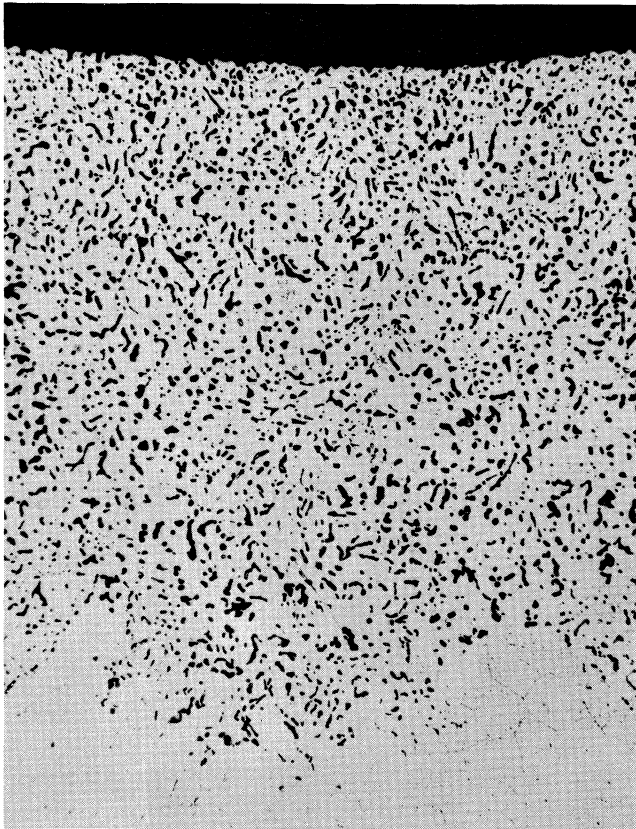


Herb McCoy first worked at ORNL as an undergraduate coöp student out of Virginia Polytech in 1953. In 1955 he married Ann Thompson, a Laboratory Personnel Division employee, and transferred to UT, where he received his M.S. in metallurgy in 1958, the year he joined the ORNL staff. His work at the Laboratory has been with Aircraft Nuclear Propulsion, the Gas-Cooled Reactor, and currently the Molten Salt Reactor Experiment. McCoy heads up a group that is engaged in fundamental studies on the mechanical properties of metals in the Metals & Ceramics Division. The story he tells here of the development of the particular alloy that would stand up under the exacting demands peculiar to the MSR is one of innovation and ingenuity.

## The INOR-8 Story

By H. E. McCoy

**T**HE PHYSICISTS' NOTEBOOKS are filled with attractive reactors that probably will never be built because of inherent materials problems. The factors usually involved are excessively high operating temperatures and corrosiveness of the fluids involved. Other reactors have been constructed without full consideration of the component materials, and their operation has been plagued with problems. The Molten Salt Reactor Experiment at ORNL might well have been one of these problem cases, had not the talents of several individuals and the facilities of the Laboratory and several commercial metal producers been applied to developing a structural material for the metallic parts of the reactor.



*Figure 1. Photomicrograph of a sample of INCONEL 600 (20%Ni-15%Cr-5%Fe) after exposure to fluoride salt in a pumped loop for 15,000 hours at 1300°F. Voids near the surface are formed as chromium is removed selectively by the salt.*

This material had to be chemically compatible with molten fluoride salts and capable of being fabricated into complicated shapes such as characterize the containment vessel, piping, and the heat exchangers.

Such a material was developed; it was called INOR-8 at the Laboratory, but commercially it is known as Hastelloy N and Allvac N. This alloy has performed admirably in the MSRE, but the prospects of molten salt power reactors with plant lives of 30 years means that we must develop a modification of this alloy that is more resistant to embrittlement by long-term neutron irradiation. Let us look briefly at the development of INOR-8 and then analyze the progress toward developing an improved modification of this alloy for future molten salt power reactors.

During the 1950's when the United States was attempting to develop a nuclear-powered aircraft, one of the concepts considered was a reactor fueled with  $UF_4$  contained in a mixture of other fluoride salts. A relatively complicated reactor called the Aircraft Reactor Experiment (ARE) was constructed and operated to demonstrate this concept. The fuel, a mixture of  $NaF$ ,  $ZrF_4$ , and  $UF_4$ , was pumped through

small Inconel 600 tubes at temperatures up to 1620°F. Inconel 600 is a nickel alloy containing chromium and iron. The tubes were surrounded by blocks of beryllium oxide that served as moderator and reflector. The reactor achieved criticality in November 1954 and operated 221 hours before being dismantled for examination.

The ensuing period between the successful operation of the ARE in 1954 and criticality of the MSRE in June 1965 saw a change from thinking of molten salt reactors in terms of military applications to the concept of their use as civilian power plants. The work on molten salt chemistry and materials development that took place during this period resulted in a vastly simpler core design than that of ARE.

Much of the complication of the ARE core came from the fact that the Inconel 600 tubes were necessary to separate the molten salt from the beryllium oxide moderator-reflector, which was not compatible with the salt. Graphite is also a good moderator, and the discovery that graphite and salt are compatible allowed the core to become a block of graphite with small holes for fuel passages. Assuming that the graphite is available, the big materials question becomes, What material can be used for the containment vessel and the other metallic parts of the system?

And this is where INOR-8 was used.

## **Requirements of a Structural Material**

One of the questions that we usually ask in choosing a material is whether it will corrode. This question applies equally well to many objects that we touch each day as well as to nuclear reactors. Rusty tin cans, pitted automobile trim, and tarnished silverware all represent various types of corrosion. The severity of corrosion can vary from the very thin oxide film that gives the penny its tarnished appearance to the complete dissolution that we observe when a penny is dropped in nitric acid. The former type of corrosion is ignored; the latter type is intolerable.

	Element	Most Stable Fluoride Compound	Stability*
Structural Metals	chromium	CrF <sub>2</sub>	72
	iron	FeF <sub>2</sub>	66
	nickel	NiF <sub>2</sub>	59
	molybdenum	MoF <sub>2</sub>	57
Carrier Salts	lithium	LiF	120
	sodium	NaF	110
	potassium	KF	108
	beryllium	BeF <sub>2</sub>	103
	zirconium	ZrF <sub>4</sub>	92
	boron	BF <sub>3</sub>	86
Active Salts	uranium	UF <sub>4</sub>	92
		UF <sub>3</sub>	93
	thorium	ThF <sub>4</sub>	99

\* Negative standard free energy of formation @ 800°C.

Table 1. Relative thermodynamic stabilities of fluoride compounds.

Fluorine is very reactive with metals, so many jump to the conclusion that the fluoride salts are equally reactive. The free energy of formation is commonly used to measure the stability of a compound; a compound is stable if the free energy is negative and the stability is greater the more negative the free energy. Table 1 shows the relative stabilities of several fluorides of interest, including the potential fuel salt constituents as well as the structural metals under consideration.

