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HIGH TEMPERATURE CLADDING ALLOYS FOR REACTOR APPLICATIONS

by

J. F. Collins and J. A. McGurty

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Presented at the AIME-IMD Nuclear Metallurgy Symposium on Metallic Moderators and Cladding Materials, Philadelphia, Pennsylvania

October 19, 1960

GENERAL ELECTRIC

Facsimile Price \$ 2.60

Microfilm Price \$ 1.10

Available from the
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903/64

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ABSTRACT

For high temperature applications, fuel element cladding materials are required to protect the base metal structure and to contain the fuel so as to minimize fission product release and fuel loss.

The development of several metallic fuel element systems for air cooled reactors is reviewed and the high temperature properties of Type 310 stainless steel and Nichrome V clad fuel elements are discussed. Early work on cladding of molybdenum is reviewed and recent developments in ferrous-base alloys and chromium-base alloys as high temperature cladding materials are presented.

INTRODUCTION

The primary energy product of nuclear fission is heat. The problem has been to devise methods for converting such thermal energy into other useful forms. Great progress has been made in this field and further accomplishments are pending.

In general, the efficiency of any process for converting heat to other forms of energy (especially mechanical) is directly proportional to the temperature of the system. A nuclear heat source may exist in any one of the three physical states: gaseous, liquid or solid. An atomic bomb immediately after detonation is an example of the gaseous state. A homogeneous reactor in which the fuel is contained in a fused salt and heat is removed by means of heat exchangers is an example of the liquid state.

An example of the solid state is the swimming pool type reactor in which the fuel is contained in a stable aluminum matrix and water functions as the liquid coolant. Another example is the GE-ANPD Heat Transfer Reactor Experiment (HTRE-1) with air serving as the coolant.

Several operating reactors today are making use of solid stable fuel elements in combination with liquids or gaseous coolants to remove the thermal energy which is converted to mechanical energy external to the reactor. This review of high temperature cladding alloys is limited to such solid fuel element structures used in combination with gaseous coolants, primarily air. The intent is to summarize some advancements which have been made in the past ten years relative to metallic fuel element materials operating at temperatures above 1500°F.

Since we are primarily concerned with cladding materials it is well to define the functions of a fuel element cladding alloy. Since the fission of a nuclear fuel results in the release of radioactive substances or fission products, the cladding must contain within the solid fuel element structure such lethal radioactive particles which otherwise would contaminate the coolant. Thus, one of the primary functions of a cladding alloy is the retention of fission products.

The general concept of a high temperature fuel element core is based on the dispersion of uranium dioxide in a metallic matrix. This core composite must be protected from corrosion by the coolant, i.e. air. Thus another important function of an alloy is to provide oxidation resistance. Additionally, the cladding contributes to the structural strength and stability of the fuel element.

The requirements for a cladding material are rigorous. It must have a low neutron absorption cross-section, good thermal conductivity, adequate high temperature strength under irradiation, compatible thermal expansion, workability and weldability. In addition there must be a minimum of diffusion between the core and clad -- only enough to establish a permanent bond between the two materials.

The selection of materials for fuel element cladding depends on such considerations as type of reactor, temperature of operation, corrosiveness of coolant and availability of material. Stainless steel, Nichrome V and Inconel are useful materials for air cooled reactors at temperatures of 1500 to 1950°F. Above 2000°F the strength requirements are met only by refractory metals such as molybdenum, columbium, chromium and tungsten and these materials must be

protected from oxidation by a suitable coating or cladding material if they are to be used with an air coolant. The applications of stainless steel and nickel alloys to fuel elements are well established, whereas work on the clad refractory metals is limited by developments in the technology of refractory metal alloys, and is treated in less detail in the following.

STAINLESS STEEL

The stainless steels as a group comprise some 27 different types or compositions, including both austenitic and ferritic steels. The selection of any one of these 27 types for cladding of fuel elements or other reactor components must be based on all those requirements mentioned above, but primarily on its high temperature oxidation resistance and strength and its neutron absorption cross-section.

