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CONSIDERATIONS OF ALLOY N FOR FLUORIDE SALT-COOLED

HIGH-TEMPERATURE REACTOR APPLICATIONS

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ABSTRACT

Fluoride Salt-Cooled High-Temperature Reactors (FHRs) are a promising new class of thermal-spectrum nuclear reactors. The reactor structural materials must possess high-temperature strength and chemical compatibility with the liquid fluoride salt as well as with a power cycle fluid such as supercritical water while remaining resistant to residual air within the containment. Alloy N was developed for use with liquid fluoride salts and it possesses adequate strength and chemical compatibility up to about 700°C. A distinctive property of FHRs is that their maximum allowable coolant temperature is restricted by their structural alloy maximum service temperature. As the reactor thermal efficiency directly increases with the maximum coolant temperature, higher temperature resistant alloys are strongly desired. This paper reviews the current status of Alloy N and its relevance to FHRs including its design principles, development history, high temperature strength, environmental resistance, metallurgical stability, component manufacturability, ASME codification status, and reactor service requirements. The review will identify issues and provide guidance for improving the alloy properties or implementing engineering solutions.

INTRODUCTION

To achieve a secure and low-carbon energy future through a new generation of high temperature, high efficiency, affordable, and safe nuclear energy systems, the Fluoride Salt-Cooled High-Temperature Reactor (FHR) concept has drawn significant interest for development considerations because of several technical advantages it possesses over other reactor concepts. Many industries that support our modern civilization and continued economic growth require high temperature processing heat. Petrochemical refining requires heat from sources in the temperature range of 250°C to 550°C, electricity generation requires 350°C to 800°C or even higher, and hydrogen production and coal gasification can employ 800°C to 1000°C. Within these feasible processing temperature ranges, the actual operating temperatures of the heat generation systems are increasing towards the maxima for improved energy efficiency.

Useful fluoride salts for nuclear reactor heat transport have liquid temperature ranges starting from about 450°C and boiling points near 1400°C providing several hundred degree margin from operating temperature to boiling. Operating as a single-phase heat transfer fluid enables low-pressure reactor operation minimizing the required structural boundary thickness (primarily determined by seismic and impact loads). Liquid fluoride salts have high thermal capacity and low viscosity at operating temperature enabling effective heat transfer. Fluoride salts also have large coefficients of thermal expansion facilitating natural circulation based decay heat removal. Further, liquid fluorides are not highly chemically reactive avoiding the potential for energetic chemical reactions with the coolant as in sodium-cooled reactors. The

intermediate loop of an FHR also physically separates the power cycle or chemical process (e.g. hydrogen production) from the reactor core avoiding possible reactor damage from accidents in connected facilities. Fluoride salts also have high solubility for both actinides and fission products providing an addition radioactive material retention barrier in the event of a fuel damage accident.

However, liquid fluoride salts without proper chemistry control can create a very corrosive environment. Combined with the intended very high operational temperatures, various component geometries, and different materials for construction of the reactor system, application of liquid fluoride salts in the FHR becomes predicated on the availability of a structural alloy that can contain the salts over long period of time, afford useful mechanical properties, be easily formed and welded into relatively complicated shapes, and be metallurgically stable over a wide temperature range. In addition, this containment alloy must be compatible with not only the internal molten fluoride salt, but also with the other materials in the reactor system such as the graphite, as well as with the power cycle fluids and the containment environment which could be dry nitrogen, air, argon, or helium.

While Alloy N is a reasonably well proven alloy for structural components that operate at temperatures less than or equal to 704°C in low neutron flux regions, at higher temperatures, improved structural alloys are needed or strategies must be developed to allow for the use of clad material. It should be noted, however, that in high neutron flux regions, high nickel alloys, due their embrittlement characteristics, are not applicable, and thus current FHR designs do not employ structural alloys in core.

In the 1960s and 1970s, a research program was conducted at the Oak Ridge National Laboratory (ORNL) to investigate fluoride salts and structural alloys for the development of a molten salt reactor with an operational temperature of 650°C and a basic plant life of 30 years. Extensive studies were carried out through the Molten Salt Reactor Experiment (MSRE), an 8 MW test reactor, which allowed for the accumulation of significant knowledge and experiences in alloy development for nuclear molten fluoride salt containment. The FHR concept differs from the Molten Salt Reactor (MSR) concept in that no nuclear fuel is dissolved in the salt. Therefore the terms of art differentiating the two concepts are "salt cooled" vs. "salt fueled" reactors.

As over forty years have passed since the MSRE a reevaluation of the past studies at ORNL and worldwide is appropriate, so that the new reactor design can make use of both historical and more recent alloy development experience. This paper is intended to review the current status of Alloy N focusing on aspects relevant to the desired application including its development history, design principles, high temperature strength, environmental resistance, metallurgical stability, component manufacturability, ASME codification status, and reactor service requirements. The review is aimed at identifying major technical issues and providing guidance for improving the alloy properties.

DEVELOPMENT HISTORY

In the early work of 1950s and 1960s to develop the molten salt breeder reactor, several commercially available high-temperature alloy systems were initially evaluated for their feasibility [1, 2]. The evaluation results suggested that Alloy 600, a Ni-base alloy containing 15% Cr and 7% Fe, afforded the best combination of desired properties [3]. However, because the corrosion rates of the alloy above 700°C were too high for long-term exposure to most fluoride salt systems, a research program was established at ORNL to develop a new alloy for the reactor system. The program settled on Ni-base alloys solution strengthened with 15 to 20% Mo, which showed very good resistance to salt attack but lacked sufficient mechanical strength and oxidation resistance at the desired service temperature. Hence, various additional solid-solution alloying agents were evaluated, including Cr, Al, Ti, Nb, Fe, V, and W. Eventually, a tradeoff between corrosion and mechanical properties was made, and as a result an alloy composition within the range of 15 to 17% Mo, 6 to 8% Cr, 4 to 6% Fe, 0.04 to 0.08% C, and balanced by Ni was developed. This alloy was designated as INOR-8 and later commercialized as Alloy N [4].

THE MATERIAL

Alloy N (UNS No. N10003), also known as Hastelloy® N or INOR-8, is a Ni-base alloy containing Mo, Cr, Fe, C, and small amounts of several other elements. Developed at ORNL specifically for applications in molten fluoride salt systems, the alloy provides good oxidation resistance to molten fluoride salts in the temperature range of 704°C to 871°C. Test results indicated that corrosion attack on Alloy N in molten fluoride salts at temperatures up to 704°C was less than 25 microns per year over two years duration. Alloy N also has good oxidation resistance in air environment and may be used for continuous operations at temperatures up to 982°C.

Nominal composition of Alloy N is given in Table 1. The alloy is a solid solution material, and it is normally solution annealed in the temperature range of 1093°C to 1177°C followed by rapid air cooling. Metallographic examinations have shown that its strengthening elements remain in solid solution in the 593°C to 871°C range. Carbide precipitates appear randomly distributed in the grain boundaries and matrix of the grain. Agglomeration of the carbides is observed after long-term exposure at 649°C to 760°C. However, there is no precipitation hardening indicated by high temperature mechanical testing; and for prolonged periods at 816°C, tensile test results indicated no tendency toward embrittlement either. Furthermore, the alloy did not exhibit marked notch sensitivity during stress-rupture properties evaluation using smooth and notched specimens [5, 6].