Since the fuel compounds are more stable than the structural materials, the salts and the metals should be satisfied with their respective roles and the corrosion rate should be low. However, the relative ranking of the metals indicates that nickel and molybdenum are least likely to form fluorides and that chromium is most likely. Thus, a reasonable container material for these salts would be a nickel or molybdenum base alloy with minimum quantities of chromium and iron. The question arises, Why not use pure molybdenum or nickel? Pure molybdenum is difficult to fabricate and is quickly relegated to the role of alloying addition to nickel to give strength. Pure nickel is quite weak at high temperatures and acutely sensitive to impurities such as sulphur and phosphorus and would not be suitable for use in an engineering system. Both

nickel and molybdenum oxidize rapidly at high temperatures and would have to be protected from exposure to air; alloying with chromium is normally used to alleviate this problem in nickel base alloys. We have already mentioned the Inconel 600 that was used in the ARE. However, this alloy corroded to depths of 10 mils in 1,000 hours when exposed to circulating salt at a maximum temperature of 1500°F and would not be suitable for a long-term application. The nature of the attack is shown in Figure 1.

The list of available commercial alloys was searched further. Two, Hastelloys B and W, satisfied the corrosion requirements, but "aged," i.e. became very brittle, after being heated for long periods of time.

## Development of INOR-8

This completed the screening tests on the available commercial alloys and all attention was turned toward developing a new alloy in late 1956. The application was still the ANP program where the service temperature was 1500°F. The requirements for this alloy were 1) good corrosion resistance to fluoride salts, 2) good oxidation resistance, 3) moderate strength and ductility at high temperatures,



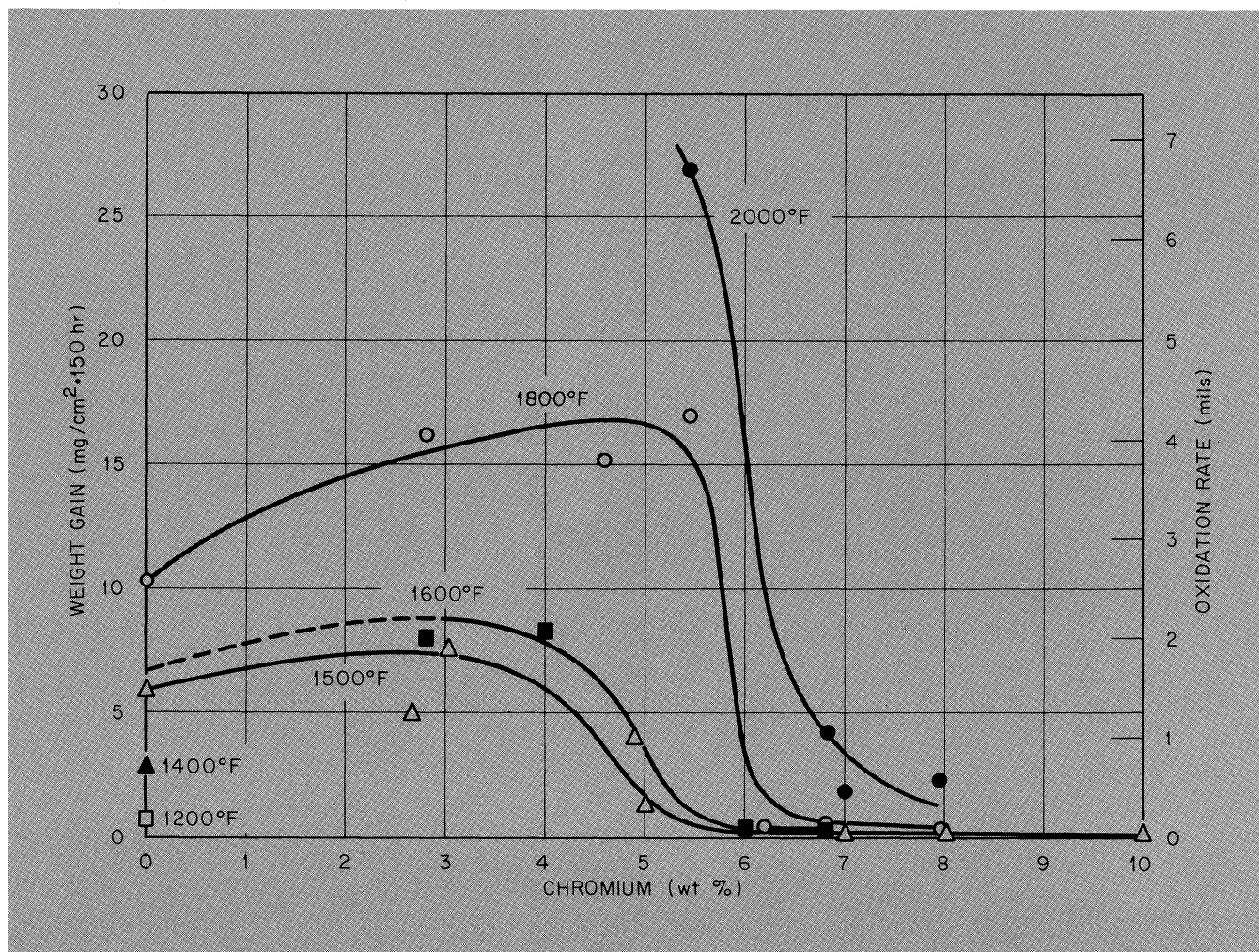


Figure 2. Variation of the rate of oxidation of an 80%Ni-20%Mo alloy with chromium content. Note the very sharp decrease in rate at chromium levels of 5 to 7%.

4) stable properties at the service temperature, 5) ability to be melted and fabricated into complex shapes, and 6) ability to be joined by welding and brazing. As you may have already gathered, such a program involved several experimental disciplines. We have already mentioned corrosion, mechanical properties, fabrication, joining and physical metallurgy. Fabrication in this case involved shaping 5-ton ingots into useful items like plate, pipes, rods and sheets, using such techniques as forging, rolling, swaging, extrusion, and drawing. Physical metallurgy is a term that covers about everything that is not included in the other terms, but its principal aspect here was a study of the stability of the various alloys by aging at temperatures of 1200°F to 1500°F.

This program was directed by W. D. Manly of Union Carbide; ORNL's H. Inouye served as the program's technical conscience in addition to being involved in much of the experimental work.

The facts accumulated at this point indicated that the alloy base should be nickel, with molybdenum (less than 20%) for strengthening, and some chromium for oxidation resistance (less than the 15% in Inconel 600). The melting practice used at that time introduced small amounts of manganese, silicon, boron, oxygen, nitrogen, and some iron since some of the chromium was charged as ferrochrome. The metals used for melting stock also contain small amounts of sulphur, phosphorus, carbon, and myriad other impurities since scrap from previous melts is quite often used. And so a commercial melt

becomes a multicomponent system, and the so-called scale-up from small laboratory to large commercial melts is an important and unforeseeable experience.

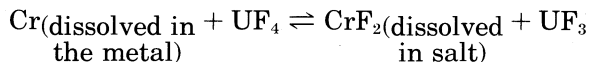
The largest portion of the development program spanned the years of 1956 to 1958. Small melts up to 100 lb could be made at ORNL and larger ones of 5,000 to 10,000 lb were made by Battelle Memorial Institute, International Nickel Company, Westinghouse, and Haynes Stellite. The small ingots were used as a screening step and larger melts were made of only the compositions that appeared attractive. (The screening step was taken because these alloys cost about \$6 per lb.) The large batches of metal, or "heats," were fabricated by the vendors with ORNL personnel on site in most cases. The fabrication data derived from this were extremely valuable to both parties involved, since this was an unknown alloy, of which a 10,000-lb mass had to be gotten to a useful shape. Fabrication was in the form of tubing for corrosion studies, sheet for mechanical property measurements, and thick plate for joining studies. The New England Testing Laboratory near Boston assisted in the mechanical property studies, and welding assistance was available from Rensselaer Polytech.