The most common types of stainless steels are those of the austenitic 18 chromium-8 nickel series which includes Types 302, 304, 316, 321 and 347. These steels are limited in strength and oxidation resistance to about 1550°F.

The more highly alloyed stainless steels, such as Type 309 (25 Cr-12 Ni) and Type 310 (25 Cr-20 Ni), have good heat resistance and strength to 2000°F but due to their higher nickel content have somewhat higher neutron absorption cross-sections than the 18-8 type steels.

The ferritic alloys contain chromium ranging from 12 to 27 percent and generally are nickel-free. These alloys have a low cross-section and the higher chromium alloys, such as Type 446, are heat resistant

to 2100°F. However, at temperatures above 1500°F, these ferritic alloys lose their strength rapidly with increasing temperature and unless used as a cladding over a strong base material would not be adequate for fuel element applications. The obvious choice for a fuel element having both core and cladding of stainless steel is Type 310 based on its combination of strength and oxidation resistance.

Commercial Type 310 stainless steel has a tensile strength of 95,000 psi at room temperature and 14,000 psi at 1800°F. Its thermal neutron absorption cross-section is a reasonably low $.252 \text{ cm}^{-1}$. The thermal conductivity of 310 stainless steel is one-tenth that of copper having a value of 10.8 Btu/hr/sq ft/°F/ft at 1500°F. It is readily fabricated into useful shapes and can be welded or brazed by any one of several techniques.

Fuel Element Concept

What is a stainless steel fuel sheet and how is it made? The early concept of heterogeneous fuel elements for a direct cycle reactor was that of thin sheets containing a dispersion of uranium dioxide fuel particles in the core with the thinnest possible cladding to contain the fuel. A typical section of this sandwich type fuel sheet is shown in Figure 1.

Fabrication Technique

This fuel sheet is made by first blending stainless steel powder with UO_2 powder of 10 to 44 micron particle size and pressing this powder blend in steel dies to form rectangular plates of suitable size and thickness. These core plates are sintered in dry hydrogen at 2200°F to consolidate the powder pressed compact and give it strength.

Fig. 1. Section of 310 stainless steel fuel sheet with .004 inch cladding over core containing 30% UO_2 as fuel dispersion. Sheet has been tested at 1800°F for 100 hours under 1000 psi stress.

This core containing the UO_2 fuel is enclosed in a picture frame as shown in Figure 2. The frame is made of 310 stainless steel and may be wrought material or more commonly is made by powder metallurgy and sintered around the core. Cladding plates of 310 stainless steel sheet stock are carefully cleaned and applied to both sides of the framed core in sandwich fashion. This billet is then hot pressed at high pressure and temperature in inert atmosphere to establish a bond between the core and cladding. The billet is then hot rolled at 1900°F to thin sheet, cleaned and cold rolled to final thickness ranging from .025 down to .012 inch. Such a fuel sheet may be 3 to 4 feet long. The cladding thickness of the final sheet is pre-determined by the ratio of core-clad thickness of the starting billet. Such fuel sheet has useful ductility and properties similar to standard 310 stainless steel sheet.

Fig. 2. Exploded view of fuel element billet using picture frame technique.

The earliest attempt to utilize the stainless steel-UO₂ dispersion type fuel element for high temperature applications was that of the Aircraft Nuclear Propulsion Project in 1951 and with the selection of the direct cycle reactor for development by GE-ANPD, the 310 stainless steel fuel element became highly developed and thoroughly evaluated. The following properties data resulted from the GE-ANPD evaluations conducted between 1952 to 1954. Although these data represent overall properties of clad fuel sheet, in most cases it is the 310 stainless steel cladding which provides the stability and is therefore on trial in these tests.

Tensile Strength of 310 Stainless Steel Fuel Sheet

Fuel sheet containing 10 volume percent UO_2 with .004 inch of cladding, overall thickness of .012 inch, has the tensile properties shown in Table I.