Table 1: Nominal composition (wt.%) of Alloy N

Ni	Mo	Cr	Fe	Si	Mn
Bal.	16	7	≤ 5	≤ 1	≤ 0.08
C	Co	Cu	W	Al + Ti	
≤ 0.08	≤ 0.20	≤ 0.35	≤ 0.50	≤ 0.35	

Various product forms of Alloy N can be manufactured by processing methods regularly used for Ni-base alloys, such as forging, extrusion, hot rolling, and cold rolling. The hot working range for Alloy N is between 871°C and 1177°C. Forging can be conducted in the temperature range from 1038°C to 1232°C and hot rolling from 1024°C to 1204°C. Because the material work hardens readily, intermediate annealing is normally required after cold rolling of sheets. The alloy has good weldability and can be readily welded by the inert gas metal arc welding process. The weldment normally requires no preheat nor postheat, and is not subject to air hardening during welding [5, 6].

REACTOR SERVICE REQUIREMENTS FOR STRUCTURAL ALLOY

The FHR and the MSR concepts are both low-pressure, high-temperature reactor types. Both reactor classes employ primary, intermediate, and secondary (or power cycle) heat transfer loops. The FHR uses clean fluoride salt, most likely $2^7LiF-BeF_2$, as its primary coolant and a non-lithium bearing intermediate salt such as $KF-ZrF_4$ as its intermediate salt while the MSR employs a fissile material containing primary fuel salt. Although the design intent of both reactor classes is to employ Alloy N as their primary structural material, the FHR concept is currently under more active investigation. Thus, this material evaluation will focus on the performance requirements for salt-cooled rather than salt-fueled reactors.

Several designs are currently under consideration for the FHR concept. The design output temperature of all these proposed FHRs is 700°C and their core inlet temperature is 650°C. Thus, the input to the salt-to-salt primary-to-secondary heat exchanger will be at 700°C. All currently proposed FHRs configure the hot coolant for up flow through the reactor core and the cold coolant (650°C) for down flow within a downcomer annulus just inside the reactor vessel, as shown in Fig. 1. Hence, the reactor vessel operates at 650°C. The intermediate coolant loop transfers heat from the primary loop to the secondary or power cycle loop. Several different power cycles are under consideration for the FHR, including supercritical water, supercritical carbon dioxide, helium, and direct air power cycles.

The secondary heat exchanger transferring heat from the intermediate salt to power cycle features a large pressure differential. An ultra supercritical water power-cycle can have pressures up to 35 MPa whereas a supercritical carbon dioxide power-cycle can have pressures up to 30 MPa. For a tube and shell heat exchanger, the full pressure differential will appear across the thin tube walls.

Alloy N is considered as the structural material for the reactor vessel, heat exchangers, pumps, and piping for all current FHR design studies. Various other mechanical parts in contact with the liquid fluoride salt may also be included. The structural alloy of these components must withstand thermal stress fatigue, low and high cycle fatigue, creep-fatigue, static tensile and compressive load types at high temperature, and remain compatible with the core graphite and the liquid fluoride

salt. Therefore, while the reactor vessel and large pipes may alternatively be fabricated from another high temperature alloy clad with a Ni-based cladding layer to provide chemical compatibility with the fluoride salt. Significant performance improvement accrues by using a monolithic structure for the thin walled heat exchanger tubing.
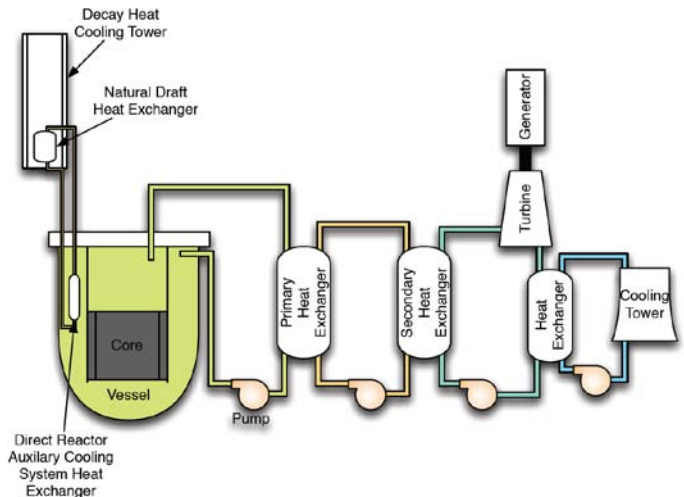

Fig. 1: A conceptual schematic of the FHR system

The FHR core features thick graphite reflectors and downcomer annuli, thus the reactor vessel is in a low neutron flux region with well less than 10^{20} neutrons/cm^2 total lifetime exposure. As the FHR features a low-pressure primary system, the reactor vessel wall thickness is primarily determined by welding attachment and seismic requirements with ~25 mm thickness being anticipated. The reactor vessel service lifetime design goal should be at least 60 years. However, as a thin wall component an FHR reactor vessel could be replaced as part of a major service outage.

Although the design output temperature of all the currently proposed FHRs is 700°C and their core inlet temperature is 650°C, higher operational temperature is desired to increase the efficiency of both electricity generation and high-temperature steam electrolysis based hydrogen production, which requires processing temperature of ~850 °C for efficient operation.

CODIFICATION STATUS AND DESIGN STRESSES

For design and construction of boilers, pressure vessels, and other related components in both the United States and Canada, the structural materials must be accepted into the Boiler and Pressure Vessel Code (BPVC) or Code Case developed and maintained by the American Society of Mechanical Engineers (ASME). Properties data of Codified structural materials in specific product forms for design and construction consideration are published in BPVC Section II Part D. If the components are intended for nuclear

applications, the materials must be further accepted into ASME BPVC Section III.

After its development, Alloy N was first approved by the ASME for use in pressure vessels under code cases 1315 and 1345 [7]. Currently, several product forms of the alloy including plate, sheet, welded pipe and tubing, seamless wrought pipe and tubing, fittings, strip, and rod are accepted in the BPVC and also approved for bolting application [8]. The maximum Codified design temperature for Alloy N is 704°C, which is applicable to pressure vessels. Applications to bolting and transport tanks are limited to lower maximum permissible temperatures of 427°C and 343°C, respectively. A summary of the Codification status for the alloy is given in Table 2. The maximum allowable stress value S and maximum allowable stress intensity value S_m are provided in BPVC Section II Part D Table 1B, Table 3, and Table 5B. These values as a function of time are presented in Fig. 2. When the values vary for different product forms, the average values are used to construct Fig. 2 for clarity.

Table 2: Current codification status of Alloy N

Code Book Information Summary				Maximum Permissible Temperature	Maximum Temperature Listed for Allowable Design Stress (S, S_m)	Allowable Design Stress Type
Applicability	Code Section	Code Table	Product	°C	°C	
Pressure Vessel	Section VIII Division 1	Sect. II-D Table 1B	Various Forms	704	725	S
Transport Tanks	Section XII	Sect. II-D Table 1B	Various Forms	343	725	S
Pressure Vessel	Section VIII Division 1	Sect. II-D Table 3	Bolting	704	725	S
Pressure Vessel	Section VIII Division 2	Sect. II-D Table 3	Bolting	427	725	S
Transport Tanks	Section XII	Sect. II-D Table 3	Bolting	343	725	S
Pressure Vessel	Section VIII Division 2	Sect. II-D Table 5B	Various Forms	427	450	S_m

