# *Metallography and Corrosion*

## *Proceedings of the Metallography and Corrosion Symposium*

*Sponsored by*

*National Association of Corrosion Engineers*
*American Society for Metals*
*International Metallographic Society*

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# Preface

Detailed laboratory studies of corrosion phenomena have contributed much to their practical and theoretical understanding. A number of new and improved analytical tools and methods have been developed in recent years and many of these have found usage in the corrosion field. Among these are many methods that can be characterized as generally belonging to the field of metallography.

In recognition of the important role that metallography plays in the study of corrosion phenomena, the absence of a text that specifically discusses this subject, and the belief that communication of information on the subject would be of technical interest, the National Association of Corrosion Engineers (NACE), the American Society for Metals (ASM), and the International Metallographic Society (IMS) sponsored a symposium. The intent was to bring together world-recognized authorities working in various aspects of the corrosion and metallographic fields to share methods they use, results they have obtained, and the purposes to which they utilize these results. The symposium, entitled "Metallography and Corrosion," was held in Calgary, Alberta, Canada, July 25-26, 1983. It followed 8 prior symposia which the IMS cosponsored with other societies on subjects such as "Metallography in Failure Analysis" (1977), "Metallography as a Quality Control Tool" (1979), and "Practical Applications of Quantitative Metallography" (1982).

The widespread interest in the symposium, shown specifically by the large attendance and enthusiastic participation, has encouraged us to publish the formally presented papers. These papers constitute the current volume. Our hope is that these proceedings will serve as a useful reference for individuals active either full- or part-time in the combined fields of metallography and corrosion.

Organizing a symposium of the size that resulted would not have been possible without contributions from numerous individuals. To all we owe a deep debt of gratitude, but especially we want to mention William E. White, General Chairman of the 1983 International Metallographic Convention of which the symposium was a part. The cooperation of the cosponsoring societies was assured through several individuals, most directly P. Crevolin of the National Association of Corrosion Engineers, Alan Gray of the American Society for Metals, and James E. Bennett of the International Metallographic Society. We also give special thanks to Anne Louise Egan for putting the entire proceedings in a uniform format and typing them in camera-ready form. Finally, we thank all the authors and session chairmen without whose participation the symposium would not have been possible.

We hope the combined efforts of these and many more unnamed individuals has resulted in a publication that will prove to be useful to the scientific community.

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# NUCLEAR TECHNOLOGY, CORROSION SCIENCE AND THE LESSONS FROM HISTORY

J. E. Harris*

## INTRODUCTION

From the very commencement of the nuclear power program the subject of corrosion has been of dominating importance. In many cases it was their relative corrosion resistance that governed the choice of materials and corrosion considerations which defined reactor operating temperatures. The nuclear technologist had also to deal with a relatively new and little understood process - radiolytic corrosion. This occurs when radiation of the gaseous or liquid medium creates active species which enhance chemical attack of the components.

Broadly speaking, the corrosion scientist in the nuclear field will be required to predict the endurance of materials over four widely differing timescales, as follows;

| Item | Approximate Timescale (years) |
|---|---|
| Fuel Element Materials | 5 |
| Reactor Core (plus decommissioning period) | 50 |
| Containment for Fission Product Wastes | 500 |
| Containment for Actinide Wastes | 500,000 |

It is, of course, the final item, the need to protect the biosphere from the actinides in the highly active waste for an appreciable fraction of a million years, which has captured the imagination of the public.

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Of the four timescales referred to above, by far the easiest to deal with is, of course, the shortest - the five years lifetime of the fuel element. This is a sufficiently short period for meaningful extrapolations to be possible from the results of laboratory experiments of reasonable duration. In addition to this, trials can be carried out in test reactors and as soon as the commercial reactor is commissioned, fuel elements can be withdrawn progressively from the reactor and examined in shielded facilities for evidence of deterioration [1,2]. These advantages led to the evolution of successful corrosion-resistant canning alloys at an early stage of reactor development. Perhaps the best known of these nuclear fuel canning alloys are the Zircaloy and Magnox series developed for American Water Cooled and British Gas Cooled Reactors, respectively. Both these groups of materials have stood the test of time to quite an astonishing degree. However, in spite of this success, the in-pile performance of fuel elements has still produced some surprises, as will be described.

