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"R & D ADVANCES IN HIGH TEMPERATURE THERMOCOUPLES FOR NUCLEAR UTILIZATION IN SEVERE ENVIRONMENT"

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ABSTRACT

Safety experiments for water reactors in Cadarache have made necessary a research program for developing special thermocouples for use in severe fuel damage conditions (superheated steam).

Standard cladding thermocouples (type K, alumina insulated, zircaloy sheathed, O.D. 0.7 mm) must be replaced by others with W3Re versus W25Re legs, Ta sheath protected by a zircaloy outer sheath, and hafnia or thoria insulation. The zircaloy sheath will be sufficient to protect correctly Tantalum.

Fuel centerline thermocouples have W5Re versus W26Re or W3Re versus W25Re legs, hard-fired thoria insulation and rhenium CVD sheath (O.D. 1.1 mm). A protective $ReSi_2$ coating is applied. This protection withstands at least 1600°C, 45 minutes in steam.

Tests are done concerning: a) materials compatibilities in helium between 1400°C and 2000°C, b) prototypes qualification (in Saclay or Grenoble), c) determination of errors due to degradation of insulation resistance of thermocouples cables (with magnesia, hafnia, alumina), d) Ir or Re protective coatings by CVD process, other coatings by ionic bombardment, etc...

A completely new type of hot junction has been patented.

Future works will include: completion of these tests, Mo-Nb alloys thermocouples legs realization withstanding heavy neutronic fluence, and use of ceramics glues.

1 - INTRODUCTION

Safety experiments for Water Reactors performed in Cadarache (France), in Severe Fuel Damage Conditions (PHEBUS parts III and IV) have made necessary a research program for developing new thermocouples to be used in superheated steam.

Some developments of these techniques are used or foreseen in other environments such as sodium reactors: PAHR project in Grenoble (France) or Mol (Belgium), Scarabée tests (Cadarache), or non-nuclear applications: space industry or isostatic furnaces.

To perform these developments, we dispose of tests and fabrication tools such as insulation measurement apparatus, compatibility tests installations, high temperature steam qualification tests and a thermocouple prototype fabrication work-shop.

2 - PRE-EXISTING TECHNOLOGY

At the end of PHEBUS part II (LOCA) experiments, two types of thermocouples are currently available:

a) Standard thermocouples (type K, alumina insulated, zircaloy sheathed, O.D. 0.7 mm) for external (laser welded) or internal temperature measurement on the fuel rod cladding (Fig. 1).

b) Fuel centerline thermocouples with W5Re versus W26Re or W3Re versus W25Re legs, hard fired thoria insulation and rhenium CVD sheath (O.D. 1.1 mm).

3 - AIM OF THE PROGRAM

a) - PHEBUS Part III (1985-1987) experiments need to measure steam temperatures between 1600°C and 1800°C. In order to be easily implanted on the test train, these thermocouples must allow reasonable bendings.

In PHEBUS Part IV (1988-1989), the steam measurements will be between 1800°C and 2200°C.

b) - The temperatures involved have led to the choice of W-Re alloys as thermoelements [1],[2],[3]. But W5Re versus W26Re are brittle, so we prefer W3Re (doped) versus W25Re. A normal elongation is 10 to 20% of the initial length. We have also remarked that some of commercially available WRe thermoelements (Hoskins, Engelhard, Cime-Bocuze) have one or both wires presenting an axial fissuration (Fig. 2).

We also encounter a problem concerning the compensating cable adapted to the W3Re versus W25Re type. Both Engelhard's alloys 300-P/300-N and Hoskins's alloys 203/225 match the W3Re versus W25Re F.e.m. curve only between 0° and 371°C (resp. 260°C). So our connection box operating in the range 0-870°C, we have either to use a 3 or 4-wire compensating cable, or to reduce or measure the box temperature, or to sacrify the precision.

Five insulation materials were easily available. But we rejected magnesia because of its low maximum usable temperature: 1650°C [2], its water affinity and its poor insulating qualities at high temperature (as we verify with the help of the Nancy School of Mines). Alumina was rejected because of its 2010°C Melting Point, and its approximate usable temperature of 1540°C [2].