Note: The temperatures in the S, S_m column are intended for purposes of interpolation between 700 and 725°C, and 425 and 450°C to get the value for 704°C and 427°C, respectively, the maximum permissible temperature, and are not considered for design.
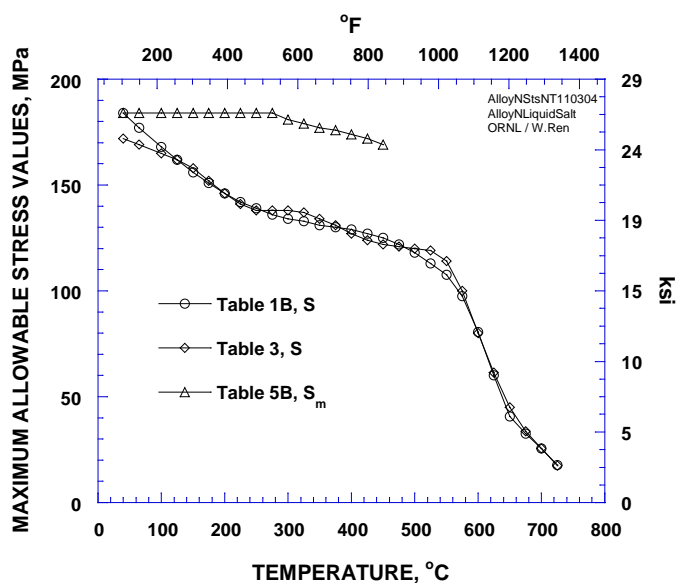

Fig. 2: Maximum allowable stress value S of Alloy N by ASME BPVC.

Compared to the leading candidate materials that are usually considered for advanced nuclear reactor construction, the high temperature strength of Alloy N is noticeably weaker.

For long-term time-dependent strength, comparison can often be made with respect to 100,000-hour creep strength at the temperature of interest. The 100,000-hour creep strengths of Alloy N and several leading candidate materials for advanced nuclear reactors are compared in Fig. 3. The 100,000-hour strength values are extracted from the stress allowables of ASME BPV Code Section II Part D [8]. At temperatures around 630°C, Alloy N becomes weaker than the other candidates. Creep data for Alloy N at temperatures above 760°C are needed to complete the comparison curves.

For short-term time-independent strength, typical ultimate tensile stress (UTS) and yield stress (YS) of Alloy N are compared with those of several other candidate materials in Fig. 4 and Fig. 5, respectively, for temperatures up to 525°C. It appears that Alloy N is only weaker than Alloy 230 in this temperature range.
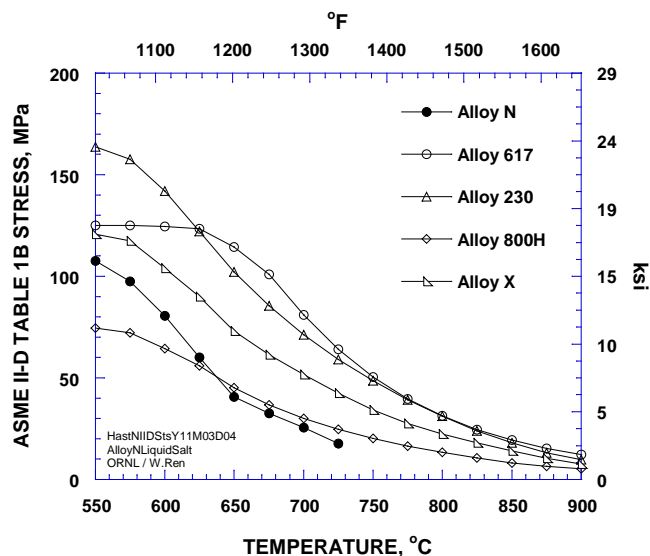
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Fig. 3: Comparison of the strength based on 100,000 hours for candidate materials considered for service at temperatures up to 900°C.
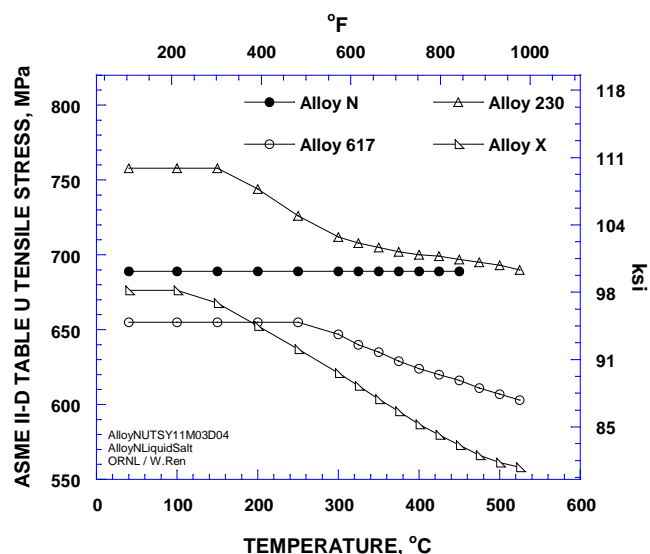
Fig. 4: Comparison of typical UTS values of Alloy N and other candidate materials at various temperatures.

It should be noted from Table 2 that although Alloy N was developed for nuclear applications and extensively investigated for nuclear reactor application during the MSRE program in a 8 MW test reactor at ORNL, it has not been Codified into BPVC Section III - Rules for Construction of Nuclear Power Plant Components, particularly not into Subsection NH - Class 1 Components in Elevated Temperature Service. This means that the current qualification status of Alloy N does not allow it to be used for design and construction of any commercial nuclear reactors in the United States and Canada. To qualify an alloy

for Subsection NH, certain behavioral features are required for preventing seven structural failure modes: [9]

1. Ductile rupture from short-term loading;
2. Creep-rupture from long-term loading;
3. Creep-fatigue failure;
4. Gross distortion due to incremental collapse and ratcheting;
5. Loss of function due to excessive deformation;
6. Buckling due to short-term loading; and
7. Creep-buckling due to long-term loading.

For some advanced nuclear reactor applications, an additional failure mode, i. e., non-ductile rupture, is also included in the failure prevention list [10].
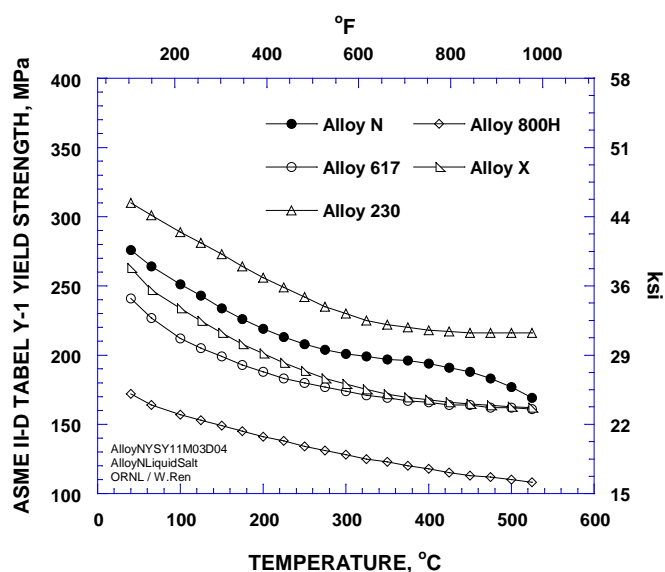
Fig. 5: Comparison of typical YS values of Alloy N and other candidate materials at various temperatures.

To qualify an alloy for Class 1 components in elevated temperature nuclear service regulated by Subsection NH of the ASME BPVC does not require consideration of environmental resistance. However, for the FHR applications, it is unlikely the consideration of environmental resistance can be avoided due to the significant effects of liquid fluoride salts on metallic materials. Apparently, to consider Alloy N for commercial FHR design and construction, more research and development (R&D) are needed to address the Codification issues, particularly to generate the material properties data and information required by Code Section III Subsection NH.

