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THERMOCOUPLES FOR CONDITIONS OF AGGRESSIVE ENVIRONMENTS

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THERMOCOUPLES FOR CONDITIONS OF AGGRESSIVE ENVIRONMENTS
THERMOELEMENTE FüR SCHWERE UMWELTBEDINGUNGEN

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SUMMARY

Two new kinds of thermocouples have been chosen for temperature measurements in the in-pile safety program for light water reactors performed in France. They must give fuel centerline or rod cladding temperatures and withstand steam oxidation between 1000°C and 1800°C or higher, under Severe Fuel Damage conditions.

We describe briefly both types, then we emphasize on improvements under way concerning the tungsten-rhenium legs, the hafnia insulation and the sheaths materials. Oxidation resistance is achieved mainly by silicides layers, but other possibilities are considered, such as iridium coatings. Some details of insulators manufacturing or sensor assembly are given, as well as other high temperature applications for these thermocouples.

KURZFASSUNG

Zwei neuen Arten von Thermoelemente sind für Temperaturmessungen in dem französischen in-Reaktor nucleare Sicherheit Versuchsprogramm für Wasserreaktoren ausgesucht worden.

Sie müssen Temperaturen in der Mitte der UO_2 Pellets oder über der Stäbehüllrohr geben, und sie müssen Dampfoxydation zwischen 1000°C und über 1800°C in schweren Kernschädenbedingungen widerstehen.

Zuerst beschreiben wir kurz die beiden Sorten, dann geben wir einen Ueberblick über das aktual Versuchsprogramm für Wolfram-Rhenium Elemente, HfO_2 Isolierungen und Mantelmaterialen für diese Thermoelemente.

Die Oxydationbeständigkeit wird durch Siliziumschichte erhalten, andere Möglichkeiten aber sind studiert, beispielsweise Iridiumschichte.

Wir geben die Isolierherstellung und die Messinstrumentverbindung an, so wie andere Hochtemperaturverwendungen für diese Thermoelemente.

INTRODUCTION

Since 1986, French Safety Authorities have undertaken a series of experiments in the PHEBUS reactor, at the Cadarache Nuclear Center. The Severe Fuel Damage Programme is characterized by hard environmental conditions : steam oxidation, hydrogen or helium atmospheres, and temperatures rising up to 1800°C or even higher.

In these small-scale accident simulations, temperatures are measured inside and outside the nuclear fuel bundle, which comprises 21 fuel rods, approx. 1 meter-long. Starting from thermocouples used in the former Loss-Of-Coolant-Accident PHEBUS experiments, a choice was made of two new types of sensors, as explained in a previous report [1].

BASIC THERMOCOUPLES CHOICES

a) "$ReSi_2$" thermocouple description

This first type was originally designed to measure fuel centerline temperature inside the UO_2 fuel pellet stack, but was also mounted afterwards on rod cladding, or near the bundle.

It has W 5% Re versus W 26% Re legs, a hard-fired HfO_2 insulation, a Rhenium Chemical Vapor Deposited (C.V.D.) sheath protected by a $ReSi_2$ layer. This high temperature part cannot be easily bent, so a flexible zircaloy-sheathed extension cable was necessary in a medium temperature area. This was spliced on one end to the rhenium by a zircaloy connecting-box , and on the other end to a stainless-steel sheathed extension cable with compensating wires, by a second connecting-box made of a zircaloy-stainless steel diffusion bonding (Fig. 1).

b) "Duplex" thermocouple description

This second type is usually, but not always, a cladding thermocouple.

It has W 5% Re versus W 26% Re legs, a crushable and compacted HfO_2 insulation, and a "duplex" sheath made of an outer zircaloy tube separated from the insulators by an inner tantalum tube. The zircaloy sheath is spliced to a stainless steel extension cable with a zircaloy/stainless steel diffusion bonding connecting-box (Fig. 2).