Table I. Short-Time Tensile Properties of 310 Stainless Steel Fuel Elements

<u>Temperature, °F</u>	<u>Ultimate Strength, psi</u>	<u>Elongation, pct.</u>
1500	23,000	11
1650	16,500	10
1800	12,000	13
2000	7,000	19
2200	4,800	16

Stress-Rupture Strength

Stainless steel fuel sheet as described above when heated in air at temperatures ranging from 1200 to 2000°F has the stress-rupture properties shown in Table II.

Table II. 100 Hour Rupture Strength of 310 Stainless Steel Fuel Sheet

<u>Temperature, °F</u>	<u>Stress, psi</u>
1200	15,000
1500	4,000
1650	2,200
1800	1,200
2000	680

However, at the higher temperature and especially at 2000°F, failure is caused primarily by oxide penetration rather than weakness of material, as will be shown in a later discussion of oxidation resistance.

Transverse Rupture Strength

In an effort to determine the magnitude of the fission gas pressure developed within the core of 310 stainless steel fuel elements at 1800°F as a function of fuel burn-up, a transverse rupture test was devised to determine the strength of the core of clad fuel sheet. Stainless steel shanks were brazed to coupons of 310 stainless steel fuel sheet, using a specially developed braze alloy which did not affect the mechanical properties of the fuel sheet.

Initially a series of such brazed fuel element specimens were subjected to tensile tests at temperatures ranging up to 1800°F to determine the core strength as a function of temperature. The ultimate strengths at rupture are shown in Table III.

Table III. Transverse Rupture Strength of 310 Stainless Steel Fuel Sheet

Room Temp.	17,685 psi
1200°F	14,680
1400	12,760
1600	11,750
1800	8,350
1800	7,950
1800	8,020

Rupture in each case occurred within the fueled core rather than at the interface or in the brazed joint.

A series of eight such fuel element specimens were irradiated at room temperature in the Low Intensity Test Reactor (LITR) to produce a fuel burn-up of 0.4 percent. Tensile tests were then conducted at 1800°F in the hot cells at Oak Ridge National Laboratory (ORNL).

The rupture strength of the cores which were irradiated ranged from 6925 to 8100 psi at 1800°F while unirradiated specimens had core strengths ranging from 7950 to 8350 psi. In general, while the average strength of the irradiated fuel sheet was lower than the unirradiated fuel sheet, there was no indication that irradiation significantly affected the core strength of 310 stainless steel fuel sheet.

Oxidation Resistance of 310 Fuel Sheet

When fuel sheet clad with .004 inch of stainless was heated in air under a load of 1000 psi, the intergranular oxide penetration in 100 hours at temperatures of 1500 to 1800°F measured as follows:

1500°F	.0004 inch
1650	.0008
1800	.0030

From this preliminary data it became apparent that the limitations of this material were set by the degree of intergranular penetration rather than by mechanical properties.

A graphical presentation of the operating limitations of Type 310 fuel sheet is shown in Figure 3. Failure is defined as oxide penetration in excess of .002 inch. If operating conditions of stress and temperature fall above the lower line failure may be expected short of 100 hour design operating life. Between the two lines is an area of uncertainty. For example, in order to operate safely for 100 hours under 1000 psi stress the fuel ribbon temperature must not exceed 1740°F.

Fig. 3. Operating limitation for 100 hour life for 310 stainless steel fuel ribbon based on oxide stringer penetration.

Fission Product Retention of 310 Stainless Steel

After a series of successful tests of 310 stainless steel fuel element plates under irradiation, a multi-stage fuel element assembly of enriched stainless steel fuel ribbon was tested in the Materials Test Reactor (MTR) in 1953. This test assembly was operated at 1550°F for 100 hours with flowing air as the coolant. The burn-up was 1.26 percent under a flux of 4×10^{13} n/cm²/sec with no fission product release detected and no damage to the fuel element specimen. This was the first physical demonstration that a metallic fuel element could be designed and fabricated to operate as an elevated temperature, high flux, direct cycle fuel element.