ENVIRONMENTAL RESISTANCE

Depending on the FHR system design and the specific components that Alloy N is employed to construct, the alloy may be exposed to different environments such as air, liquid fluoride salt, or power cycle working fluid individually or in

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combination. Environmental resistance, particularly the resistance to liquid fluoride salts, is essential for its intended applications in the FHR system.

Thermodynamics of the Liquid Fluoride Salt - Alloy N System

Liquid fluoride salts act as fluxes and remove any oxide layer that may be present on the metallic material. As a result, the normally used approach for providing high temperature oxidation resistance, i.e., the development of an alloy composition that provides for an extremely slow growing protective oxide layer on the surface of the material, cannot be employed in the presence of liquid fluoride salts. Typically, for structural materials, this oxide layer is, in general, either chromium oxide or, at higher temperatures, aluminum oxide. Thus, the choice of a structural material for containment of liquid fluoride salts begins with a consideration of the reduction-oxidation (redox) potentials of the component elements of the material with respect to components of the salt. Typically, standard free energies of formation per gram atom of fluorine are evaluated for the potential elemental components of the structural material versus that of the fluoride salt at the temperature of interest. The desire is to have the components of the molten fluoride salt be more stable than fluoride compounds that could form with the components of the structural material, and so have a non-reactive system. Hence, Ni-base alloys, such as Alloy N, become the choice for use in liquid fluoride salts. Other alloying elements are then added to the composition to increase the mechanical properties and provide resistance to oxidation in air or other environments.

Kinetics of the Liquid Fluoride Salt - Alloy N System

Beyond thermodynamics, kinetics of reactions defines fitness of a material for use in its environment. In the early development at ORNL during the 1960s and 1970s, corrosion of a variety of structural alloys by the MSRE salt mixtures resulted from a combination of reactions that involved impurities in the salt:
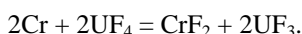
$$2HF + M = MF_2 + H_2$$

where M = Ni, Cr, Fe

and

$$XF_2 + Cr = CrF_2 + X$$
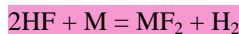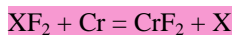
where X = Ni, Fe

and reactions involving fuel components, for example:

$$2Cr + 2UF_4 = CrF_2 + 2UF_3.$$

These products readily dissolve into the molten salt mixture. As shown in Fig. 6, the levels of impurities in the salt significantly impact the material's performance and a great effort was made to minimize impurity concentrations in the fluoride salt and maintain clean alloy surfaces. However, the reaction with UF_4 is intrinsic and depends on the redox potential of the salt, which can be described in terms of the ratio of activities of quadrivalent-to-trivalent uranium ions.

FLUORIDE BATCH HIGH IN FE & NI · 250X
FLUORIDE BATCH MODERATE IN FE & N · 250X
FLUORIDE BATCH LOW IN FE & NI · 250X
FLUORIDE BATCH HIGH IN HF · 250X

INCONEL THERMAL CONVECTION LOOPS-500 HRS. AT 1500°F
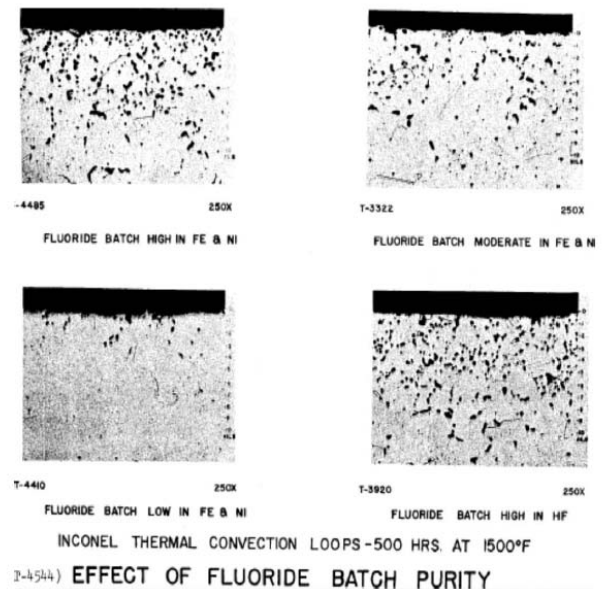P-4544) EFFECT OF FLUORIDE BATCH PURITY

Fig. 6: The greater the impurities in the fluoride salt, the greater the corrosion.

Kinetics of the reactions were evaluated during several hundred thousand hours of corrosion testing with Alloy N and fluoride salts using thermal convection loop tests [1 - 3, 11] and pumped loop [12] tests in addition to experience from the MSRE. Two general mechanisms of corrosion, metal dissolution and oxidation of metal to ions, can occur in molten salt systems. Because of low solubility of most structural metals in salt systems, one mechanism, metal dissolution due to solubility in the melt, is not a common form of attack. The second mechanism, oxidation of metal to ions, is more likely. In addition to anodic dissolution and cathodic reduction of an oxidant, in the salts that are electronic as well as ionic conductors, reduction reactions can occur in the melt as well as at the metal-melt interface. In many molten salt systems, the rate controlling step is ion diffusion from the alloy into the bulk solution, rather than charge transfer.

Mass Transfer Induced by Temperature Gradient

Gradients in the chemical activities of constituents caused by temperature differences can result in dissolution of metal in one region of the system with subsequent deposition in other portions of the system. The amount of attack will depend on the driving force and dissolution or deposition kinetics for reactions that result in transporting the corroding species to a different part of the loop circuit where they might deposit. Hence, a non-isothermal system could also be subject to corrosion from thermal gradient mass transfer if the chemical potential of the corrosion product fluoride or chloride, at a given concentration, is a strong function of temperature, and

deposition of the corrosion species occurs in the cooler regions of a loop operating with a relatively high temperature differential. This effect is shown in Fig. 7, where an Alloy N loop which was operated for 9 years, with a T_{max} of 700°C and T_{min} of 560°C, presents attack and mass loss (void formation 0.0508 mm into matrix) in the hotter area and deposition in cooler regions. More recently, similar void formation deposition at much higher temperature has been reported [13]. However, the overall corrosion at this higher temperature was much less than of previous studies at lower temperature due to being able to produce much cleaner fluoride salts.
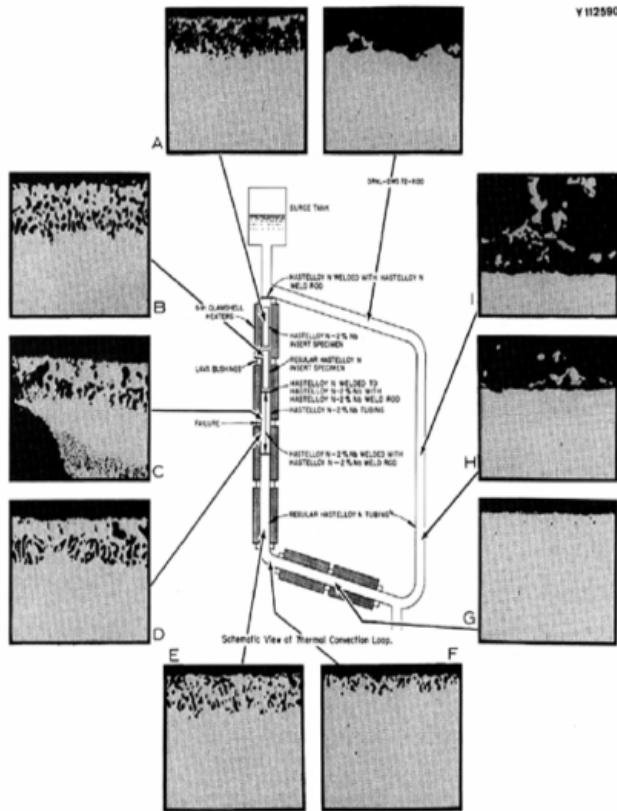
Fig. 7: Alloy N loop mass loss at the hotter temperature and material deposition at the colder temperature [14].