Hundreds of small melts were made by metallurgists at ORNL and large melts were made by the vendors of the alloys shown in Table 2. All of these alloys fabricated well except INOR-4. This alloy contained 1.5% titanium and 2% aluminum. These elements in this concentration form a very brittle intermetallic compound with nickel called "gamma prime." It forms the basic hardener in a series of nickel base alloys developed in recent years. Such alloys require special fabrication procedures not practicable for our purposes.

My casual mention that most of the alloys fabricated well does not pay adequate tribute to the team (Inouye, T. K. Roche, D. E. Rosson and G. Golston) who worked many hours at ORNL and in the fabrication shops of the vendors. At this time most of the tubing available was made by forming flat strips into a cylindrical shape and welding the contacting pieces together. This was called "welded tubing" and had a terrible reputation for being badly flawed. What we really wanted was a seamless tubing. The normal procedure for getting this is to deform an ingot some by forging (hammering), extrude this forged piece to obtain a tube shell (a crude pipe with a thick wall), and draw, i.e., stretch, this tube to obtain high quality, thinwalled tubing. The extrusion step was the difficult part. Extrusion

involves simply pushing the metal through a die to obtain a particular shape. This is what you do to tooth paste, but metals take a good deal more push. To minimize the energy required, the metal is usually heated nearly to melting point, transferred quickly to the extrusion press, and shoved through the die in a matter of a few seconds. This procedure, however, consistently gave scrap instead of a tube shell. One of the team, in a moment of inspiration, reasoned that the energy of extrusion alone could be enough to heat it up and might even exceed the melting point. The solution? Slow down the rate of extrusion. We ended up with good tube shells that were later drawn into miles of tubing by Superior Tubing Company.

The corrosion experiments on these alloys showed that the corrosion susceptibility increased in this order: iron, niobium, uranium, chromium, tungsten, and aluminum. It is very close to that predicted by the relative stabilities of the fluorides, i.e., aluminum would like to be a fluoride more than any of the elements listed and will be attached preferentially by a fluoride salt. Tungsten is the only element that fell appreciably out of place. The corrosion rates of alloys containing only nickel, molybdenum, iron and chromium were found to be quite acceptable. Jack Devan and Bob Evans showed by two very good tracer experiments that the corrosion rate of such alloys in a fluoride salt containing  $UF_4$  was controlled by the diffusion rate of chromium in the metal. The corrosion reaction involved chromium in the alloy reacting with  $UF_4$  in the salt to produce  $UF_3$  and  $CrF_2$ , both of which are soluble in the salt. This reaction can be written:



Alloy	Composition, % by weight (Base: Ni)						
	Mo	Cr	Fe	Ti	Al	Nb	W
INOR-1	20						
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		
INOR-7	16	6			1	1	
INOR-8	16	6	5				
INOR-9	17		5			3	

Table 2. Several promising nickel base alloys melted in the course of developing INOR-8.

Element	Content, % by weight*	
	Standard Alloy	Modified Alloy
nickel	Base	Base
molybdenum	15 to 18	11 to 13
chromium	6 to 8	6 to 8
iron	5	.1**
manganese	1	.15 to .25**
silicon	1	.1
phosphorus	.015	.01
sulphur	.020	.01
boron	.01	.001
titanium & hafnium	----	about 1% of each
niobium	----	1 to 2

\*Single values are maximum amounts allowed. The actual concentrations of these elements in an alloy can be much lower.

\*\*These elements are not felt to be very important. Alloys are now being purchased with the smaller concentration specified, but the specification may be changed in the future to allow a higher concentration.

Table 3. Chemical composition of INOR-8.

The reaction is temperature-dependent and the net effect is that chromium is removed from the hotter parts of the system and deposited in the cooler parts. Thus, the chromium level should be as low as possible to obtain the lowest corrosion rate in fluoride salts.

However, Inouye's studies of oxidation in air revealed a need for chromium. As Figure 2 shows, the oxidation rate decreased markedly as the chromium level was increased. In fact, as much as 6% chromium was required to obtain an oxide that was adherent and kept the metal from oxidizing too rapidly. And the need for 6% chromium was corroborated by the observation that of the alloys shown in Table 2 only INOR-7 and INOR-8 had acceptable oxidation resistance at 1500°F.

All of the alloys had adequate strength, because of the 15 to 20% molybdenum present. Titanium and aluminum increased the strength even further, but the gains in strength were not worth the fabrication problems mentioned earlier. The precise levels of chromium and iron did not affect the strength appreciably.

All of these alloys could be welded by the tungsten electrode with inert cover gas (TIG) process as long as the boron, sulphur and phosphorus levels were each below 0.01%. These are impurity ele-

ments and they can be kept at this level with reasonable care.

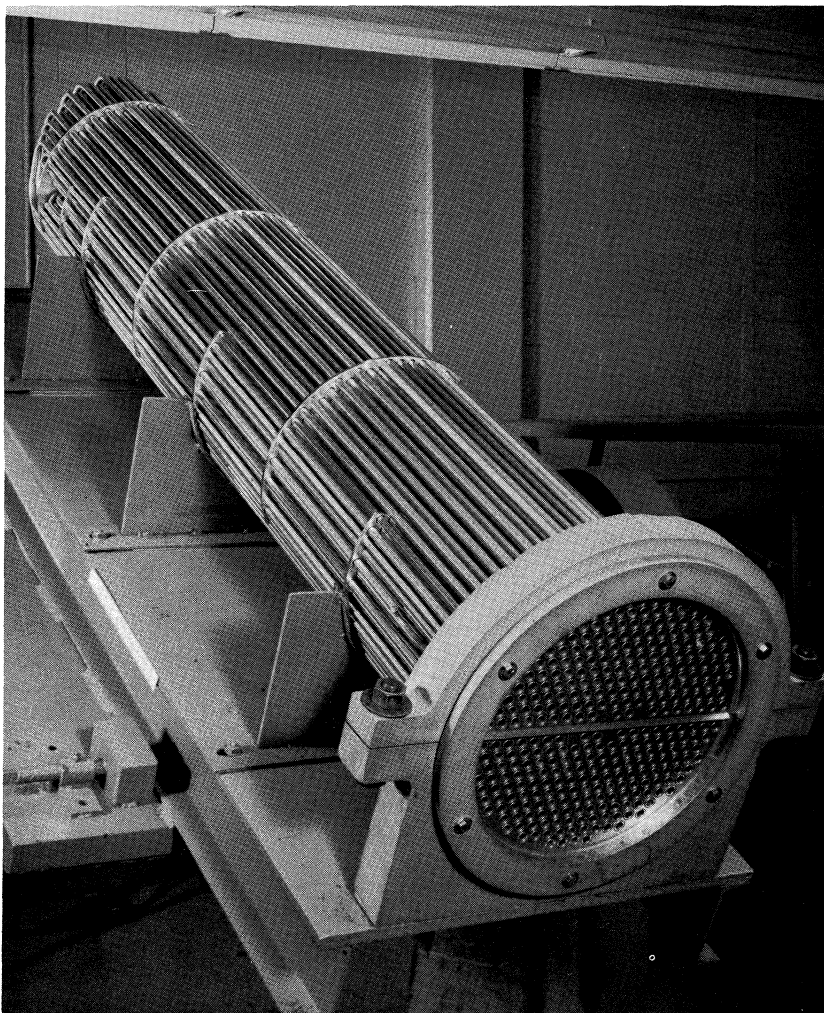
All of these factors led ultimately to the alloy composition specified in Table 3. The final composition is nearest to that of the experimental alloy INOR-8, which is how the alloy has always been known at ORNL. A patent application was filed on March 3, 1958 and patent No. 2,921,850 was issued on January 19, 1960 to H. Inouye, W. D. Manly, and T. K. Roche.