Beryllia would be a good choice until 2300°C-2430°C [2],[4], but its chemical toxicity creates many fabrication difficulties. So we prefer to choose thoria (M.P. 3290°C), with an usable temperature of about 2760°C. Thoria is now currently available in hard-fired or crushable two-holes insulators, in small diameters (0.7 mm to 3 mm). But thoria has two drawbacks: its high price and its radioactivity.

Another choice is hafnia (HfO_2) with a low price, and crushable products (Fig. 3).

4 - DIRECT DEVELOPMENTS

Some improvements were done directly from the preexisting thermocouples. a) For the **fuel centerline thermocouple**, in order to have a better fiability of the product, we introduce in the specification a test to 1600°C in vacuum, before use. The first results were very satisfactory, and this test eliminates any unsound thermocouple. We also verified its resistance to vibrations due to the shipping.

Another improvement would be to change the junction between the rhenium tube and the stainless steel connecting box done normally by Nicrobraze 50, by a direct laser welding.

We also tried with success two prototypes with a normal Re CVD sheath covered by a $ReSi_2$ layer. This thermocouple withstands at least 1570°C in steam during 3 temperature levels of 15, 15 and 10 minutes. The Re sheath (Fig. 4) and its $ReSi_2$ layer (Fig. 5) were produced by Ultramet (California).

This result was confirmed by the second prototype withstanding temperatures around 1600°C during 10 minutes in good temperature accordance with the first one. The breakage of both thermocouples was due to sticking of the sample to the sheath. Two cylindrical samples of the same material (Rhenium plus $ReSi_2$) withstood 1700°C-1800°C during 16 minutes in water steam.

Other experiments will be soon performed with six new thermocouples.

b) For cladding measurements, we try a new kind of thermocouple that we call **"duplex"**. It will be constituted by W3Re(doped) versus W25Re legs, thoria or hafnia insulation, a Tantalum inner sheath and a zircaloy outer sheath. It can allow bendings. The preliminary experiments were conducted with MgO instead HfO_2 insulation, for cost saving and availability reasons.

The zircaloy sheath will be sufficient to protect correctly Tantalum, by a formation of a protective oxide layer, during the time of the test (about 20 or 30 minutes).

The zircaloy is necessary to enable easy laser welding to the cladding. The outer sheath is put on the inner one only when the hot junction has been made.

The difficulty to realize a classical hot junction and to close together the two sheaths has permitted to invent a new type of junction and to patent it [5].

In this case there is no welding of the thermoelement wires, but the ends of the two legs are inside a refractory metal (Nb or Ta) powder which fills the end of the micro-conductor (inside the sheath). An advantage is to allow the wires little displacements due to differential dilatation, and to keep a good electrical contact.

In the "duplex", the inner sheath serves as mechanical protector of the elements and also for gettering impurity gases coming from the insulator [6].

c) As for the $ReSi_2$ layer, **qualifications tests** are performed in two installations: Vapoflash at C.E.N. Saclay, and Heva at C.E.N. Grenoble [7]. These out-of-pile tests have a steam generator (boiler) at normal atmospheric pressure, and a heating part constituted by a H.F. generator outside a quartz tube.

One of the main problem is to find a support piece (ZrO_2 or Al_2O_3) which can withstand temperature and steam without interfering with the test sample.

Different types of susceptor are used: graphite, iridium or zircaloy (which is destructed during the test with exothermic reaction).

Difficulties are also encountered with temperature measurements, so we use either 60 % Ir-40 % Rh Versus Ir wires, or a W5Re versus W26Re thermocouple with Re, $ReSi_2$ sheath, or an optical pyrometer.

d) Preliminary results on the "duplex" thermocouples are contradictory. In Vapoflash, a prototype withstood two heatings to 1600°C (speed: + 5°C/mn); it broke at the beginning of the second 1600°C step. In Heva, a prototype failed suddenly during the heating at 1540°C (speed: + 1°C/mn).

Five other prototypes must be tested in the near future. We have also realized powder hot junctions on rigid high temperature Re thermocouple to test them.

5 - COMPLEMENTARY STUDIES

We have also undertaken some studies to support thermocouple prototype fabrication in four different ways:

a) compatibility between insulators and sheath material to compare with previous bibliographical reports [8].

b) Some insulation measurements and tests to appreciate the f.e.m. drift due to hot point or shunting problems [9], which are classical problems [10],[11],[12],[13].

c) Development of layer materials to withstand Phébus SFD environment.

d) Development of a Hafnium-27% Tantalum alloy, which is said to resist to high temperature oxidization in steam [14],[15].