"Duplex" thermocouples were originally developed by Curt Wilkins at the Idaho National Engineering Laboratory |2|, and have obtained good results in S.F.D. experiments performed in the Power Burst Facility |3|.

In our case, BeO was replaced by HfO_2 insulation, and manufacturing of thermocouples was different. In Wilkins's thermocouples, the tantalum was only a layer deposited inside the zircaloy, instead of being a separated tube. Tantalum is a barrier to prevent chemical interaction between Zy and HfO_2, which could be quite significant at 1500°C |4|.

DEVELOPMENTS ON THERMOCOUPLES COMPONENTS

a) Thermoelements

W 5% Re versus W 26% Re was finally preferred to other W Re alloys combinations (i.e. W 3% Re versus W 25% Re), because of the availability of AISI 347 stainless steel-sheathed extension cable with compensating wires, which could be used up to 870°C. Tungsten-rhenium alloys wires exhibit quite often some radial fissuration. This could be detected by a destructive micrographic examination. In some cases, a very simple vibration test (a weight is suspended at one end of the wire) is sufficient to break a faulty thermoelement. A feasibility study has recently begun to detect radial fissuration by a non-destructive eddy-current method, during wire manufacturing.

b) Insulation

Crushable and hard-fired hafnia insulators were developed, with the help of a french ceramics manufacturer, and are now available.

HfO_2 is chosen because of the toxic nature of BeO, and because of the handling problems with crushable ThO_2, and also due to the difficulty to find a thoria supplier at a reasonable cost. Insulations resistances of HfO_2 and BeO are quite similar at high temperature |5, 6|.

In-pile tests design demonstrated the importance of the thermocouple position in the temperature gradient : for example when the external cladding thermocouple goes from the bottom of the fuel rod (1000°C) to the upper part (1600°C), passing through the hotter zone (maximum power level). In this case, the hot junction is not located at the hottest point. At high temperature (1800°C-2200°C), the insulation resistance of hafnia (or thoria or beryllia) decreases, and causes a drift. This phenomenon seems worse for crushable products than for hard-fired products. Insulation measurements have been performed and tentatively modelized.

To limit this problem, care will be taken of hafnia chemical purity by using a cleaner workshop where dusts and moisture are controlled and limited. Analyses showed a slight pollution during extrusion of hafnia insulators : iron, chromium (due to the dies) and alumina, silicon, calcium (due to furnace materials) contents became greater (Table 1).

We have also remarked that it was difficult to obtain hard-fired hafnia products with a very high density, in opposition to thoria hard-fired insulators.

Another way to limit thermal shunting effect at high temperature is to increase the diameter of the wires (i.e. from 0.005 inch to 0.01 inch) which decreases the loop resistance.

c) Sheaths and connexions

Cleaning the inner surface of thermocouples tubes appeared to be a basic problem, especially for tantalum. Any dirt could decrease the insulation resistance. A method consisting of heating the tubes under vacuum with alumina ceramics inside, which could be regenerated afterwards, led to grain growth, when it was necessary to repeat the same operation several times. Other methods are also used, such as solvant, alumina slurry or acid circulation inside the tubes.

Connecting-boxes are generally laser-welded to sheaths and to extension cables. For example, the junctions between zircaloy sleeves and rhenium tubes are realized by this process, in the "$ReSi_2$" type thermocouple. These sleeves must be very carefully made, and they must be mounted in acceptable temperatures areas, generally lower than 800°C. Some troubles have been attributed to poor metallurgical quality of the compensating cables called "X" and "Y", when swaged in the stainless-steel sheathed extension leads.

DEVELOPMENTS ON PROTECTIVE SHEATHS

"$ReSi_2$" or "duplex" thermocouples were satisfactory basic choices. But other protective materials have been studied to protect thermoelements from high temperature steam, or to reduce manufacturing cost, particularly high for $ReSi_2$.

a) Hafnium - tantalum alloys

73 % hafnium 27 w/o tantalum alloy was suggested by a previous author |7| as a candidate sheath material, because of good oxidation resistance at high temperature (1650°C - 2200°C).