## Molten Salt Reactors for Civilian Power

The ANP program was discontinued in 1960 and the mission of the program was shifted to civilian power reactors and became known as the Molten Salt Reactor Program. A demonstration reactor was needed and construction on the Molten Salt Reactor Experiment (MSRE) began in 1961.

Very little additional development was done. Long-term corrosion experiments were conducted and the mechanical properties were measured on several heats procured for the MSRE to insure that the properties were equivalent to those measured for the development heats of INOR-8. One problem





*Figure 3. Completed tube bundle for the MSRE primary heat exchanger. The bundle consists of 163 half-inch OD tubes of INOR-8 joined to a 1½" thick header.*

worthy of mention developed in the form of cracks that occurred during welding. The cause of this was never determined, but as a consequence the heats of INOR-8 for the MSRE were purchased from Haynes Stellite (now Materials System Division of Union Carbide) on the specified condition that their weldability be first demonstrated by the vendor. The actual number of heats rejected as a result of this clause is not known, but we got the general impression that the markedly improved quality resulted from some revisions in the melting practice.

The fabrication of the metal components of the MSRE proceeded without major incident and the reactor went critical on June 1, 1965. The heat exchanger shown in Figure 3 gives an idea of the complexity of the structure. In all, some 100,000 lbs of INOR-8 went into fabricating the system. The performance of the MSRE has been extremely satis-

fying to all concerned and the role of INOR-8 in this success story is a vital one. We have removed several pieces of INOR-8 for examination and have not been able to detect any corrosion. In spite of this, however, the salt in the MSRE continues to pick up chromium from the metal, and the amount after about 30,000 hours at 1200°F is equivalent to removing the chromium from a surface to a depth of about 0.7 mil (a human hair is one to three mils thick).

### **Need for Improvement**

Since the MSRE was fabricated, we have found that INOR-8, like most iron and nickel base alloys, is embrittled by neutron irradiation. Metallurgists and solid state physicists have known for many

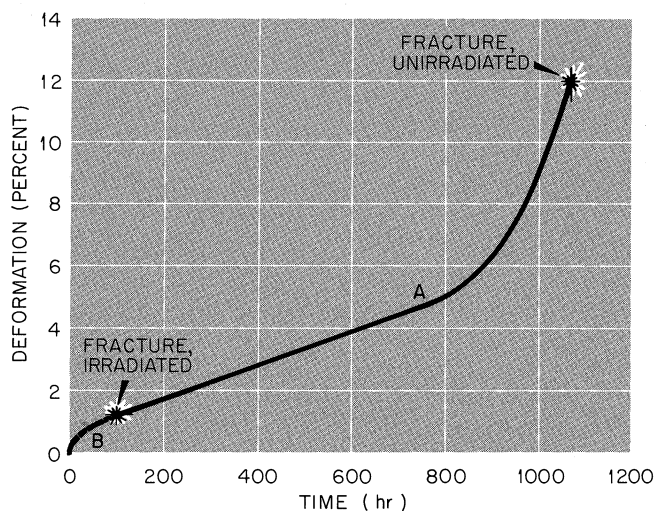
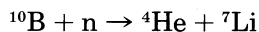


Figure 4. Results of creep tests on irradiated (curve B) and unirradiated (curve A) samples of INOR-8. The samples were stressed to 30,000 psi at 1200°F.

years that metals are hardened when they are irradiated at relatively low temperatures. This hardening is referred to as "displacement damage," since it is caused by atoms being displaced from their normal positions by neutrons. These displaced atoms interfere with the normal mechanisms of deformation and make the metals stronger. If the neutron irradiation occurs at higher temperatures, thermal motion enables the displaced atoms to return to their normal positions and no hardening is observed. This self-annealing temperature is about 1000°F for alloys such as INOR-8 and the general conclusion until about 1966 was that these materials could be used in a neutron environment at higher temperatures without significant change in properties.

However, more recent work has shown that this assumption was wrong and that the ductility of alloys such as INOR-8 at 1200°F is reduced drastically by neutron irradiation. This embrittlement has been attributed to the helium that is produced by the transmutation of boron-10. A thermal neutron reaction, it can be written:



Cyclotron injection experiments have shown that the damage is due to the helium rather than the lithium. Boron is present in these alloys as an impurity that comes primarily from the refractories used during melting ( $^{10}\text{B}$  constitutes only 18.2% of natural boron). The cross section for this transmutation is quite high and all of the  $^{10}\text{B}$  will be transmuted to helium in a molten salt reactor after a neutron fluence of about  $1 \times 10^{21}$  neutrons/cm<sup>2</sup>.

The exact mechanism by which helium embrittles these alloys is not understood, but ease of crack

propagation seems to be the most dramatic effect. This is best measured in the response of a metal sample to a sustained load in the irradiated and unirradiated conditions. Such tests are normally referred to as "creep tests," and simulate the type of loading experienced by a reactor vessel under steady-state operation. The load (force) or stress (force per unit area) is applied and the resulting deformation is observed. This deformation or creep will cause small cracks to form in the metal that eventually link together until the sample fractures. A well-behaved engineering material such as INOR-8 will respond as shown in curve A in Figure 4. When this same material is stressed while being irradiated, curve B is obtained. A lot of metallurgy is tied up in the shape of these curves, but the important fact for our analysis is that the curves are identical for the irradiated and unirradiated samples for the first 100 hours, or up to where the irradiated sample fractures. Thus, the processes that cause the stressed metal to deform (creep) are not influenced by irradiation, but the irradiated sample fractures in a shorter time owing to the easier propagation of cracks. This is illustrated further by the photomicrographs shown in Figure 5.

Tests were run to determine quantitatively the effects of this embrittlement on the materials used in the MSRE structure. These tests showed that the fracture ductility was reduced as the quantity of helium in the metal was increased by going to higher thermal neutron fluences. Another important observation was that the fracture ductility depended heavily upon how fast the metal was deformed. The lowest fracture ductilities occur at a deformation rate of about 0.1% per hour. Such high deformation rates would not be encountered normally in a reactor system but may occur during transients involving rapid change in temperature and pressure. The ductility then improves slightly as the deformation rate is reduced further to a more realistic rate of 0.001% per hour. (The MSRE was designed to deform at a rate no higher than 0.00001% per hour.)

The properties of INOR-8 are adequate for the MSRE where the anticipated thermal neutron fluence is less than  $5 \times 10^{19}$  neutrons/cm<sup>2</sup>. However, the design lifetime of a power reactor such as the Molten Salt Breeder (MSBR) is 30 years and the fluence on the vessel will be at least  $1 \times 10^{21}$  neu-



trons/cm<sup>2</sup>. The need for an alloy with better resistance to embrittlement, therefore, is evident.

