloy is undertaken, experience with the Code qualification of Alloy 709 for the Advanced Reactor Technologies (ART) Fast Reactor Program can serve as a model for how to proceed and what the likely timeframe for success will be. An outline of the alloy 709 development approach is given in Table 9. This stepwise approach initiates testing with the characterization that supports restricted qualification of the alloy simultaneously with very long term testing that will eventually be required for full qualification for the Generation IV goal of a sixty-year design life. A schematic of the testing schedule is also shown below in Table 10.

Table 9. Pathway toward Code qualification for a new alloy that supports different design phases of the deployment of a sodium fast reactor.

Milestone	Alloy 709 implementation milestone	Delivery schedule from initiation of long term testing (y)	Required data
A	Develop Conceptual Design Guide, 500,000 h life time	2.5	10,000 h creep rupture and thermal aging data and initial fatigue and creep-fatigue data from plates, and data from applicable key feature tests
	Develop Division 5 Alloy 709 Code Case for Class B construction	2.5	Creep and thermal aging data that support development of Conceptual Design Guide also support Class B Code Case
B	Develop Division 5 Alloy 709 Code Case, 100,000 h life time	5	25,000 h creep rupture and thermal aging data and intermediate fatigue and creep-fatigue data from plates
	Project approximate, 500,000 h allowable stress values		
C	Incorporate Alloy 709 in Division 5, Subsection HBB, 300,000 h life time	8.5	60,000 h creep rupture and thermal aging data and all other code case supporting data from plates, pipes, forgings and bars
	Refine the approximate, 500,000 h allowable stress values		
D	Extend Alloy 709 to 500,000 h life time in Division 5, Subsection HBB	13	100,000 h creep rupture and thermal aging data from plates

Table 10. Timeline for testing to complete actions in Table 9.

Miles-tone	Time from initiation of long term testing (year)																									
	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	11	11.5	12	12.5	13
A	▥	▥	▥	▥	▨																					
B	▥	▥	▥	▥	▥	▥	▥	▥	▨	▨																
C	▥	▥	▥	▥	▥	▥	▥	▥	▥	▥	▥	▥	▥	▥	▨	▨	▨									
D															▧	▧	▧	▧	▧	▧	▧	▧	▧	▧	▨	▨

Legend	
▥	Testing: creep, thermal aging, fatigue, creep-fatigue, Huddleston, constitutive, two-bar, SMT, etc. from Test Tables A
▧	Continuation of testing: creep and thermal aging only
▨	Development of design procedures and drafting of rules

The qualification path and time period for code qualification of Alloy 709 followed several years of investigation of alloy chemistry, processing, welding, sodium compatibility and scoping studies of mechanical properties. This process was accelerated in the case of the Fast Reactor Program by substantial experience with this type of reactor and prior alloy-development efforts and irradiation testing. MSRs, by contrast, have a limited experience base, and it is likely that a scope of effort similar to that described above for Ti-alloyed Hastelloy N—i.e., 100 one kg experimental heats, and twenty 22 to 45 kg heats—might be required to form the technical justification for proceeding to commercial-scale heats. For the Hastelloy N plus Ti development, the Oak Ridge Reactor irradiated a large number of samples that were subsequently creep-tested in hot cells. That sort of testing program is not feasible with currently available resources, and it is likely that the majority of irradiation testing would be carried out with ion-beam implantation of He.

Details of many of the potential designs for MSRs are being closely held as trade secrets or have limited disclosure. This makes it difficult to set requirements for screening studies during alloy development. A reasonable operating temperature goal would be in the range 750 to 800ºC.

An initial goal for creep rupture properties would be an improvement over Hastelloy N that is sustainable up to the upper temperature limit for 300,000 hours. There are apparently no data available for creep-fatigue of Hastelloy N; Type 316 stainless steel has been very well characterized and could serve as a basis for comparison.

It appears that He content of a little as one atomic part per million reduces the creep ductility of solid solution Ni based alloys to an unacceptable value. A goal for alloy development could be no grain boundary bubbles for He content of 5 atomic ppm after ion irradiation and aging for a period of 1000 hours at the upper temperature limit. The thermal stability of a particle dispersion with respect to thermal aging at the same temperature and time would also need to be demonstrated.

Any alloy that could be considered for further development must be weldable using commercial practice. The baseline corrosion properties should be comparable or better than Hastelloy N in the fluoride salt environment up to the upper temperature limit.

8. CONCLUSIONS

The material challenges for molten salt reactors ranked in order of importance are irradiation effects, corrosion, and elevated-temperature strength. The majority of information available is for thermal-spectrum fluoride-salt reactors with U fuel dissolved in the salt. Much less is known about chloride-salt reactors, and alloys for those systems will not be explicitly discussed further here.

The primary candidates for MSR application are nickel-based alloys because of their intrinsic resistance to creep (compared to ferritic alloys) and demonstrated resistance to salt corrosion when the alloy chemistry and salt redox chemistry are both carefully controlled.

Hastelloy N was used for all structural components of the MSRE. Its performance in service for several years with an outlet temperature of approximately 650°C was judged to be adequate. Subsequent post-decommissioning analysis showed intergranular cracking from grain-boundary embrittlement by the fission product tellurium. Embrittlement by formation of grain-boundary He bubbles, resulting from transmutation of Ni, was also recognized as a significant issue. While the alloy received ASTM standardization in several produced forms, it was not qualified for nuclear construction in the ASME code.

Given limitations with this alloy in terms of both resistance to He embrittlement and mechanical properties above 650°C, it is not recommended that the significant additional effort to characterize the properties necessary for qualification for nuclear components be undertaken. For relatively short-time operation of MSRs at 650°C, it may be possible to use Type 316 stainless steel. This alloy is fully ASME code qualified for nuclear construction.

It is recommended that a systematic development program be initiated to develop new nickel alloys that contain a fine, stable dispersion of intermetallic particles to trap helium at the interface between the matrix and particle, and with increased solid-solution strengthening from addition of refractory elements. Extensive screening of attractive alloy compositions for elevated-temperature strength, microstructural stability, weldability, corrosion resistance and resistance to He embrittlement (characterized using ion implantation) will lead to an alloy down-selection for commercialization and Code qualification. With support from computational materials science tools, a speculative time frame for a down-selection program, using 20-30 kg heats, is about four to five years. It would be followed by fabrication scale-up before the Code qualification process can begin.

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