But attaining chemical homogeneity with two materials that have very different melting points was difficult.

Metallurgical transformation of this alloy at low or medium temperature was also a problem because of its hardness and oxygen affinity. Moreover, 73%Hf27% Ta exhibited a particularly fast oxidation at about 850°C, while better resisting to steam at higher temperatures. This peculiarity was found by a more careful bibliography |8| and confirmed by further experiments.

b) Molybdenum-rhenium alloy with silicide coating

A way to reducing the cost of "$ReSi_2$" thermocouples sheath is changing the rhenium C.V.D. substrate by more conventional and cheaper tubes such as molybdenum 50% - rhenium 50 w/o sheaths |9|. Uncoated, such thermocouples can survive approximately a quarter of an hour at 1400°C in steam.

At CEA-GRENOBLE, a $MoSi_2$ layer (thickness : 30 to 50μm) could be deposited on Mo-Re tubes. With such a coating, Mo-Re samples withstood a quarter of an hour at 1800°C in steam, but were destroyed at 1830°C. Manufacturing of thermocouples was tried, and a limited amount of swaging or bending could be allowed on Mo-Re tubes. Feasability studies of laser welding of sleeves representing the thermocouple connecting-boxes are satisfactory between stainless-steel and Mo-Re, and can also be successful between zircaloy and Mo-Re if some precautions are taken during laser welding to avoid crack formation.

Up to now, the mounting of a $MoSi_2$-type thermocouple has not been decided in a test train for in-pile experimentation, but this could be done easily.

c) Niobium with silicide coating

Another way to cutting costs is using, instead of a Re-silicided sheath, a niobium tube protected by a silicide layer deposited by a U.S. Company |10|. This slurry (Si - 20Cr - 20Fe) is applied on the niobium tubes and fired for diffusion into the substrate ; it is composed of several discrete layers and presents some cracks.

For better protection, the coating is preoxidized beforehand. Out-of-pile qualification tests have demonstrated that such tubes survived a quarter of an hour at 1800°C under our steam conditions, in the best case. But samples exhibit an important grain growth in the substrate, some hardening of the niobium perhaps due to oxygen penetration, and a great brittleness. The silicides seem to be slightly flowing at high temperature. Tightness of laser junctions between Zy sleeves and silicide protected niobium tubes was also checked.

A prototype of such thermocouples will be tested in the third PHEBUS S.F.D. experiment to be performed in February-1988.

d) Iridium

The use of an iridium-made thermocouple sheath was suggested, because of the intrinsic quality of this material : iridium could resist several hours at 2200°C under oxidizing atmospheres |11|. But qualification tests required samples to study weldability between Zy or S.S. sleeves and iridium, or to check airtightness of candidate sheaths, and this was considered as too expensive.

A cheaper utilization of iridium material was tested in the first S.F.D. in-pile experiment in december 1986. An iridium versus iridium 40% rhodium bare thermocouple gave acceptable results up to 1300°C under steam. But there was some noise in the signal, and extension cables with compensating wires were not available for this Ir/IrRh combination. Other prototypes are mounted in the third test train, and will possibly reach higher temperatures.

The last attempt for improving the oxidation resistance above 1800°C is the use of a rhenium sheath protected by an iridium C.V.D. layer (thickness = 15 to 30 μm) |12|. Three thermocouples have been manufactured and will be tested very soon.

IN-PILE RESULTS

By november 1987, two PHEBUS S.F.D. experiments out of seven have been performed satisfactorily.

In the first one, in steam at about 1800°C (max. 1930°C), about two thirds of the $ReSi_2$ and duplex thermocouples survived the entire test, and some of the duplex that were destroyed, reached their technological limit with a complete oxidation of the Zy cladding.