Applications for Stainless Steel Fuel Sheet

The fabrication of 310 stainless steel fuel ribbons into specific designs is relatively simple and straightforward by brazing. A boron-free braze alloy was developed at GE-ANPD specifically for reactor application and is now designated as GE-81.* This braze material is applied to the joint as a powder dispersed in an organic vehicle and when heated to 2200°F in hydrogen flows into the joint to make a fillet braze. A typical joint between two pieces of stainless steel fuel sheet is shown in Figure 4. By this technique configurations such as corrugations or honeycomb structures can be fabricated into strong, oxidation resistant fuel elements. A plate and fin type of brazed fuel element assembly is shown in Figure 5. Type 310 stainless steel fuel elements are as easily formed into complex shapes as 310 sheet stock.

While the foregoing discussion has been concerned only with sheet type fuel elements, stainless steel has been used for other types of fuel elements such as rods, pins, wire and pebbles. A number of operating reactors today are using stainless steel clad fuel elements of various configurations with satisfactory performance.

NICKEL-BASE ALLOYS AS CLADDING MATERIALS

As a family the nickel-base alloys include several hundred compositions designed for a wide variety of applications. Nickel-base alloys are among the strongest materials known for high temperature service combined with good corrosion resistance. Nickel itself forms an adherent oxide film at temperatures of 1400°F and resistance to further oxidation at higher temperatures makes the metal

*Composition of GE-81 is 70 Ni-20 Cr-10 Si

Fig. 4. Brazed joint between two sandwich fuel element sheets of Type 310 stainless steel. No trace of the original surfaces between the two components remains.

Fig. 5. A brazed plate and corrugated fin type fuel element of Type 310 stainless steel.

useful to 2000°F. Alloying nickel with chromium makes its oxidation resistance superior to pure nickel and forms the basis for a series of heat resistant alloys. High temperature alloys of particular interest are those commonly known by their trade names as Inconel, Nimonic 80, Hastelloy A and Nichrome V. Inconel is an alloy of 77 nickel-15 chromium-7 iron and Nichrome V is an 80 nickel-20 chromium alloy. Both of these alloys are attractive as cladding materials because their oxidation resistance is good to 2200°F and their strength does not decrease rapidly at elevated temperatures. Nimonic 80 and Hastelloy A are high strength alloys but do not have as good oxidation resistance as Nichrome V.

Nichrome V has long been used for electrical heating elements operating as high as 2200°F. Its tensile strength is 100,000 psi at room temperature and 15,000 psi at 1800°F. Its thermal conductivity is 7.75 Btu/hr/sq ft/°F/ft (450°F). Nichrome V is ductile and easily worked at room temperature. It can be welded with ease. Its neutron absorption cross-section is 4.5 barns/atom which was once regarded as too parasitic for use in an efficient nuclear reactor, but as designs were modified and higher fuel loadings were found to be feasible, the cross-section of Nichrome V became acceptable.

Inconel is similar to Nichrome V in its mechanical properties and high temperature oxidation resistance. The choice of Nichrome V over Inconel for fuel element cladding would be based only on the slightly better quality and workability of Nichrome V.

The first application of Nichrome V to fuel elements was in the fabrication of wire type fuel elements. This consisted of .020 inch diameter wire containing a .012 inch diameter core bearing the dispersion of the UO_2 fuel and a .001 inch cladding of Nichrome V. This type fuel element was made by blending powders of nickel and chromium with UO_2 , pressing this powder blend into $3/8$ inch diameter slurs and sintering in dry hydrogen at 2200°F for 3 hours. These sintered cores were then pressed into the bore of Nichrome V capsules and a plug was welded in place to seal the assembly. The capsules were then hot rod rolled or swaged at 1850°F to 8% reduction and from this point the material could be cold drawn to .020 inch wire by making intermediate anneals in hydrogen at 2000°F . A section of such a wire fuel element is shown in Figure 6 with the UO_2 dispersion encased in a layer of Nichrome V.