### Reduce the Boron Content?

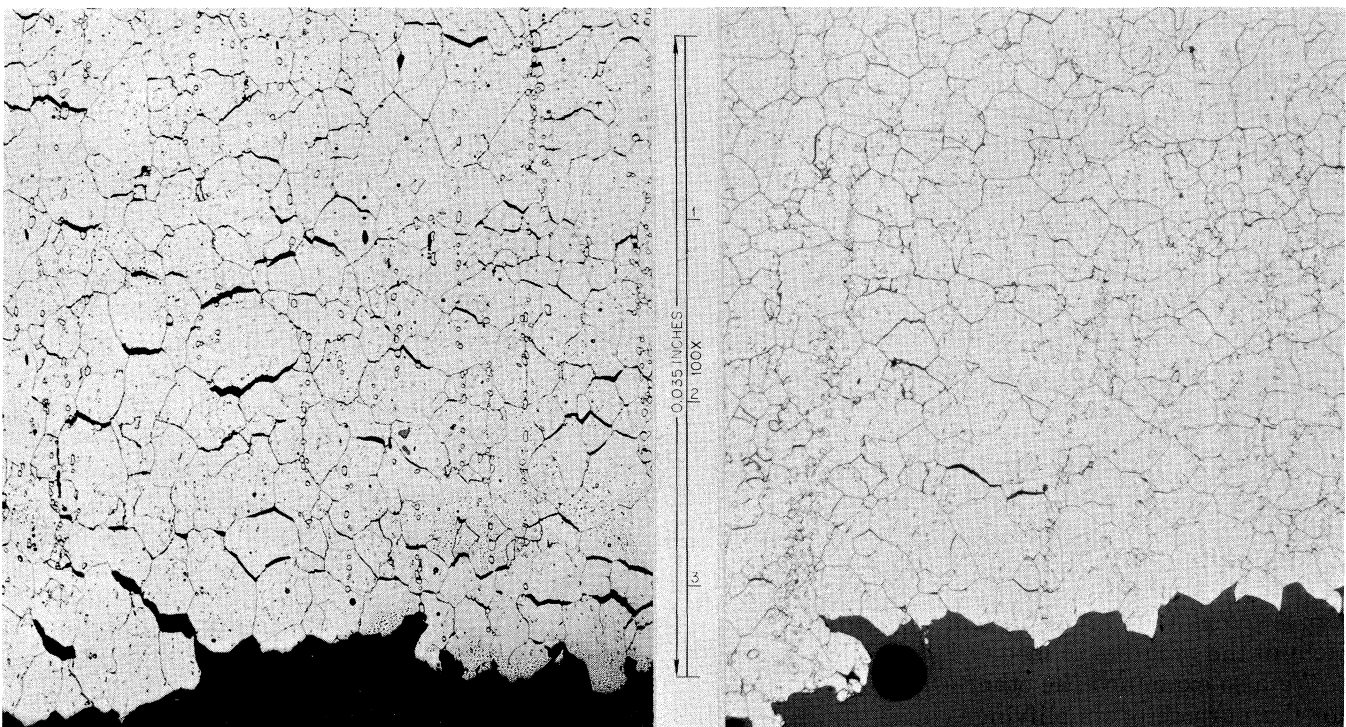
You might think the obvious solution to a problem that results from the presence of boron would be to get rid of the boron. And although at low deformation rates the fracture ductility is reduced from 30 to 3% by the presence of only 1 ppm helium, we pursued this avenue for a short time. The main source of boron is from the refractories (ceramic vessels) used in melting the alloys. The regular melting practice used in making the metal for the MSRE produced material with 20 to 50 ppm boron. By employing vacuum melting practice and using very pure components the content was reduced to 1 to 2 ppm, probably the lowest attainable by commercial vendors. We have even made small laboratory melts containing .02 ppm boron, but we found that even these alloys were very brittle after irradiation. Thus we have been forced to conclude

that the levels of helium required to embrittle this alloy are so low that reducing the boron level will not offer much improvement.

### Modification of the Chemical Composition

A closer look at the mechanism of embrittlement by helium reveals several other important characteristics. Metals are made up of grains, or small crystals. At low temperatures they usually fracture across the grains (intragranular) and at elevated temperatures they fracture along the grain boundaries (intergranular). Helium is embrittling to these alloys only in the temperature range where the fracture is intergranular. Since helium is nearly insoluble in metals and moves very slowly, it follows that only the helium that is generated near the grain boundaries can have an effect on the fracture process. Since the range of the transmuted helium atom is only about two microns in iron and nickel, the <sup>10</sup>B atoms must be located very near the grain boundaries. With the boron present in parts-

*Figure 5. Photomicrographs of the samples plotted in Figure 4. The irradiated sample on the right shows relatively few cracks that occurred before they linked together to cause fracture, in contrast with the unirradiated sample ( left ) which deformed 13% before fracturing but showed numerous cracks*

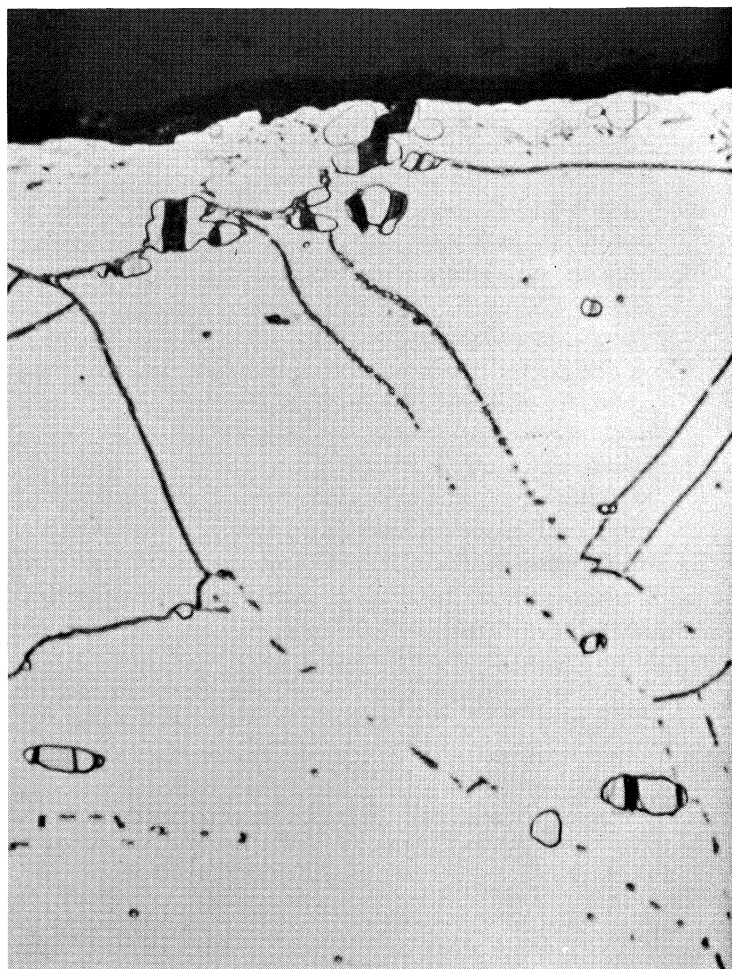


per-million concentrations the shattering effect it has is surprising. However, the boron atom is smaller than that of iron and nickel and is not accommodated easily in the crystal structure. Thus boron gravitates toward the grain boundaries where the arrangement of atoms is interrupted by the intersection of grains of different orientations. Hence, the laws of nature provide a mechanism for concentrating boron in a region where it is most detrimental.

