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THERMOCOUPLE FAILURES IN GRAPHITE IRRADIATION RIGS FOR BR 2 REACTOR, MOL

by

M. PATANE

1967

Report prepared at the C.E.N.
Centre d'Etude de l'Energie Nucléaire, Mol-Belgium

Association No. 006-60-5 BRAB

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SUMMARY

This report discusses the probable reasons for thermocouple failure during irradiation in graphite experimental devices. It was found that an adverse combination of the thermocouple sheath material, the purity of the insulation used for the thermocouple wires and the ambient atmosphere during irradiation, can give the sort of destruction observed in these thermocouples during the disassembly of the experimental device in the hot cell.

Thermocouple Failures in Graphite Irradiation Rigs for BR2 Reactor, Mol (+)

1. Introduction

Have you ever wondered about the money and time lost when an experiment fails to provide useful results?

Generally, the main question that should be asked when a mishap during the experiment gives rise to uncertainties in the interpretation of the results is: How is it possible to avoid any undesirable incidents?

1.1. The aim of the present paper is to draw the attention of project engineers to the proper use of materials destined for the construction of experimental rigs.

It is very important that the correct choice of material be made in each case because the results of experimental irradiations will be worthless if troubles occur during the experiment.

1.2. A further question now arises, namely: What is understood by "a correct choice of material"? Because nowadays, with all the existing specifications, it is normally not possible to make a wrong choice of the various materials for the construction of the rigs and of the materials to be used during the experiment.

1.3. When a type of material is chosen it is not only necessary to be sure of its suitability as recommended by the supplier but it is also advisable always to check the quality of the product, in other words, to ascertain whether this material conforms to the acceptance standard: for instance, whether the inclusions in a type of austenitic stainless-steel thermocouple sheath are acceptable[1], whether there is carbide precipitation, whether the impurities in an inert gas (used for filling the rig) are compatible with the materials that this gas must protect at high temperatures, whether the insulation material in sheathed thermocouples contains any impurities, and what is the probable influence of these impurities on the corrosion-resistance of the sheath.

1.4. These factors were considered when severe intergranular corrosion was observed on the Chromel-Alumel thermocouple sheath of a 700° C graphite rig (47/23) after seventeen days (~ 400 hours) of irradiation in BR2.

(+) Manuscript received on May 11, 1967.

2. The following sections give an account of the information required for the understanding and elimination of the problem of intercrystalline disintegration of thermocouple sheaths.

2.1. These thermocouples were in the rig for the measurement of graphite temperature during the experiment. There were two sizes of thermocouple: 1/2 mm and 1 mm diameter.

2.2. The vendor had supplied these sheathed Chromel-Alumel thermocouples in "stainless steel", type 304 (AISI).

2.3. The rig was filled twice with neon, before and during the experiment. The pressure in the rig was variable: 23 p.s.i. on the first and second days of the experiment, decreasing linearly to 10 p.s.i. on the eleventh day. After the second filling the pressure was 25.5 p.s.i., decreasing linearly to 15 p.s.i. on the seventeenth and last day of the experiment.

2.4. The temperature registered during the irradiation period was about 500^{o} C for the bottom capsule and about 600^{o} C for the top capsule, but there is reason to believe that the temperature actually reached about 900^{o} C in both zones (1 and 2) of the rig (fig. 1 A). In figure 1 B the arrangement of thermocouples inside the capsule can be seen.

3. Analysis of materials

We shall now turn our attention to the material of the thermocouples and the nature of the environment.

3.1. Thermocouples

A microprobe analysis of a non-irradiated stainless steel sheath gives the following composition: Cr 20 %, Ni 11,8 %, Mn 0,7 %, Si 0,35 %, Nb 0,2 %, Pb 0,07 to 0,1 %.

The declared carbon content was $<$ 0,04 %.

The composition of this stainless steel corresponds to an unstabilised austenitic stainless steel.

3.2. MgO Insulation

An analysis carried out on the MgO insulation of some unirradiated thermocouples of the same batch gave the following results[2].

	B_2O_3	SiO_2	MnO	NiO	Fe_2O_3	Al_2O_3	CaO	V_2O_5	CuO	ZrO_2	S
%	0.008	0.1	0.004	0.002	0.1	0.004	0.15	0.006	0.00003	0.003	0.02

We can consider this analysis as valid also for the insulation of the irradiated thermocouples.