Mass Transfer Induced by Material Dissimilarity

Mass transfer can also occur when dissimilar structural materials are included in the same system. The dissimilar materials do not have to be electrically coupled. Two things are required for dissimilar material mass transfer to become a factor. First, an element contained in one of the materials has to have a strong tendency to form an alloy or compound with the second material. More importantly, an element in one of the materials must be subject to oxidative attack or suffer dissolution within the salt solution. The oxidative attack can be either by reaction with impurities or, if a reactive element, with the salt constituents. In either event, once the element goes into

solution, it can then migrate through the solution and form the required product if the chemical driving force (activity gradient) is sufficient. If the product does form, this will allow the mechanisms of corrosive attack or dissolution to continue (i.e., favorable thermodynamics) although kinetics may be limited by solid state diffusion. If the attack is solely by reaction with impurities, the problem may dramatically slow with time. However, the reaction will not stop if there is solubility in the salt for a specific element. Such an attack is shown in Fig. 8 where Co is deposited from high activity alloy onto a low activity alloy.
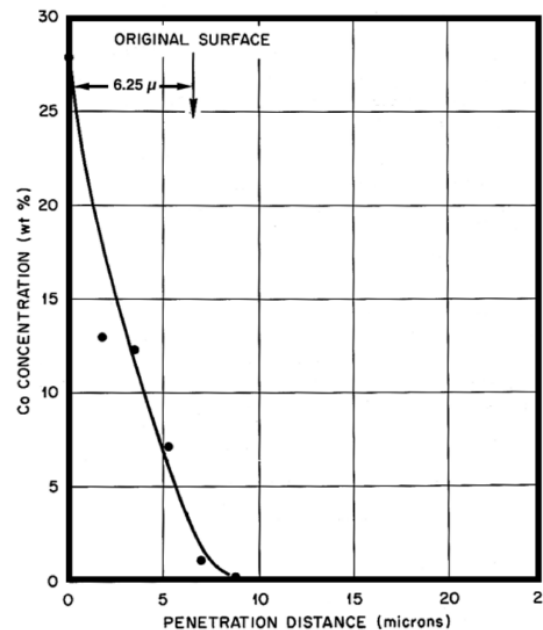

Fig. 8: Desposition of Co from Alloy 25 (53.0% Co) onto Alloy N (0.1% Co) [14].

Fission Product Induced Cracking

While the corrosion rate of Alloy N measured during operation of the MSRE was relatively low and of the same order as that for forced-convection loops operating under similar temperatures, tensile specimens that were exposed to the fuel salt and then tested to failure showed shallow surface cracks (150 to 250 μm) along the gage length at grain boundaries that connected to the salt-exposed surfaces [15]. These cracks were determined to be due to the fission product tellurium and modification of Alloy N with approximately 2% Nb significantly reduced the cracking, as shown in Fig. 9 [16].

Electrochemical studies also demonstrated that the cracking could be controlled by the redox potential of the salt, which in this case, was controlled by the ratio of U^{+4} to U^{+3} in the salt. Results of studies with this ratio varied between 10 and 300 are shown in Fig. 10 where for a redox potential of less than approximately 70, tellurium embrittlement of grain boundaries is greatly reduced.
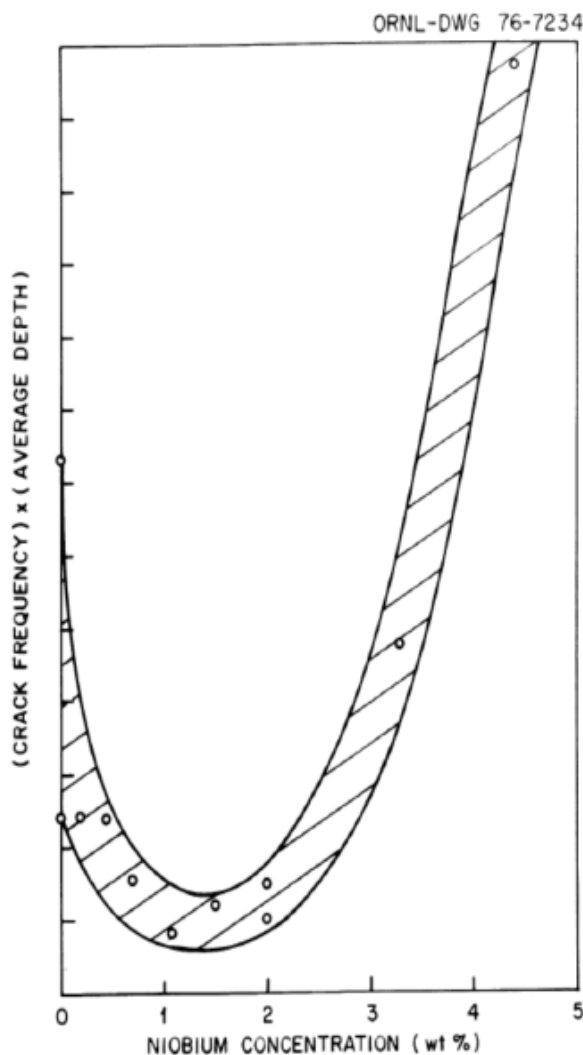
Fig. 9: Effect of Nb in modified Alloy N on grain boundary cracking when exposed to fluoride salt with $Cr_3Te_4 + Cr_5Te_6$ for 250 h at 700°C [16].

Alloy N in Other Salts

The compatibility behavior of Alloy N has also been evaluated, though less extensively, for fluoroborates [17] and chlorides [18, 19]. Based on the scant data, the corrosion rate in fluoroborates is approximately 1 mil/year, which is larger than for fluoride salts under comparable conditions. In the case of the chlorides, at 500°C for 1000 h, intergranular corrosion was observed for static tests and transgranular corrosion under rocking conditions for a temperature differential of 50°C.

General Evaluation of Environmental Resistance of Alloy N

Experimental results from materials industry show that Alloy N has excellent oxidation resistance in air at temperatures up to 1038°C. After exposure to high temperatures for 1,000 hours, the weight gain was only 2 µg/cm² at 1038°C and essentially zero at 649°C, as shown in Fig. 11. The alloy also

appears to have good corrosion resistance in steam and water. Stress corrosion tests in pressurized water showed no evidence of stress corrosion cracking, as is typical of Ni base alloys. More importantly, test results indicated that Alloy N has excellent corrosion resistance to liquid fluoride salts in the temperature range of 704°C to 871°C. The corrosive attack rate for Alloy N is less than 25.4 µm/year in this temperature range, as compared to 889 µm/year for Inconel at 650°F [6].
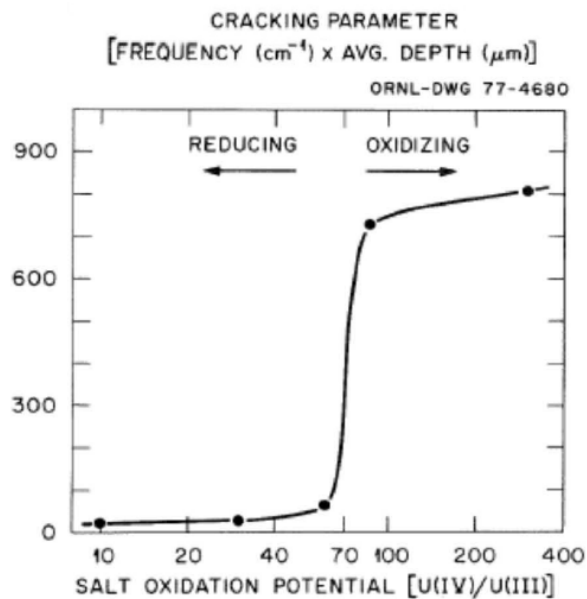

