NEW DEVELOPMENTS IN MATERIALS FOR MOLTEN-SALT REACTORS

REACTORS

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Operating experience with the Molten-Salt Reactor Experiment (MSRE) has demonstrated the excellent compatibility of the graphite-Hastelloy-N-fluoride salt system at 650°C. Several improvements in materials are needed for a molten-salt breeder reactor with a basic plant life of 30 years; specifically: Hastelloy-N with improved resistance to embrittlement by thermal neutrons; graphite with better dimensional stability in a fast neutron flux; graphite that is sealed to obtain a surface permeability of $<10^{-8}$ cm²/sec; and a secondary coolant that is inexpensive and has a melting point of ~400°C. A brief description is given of the materials work in progress to satisfy each of these requirements.

INTRODUCTION

Our present concept of a molten-salt breeder reactor[1] utilizes graphite as moderator and reflector, Hastelloy-N for the containment vessel and other metallic parts of the system, and a liquid fluoride salt containing LiF, BeF_2, UF_4, and ThF_4 as the fertile-fissile medium. The fertile-fissile salt will leave the reactor vessel at a temperature of ~700°C and energy will be transferred to a coolant salt which in turn is used to produce supercritical steam.

Experience with the Molten-Salt Reactor Experiment (MSRE) has demonstrated the basic compatibility of the graphite-Hastelloy-N[a]-fluoride salt (LiF-BeF_2-ZrF_4-UF_4) system at 650°C. However, a breeder reactor will impose more stringent material requirements; namely: the design life of the basic plant of a breeder is 30 years at a maximum operating temperature of 700°C; the power density will be higher in a breeder and will require the core graphite to sustain higher damaging neutron flux and fluence; and neutron economy is of utmost importance in the breeder and the retention of fission products (particularly ^{135}Xe) by the core graphite must be minimized. Each of these factors requires a specific improvement in the behavior of materials.

Experience has shown that the mechanical properties of Hastelloy-N deteriorate as a result of thermal-neutron exposure and a method must be found of improving the mechanical properties of this material to ensure the desired 30-year plant life.

Similarly, graphite is damaged by irradiation. Although the core graphite can be replaced, the allowable fast neutron fluence for the graphite has an important influence on the economics of molten-salt breeder reactors. Thus, a program has been undertaken to learn more about irradiation damage in graphite and to develop graphites with improved resistance to damage.

A big factor in neutron economy is reducing the quantity of ^{135}Xe that resides in the core. This gas can be removed by continuously sparging the system with helium bubbles, but the transfer by this method probably will not be rapid enough to prevent excessive quantities of ^{135}Xe from being absorbed by the graphite. This can be prevented by reducing the surface diffusivity to $<10^{-8}$ cm²/sec, and we feel that this is best accomplished by carbon impregnation by internal decomposition of a hydrocarbon.

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[a] Hastelloy-N is the trade name of UCC for a nickel-base alloy containing 16% Mo, 7% Cr, 5% Fe, 0.05% C. This alloy was originally developed at ORNL specifically for use in molten-salt systems. It has been approved by the ASME for use in pressure vessels under code cases 1315 and 1345.

A new secondary coolant is also needed that will allow us greater latitude in operating temperature. Sodium fluoroborate has reasonable physical properties for this application, and the compatibility of Hastelloy-N with this salt is being evaluated.

Our work in each of these areas will be described in some detail.

EXPERIENCE WITH THE MSRE

Other papers in this series have elaborated on the information gained from the MSRE regarding operating experience, physics, chemistry, and fission-product behavior. Additionally, valuable information has been gained about the materials involved.[2-4]

There are surveillance facilities exposed to the salt in the core of the reactor and outside the reactor vessel, where the environment is nitrogen plus ~2% O_2. Hastelloy-N tensile rods and samples of the grade CGB graphite[b] used in the core of the MSRE are exposed in the core facility. The components are assembled so that portions can be removed in a hot cell, new samples added, and the assembly returned to the reactor. Samples were removed after 1100, 4400, and 9000 h of full-power (~8 MW) operation at 650°C. As shown in Fig. 1, the physical condition of the graphite and metal samples was excellent; identification numbers and machining marks were clearly visible. The peak fast fluence received by the graphite has been 4.8×10^{20} n/cm^2 (>50 keV) and the dimensional changes are <0.1%. Pieces of graphite from the MSRE have been sectioned and most of the fission products were found to be located on the surface and within 10 mils below the surface. However, a few of the fission products have gaseous precursors and penetrated the graphite to greater depths. The microstructure of the Hastelloy-N near the surface was modified to a depth of ~1 mil, but a similar modification was found in samples exposed to static nonfissioning salt for an equivalent time. The near-surface modification has not been positively identified, but its presence is likely of no consequence. The very small changes in the amounts of chromium and iron in the fuel salt also indicate very low corrosion rates and support our metallographic observations.