The lifetimes of nuclear core and boiler materials are an order of magnitude longer and the task of predicting performance ten times as difficult. The chemical environments are formidable -- swirling super-heated water or the unremitting gale of a hot gas for up to forty years with little opportunity in many cases for repair or replacement or even for inspection. It is almost impossible to simulate such conditions in the laboratory and in any case the extrapolation would be too long to provide meaningful predictions. The corrosion scientist has to do the best he can and rely on in-service monitoring to confirm or deny his predictions. On the whole, the developments have been successful but two examples of shortfalls in performance will be described -- the occurrence of mild steel oxidation in Magnox reactors and "denting" in PWR steam generators.

To assist in making forecasts over a fifty year timescale the scientist must take into account the wealth of information on the corrosion behavior of a range of materials used in more conventional applications. Circumstances force him to consider his industry as part of an evolving technology. Some examples of corrosion problems in more familiar structures and historic monuments will be described.

When it comes to the five hundred year timescale necessary to contain the fission products, the only source of information is the archaeological evidence for the survivability of buildings and artefacts. The relevance of this archaeological evidence will be discussed and some examples given.

When the timescale is extended to the 500,000 year period of separation of the actinides from the biosphere then even the archaeological evidence becomes irrelavant and the scientist is forced to seek information from the work of the geologists. Studies of the corrosion of minerals, natural glasses and metals (mostly from meteorites) become of especial interest. Some of this work will be discussed briefly at the conclusion of this paper.

## VOLUME CHANGES DURING CHEMICAL AND PHYSICAL PROCESSES

A comprehensive survey of the corrosion of materials in all reactors would, of course, be a vast task and is not attempted here. To narrow the field, attention is focussed on examples where it is the volume expansion taking place during corrosion of metals which causes the problem. As is well known, if the reaction is taking place in a confined space, there is always sufficient energy released by the oxidation process to deform the metal thereby providing the required additional volume. At the risk of some oversimplification this can be explained as follows.

If the additional volume to accommodate the oxide is $\Delta V$ and if $\sigma$ is the average stress required to cause the metal to yield or to creep, then the work done in providing space is $\sigma\Delta V$. For the reaction to proceed then the energy released by oxidation, $\Delta F$, must be of sufficient magnitude to do this work. Thus the condition for oxidation-induced deformation is:

$$\Delta F > \sigma\Delta V$$

Setting reasonable values for the above parameters, it is found that the left hand side of the inequality exceeds the right hand side by typically three orders of magnitude [3].

The huge amount of energy released by oxidation processes should come as no surprise -- the oxidation of a liter of petrol (gasoline) will propel a fully laden vehicle to the top of a very high hill and the effort is in fact equivalent to the total work output of an average man toiling for several weeks. During the normal corrosion of everyday metal objects the energy is released so slowly that the associated temperature rises are too small to be detected by the senses. Nevertheless, the total energy release is enormous and it can sometimes be experienced, e.g., the explosive release of oxidizing metal powders in a firework. It is interesting that the heats of combustion per unit volume of magnesium and iron are greater than those of wood or oil.

Incidentally, while the energy releases do not compare with those of chemical changes, the above inequality is also satisfied for a number of important physical changes. Examples of these are crystallization from supersaturated solutions, allotropic changes and, in particular, the freezing of water. While their potential energy release is much less than oxidation [$\Delta F$ (oxidation) $\sim$500 kJ/mole; $\Delta F$ (heat of solution) $\sim$50 kJ/mole; $\Delta F$ (fusion of ice) $\sim$5 kJ/mole ] they are nevertheless sufficiently powerful processes to break down rocks to form soil -- an essential precondition for agriculture in support of human life.