Fig. 10: Effect of redox potential on cracking behavior of Alloy N exposed 260 h at 700°C to fluoride salt containing Te [16].
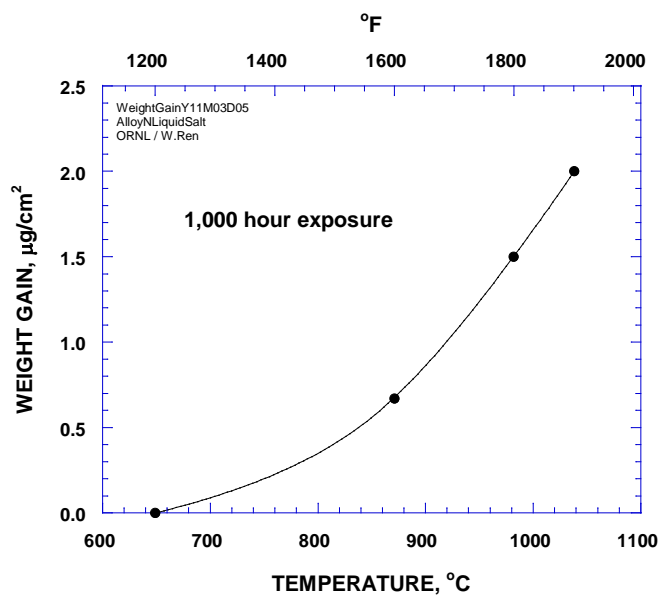

Fig. 11: Weight gain of Alloy N after 1,000 hours exposure in air at various temperatures [6].

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HIGH TEMPERATURE STRENGTH

For applications at high temperatures, properties related to creep and stress-rupture often become the controlling factor. To develop an FHR design with higher allowed operating temperature and longer service life, these properties are major factors that significantly affect the success of design.

Stress-Rupture Life

In the previous discussion on Fig. 3, design data of Alloy N from ASME BPVC based on long-term time-dependent properties were compared with those of several other leading candidate alloys considered for the Gen IV Nuclear Energy Systems development. Without knowing the derivation details of these design data, raw test data would provide more direct comparison between the time-dependent properties of these alloys. In Fig. 12, creep-rupture data of Alloy N are plotted along with that of Alloys 617 and 230 for 704°C, the maximum allowable temperature for its application permitted by the ASME BPVC. The data for Alloy N were generated from thin sheet specimens and other smooth and notched specimens [5, 6]. It appears in Fig 12 that the alloy does not exhibit any noticeable effect on creep-rupture properties from notch sensitivity or different product forms. Meanwhile, it is obvious that for a given stress level, the creep-rupture life of Alloy N is about 2 to 3 orders shorter than that of Alloys 617 and 230 at 704°C. For higher temperatures desired for advanced FHR applications, the same trend of weakness can be observed in Fig. 13 for 816°C and Fig 14 for 927°C. Its seems that at 927°C, the creep-rupture strength of Alloy N is comparable to that of Alloys 617 and 230 at 1093°C, as shown in Fig. 15. Unfortunately, Alloys 617 and 230 do not possess the same environmental resistance found in Alloy N. Obviously, for operations above 704°C, a new alloy is desirable that can provide the high temperature strength at least equal to, preferably better than, that of Alloy 617 and 230, while offering the same or improved environmental resistance possessed by Alloy N.
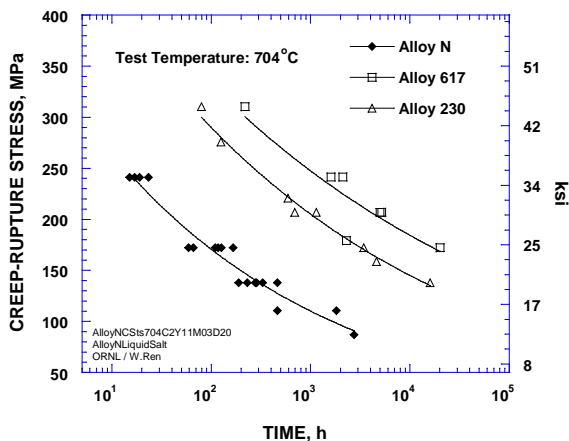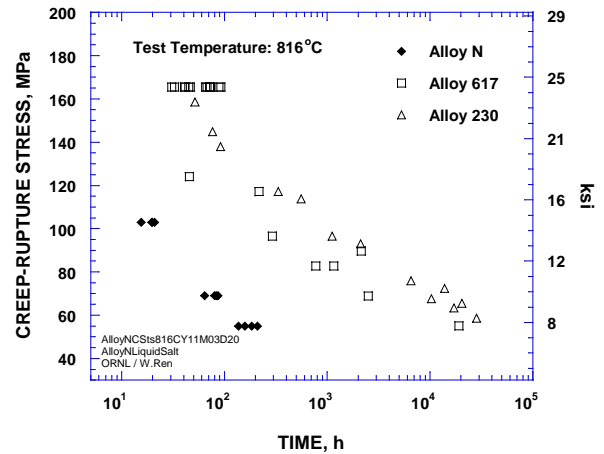

Fig. 13: Creep-rupture stress of Alloy N at 816°C in comparison with that of Alloys 617 and 230 [5, 6, 20].
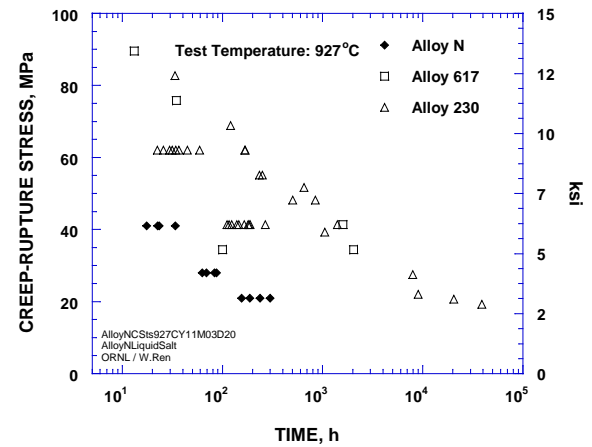

Fig. 14: Creep-rupture stress of Alloy N at 927°C in comparison with that of Alloys 617 and 230 [5, 6, 20].
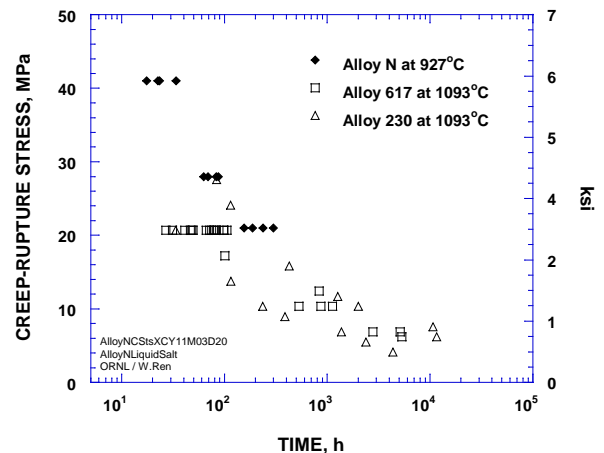

Fig. 12: Creep-rupture stress of Alloy N at 704°C in comparison with that of Alloys 617 and 230 [5, 6, 20].