3.3. Neon gas

The purity of this gas as supplied to the rig at Mol was 99.83 %.
Its analysis gave the following impurity contents:
CO_2 - 1200 ppm
H_2 - 500 ppm
No moisture was detected in the gas.

3.4. Graphite

Some humidity, air and sulphur may have been present in the graphite charged into the capsules of the rig.

4. Microscopic examination and findings

During the hot-cell extraction of the irradiated graphite capsules from the rig it was observed that the thermocouple sheaths were very brittle.

Generally, a sudden decrease of plasticity occurs in austenitic stainless steels as a result of irradiation at an integrated flux of 0.9 to 3.4×10^{20} nvt at 450° C - 650° C[3]. But this plasticity decrease due to irradiation damage does not explain the excessive embrittlement observed.

For this reason it was decided to conduct a complete investigation of the causes of this embrittlement.

As mentioned above, this embrittlement was particularly severe in zones 1 and 2 of the rig shown in fig. 1 A.

The colour of the external surface of the sheath was grey-black, showing clearly that carbon deposition had occurred during the experiment.

4.1. Examination of irradiated thermocouple sheath

As shown by the photomicrographs in figures 2 and 3, a catastrophic destruction of the thermocouple sheath occurred during the experiment.

This catastrophic destruction proceeded in two directions: from the outside to the inside and from the inside to the outside of the sheathing tube.

In figure 2 b a large concentration of carbides underlying the external surface of thermocouple sheath can be observed.

4.2. Stainless steel of thermocouple sheath

The kind of stainless steel examined, as confirmed by microprobe analysis, is an unstabilized austenitic stainless steel. We know that the austenite is a metastable condition in which all the carbon present in the steel is completely dissolved in the iron, but this complete dissolution of carbon depends on correct heat treatment. Microscopic examination of non-irradiated and unetched stainless-steel and thermocouple sheath revealed extensive carbide precipitation and the inclusion of several oxide particles (see figs. 4 a, b, 5, 6a, b). In some cases the thickness of the precipitate and of the impurities was much greater that 1/10 of the thickness of thermocouple sheath.

It is necessary to remember that tubing have defects greater than 0.0015 inch must be rejected[1, 13].

It is well known that an austenitic stainless steel which shows extensive carbide precipitation when heated to a temperature between 550° and 850° C becomes susceptible to intergranular corrosion[6], but the contribution to this attack is greatly influenced by the environment within the above-mentioned temperature range.

The external surface condition of the non-irradiated thermocouple sheath was very bad (see top of figs. 4 a, b). At several points the protective oxide layer was certainly very irregular and pitting was apparent (see figs. 4 and 5). On the other hand, the lead content is very harmful to the corrosion-resistance, especially when the stainless steel is subjected to a reactive environment under irradiation effects[4].

4.3. Protective oxide layer

On the external and internal surfaces of austenitic stainless-steel sheathing tube there is a protective layer of oxide. This consists largely of a protective Cr_2O_3-rich oxide with the source NiO and also a spinal[7, 14].

5. Some probable causes of corrosion

The photomicrographs in fig. 3 show that the attack on the stainless-steel thermocouple sheath proceeded in two directions.

5.1. Attack from inside

As is shown by the chemical analysis of the MgO, various oxides are present as impurities. These include V_2O_5, one of the most serious offenders against the protective Cr_2O_3-rich oxide layer of the type which react with Cr_2O_3 to produce a volatile oxide, molten oxide or eutectic mixtures[7]. The presence of V_2O_5 probably caused the formation of low-melting-point vanadate in several internal-surface zones of the sheathing tube[7, 15].

The presence of sulphur (about 200 ppm) is also dangerous because this element is a redoubtable enemy of the Ni and reduces its capacity to protect against oxidation[8].

The sulphur content presumably originates from residual traces of drawing compounds used during the manufacture of the sheathing tube[8].

5.2. Attack from outside

The impurities present in the filling gas and in the graphite played an important role.