## THE MAGNOX AND AGR REACTORS

The Magnox reactor is fuelled by a natural uranium rod encased in a finned magnesium alloy can. The elements are stacked vertically in channels in the graphite moderator and the coolant is carbon dioxide gas under pressure. For the early stations a steel pressure vessel was used, but for the later designs, at Oldbury and Wylfa, concrete vessels were employed. These reactors were the first "commercial" nuclear stations in the world and they still provide about ten percent of the electrical output of the Central Electricity Generating Board (the CEGB is the single Utility which supplies the whole of England and Wales with electricity). Besides the sixteen reactors operated by the CEGB, the eight prototypes at Calder Hall and Chapel Cross are still operating successfully (as they have done for the past 27 years). There is a twin reactor Magnox station in Scotland (Hunterston) and single reactor stations in Italy and Japan (Latina and Tokai Mura, respectively). There is also an extensive series of independently-developed "Magnox type" reactors operating in France.

The next stage in gas-cooled reactor technology in the UK was the development of the Advanced Gas Cooled Reactor (AGR). Again the coolant is carbon dioxide and the moderator is graphite with concrete pressure vessels. The principal difference is the design and materials of the duel element which consist of an array of "pins" consisting of lightly enriched uranium oxide pellets inside a stainless steel can. This permits higher operating temperatures and hence greater thermal efficiency. Currently, there is 9.4 GW(e) of AGR plant in operation or under construction in the UK. It is a unique system to the United Kingdom -- unlike Magnox there have been no foreign sales.

## THE MAGNOX ELEMENT

Over the years a number of different designs of Magnox fuel element have been developed and the one illustrated in Figure 1 has become known as the "polyzonal" type. The complete element consists of a solid rod of natural (i.e., enriched) uranium about one meter long and almost 3 cms in diameter. It is protected from corrosive attack by the reactor coolant gas by inserting it inside a finned can made from a magnesium -- 0.8 wt.% aluminum alloy known as Magnox AL80. The can is produced by first extruding a finned tube and then twisting it to give a helical pattern to the fins. The finned heat transfer surface is then divided into quadrants by cutting longitudinal grooves and inserting into them magnesium alloy strips, known as "splitters". The splitters are held in place with welded "braces" and the can is sealed by welding on "caps" at either end after insertion of the fuel rod. The polyzonal can is being replaced at a number of stations by the rather superior "herringbone" design which has sturdier, machined fins. It is not necessary to describe this design further here because the phenomenon of interest, fin waving, is essentially confined to the polyzonal type. It is, however, of interest to trace the development of the fuel element over the years, paying especial attention to the fins.

## THE EARLY DEVELOPMENT OF THE FUEL ELEMENT

The progenitor of the Magnox element was the uranium rod in a plain aluminum can used to fuel the low energy graphite pile known as GLEEP. This was constructed at Harwell shortly after the end of World War II. It marked the beginning of Britain's independent development of nuclear energy. There followed the construction of the medium energy pile, BEPO, at Harwell and then the plutonium-producing piles at Windscale. All of these air-cooled graphite-moderated piles used natural uranium rods in aluminum cans. During the course of these development, fuel element fins evolved, rather like the dorsal spines on the plated dinosaur, and for the same reason, to dissipate heat. Fins were first used on fuel for BEPO -- the forerunner for Windscale. At that time it was considered that the Windscale piles would have to be pressurized involving the construction of a large steel pressure vessel around the reactor core. It was then found that the fins were so efficient in improving heat transfer that pressurizing was not necessary and this hugely eased the constructional difficulties and permitted the piles to be completed on a short timescale. Subsequently it was realized that a combination of finned fuel elements and pressurizing opened the door for the development of the first commercial electricity-producing pile, the Magnox reactor. Thus it can be seen that the evolution of fuel element fins has played an important part in the development of nuclear power.