5a) Compatibility Studies :

We intent to verify the reaction that occurs (or does not occur) between two cylindrical samples (£: 8 mm, height: 4 mm) of a refractory metal (or Zy) and a refractory oxide or BN. We include BN in this test, because of its use in heating elements. The samples are placed in a cylindrical container (in Nb or Zy), under He atmosphere, and then heated to a high temperature.

After treatment, a X-ray diffraction is performed, and sometimes also a scan microscopy, or a microprobe analysis. A total of 30 containers have been prepared, but unfortunately, only a few complete conclusions are available (mid-May 1984).

The preparation of the containers is carried in Saclay, but treatments and analysis are done by the "Laboratoire de Gênie Métallurgique" of the Nancy School of Mines (France).

These are the first results.
1) There is a good compatibility between HfO_2 and Ta, and between HfO_2 and Nb, for 1 hour at 1700°C. X-rays indicate Ta_2O_5 and Nb_2O_5 (resp.) formation, but only superficially. But the oxygen of these oxides can come from either a HfO_2 dissociation, or from the oxygen dissolved in Ta or Nb.

2) BN interaction was studied with Ta, Ta with a rhenium layer, during 1 hour at 1700°C, and with zircaloy during 15 minutes at 1400°C. BN reacts with these metals to give borides. This means a BN dissociation at the interface with the metal. We cannot find the nitrogen released in the samples. We notice an important loss of weight in boron nitride during the experiment.

The rhenium layer (50-60 µm) reduces the speed of the reaction (four times less important than with pure tantalum).

The borides constituted with zirconium are particularly brittle (ZrB_2, ZrBN). The oxygen present in BN (1.5-2.5%) reacts with metals and gives very superficial metal oxides (Re_2O_7) on Ta with Re layer, except with pure tantalum (Ta_2O_5, 6 µm). Oxygen observed on X-ray images done by electronic microprobe is only put in evidence in the porosities.

All these results must be confirmed and completed with the achievement of all the containers.

5b) <u>Insulation and drift problems</u> :

One of the most important preoccupation of Safety Test Organization is to avoid shunting problem or hot point phenomena before the hot junction itself. For this reason, tests have been performed in Nancy, using a five elements furnace to create a non uniform temperature gradient with a maximum on the middle of the microconductor. Results indicate that for temperatures below 1200°C errors were low [9]. For temperatures above 1200°C, we use a high temperature furnace (2000°C) in Nancy. For MgO, the errors above 1200°C increase very rapidly (Fig. 6). Complete results for ThO_2 and HfO_2 are not (May 1984) available. But a whole series of tests must be performed either in abnormal gradient, or normal one (in Nancy and in Paris).

Estimation of the effects of thermocouple location have also been performed (Edgar tests) in Saclay, to be compared with other bibliographical reports [16],[17]. But they are not in the subject of this text.

Some analysis were performed in C.E.N. de Grenoble (France), with the help of scan electronic microscope on different samples of insulators used in thermocouples. Crushable HfO_2 seems the best choice with regular small grains ($\sim$ 0.5 µm), Al_2O_3 presents two classes of grains (small and great), and ThO_2 has a foil structure. But it is difficult to say whether these results can be generalized to other fabrications. We also determine crushable heating temperature for Thoria (1320-1350°C).

5c) Development of layer materials :

These studies concerning both thermocouples and test trains materials for Severe Fuel Damage environment are performed by the COMURHEX Company (Bollène-France) on behalf of C.E.N. Cadarache (Safety Dpt.) and C.E.N. Saclay. The work done by Ultramet has already been related above. Qualifications tests are also performed in Heva and Vapoflash installations.