Fig. 6. Section of Nichrome wire fuel element containing 30 percent UO_2 .

As a result of its success in wire fuel elements and because of its potentially superior elevated temperature strength and oxidation resistance, Nichrome V was investigated as a substitute for 310 stainless steel in fuel ribbon.

Fabrication procedures were quite similar to those of 310 stainless steel fuel sheet previously described. The cladding and core were of the following composition:

<u>Cladding</u>		<u>Core</u>	
Cr	19.34%	Cr	20.0%
Si	1.35	Ni	80.0
Fe	0.67	plus 30 w/o UO ₂	
S	.006		
C	.036		
Ni	Balance		

Ribbons were hot and cold rolled to .012 inch thickness with .004 inch of cladding. Such fuel sheet when fully annealed in hydrogen at 1850°F has excellent ductility and workability.

Tensile Properties of Nichrome V Clad Fuel Sheet

Tensile data were obtained for .012 inch thick Nichrome V fuel sheet over the temperature range of 1200 to 2000°F. These data are presented in Figure 7 and show that the short-time tensile strength of Nichrome V fuel sheet is about 10 percent less than that of Type 310 stainless steel fuel sheet. Tensile tests of Nichrome V fuel sheet having higher core-to-clad thickness ratios and overall thickness up to .026 inch showed somewhat higher strength in the 1600-1800°F temperature range. However, the strength of fuel sheet is little more than half the strength of wrought Nichrome V stock.

Fig. 7. Tensile properties of Nichrome V fuel ribbon based on .012 inch stock, 30% UO_2 in central .004 inch core.

Stress-Rupture Properties of Nichrome Clad Fuel Sheet

Stress-rupture tests were conducted in air at temperatures of 1650, 1800 and 2000°F. These data are shown in Figure 8 in comparison with 310 stainless steel fuel ribbon. It will be noted that an increase in stress or temperature can be tolerated in the vicinity of 10 hour rupture life if Nichrome V is substituted for 310 stainless steel. For 100 hour rupture life under 1000 psi, Nichrome V will withstand 2000°F whereas 310 stainless steel is limited to 1850°F under these conditions.

Fig. 8. Comparison of stress-rupture properties of Nichrome V fuel strip with those of 310 stainless steel fuel strip.

While 310 stainless steel can be subjected to higher loads for short periods of time, for the long term test Nichrome V is superior.

Oxidation Resistance of Nichrome V

Stress-oxidation test data for Nichrome V fuel ribbon (.012") was obtained at 1800, 1900 and 2000°F at 1000 psi for 100 hours. The maximum oxide penetration was .0014 inch at 1800°F, .004 inch at 1900°F and .005 inch at 2000°F. However, the specimens run at 2000°F were brittle and approaching failure. It was apparent that the

maximum operating temperature should not exceed 1900°F since under these conditions (1000 psi for 100 hours) the oxide stringer penetration could contact the fuel-bearing core.

The oxidation of Nichrome proceeds by three modes of attack. In addition to uniform surface attack and oxide stringer penetration, small local voids develop internally. There is some evidence that the voids are associated with the presence of a second phase detected in Nichrome fuel sheet.

Since oxide stringer penetration is a criterion for performance of Nichrome clad fuel ribbon under stress and temperature, then a curve, such as Figure 9, can be utilized to determine safe operating conditions. For 100 hour operation under 1000 psi stress, Nichrome fuel ribbons should not exceed 1830°F. This is an advantage of 90°F over 310 stainless steel fuel elements. If design stresses can be limited to 500 psi then Nichrome fuel elements might be operated as high as 1950°F.