The deposition of fine C particles on the external surface of the sheathing tube reduced part of the Cr_2O_3-rich layer and favoured the carburisation of underlying metal (fig. 2 b).

These fine particles of C have two sources: they originate directly from the graphite and indirectly from a chemical back-reaction of CO at high temperature which is catalysed by the steel[8].

The main source of monoxide was the decomposition of the CO_2 in zones 1 and 2 of the rig according to the reaction $2\ CO_2 \longrightarrow CO + O_2$.

Some recent work by the Dragon Project staff at A.E.E., Winfrith, on the corrosion of austenitic stainless-steel thermocouple sheathing in a high-purity helium atmosphere, has shown that serious carburisation and embrittlement of the stainless-steel thermocouple sheath occurred when the sheath was exposed only to the rig atmosphere at temperatures of 500° - 800° C, in a region where the carbon monoxide concentration could not have been higher than 1000 ppm[8].

The carbon atoms in the carbon monoxide do, however, carburize a metal much more readily than carbon atoms coming from the solid graphite, owing, as mentioned above, to the steel-catalysed back-reaction $2\ CO \longrightarrow CO_2 + C$.

In cases where the inert rig atmosphere was contaminated with oxidising impurities as a result of imperfect outgassing of the graphite, the 18/8 stainless-steel had suffered appreciably[7].

From the impurities present in the filling gas and from the air and humidity probably present in the graphite it is possible to detect several of these oxidising impurities.

A double attack was possible during the experiment:
a) by the C, which reduced Cr_2O_3 to form CO,
b) by the oxidising impurities which caused severe internal oxidation.

In almost all cases, water vapour in small quantities increases the sealing rate of austenitic nickel-chromium steels[7]. But the presence of the water vapour together with small quantities of CO and CO_2 in the filling gas probably caused a dilution of the initial Cr_2O_3-rich layer by iron and some carburisation, but not a break-through, as occurs in the presence of an excess of O_2.

However, if the gas also contained small quantities of SO_2 (in our case probably formed by oxidation of the sulphur impurity in the graphite), this impurity may have considerably stimulated the attack, and its influence is therefore greatest at very moderate CO contents[7, 8].

Alternate oxidising and reducing conditions may also have been produced. When these conditions occur the attack on grain boundaries depleted in chromium for the carbide precipitation phenomenon is severe.

In any case, when graphite is present in the rig the use of 18/8 unstabilized stainless steel as thermocouple sheathing is not advisable, because this type of steel is particularly susceptible to carburisation in the temperature range 650° - 850° C[9, 10].

5.3. If it is possible for carbon to dissolve in the sheath and hence diffuse through it, then the MgO insulation of the inside of the sheath will slowly become contaminated. Tests carried out by Reichardt[8] on thermocouples subjected to high temperatures in contact with graphite showed a marked drop in resistance between wires and sheath. When selecting a sheath material it is therefore important to consider not only the compatibility but also the amount of carbon that can be dissolved in the sheath, since this determines the diffusion rate of carbon through the sheath at the temperature of the experiment.

5.4. Influence of surface finish on the corrosion

The surface finish may have had an appreciable effect on the reaction rate of carburisation and oxidation[7]. The condition of the dies during the manufacture of the sheathing tube may have been responsible for considerable abrasion of the external surface.

In this case a surface is obtained which consists of internally stressed, disarrayed alloy containing entrained oxide and covered with an oxide formed by preferential oxidation. The photomicrographs in figures 4 a, b (top) show very clearly the bad external surface condition of the non-irradiated thermocouple sheath.

6. Discussion

The factors enumerated above caused a radical change in the nature of the sheath metal (fig. 2 b).

When intergranular attack had occurred during the experiment in the hot cells there was frequently no outward sign of corrosion until the thermocouple sheath broke during the handling operations. This is one of the chief dangers of intergranular corrosion: it may progress to a very dangerous extent without any visible warning. But what, in our case, is the damage resulting from this corrosion? During the experiment the complete destruction of the protective sheath caused an attack on the thermocouples wires, especially the chromel wire, by oxidation and carburisation.

Recent American work on the influence of the environment on the chromel-alumel thermocouple wires has shown that oxidation and carburisation of the chromel wire can produce a negative drift of up to 100° C during the experiment[11, 12].