Fig. 15: Creep-rupture stress of Alloy N at 927°C in comparison with that of Alloys 617 and 230 at 1093°C [5, 6, 20].

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High-Temperature, Neutron Irradiation Stress-Rupture Life Reduction

The MSRE found that Alloy N is subject to a type of high-temperature, neutron irradiation damage that reduces the stress rupture life and the fracture strain [21 - 24]. Severity of the reduction in rupture life appeared to be affected by the applied stress level. An example was reported that after irradiation to a thermal fluence of about 5×10^{20} n/cm^2, the average rupture lives at 650°C for irradiated and non-irradiated Alloy N specimens were about the same for materials tested at stresses below 138 MPa, but as the stress level was increased to 276 MPa, the average rupture life of the irradiated specimens was shortened more than 100 hours compared to that of the non-irradiated specimens, as shown in Fig. 16.
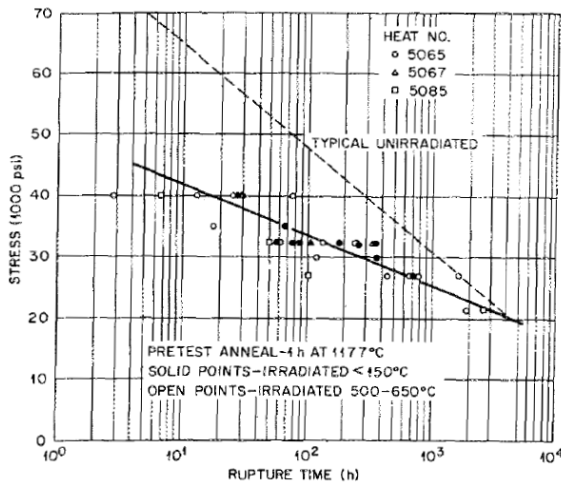

Fig. 16: Creep-rupture stress of Alloy N at 650°C after irradiation to a thermal fluence of about 5×10^{20} n/cm^2 [7].

Irradiated Fracture Strain Reduction

Reduction in fracture strain in both tensile and creep tests on Alloy N were also reported after irradiation. Such reduction was found to be related to the strain rate, and a minima in fracture strain was observed at the strain rate of 0.001/h, as shown in Fig. 17, in which the strain rate represents tensile strain rate for tensile data and minimum creep strain rate for creep data. This observation certainly raises concerns that the alloy could fail under transient conditions that impose higher stresses or require that the material absorb thermally induced strains. Consequently, it should be noted that no FHR designs intend to use Alloy N in high neutron flux (i.e. near core) locations.

FURTHER INVESTIGATION ISSUES AND STATUS

Based on the FHR operational requirements for its structural materials and our extensive reviews on commercially available alloys that might satisfy those severe service conditions, Alloy N stands out as a leading candidate material. However, several issues, as discussed in the previous sections, have been identified for the alloy that would require considerable R&D activities to qualify it for commercial

nuclear reactor applications, or to improve its properties before the severe service requirements of advanced FHR can be reliably met, particularly when elevated temperature operation is considered. Efforts to improve its properties may consequently create a variant of Alloy N, or even a completely new alloy, for the intended FHR application. Among the issues to be addressed, the most essential one is the long-term strength in liquid fluoride salt environment at desirable temperatures above the current ASME BPVC permissible temperature of 704°C. The most significant challenge to addressing this issue is the difficulty in balancing between the long-term elevated temperature strength and the environmental resistance in liquid fluoride salts. This difficulty would be further aggravated under high-temperature, high neutron flux service conditions.
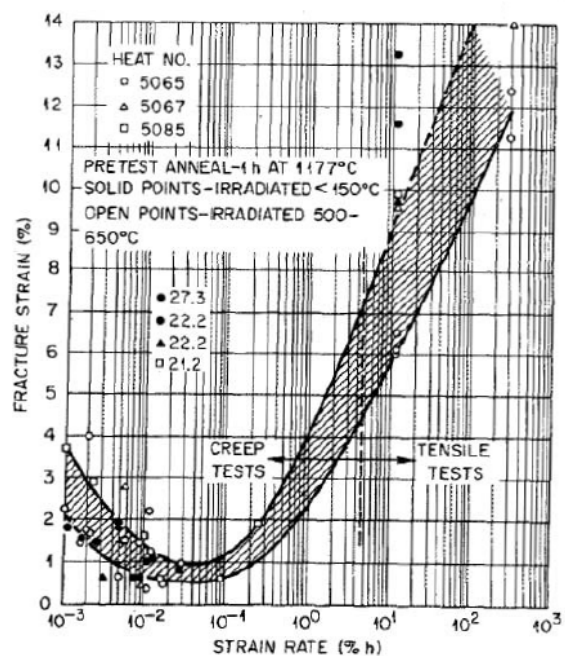

Fig. 17: Fracture strain of Alloy N at 650°C after irradiation to a thermal fluence of about 5×10^{20} n/cm^2 [7].

It is well known that the conventional approach to improving an existing alloy or developing a new one, which largely relies on a series of laboratory experiments with considerable trial-and-error efforts, is normally a time- and fund-consuming adventure. For example, the improvement of 9Cr-1Mo steel to the Modified 9Cr-1Mo steel, a successful alloy development program led by ORNL in the 1970s and 1980s, took approximately 10 years to complete [25]. To provide a satisfactory structural alloy for FHR design and construction under the current pressing demands for low-carbon energy, the conventional approach is apparently cumbersome. More time- and cost-efficient approaches must be explored.

In 2010, a project was established at ORNL to explore the potentials of modern computational simulation and advanced materials database technologies in enhancing Alloy N for the FHR system development. As shown in Fig. 18, computational

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thermodynamic models are first established based on historical data derived from extensive metallurgical experiments to predict microstructure features such as phases that would present and their relative amounts from candidate compositional variants of Alloy N. The simulated microstructures are analyzed for their weighted functions in high temperature strengthening and environmental resistance. Further predictions are then made on desired properties, particularly high temperature strength and liquid fluoride salt environmental resistance that would result from the compositional variations. Iteration of the modeling, analysis, and prediction would effectively provide guidance to narrowing down the composition and fabrication parameter windows before actual experimental heats of alloy are made for laboratory investigations, which include metallurgical characterization and mechanical testing. The laboratory investigation results are then fed back into the database for simulation of various combinations of the alloy capacities in strength and environmental resistance with regard to the chemical composition and fabrication processing. Optimization of composition, processing, and properties will be approached in this fashion with minimized actual metallurgical and mechanical trial-and-error efforts to achieve improvements in alloy properties.
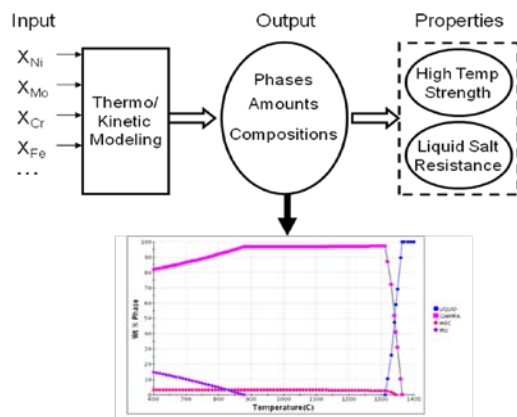

Fig. 18: Computational modeling to identify paths that increase high temperature strength and environmental resistance

To provide experimental feedback to the computational simulation, development of mechanical testing system is also underway. The FHR service conditions will be simulated for the experimental alloy specimens to be tested in long-term exposure to liquid fluoride salt environment under load at temperatures up to and 50°C above the intended service temperatures. This requires creep testing of specimens from the experimental heats in liquid fluoride salt in the temperature range of 700°C up to 1000°C, if 950°C is eventually desired for the advanced FHR system. Although the requirements are much higher than those for the MSRE in the 1970s and 1980s, the creep testing for the MSRE has provided valuable

experience to draw upon in designing and building the new testing systems. A prototype of the testing system will be completed within 2011 and actual testing of the specimens will be started upon its completion.