As already mentioned, a principal theme running through this paper is the influence of volume changes taking place during chemical reactions on the development of the technology. It is then particularly interesting that it was such a volume-increasing reaction that finally forced the changeover from aluminum to magnesium cans. One of the main disadvantages of aluminum was that it reacted chemically with the uranium producing $UAl_3$ particles. The resultant volume change caused "pimpling" on the surface of the uranium bar and distortion, and even fracture, of the aluminum cladding. This chemical interaction was minimized by inserting a graphite barrier between bar and can but at high temperatures and burn-ups (such as would be experienced in the projected commercial reactors) the barrier was no longer very effective. Of course, the changeover to magnesium would not have been possible had not Littler and Colmer [4] previously discovered that, contrary to earlier findings, the neutron absorption cross-section of this chemical element was acceptably low. Also vital was the development by Huddle and others of the corrosion-resistant magnesium-aluminum canning alloy. Incidentally the alloy's name, Magnox, (MAGnesium No OXidation) has been chosen for the complete reactor system, thereby perpetuating an acknowledgement of the importance of corrosion in early reactor technology. An interesting development was the finding that trace quantities of beryllium improved the ignition characteristic of the Magnox alloy.

## OXIDATION OF URANIUM

Another volume-increasing chemical process had manifested itself from the very early stages of the fuel element development program. When the cladding was punctured during service, and carbon dioxide came into contact with the hot uranium, it oxidized it with an associated unusually-large increase in volume (approximately a factor two). An example of an oxidized fuel element is shown in Figure 2. This increase in volume is normally very beneficial because it opens up the original leak path making it detectable by the burst cartridge detection gear (the instrument which measures the release of fission products into the gas stream thereby detecting a fuel element failure). As soon as it is discovered, the failed element can be discharged on load without difficulty. On rare occasions the oxidation occurs at a site remote from the primary leak so that the final (detectable) rupture of the can wall only takes place after very extensive oxidation has occurred. Such failures, known as "fast bursts", because of their final rapid failure mode, have been very troublesome. The discovery that the bar could oxidize completely, yet still support the weight of those elements above it in the reactor channel without collapsing, was very reassuring.

## FIN WAVING

The fuel element fins are fragile appendages, only ∿1 mm thick at their tip yet operating at three-quarters of their absolute melting temperature. Their development forced the metallurgist to become interested in deformation processes at very low stresses and high temperatures. Interestingly, it led to the recognition that a dominant deformtion mode in the fuel can during its life in the core was Nabarro-Herring (diffusion) creep [5,6,7]. This was the first occasion that this fundamental deformation process had been identified as having practical significance in engineering [5,6,7]. However, early experience confirmed that the fins did not flatten in the gas stream and this was encouraging. Everything appeared satisfactory until it was found, upon examining some fuel elements after three years irradiation in a reactor at Dungeness, that the fins had become deformed and adopted a waving configuration, see Figure 3. Clearly the tips of the fins had grown longer than their bases and the additional strain had been accommodated by waving.

It was first thought that the strain was due to some thermal cycling ratchetting occurring in the reactor, but the effect could not be simulated in the laboratory. A suggestion by Eldred that the effect may be associated with the formation of the thick dark deposit on the fin surfaces was first of all rejected out of hand. Microscopic studies of the fin tips revealed a flowed layer of metal beneath the deposit, thereby lending support to Eldred's proposal. At this stage serendipity played a part -- some heat transfer tests were performed on complete fuel can assemblies involving heating them up to a high temperature in a furnace. As a fire precaution, a mixture of bitumen and slate was placed in the bottom of the furnace and the fumes from this caused the fins to wave in a manner closely similar to that which had taken place in the reactor. "Oxide stretching" had been demonstrated -- the first time the elongation of an essentially plane metal substrate had been recorded as occurring in an engineering component. A literature search revealed that Darras [8] and his co-workers had indeed found that their thin magnesium alloy specimens had increased in length (by up to 14%) upon exposure to hot carbon dioxide gas, see Figure 4. Although the length change was recorded it was not thought to have any particular significance at the time.