6.1. In general it is necessary to pay particular attention during the handling of irradiated experimental capsules in hot cells. Every appreciable change in the material properties must be noted. All the observations are useful to scientists and engineers concerned with the evaluation of experimental results, and, if trouble is experienced, for correcting the next experiment.

6.2. It is also desirable, however, to guard against any trouble before and during the experiment, and, if something goes wrong, to know the effects of all parameters which have ever interfered with the normal behaviour of an experimental run.

6.3. For the particular case discussed the suggestions are as follows:

a) Before the construction of the rig and its thermocouples:
   1 - a correct choice of material,
   2 - an acceptance test on this material,
   3 - a study of the compatibility of this material with the possible environment in the conditions of the experimental run,
   4 - a check on the purity of the graphite.

b) During the experiment:
   1 - use of a higher-purity filling gas,
   2 - periodic sampling of the gas during the experiment.

This last suggestion is the most important, because every chemical reaction that can occur under the experimental conditions can be reconstructed to give an explanation of the probable phenomena, thus making for optimum interpretation of the results.

7. Conclusions

It is clear from the foregoing that no detail must be overlooked during the study and the choice of materials for an experimental rig to be irradiated in a material testing reactor. This example will result in the exercise of better surveillance in the future.

An experiment giving unreliable results is a waste of money, time, effort and ingenuity.

Acknowledgements

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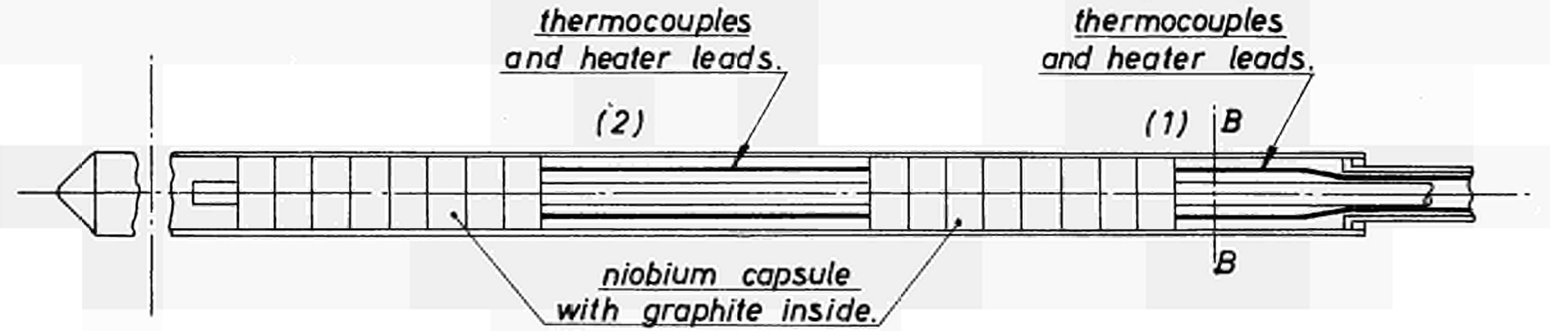
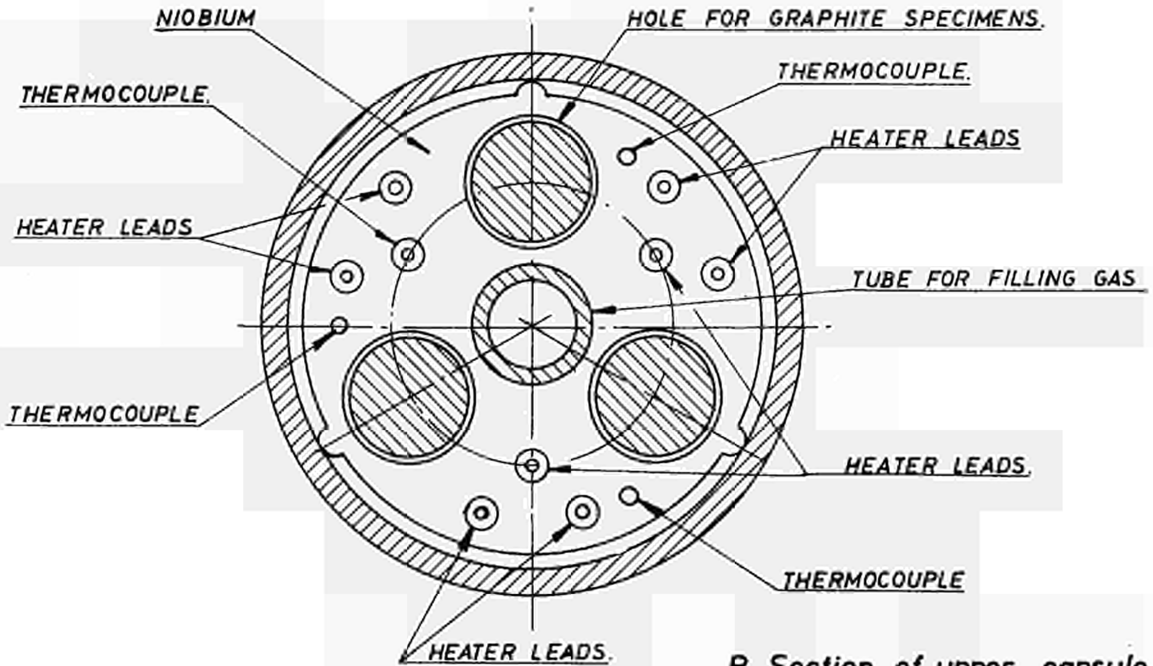
I am also grateful to Mr. N.H. Hancock, who has made this work possible, to Mr. H. Venables for his assistance and his suggestions to my work in 393.6 Laboratory, to Mr. J.H. Evans and Mr. P.J. Bronsdon for their collaboration in photomicrographic work and helpful discussions, and to Miss P.M. Thomas for the electron-probe analysis measurements.