Since strain and oxidation resistance of Nichrome are interrelated, strength data such as short-time tensile or stress-rupture figures are misleading to the designer since they do not reveal the true operating life of a fuel element. Extensive testing of Nichrome V in air at elevated temperatures established that the material, when subjected to elongations greater than 5 percent, suffered accelerated intergranular oxidation leading to early failure. In a period of 100 hours at 1850°F, oxide penetration of .003 inch may occur in a sheet which shows 20 percent elongation, but if the elongation is less than 5 percent the penetration measures only .0005 inches.

Fig. 9. Stress-temperature limitations for 100 hour operation of Nichrome fuel ribbon (.012").

It is important then that the designer know the stress levels that will provide an elongation no greater than 5 percent at a particular operating temperature. Such data was derived from a series of 100 hour stress-oxidation tests conducted over a range of temperatures from 1600 to 2200°F. From a series of elongation versus stress curves, the stresses to produce 2 and 5 percent elongation in 100 hours at each test temperature were determined. These data are shown in Figure 10 and indicate that for 1900°F operation the Nichrome fuel element should be designed for a stress of 500 psi. From these data it would also appear that Nichrome V is useful as a fuel element material to 2200°F provided a stable, low stress structure could be provided.

Fig. 10. Stress to produce elongations of 2% and 5% and rupture in 100 hours for Nichrome V sheet as a function of temperature.

Applications

Thousands of feet of Nichrome fuel ribbon have been produced by GE-ANPD in the past few years and hundreds of fuel element cartridges have been fabricated and joined by brazing with GE-81 (Ni-20 Cr-10 Si). The first air-cooled reactor experiment, HTRE-1, was operated in 1956 using Nichrome fuel elements. This reactor was operated for 105 hours at a fuel element temperature of 1750°F and 39 hours at 1860°F with no serious defects in the Nichrome fuel elements. Two additional high temperature reactors have been built around Nichrome fuel elements by GE-ANPD and operated at the predicted power levels.

CLADDING OF MOLYBDENUM FUEL ELEMENTS

Historically molybdenum was one of the first materials to receive attention for high temperature nuclear reactors because of its high strength, low parasitic cross-section and dimensional stability. As a fuel element material molybdenum would be excellent provided that it could be completely protected from oxidation at elevated temperatures. It was early recognized that molybdenum held no promise unless an oxidation resistant alloy of molybdenum or a self-healing cladding material could be developed. The problem was especially amplified in the case of fuel elements which required thin sections with cladding layers limited to .005 inch thickness. The catastrophic oxidation caused by the volatile molybdenum oxides will originate at the smallest pin-hole in the cladding and quickly destroy the fuel element structure.

Many years of research work have been expended on the problem of cladding molybdenum suitable for high temperature service and even in those applications where a heavy cladding thickness was permitted, such as jet engine parts, the bonding problems, interface reactions and fabrication difficulties have generally discouraged further efforts.

For fuel element applications, various cladding materials were investigated and included such high temperature alloys as Inconel, nickel, Type 446 stainless steel, Type 310 stainless steel and platinum-10 rhodium. Plate-type fuel elements were fabricated by sintering molybdenum-UO₂ cores at 2900°F, then framing with stainless steel and hot pressing to establish a bond between the cladding

plates and the molybdenum core. This hot pressed billet was then hot rolled to thin sheet. Due to mismatch of thermal expansion properties, the stainless steels proved difficult to bond to molybdenum and were discounted early. Both Inconel and nickel formed an intermetallic phase of nickel-molybdenum which caused a brittle bond at the core-clad interface of the final sheet. A good bond was obtained with platinum-10 rhodium alloy, but from the standpoint of nuclear properties and economics, platinum was not seriously considered.

The tensile strength of Inconel clad molybdenum sheet tested at 2000°F proved to be 15,000 psi, about double that of Nichrome or stainless steel fuel sheet. On thermal cycling tests, Inconel cladding with an intermediate layer of nickel protected molybdenum for 100 hours (40 cycles) at 2000°F but at 2200°F, the life was shortened by the catastrophic oxidation problem. Some 35 metals and alloys were surveyed for their corrosion resistance to molybdenum trioxide at 1800°F and only the high nickel alloys were found to offer suitable resistance. However, no evidence of self-healing in the event of a flaw in the cladding was found and after two years of efforts to develop a clad molybdenum fuel ribbon, the work was terminated by GE-ANPD in 1954.