In the second one, in hydrogen with a few steam mixture, at 1750°C during one hour and a half, several uncoated rhenium fuel centerline thermocouples withstood the entire experiment, and results of measurements outside the fuel rod were acceptable, when the state of the bundle is considered. In the beginning of this experiment, it seems that an important exothermic chemical reaction had occurred between the hydrogen and the zircaloy cladding of the fuel rod, at about 500°C, leading to a very rapid temperature increase up to 1100°C. This will account for some early failures at 1400°C of some duplex thermocouples welded outside the cladding.

This fast reaction was not observed in the parts of the bundle where the small steam injection was performed before reaching 500°C. Results of the temperature measurements will be checked by post-irradiation metallographic examination.

In further tests, at higher temperatures, the size of thermocouples components and particularly the thickness of Zy duplex sheath will be increased.

OTHER APPLICATIONS

Thermocouples derived from the above-mentioned technology have been used in other nuclear experiments in Cadarache, Grenoble or Saclay in France, or Mol in Belgium, etc... The same french HfO_2 insulators were inserted in thermocouples manufactured by the Karlsruhe Nuclear Center (KfK) for the CORA facility. Other thermocouples have also been tested in some non-nuclear industrial applications, such as furnaces for steel industry, or hot isostatic pressing. In this last case, qualifications are now in progress with W 5% Re versus W 26% Re type, Ta, Nb or Mo-Re sheathed thermocouples protected by P.V.D. coatings of carbides or nitrides in a carbon aggressive environment.

CONCLUSIONS

Two kinds of high temperature thermocouples protected against oxidation by either a rhenium silicide, or a Ta/Zy duplex sheath have given satisfactory results in the French Severe Fuel Damage Program for Light Water Reactor Safety performed in the PHEBUS reactor. Alternatives such as niobium silicided or MoRe silicided tubes could also be considered to reduce costs, or rhenium protected by iridium to increase oxidation resistance.

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Fig. 1 - "Duplex"-type thermocouple (schematic)

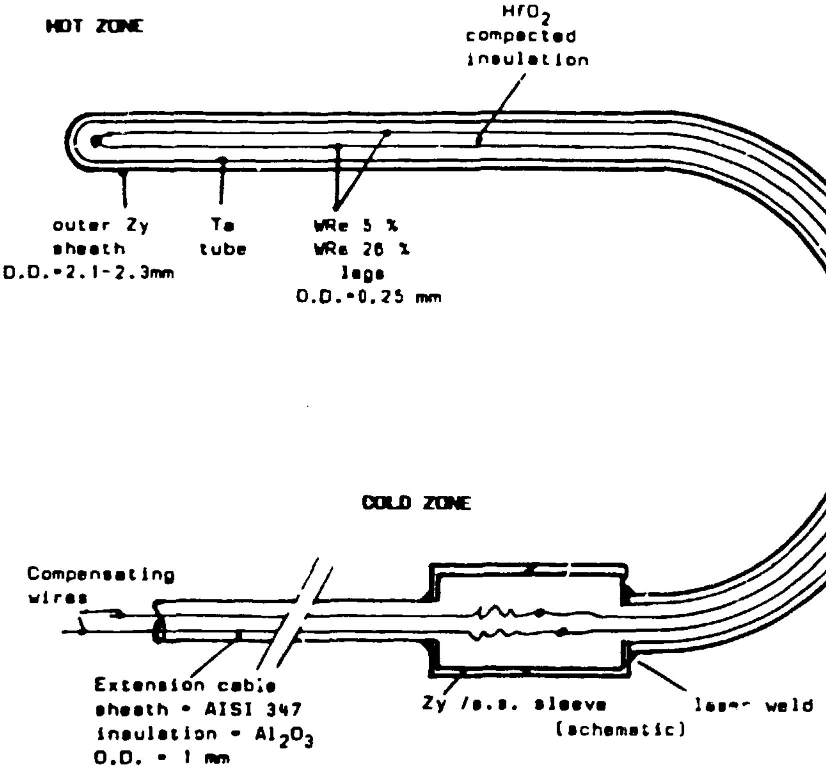

Fig. 2 - "Re Si$_2$" - Type thermocouple (schematic)