This work has been performed during a stage at A.E.R.E in Harwell (U.K.A.E.A) in the summer of 1963.

A.E.R.E. HARWELL	700° C GRAPHITE IRRADIATION RIG FOR BR2 REACTOR, MOL.	RIG 47/23.



A. Sketch of the rig showing the position of the capsule and the zones (1) and (2).

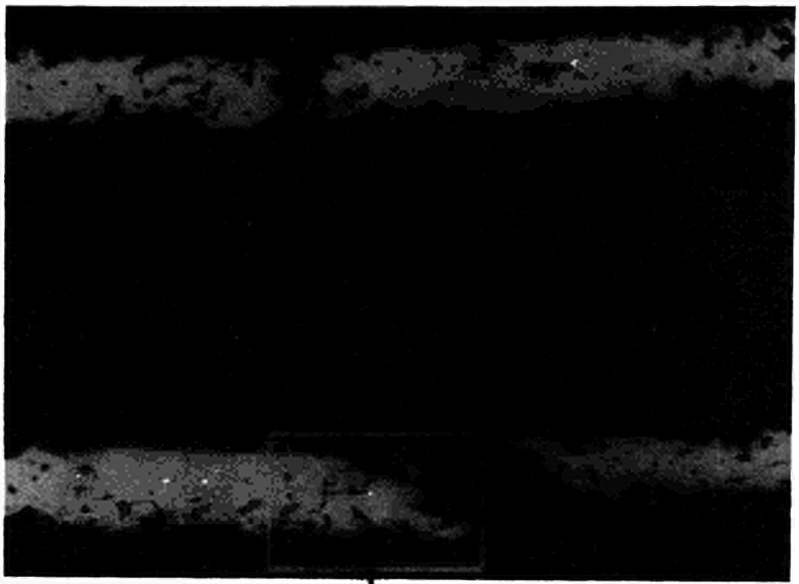


B. Section of upper capsule.

Fig. 1.