The observed low corrosion rate of Hastelloy-N in the MSRE does not come as a surprise, since thousands of hours of corrosion tests preceded construction of the reactor. Hastelloy-N is nickel based and contains about 16% Mo, 7% Cr, and 5% Fe. Under normal operating conditions, the fuel salt cannot oxidize (form fluorides) any of these elements except Cr. Since Cr is present in very small concentrations in the alloy, the corrosion is limited by the diffusion of Cr to the metal surface. Corrosion can be reduced even further by controlling the oxidation state of the salt, thus reducing the rate of the corrosion reaction at the metal-salt interface. The oxidation state of the salt in the MSRE is controlled by the addition of beryllium metal.

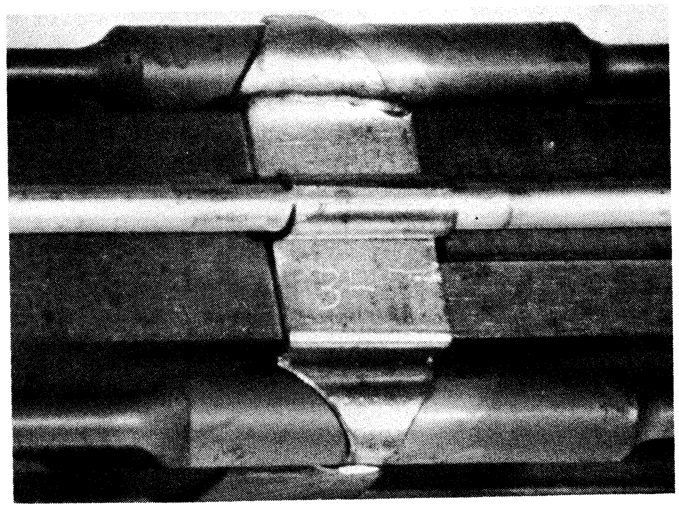

Fig. 1. Graphite and Hastelloy-N surveillance assembly removed from the core of the MSRE after 72 400 MWh of operation. Exposed to flowing salt for 15 300 h at 650°C.

Hastelloy-N samples were removed from the surveillance facility outside the reactor vessel after 4400 and 9000 h of full-power operation. This environment is oxidizing, and an oxide film ~2 mils thick was formed on the surface after the longer exposure. There was no evidence of nitriding, and the mechanical properties of these samples were not affected adversely by the presence of the thin oxide film.

Thus, experience with the MSRE has proved in service the excellent compatibility of the Hastelloy-N-graphite-fluoride salt system.

DEVELOPMENT OF A MODIFIED HASTELLOY-N WITH IMPROVED RESISTANCE TO IRRADIATION DAMAGE

Since the MSRE was constructed, Hastelloy-N, as well as most other iron- and nickel-base alloys, was found to be subject to a type of high-temperature irradiation damage that reduces the

[b]Trade name of Union Carbide Corporation for the needle-coke graphite used in the MSRE.

stress rupture life and the fraction strain.[5-10] This effect is characterized in Figs. 2 and 3 for a test temperature of 650°c. The rupture lives for irradiated and unirradiated materials differ most at high stress levels and are about the same for below 20 000 psi. The property change of most concern in reactor design and operation is the reduction in fracture strain. The postirradiation fracture strain is shown in Fig. 3 as a function of strain rate; the scatter band is based upon test results for three different heats of metal. The plot includes results from both tensile and creep tests. In tensile tests the strain rate is a controlled parameter and the test results are plotted directly. In creep tests the stress is controlled and the strain measured as a function of time. The minimum strain rate was used in constructing Fig. 3. The data are characterized by a curve with a minumum at a strain rate of ~0.1%/h, with rapidly increasing fracture strain as the strain rate is increased, and slowly increasing fracture strain as the strain rate is decreased. Thus, under normal operating conditions for a reactor where the stress levels (and the strain rates) are low, the rupture life will not be affected significantly (Fig. 2), but the fracture strain will be only 2 to 4% (Fig. 3). However, transient conditions that would impose higher stresses or require that the material absorb thermally induced strains could cause failure of the material. Therefore, a material is desired that has improved properties in the irradiated condition and a program with this as its goal has been embarked upon.[c]

The changes in high-temperature properties of iron- and nickel-base alloys during irradiation in thermal reactors have been shown rather conclusively to be related to the thermal fluence and more specifically related to the quantity of helium produced in the metal from the thermal $^{10}B(n,\alpha)^7Li$ transmutation.[11-14] The mechanical properties are only affected under test conditions that produce intergranular fracturing of the material. Under these conditions both creep and tensile curves for irradiated and unirradiated materials are identical up to some strain where the irradiated material fractures and the unirradiated material continues to deform. Thus, the main influence of irradiation is to enhance intergranular fracture.