One solution to this problem that seems reasonable is to add an element that will react with the boron to form a stable compound. Ideally, by suitable annealing, the compound could be deposited as fine precipitates located within the grains rather than at the grain boundaries. However, the location of the precipitates along the grain boundaries may be acceptable if the transmuted helium remains associated with the precipitate and does not influence the fracture process. Very fine precipitates along the boundaries can even retard the propagation of cracks and might prove beneficial from this standpoint. Hence, the key item in our thinking was to add small amounts of elements such as titanium, zirconium and hafnium that formed compounds with boron.

One thing to understand here is the extreme importance of the electron optic equipment that has only become available in recent years. An ingenious device, the microprobe analyzer, is capable of determining the chemical composition of an area about two microns in diameter, permitting analysis of both the precipitates and the surrounding areas (matrix). These precipitates can be extracted and collected by a process which involves dissolving away the matrix material. They can then be identified by x-ray diffraction, analyzed by normal wet chemistry techniques, or placed in the electron microscope for electron diffraction and for qualitative analysis by the microprobe attachment for this instrument. The metal can also be corroded with acids until it can be seen through by the electron microscope to determine its structure and the role that the precipitates play in deformation and fracture. Moreover, these same techniques can be applied to irradiated samples since very small amounts of material are involved. This work has been performed by R. E. Gehlback, J. O. Stiegler, R. S. Crouse, and H. V. Mateer and has been the key item in the program to modify INOR-8.

We also examined the other elements in INOR-8 for the purpose of simplifying the alloy as much as



possible. The microstructure shown in Figure 6 is characteristic of the standard Hastelloy N. The large precipitates are carbides of the  $M_6C$  (six metal atoms to one of carbon) type where M is 50% Mo, 40% Ni, 5% Cr, 1% Fe, and up to 4% Si. These particles are located in "stringers" in the metal, causing the grain size to be much smaller near the stringers. The particles themselves are very brittle, and fracture as the material is deformed. When the material is irradiated and is also relatively brittle these cracks can propagate to cause failure. The particles are too large to improve the strength, so we sought to eliminate these from the microstructure.

Our analysis of the matrix (excluding the precipitates) revealed that only about 12% of the Mo was actually dissolved in the alloy. The bulk of it went to form the massive  $M_6C$  carbides. We made several small melts with varying Mo content and found that alloys with 10% and 12% Mo were free of the massive precipitates and those with 14% and greater

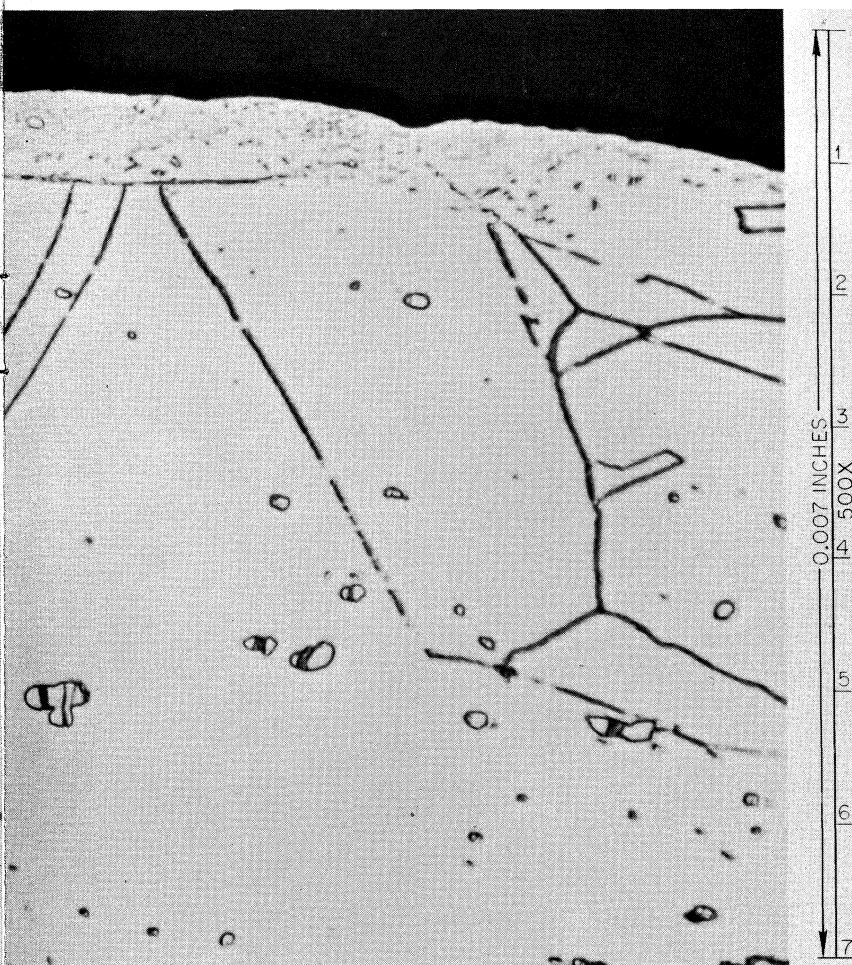


Figure 6. Polished cross section of a sample of INOR-8 deformed at 1200°F. The large carbide particles have fractured, and near the upper edge the fractures have resulted in a crack propagating to the surface.

Mo concentrations contained the precipitates. The strength penalty for decreasing the Mo content from 16% to 12% was modest enough and we decided to make this change in the alloy composition.

As mentioned previously the amount of chromium in the alloy was a compromise between resistance to oxidation and to salt corrosion. Hence, we did not alter the concentration of this element. The addition of chromium as ferrochrome also adds about 4% iron. We did not think the iron was harmful, but its elimination gave us one less variable.

Because of the very reactive elements (titanium, zirconium and hafnium) that we were adding, we chose to use the vacuum melting practice, in which the molten alloy is not exposed to air. This melting technique has become very common over the past few years and is preferred by most vendors for melting even standard INOR-8. The vacuum melting practice also reduces the amount of so-called "residual" elements introduced such as manganese,

silicon, boron, nitrogen and oxygen. Nickel-base alloys are notorious for being embrittled by small amounts of sulphur, so we retained some manganese in our specification to tie the sulphur up as a stable Mn-S compound. The other residual elements were kept as low as possible.

Recent work by C. E. Sessions has shown that the strength of INOR-8 depends very strongly on the carbon content. As the C is decreased below the normal (0.04% to 0.08%), the strength decreases dramatically; higher concentrations improve the strength gradually. Inouye had observed earlier that they could not fabricate tubing from material containing more than 0.1% C. These factors indicated that we should leave the carbon specification at 0.04% to 0.08%.

Our resulting modified alloy then contained 12% molybdenum, 7% chromium, 0.2% manganese, 0.06% carbon, and small additions of titanium, zirconium or hafnium.

*Figure 7. Transmission electron micrograph of a Ti-modified sample of INOR-8 irradiated at 1175°F and creep-tested at 1200°F.*

*The dislocations resulted from the creep test in which the sample deformed 5% before it fractured. The most important feature is the grain boundary lined with small MC-type carbide precipitates. These help to disperse boron and inhibit crack propagation along the boundary.*



## Properties of the Modified Alloys

Several small melts were made to investigate the effects of Ti, Zr and Hf on the mechanical properties after irradiation. (The behavior shown in Figure 7 is characteristic of the Ti addition.) These samples were irradiated at 1200°F and then tested in the hot cell to determine the strength and ductility after irradiation. Both parameters were improved dramatically as the titanium level exceeded 0.3% to 0.4%. Zirconium and hafnium brought about similar improvements.