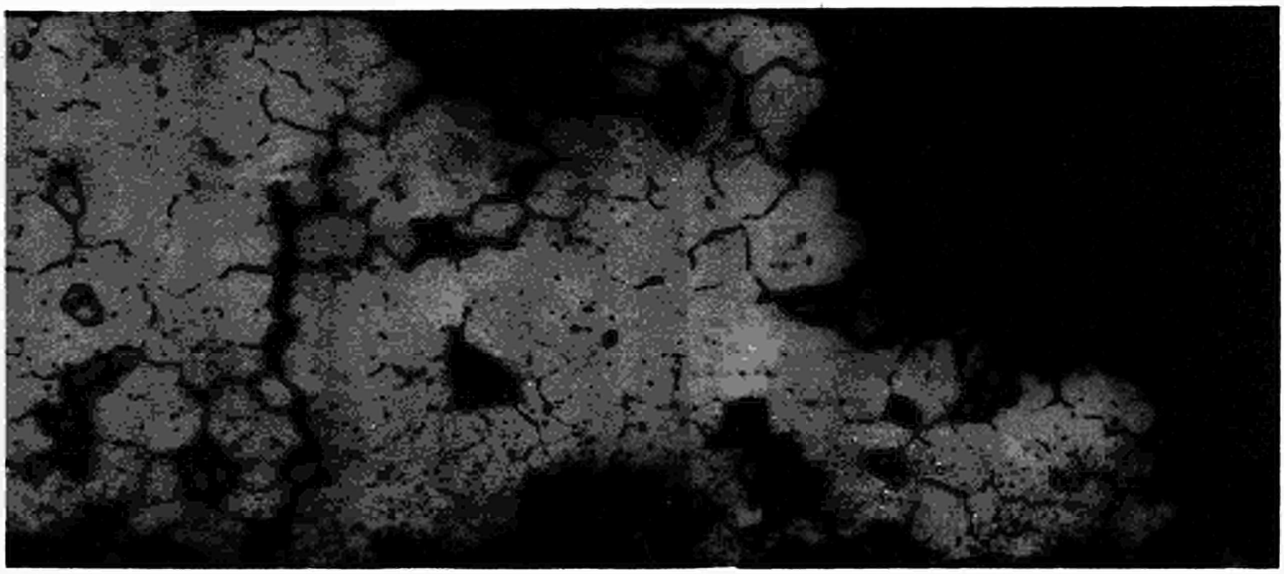
Fig. 2 a

Intergranular corrosion of an irradiated 18/8 stainless steel thermocouple sheath (longitudinal section).



A

x 50

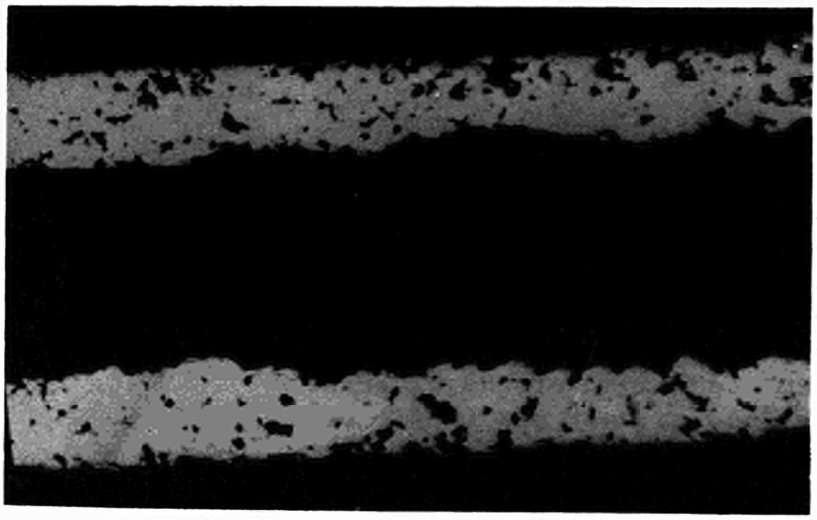


x 390

Fig. 2 b - Enlargement of region A. The corrosion has converted the solid steel into a mass of loosely held grains.