[c]Although the fast-neutron flux will be quite high in the core of our proposed breeder, the neutrons reaching the Hastelloy-N vessel will be reduced in energy by the graphite present. Thus, the fast fluence seen by the vessel during 30 years will be $<1\times10^{21}$ n/cm^2, and we do not feel that fast-neutron displacement damage is of concern. Experiments will be run to confirm this point.

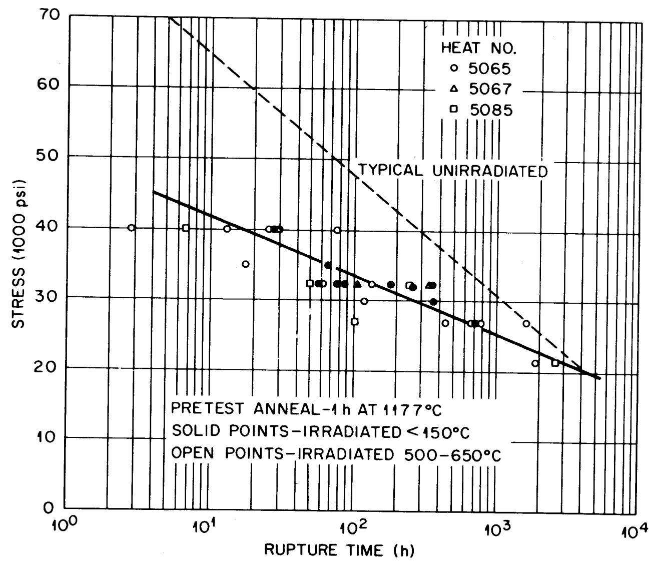

Fig. 2. Creep-rupture properties of Hastelloy-N at 650°C after irradiation to a thermal fluence of $\sim5\times10^{20}$ n/cm^2.

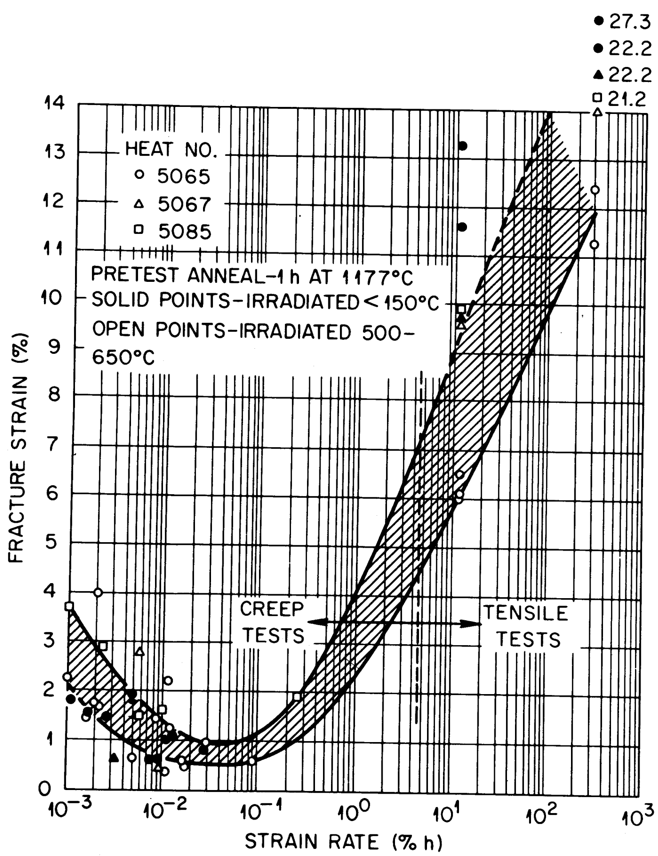

Fig. 3. Fracture strain of Hastelloy-N at 650°C after irradiation to a thermal fluence of $\sim5\times10^{20}$ n/cm^2.