We sought to keep the titanium, zirconium and hafnium additions as low as possible for two reasons. First, these elements depress the melting point of nickel-base alloys and can cause cracking in the early stages of a melt or during welding. A second reason is that these elements form brittle compounds with nickel. The exact levels required to achieve undesirable results were not known, so

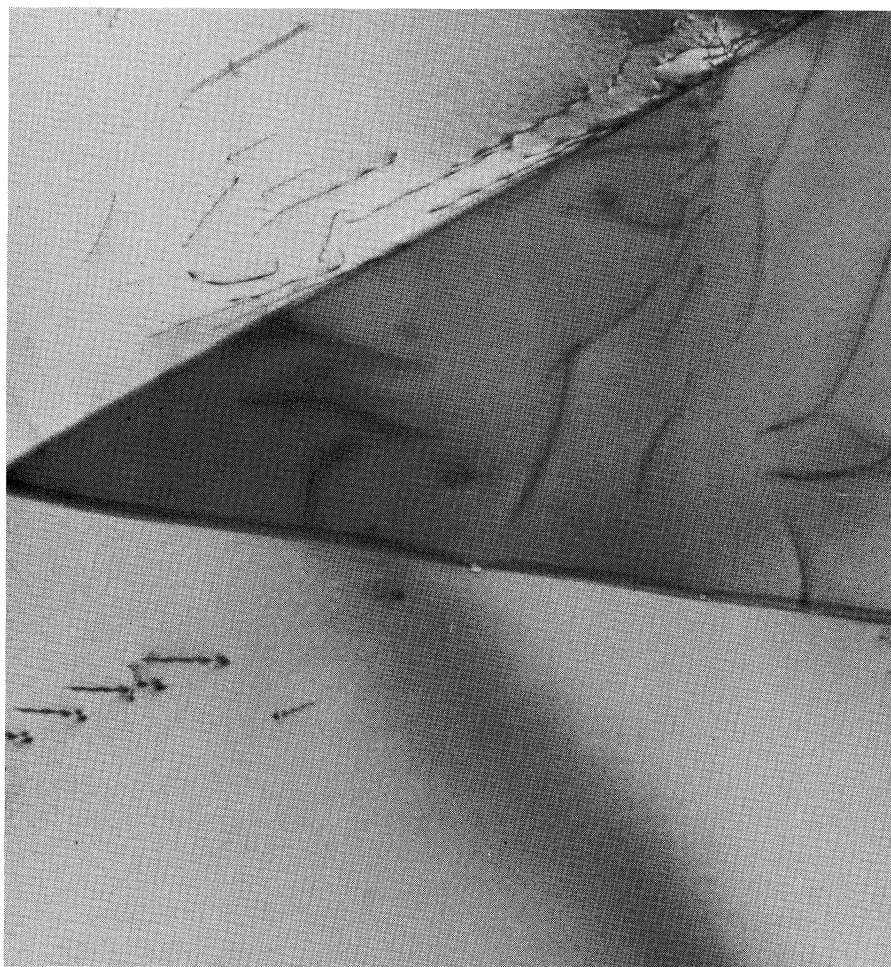
we started with very low concentrations.

We obtained a few 100-lb ingots from commercial vendors to have some plates for investigating the weldability. We found that the zirconium reduced weldability when only 0.05% was present. We did not investigate these alloys further. Alloys containing up to 1% Ti and 1% Hf had good weldability.

We could not afford to carry parallel development programs on alloys containing titanium and hafnium additions. Titanium is present in several iron and nickel base alloys, so we felt more comfortable with this addition and proceeded further with its development. Our development schedule for the near future included several 100-lb melts to study the effects of variations in titanium and carbon levels and one 5,000-lb melt. (The original development program for INOR-8 involved about 30 melts of this size, but today's austerity does not allow this approach.)

Our initial irradiation tests were carried out at





*Figure 8. Another sample of the same composition irradiated at 1300°F before creep-testing at 1200°F. This one deformed only 0.4% before it fractured, so fewer dislocations occurred. Much of the grain boundary lengths are free of precipitates and contain occasional helium bubbles. What few precipitates are present are coarse and of the  $M_2C$  type.*

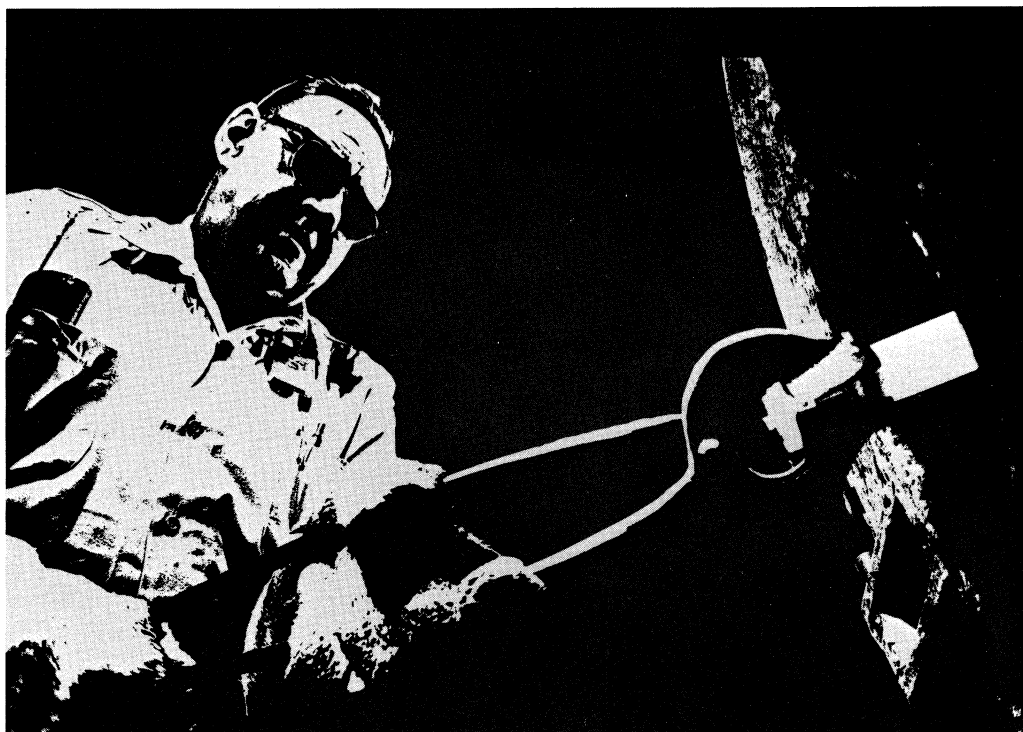
1200°F, operating temperature of the MSRE. The strength and fracture strain of the titanium-modified alloys were excellent after irradiation, and welding studies showed that they generally had good weldability. The single 5,000-lb melt fabricated well and about 50% was converted into useful products. This large heat had one idiosyncrasy: it cracked when welded with filler metal from the same heat. However, sound welds were made with eight other heats of filler wire and we were not concerned about the basic weldability of the titanium-modified alloys.