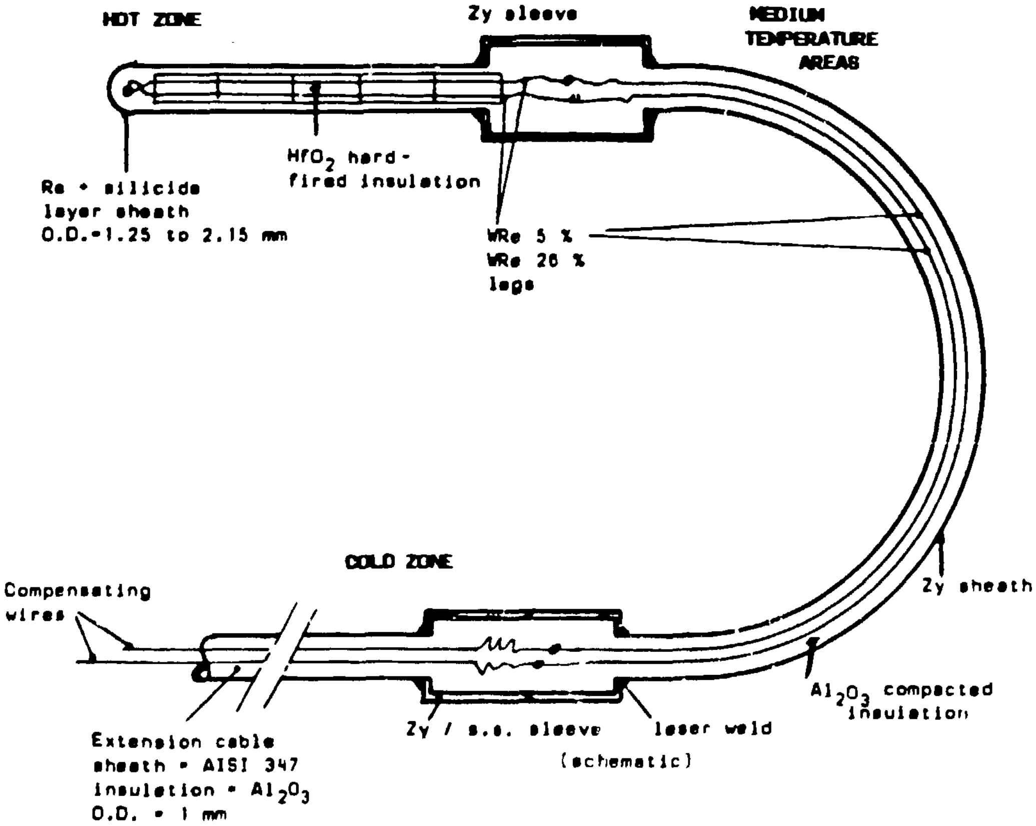

Table 1

Comparison of chemical analyses between hafnia powder and hafnia insulators

	POWDER (5 samples) Max (ppm)	INSULATORS (4 samples) Mini - Max (ppm)
Al	< 50	46 - 420
Ca	< 20	15 - 37
Cr	< 20	14 - 30
Fe	< 50	92 - 185
Mg	< 10	<10 - 21
Si	< 100	67 - 180
Zr	Ranging from 0,59 % to 1,0 %	
Other elements contents are very low : less than 10 or 25 ppm for B, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sn, Ti, U, V, W, Zn		