Fig. 3

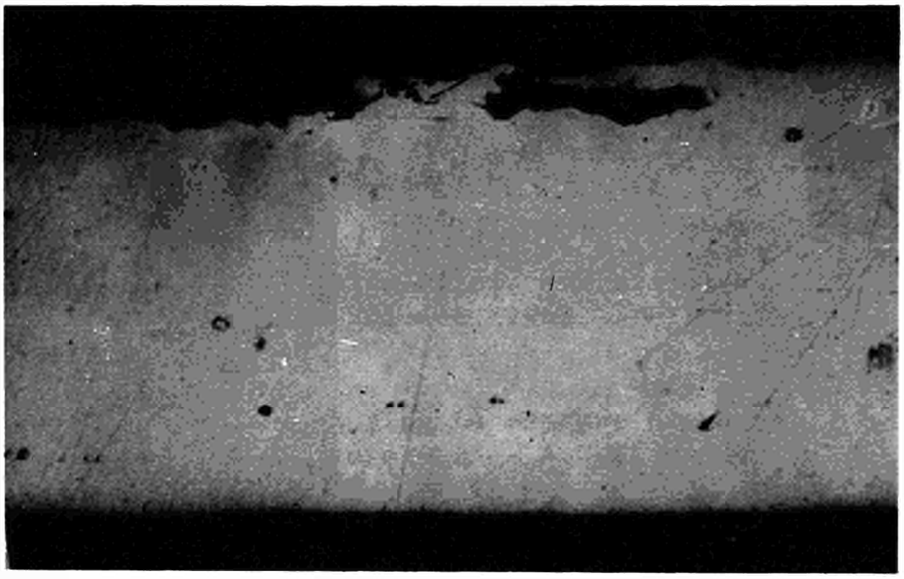
This photomicrograph of an irradiated thermocouple sheath shows that the intergranular corrosion has occurred on the internal and external surface of the sheathing tube (longitudinal section).



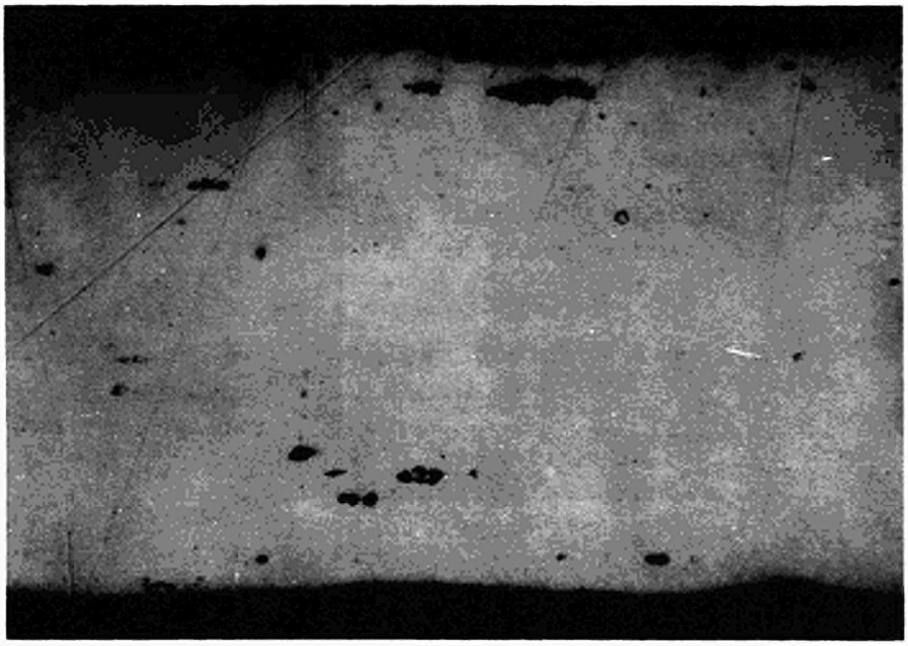
x 60

Fig. 4

Non-irradiated and unetched stainless-steel thermocouple sheath. These photomicrographs show extensive carbide precipitation. The condition of the external surface (top of the photomicrographs) is very bad. Some pitting and a very irregular appearance are revealed. In the photomicrograph b several inclusions are visible immediately below the external surface.



a x 550



b x 550

Fig. 5

Longitudinal section of sheath of half-millimetre diameter etched non-irradiated thermocouple sheath. Extensive carbide precipitation and some oxide inclusions can be seen. The appearance of the external surface is very bad (upper surface in photograph).

x 940

a x 430

Fig. 6

Longitudinal surface of wall of one-millimetre diameter non-irradiated thermocouple sheath. The photomicrographs show extensive carbide precipitation and several oxide inclusions.

b x 430

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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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