IRON-CHROMIUM-ALUMINUM ALLOYS

For high temperature oxidation resistance, aluminum-bearing ferritic alloys are unsurpassed. The formation of an aluminum oxide coating on the surface provides a barrier to oxide penetration at temperatures as high as 2500°F. The iron-25 chromium-5 aluminum alloy is

a material of this type and is especially attractive for fuel element cladding because of its low neutron absorption cross-section (2.1 barns/atom), good heat transfer properties and excellent oxidation resistance. However, the iron-chromium-aluminum alloys are ferritic and above 1100°F they lose strength rapidly with increasing temperature, as shown in Table IV. Therefore, this alloy is of little value for a heterogeneous fuel element for high temperature reactors. A program conducted at Battelle Memorial Institute⁽¹⁾ was concerned with strengthening iron-chromium-aluminum alloys by solid solution alloying of additional elements without compromising the excellent oxidation resistance at 2200°F. It was found that tantalum (5-10%) was the most effective strengthener while columbium (2-5%) and palladium (5%) resulted in some strengthening at 2200°F. But the best iron-chromium-aluminum alloy developed was considerably inferior in strength to Inconel. However, for applications as a high temperature cladding material, where strength is of minor importance, the iron-25 chromium-5 aluminum alloy has found wide application. The one disadvantage to iron-chromium-aluminum alloys is the difficulty in fabrication. Even the best vacuum melted alloys have poor formability, are difficult to weld and become coarse-grained and brittle upon prolonged heating.

(1) Saller, Stacy, Eddy - Investigation of Wrought Iron-Chromium-Aluminum Alloys for Service at 2200°F, BMI-922, June, 1954.

Table IV. Short-Time Tensile Properties of Wrought Iron-25 Chromium-5 Aluminum Alloy

Vacuum melted material, hot rolled to .040 inch sheet. Fully annealed at 2200°F in hydrogen.

<u>Temperature, °F</u>	<u>Ultimate Load, psi</u>	<u>Elongation, pct. in 2 inches</u>
Room Temp.	61,000	4.3
500	67,175	33
1000	55,420	15
1250	24,000	6
1500	10,000	19
1800	3,400	25
2000	1,950	27
2200	1,430	44
2300	940	54

CHROMIUM-YTTRIUM ALLOYS

Among the higher temperature refractory metals probably chromium offers the most resistance to oxidation and even this is far from adequate for long time protection at high temperatures. The normal chromium oxide film is no barrier to either oxidation or nitrogen penetration at temperatures above 2000°F. It was found that yttrium and certain related rare earth elements are effective for improving the barrier properties of chromium oxide to both nitrogen and oxygen penetration to temperatures as high as 2500°F.⁽²⁾ Although the solubility of yttrium in chromium is less than 1 percent, the effect of this small amount on the ability of chromium to withstand high temperatures is remarkable. Since the chromium-1 yttrium alloy has a melting point above 2800°F it offers a strong potential as a cladding alloy for refractory metals.

(2) "Applications of Rare Earths to Ferrous and Non-Ferrous Alloys" by J. F. Collins, V. P. Calkins and J. A. McGurty, Presented at ASM-AEC Symposium on Rare Earths, Chicago, November 2, 1959.

This chromium-1 yttrium alloy has been fabricated as .040 inch thick sheet stock for cladding applications and if prepared of high purity chromium has sufficient workability to be roll formed into small rings, as shown in Figure 11.

Fig. 11. Rings of chromium-1 yttrium alloy roll formed at 1800°F to 0.75 inch diameter.

At 2300°F this chromium-yttrium alloy sheet gains only 8 milligrams per square inch in 100 hours, the nitrogen absorption is less than 200 opm and the oxide penetration measures less than .001 inches. Further improvements in oxidation resistance have been made by third element additions of aluminum or thorium but at the expense of workability.