The results obtained (mid-May 1984) are summarized below.
1) Concerning tantalum substrate covered by a rhenium layer, the adhesiveness of rhenium, and deposition kinetics are established. The rhenium oxidization resistance in steam is 1400°C.
2) Deposition kinetics of silicium on rhenium ($ReSi_2$) is an acquired knowledge. The oxidization resistance in steam is 1700°C, 15 min.
3) SiC deposit on graphite has a deposition kinetics and an adhesiveness established. It withstands 1700°C, 15 min, with an approximative layer loss of 10 to 12 µm/min.
4) Iridium deposit on tantalum has an adhesiveness and deposition kinetics aknowledged, but we encounter leakage in the layer when the samples have a sharp angle. Tests with rounded angles samples are in progress.
5) Silicide deposit on zircaloy ($ZrSi_2$) is only in the beginning of the study (adhesiveness problem).
6) It is also foreseen to study WSi_2 layers, because of a high melting point (about 2115°C) compare to $MoSi_2$ for example [18].
7) Rhenium deposit on niobium substrate has also been tested (Fig. 7).

Apart from COMURHEX works, we have also realized some deposits by ionic bombardment on Ta, Nb, Re substrates, but only on small samples. These experiments are done also at the Nancy School of Mines.

5d) Hafnium - 27% tantalum alloy :

The aim of this alloy was to obtain a thermocouple sheath material able to withstand directly high temperature steam oxidization.

We undertook this project because of [14] and [15], and we found also a russian reference [19]. We realized a 70 x 40 x 10 mm^3 ingot by quadruple fusion, in arc furnace under argon. After tooling, and stainless steel covering, the cover was electron-beam welded. We obtained a 2.7 mm foil by rolling (1000°C).

Cold rolling permitted to have a 1.7 mm foil. But we had troubles to find an appropriate metallographical attack. Vickers Hardness was 412 Hv/5g in both hot and cold rolled samples.

Two qualifications tests in steam at 1800°C, 15 min were performed in Vapoflash (heating speed: + 1°C/s) and in Heva (speed: + 4°C/s). A white oxide layer, 120 µm, was observed in both cases, which is a good result (Fig. 8).

The next step of the program is to achieve thermocouple sheath fabrication. Two different ways are foreseen.

First, we take O.D. 7 mm, I.D. 3 mm cylinders in an ingot (same fabrication as above). These little cylinders will be covered with stainless steel, and the axial hole filled with a stainless steel rod, and the cover will be vacuum welded.

After swaging on a stationary spindle machine (at more than 1000°C), we hope to achieve 2.5 x 4 mm tubes, after removal of the cover and the pin.

A second method would be to obtain a cylindrical piece (1 = 200 mm, diam. = 70 mm) by a re-fusion of little ingots in electron-beam furnace.

After axial drilling, and internal and external stainless steel covering and welding, the piece will be drawn by an isostatic press (at more than 1000°C) to give a hollow cylinder (15 mm O.D.).

We hope to achieve a grain size and a ductility sufficient to allow small tubing fabrication (by cold swaging).

Another potential application of this alloy could be calorimetric fluxmeters in Aerospace applications.

6 - PROTOTYPES FABRICATION AND FUTURE WORKS

The main objective of these works was to produce thermocouples for Safety Test performed for Water Reactors, in Cadarache. But we are also manufacturing thermocouples for high temperature applications in Sodium Reactors: Scarabée (France) needs HfO_2 or ThO_2 insulated, tantalum sheathed prototypes; PAHR projects require HfO_2-Nb thermocouples (Grenoble), or ThO_2-Re (rigid) and ThO_2-Nb + 1% Zr (ductile) thermocouples (Mol-Belgium).

Isostatic press manufacturers are also interested in graphite-resistant thermocouples, and we experiment thermocouples with layer covered tantalum tubing.

When all the tests in progress will be achieved, other interesting developments could be: 1) Realization of Mo-Nb alloys thermocouples legs to withstand heavy neutronic fluence [20] (during long-time irradiation), and 2) Use of ceramics glues, or ceramic-to-metal joining to hermetically close the connection box of the thermocouple to avoid leakage problems in case of thermocouple hot part breakage.

7 - CONCLUSION

This text aims to give the present state-of-art in French Safety tests thermocouples development (mid-May 1984). The most promising points seem to be the $ReSi_2$ layer for steam oxidization resistance, the use of powder hot junction in certain cases, the manufacturing of crushable HfO_2 for low cost and easy handling reasons, and the study of different oxidization resistant materials or layers materials.

It is also clear that there is a lot more work to perform, to achieve currently available, lost cost, reliable high temperature thermocouples.

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