All seemed well with our new alloy until, anticipating that molten salt breeder reactors will operate at 1300°F, we irradiated some samples at higher temperatures. Much to our dismay, we found that the samples irradiated at 1300°F and higher reverted to about the same limitations as the standard alloy.

We examined thin sections of some of the irradiated samples in the electron microscope and found

that the microstructure varied dramatically with irradiation temperature. The microstructure shown in Figure 7 was noted after irradiation at 1175°F and creep testing at 1200°F. The most important feature is the grain boundary lined with very small particles. If you tried to shear this boundary, you would probably find that it is very strong and that these particles would make crack propagation difficult. These particles were found to be carbides of the MC type where M consists of molybdenum and the modifying elements added such as titanium, niobium, zirconium, or hafnium. A sample of the material irradiated at 1300°F and tested at 1200°F has the microstructure shown in Figure 8. The grain boundaries in this sample are free of precipitates for large distances and the precipitates present are relatively coarse. Occasional helium bubbles are visible along the grain boundaries. The precipitates in this sample are of the  $M_2C$  type with M being 90% molybdenum and 10% chromium.

*Hot swaging  
in ORNL's  
metals laboratory*



Recall that the proposed mechanism of embrittlement of this alloy during irradiation involves the accumulation of helium (from transmuted boron-10) at the grain boundaries. The fine precipitates formed at 1175°F would disperse the  $^{10}\text{B}$  and also provide a boundary that resists crack propagation. Both of these factors probably contribute to the good properties of the alloys containing the fine MC precipitate. The coarse  $\text{M}_2\text{C}$  type would not be effective in either regard.

Thus a critical part of our improved alloy seemed to be the fine MC precipitate and we looked at further chemical modifications that would make this carbide stable at higher temperatures. From our own work and from the literature, we compiled a list of those carbides which were favored by various alloying elements of interest. This list (Table 4) only indicates the trend, and the alloys have to be made to determine how much of each element is required to form the desired MC carbide. For ex-

ample, adding titanium favors the formation of the MC type, but we found in an alloy containing 0.5% Ti that MC was formed at 1200°F and that  $\text{M}_2\text{C}$  was formed after long periods of heating at 1300°F. This type of information could only have been gathered by making the experimental alloy.

We have irradiated several alloys containing various concentrations of the elements listed in Table 4. To date alloys having chemical compositions that cause the formation of the MC type precipitate have very good mechanical properties after irradiation. The properties of several of the more attractive alloys and those of standard Hastelloy N are compared in Figure 9. These alloys were all irradiated at 1400°F and retained their good properties. The properties of the alloy containing 1% Ti with 1% Hf are very good, and those of the alloy containing 0.5% Ti with 2% Nb are acceptable.

Further work will be required to decide the exact composition of the alloy to be used in future reactors. The information obtained from our small melts will be used to write specifications for several large 5,000-lb melts. These alloys will be tested to determine their strength and ductility after irradiation. Large sections will also be welded to insure that the alloys can be joined. These studies will lead to a final chemical specification that will be used for procuring materials for future molten salt reactors.

Elements	Type of Carbide Favored
Ti, Zr, Hf, Nb	MC
Cr	$\text{M}_{23}\text{C}_6$
Mo, W	$\text{M}_6\text{C}$ (high Si present)
	$\text{M}_2\text{C}$ (low Si present)

**Table 4. Carbide formation in Hastelloy N.**

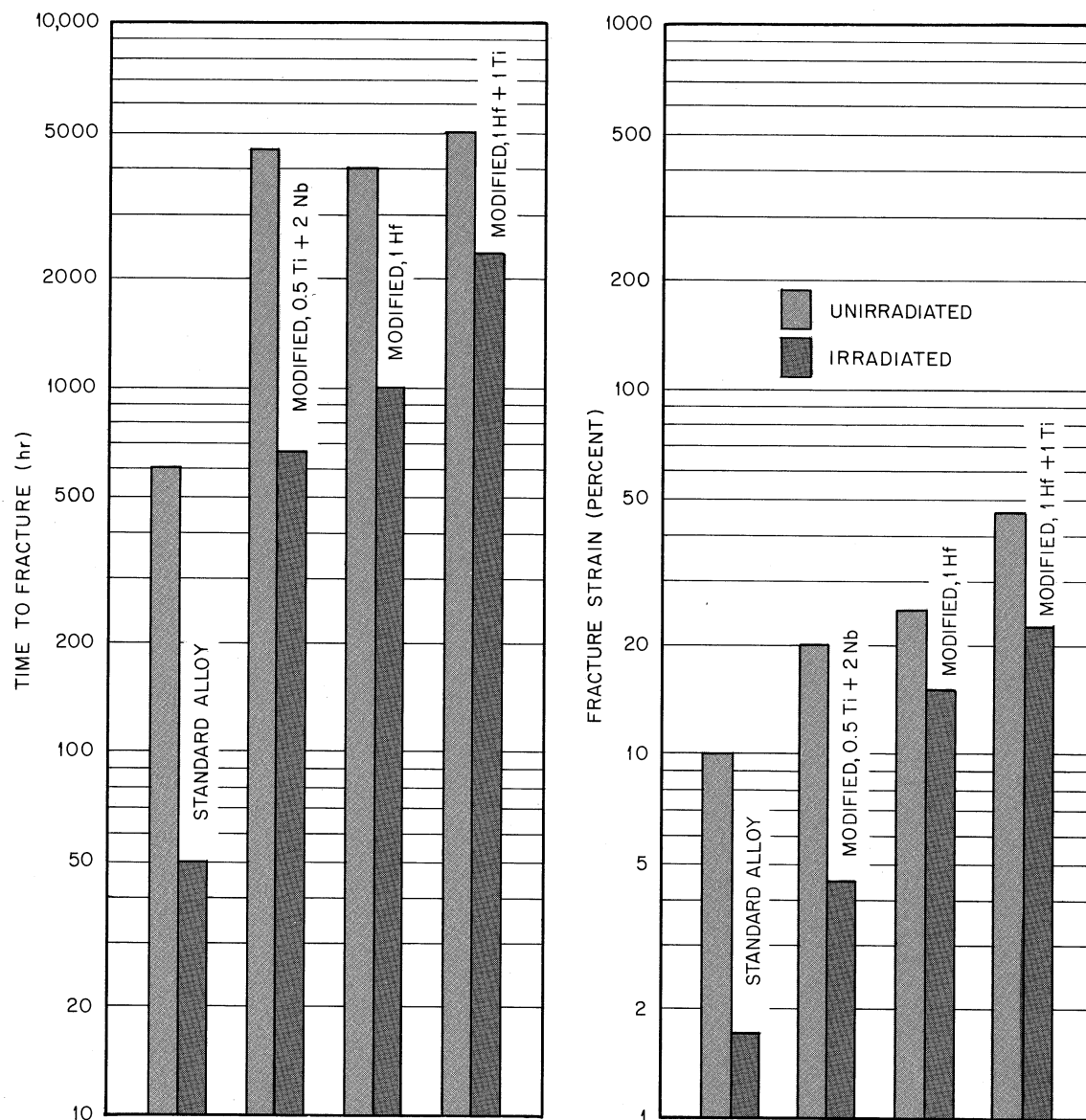


Figure 9. A comparison of the creep properties of standard INOR-8 and several modified alloys in the unirradiated and irradiated conditions. Test condition was a stress of 35,000 psi at 1200°F.