The chromium-1 yttrium alloy has sufficient strength that a useful structural material might be developed, but its immediate application is as a coating for the stronger refractory metals.

SUMMARY

For gas-cooled reactors the operating temperatures of fuel elements are being pushed to the endurance limits of metals. The design engineer and nuclear metallurgist are more or less limited to the materials summarized in Table VI.

The stainless steel fuel elements of eight years ago hardly begin to meet today's requirements from the viewpoint of either strength or oxidation resistance.

The Nichrome V fuel element has performed well at temperatures to 1900°F but is limited to less than 2000°F by oxidation effects.

Molybdenum has more than adequate strength for high temperature fuel elements, but the problem of adequate protection from rapid oxidation has not been solved.

Ferritic alloys, particularly the iron-chromium-aluminum alloy, have low strength but offer excellent oxidation resistance as a cladding material over high strength refractory metals.

For very high temperatures where the materials engineer normally turns to ceramics, the chromium-1 yttrium alloy is a strong contender for cladding over refractory metals capable of high performance.

The ability of metallic claddings to contain nuclear fuels in a stable matrix for useful reactor applications is an established fact. In addition, the claddings, such as those discussed in the preceeding, are capable of providing protection of the fuel against

Table VI. Summary of High Temperature Cladding Alloys for Nuclear Applications

Cladding Alloy	Nom. Composition	Density g/cc	Neutron Absorb. Cross-Section cm ⁻¹	Melting Temp. °F	Tensile Strength @ 1500°F 1000 psi	Oxidation Temp. Limit, °F	Relative Workability
Type 304 SS	18 Cr-8 Ni	7.9	.230	2600	19.4	1650	Good
Type 309 SS	25 Cr-12 Ni	7.8	.238	2625	26.6	2000	Good
Type 310 SS	25 Cr-20 Ni	7.9	.252	2580	25.4	2100	Good
Type 316 SS	18 Cr-12 Ni-3 Mo	7.9	.285	2550	27.5	1700	Fair
Type 347 SS	18 Cr-10 Ni-1 Cb	8.0	.237	2550	23.0	1700	Good
Type 446 SS	27 Cr	7.6	.213	2680	8.0	2050	Fair
Inconel	80 Ni-14 Cr-6 Fe	8.5	.365	2580	27	2200	Good
Nichrome V	80 Ni-20 Cr	8.4	.369	2550	36.5	2100	Excellent
Nimonic 80	Ni-20 Cr-5 Fe-2 Ti	8.2	.364	2550	72	1550	Good
Hastelloy A	Ni-20 Mo-20 Fe	8.8	.315	2420	45	2000	Fair
Fe-Cr-Al	Fe-25 Cr-5 Al	7.2	.191	2750	10	2300	Poor
Cr-1 Y	Cr-1 Y	7.2	.305	3400	30	2300	Poor

attack in air environments. Certainly similar chemical protection is possible against other corrosive environments, such as those encountered in liquid metals, liquid salts and other gaseous environments.

It is also apparent from the foregoing that the usefulness of metal claddings as a container of nuclear fuels is limited by chemical stability problems and the problems of fuel containment or fuel stability. It will be interesting to learn to what high temperature levels such metallic claddings may be heated for applications where the coolants are nonreactive gaseous substances. The melting point of tungsten is above 6000°F and nuclear fuels, such as UO₂, have melting points of about 5500°F. Is it possible that metal claddings may provide protection for fuels to such high temperatures? The answer to this stimulating question is intriguing workers in this field.

ACKNOWLEDGEMENT

The authors are indebted to Dr. J. R. Lewis and members of his staff at GE-ANPD who determined much of the properties data for Type 310 stainless steel and Nichrome V fuel sheet presented herein.

AIRCRAFT NUCLEAR PROPULSION DEPARTMENT

GENERAL ELECTRIC