FIG. 3 - High temperature thermocouples before mounting on the fuel bundle

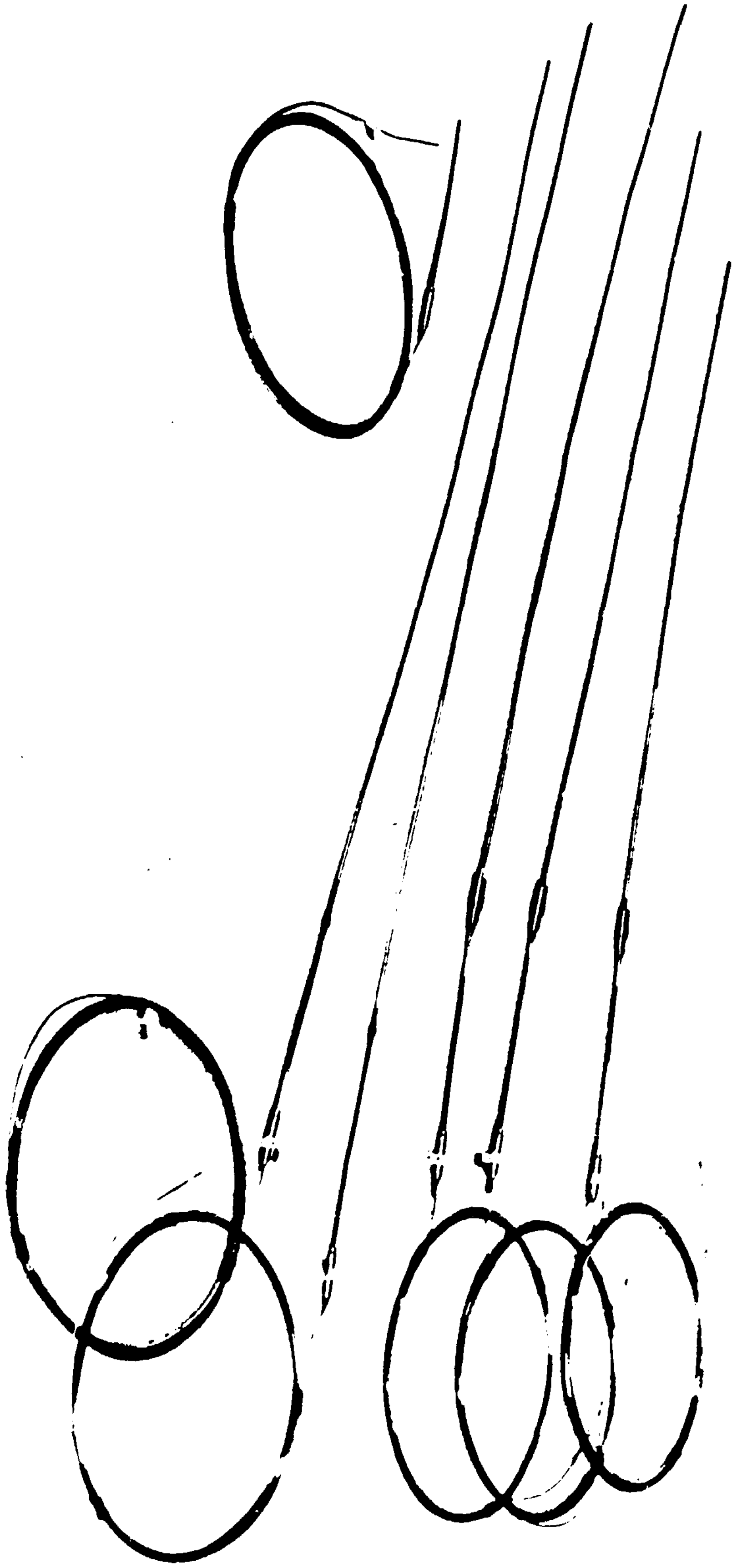

FIG. 4 - Instrumented fuel bundle : PHEBUS B9
First Severe Fuel Damage Experiment