SUMMARY

The Fluoride Salt-Cooled High-Temperature Reactor (FHR) has several technical advantages over other reactor concepts and has drawn considerable interest for development. A structural alloy is needed that can provide a combination of good environmental resistance to liquid fluoride salts and high creep strength at temperatures of 700°C up to 1000°C.

An extensive review of the commercially available alloys suggests that Alloy N, a superalloy developed at ORNL during the 1960s and 1970s, has capacities that are closest to meeting the service requirements of FHR but its permissible temperature range and the combination of high temperature strength and environmental resistance in liquid fluoride salts are not satisfactory. To enable higher temperature and increased efficiency FHR systems, a higher temperature tolerant and fluoride salt compatible alloy will be required. The conventional methods for alloy development largely rely on laboratory experiments with considerable trial-and-error efforts is normally a time- and fund-consuming adventure. To face the challenge in today's fast pace world, the potentials of modern computational simulation and advanced materials database technologies in alloy development is being explored to achieve time- and cost-efficiency. Computational simulation supported by experimental database is conducted to provide guidance for design of Alloy N variants with desired property enhancements for FHR development. Meanwhile, a system prototype for liquid fluoride salt environmental creep testing at temperatures of 700°C up to 1000°C is also being developed to support the alloy development.

ACKNOWLEDGMENTS

NOTICE

REFERENCES

[1] G. M. Adamson, R. S. Crouse, and W. D. Manly, "Interim Report on Corrosion by Alkali-Metal Fluorides," ORNL-2337, Oak Ridge National Laboratory, 1959.

Copyright © 2011 by ASME

[2] G. M. Adamson, R. S. Crouse, and W. D. Manly, "Interim Report on Corrosion by Zirconium-Base Fluorides," ORNL-2338, Oak Ridge National Laboratory, 1961.

[3] W. D. Manly et al., Aircraft Reactor Experiment - Metallurgical Aspects, ORNL-2349, Oak Ridge National Laboratory, 1957.

[4] J. R. DiStefano, J. H. DeVan, J. R. Keiser, R. L. Klueh, W. P. Eatherly, Materials Considerations for Plutonium Conversion Systems, ORNL/TM- 12925, Oak Ridge National Laboratory,1995.

[5] Haynes International, "Hastelloy N Alloy," H-2052B, 2002.

[6] Haynes International, "Nickel-Molybdenum-Chromium-Iron Alloy as Material for ASME Boiler and Pressure Vessel Construction," Document No. 5537, July 15, 1961.

[7] H. E. McCoy, R. L. Beatty, W. H. Cook, R. E. Gehlbach, C. R. Kennedy, J. W. Koger, A. P. Litman, C. E. Sessions, J. R. Weir, "New Developments in Materials for Molten-Salt Reactors," Nuclear Application and Technology, Vol. 8, February 1970.

[8] "2010 ASME Boiler and Pressure Vessel Code – II Part D Properties," American Society of Mechanical Engineers, 2011.

[9] R. I. Jetter, "Subsection NH- Class 1 Components in Elevated Temperature Service," Companion Guide to the ASME Boiler & Pressure Vessel Code, K. R. Rao, ed., pp. 369-404, American Society of Mechanical Engineers, New York, NY, 2002.

[10] J. M. Corum and J. J. Blass, "Rules for Design of Alloy 617 Nuclear Components to Very High Temperatures," pp. 147 to 153 in Fatigue, Fracture, and Risk - 1991, PVP-Vol. 215, American Society of Mechanical Engineers, New York, NY, 1991.

[11] J. H. DeVan, Effect of Alloying Addition on Corrosion Behavior of Nickel-Molybdenum Alloys in Fused Fluoride Mixtures, University of Tennessee Thesis, August 1960.

[12] R. B. Briggs, MSR Program Semiannual Program Report, August 31, 1961, pp. 93-94, ORNL-3215,Oak Ridge National Laboratory, 1962.

[13] D. F. Williams, D. F. Wilson, L. M. Toth, J. Caja, and J. R. Keiser, "Research on Molten Fluorides as High Temperature Heat Transfer Agents," Proceedings of Global 2003, New Orleans, USA, Nov. 16-20, 2003.

[14] J.W. Koger, Evaluation of Hastelloy N alloys after nine years exposure to both a molten fluoride salt and air at temperatures from 700 to 560°C, ORNL TM 4189, Oak Ridge National Laboratory, 1972.

[15] H. E. McCoy, Jr., and B. McNabb, Intergranular Cracking of INOR-8 in the MSRE, ORNL-4829, Oak Ridge National Laboratory, November 1972.

[16] J. R. Keiser, Status of Tellurium-Hastelloy N Studies in Molten Fluoride Salts, ORNL/TM-6002, Oak Ridge National Laboratory, 1977.

[17] M. W. Rosenthal, "The Development Status of Molten-Salt Breeder Reactors," ORNL-4812, Oak Ridge National Laboratory, 1972.

[18] C. J. Raseman, H. Susskind, G. Faber, W. E. McNulty, and F. J. Salzano, Engineering Experience at Brookhaven National Laboratory in Handling Fused Chloride Salts, BNL 627 (T-192), Brookhaven National Laboratory, June 1960.

[19] H. Susskind, F. B. Hill, L. Green, S. Kalish, L. E. Kukacka, W. McNulty, and E. Wirsing, Jr., Corrosion Studies for Fused Salt-Liquid Metal Extraction Process for the Liquid Metal Fuel Reactor, BNL 585 (T-146), Brookhaven National Laboratory, June 1960.

[20] U. S. Department of Energy, Background Public Information from "Gen IV Materials Handbook," an online materials information system under development since 2005.

[21] W. R. Martin and J. R. Weir, "Flow and Fracture of Metals and Alloys in Nuclear Environments," Special Technical Publication, 380, pp. 251-267, American Society for Testing and Materials, Philadelphia, 1965.

[22] J. T. Venard and J. R. Weir, "Flow and Fracture of Metals and Alloys in Nuclear Environments," Special Technical Publication, 380, p. 269, American Society for Testing and Materials, Philadelphia, 1965.

[23] W. R. Martin and J. R. Weir, "Postirradiation Creep and Stress Rupture of Hastelloy N," Nuclear Application, 3, 167, 1967.

[24] H. E. McCoy and J. R. Weir, "Stress-Rupture Properties of Irradiated and Unirradiated Hastelloy N Tubes," Nuclear Application, 4, 96, 1968.

[25] J. R. DiStefano, V. K. Sikka, et. al. "Summary of Modified 9Cr-1Mo Steel Development Program: 1975-1985," ORNL-6303, Prepared by the Oak Ridge National Laboratory for Office of Technology Support Programs, U.S. Department of Energy, October 1986.