A particular puzzle was associated with the fact that the magnesium atom occupies less volume in its oxide than it does in the metal lattice itself. (The average volume per metal atom in the oxide divided by the atomic volume in the metal is known as the Pilling-Bedworth Ratio [9]: magnesium is very unusual having a PBR of only 0.8, nearly all other metal/oxide systems have a PBR > 1). According to the simple theory, on oxidizing magnesium the oxide should be in tension and the substrate in compression, i.e., a shortening tendency for the metal rather than the observed lengthening. In fact, the value for the PBR only dictates the sign of the induced stress when the new oxide forms at the oxide/metal interface, which is not the case with magnesium. In any case, the corrosion which takes place in contaminated carbon dioxide produces a mixture of oxide, carbonate and carbon with an effective PBR which can be greater than unity.

Early work [10] on the corrosion of magnesium and Magnox AL80 in oxygen revealed that the oxidation rate was increased in the presence of hydrocarbons. These studies were subsequently extended by Antill et al [11]. Howlett and Jones [12] carried out a series of exposure tests on strip specimens of Magnox AL80 and found that significant stretching did not occur in pure $CO_2$ at high temperatures nor in $CO_2$ with deliberate additions of CO and $CH_4$, both of which are common impurities in the reactor gas. However, contamination of the gas with water vapor or higher hydrocarbons resulted in appreciable strains, see Figure 5. Attempts were made to reduce the concentration of these harmful impurities in the reactor gas, but it was difficult to determine whether or not this had a beneficial effect. In any case, considerable fin distortion, and associated degradation of heat transfer properties, had already occurred so that there was no alternative except to lower the reactor operational temperature with an associated power loss of about 40 MW(e). This was the first example of the expansive forces of corrosion leading to a loss in power output.

## THE SODIUM HYDROXIDE TREATMENT

When the important role of hydrocarbons was realized, Antill et al [11] reasoned that just as sodium ions are known to poison catalytic sites on alumina (used to crack hydrocarbons) treatment of a preoxidized magnesium sample with a sodium compound may be beneficial. They confirmed their prediction by comparing the bheavior of a preoxidized and sodium hydroxide-treated Magnox sample with one that had been simply preoxidized after exposure to $CO_2$ + 1% decane for 500 hours at 500 C. The untreated sample elongated by 6% whereas the treated specimen increased in length by <0.02%. The effect of the sodium hydroxide treatment can be quite dramatic -- Noden [13] treated two quadrants of a fuel element by swabbing with sodium hydroxide solution and left the remaining two bars untreated -- the result after exposure to a 15% butane-$CO_2$ mixture for 144 hours at 500 C can be seen in Figure 6. Unfortunately, later work by Williams [14] indicated that the effect of the sodium hydroxide was not permanent enough for it to be readily developed into a treatment which could be used routinely to protect commercial fuel elements. The phenomenon remains one of much scientific interest, however, and the further study of it might help to elucidate the mechanism of oxidation in hydrocarbon-contaminated atmospheres. Incidentally, Williams [14] also made the important discovery that a radiation field influences the stretching action.

## THE ELONGATION OF AN AGR 'PIN'

It so happened that just before the waving phenomenon was first observed, evidence of the oxide stretching of a fuel can was in fact observed [15], though not with a Magnox component but with a stainless steel "pin" developed for the AGR system. The pin sample consisted of a 20%Cr-25%Ni-Nb stainless steel tube of wall thickness $\sim$0.25 mm which was exposed to air for 887 hours at 900 C when it increased in length by 1.5%, see Figure 7. Although some of the strain could be attributed to the thermal cycling to which the pin had been subjected, separate experiments demonstrated that the major part was due to the isothermal exposure. From a knowledge of the creep properties of the steel, Noden et al [15] calculated that it must have been subjected to a tensile stress of $\sim 4 \times 10^6$ N/mm$^2$.

## THE MECHANISM OF STRETCHING

Where oxidation occurs in a confined space it is immediately obvious how the expansion can lead to stress being generated in the surrounding medium. The deformation of an essentially plane metal substrate as a result of oxide forming on its free surface, is less easy to understand. The earliest model is that due to Pilling and Bedworth [9] who suggested that if the oxygen ion only, was mobile in the scale, the metal lattice would attempt to expand or contract to its equilibrium spacing in the oxide and this would lead to the generation of stress. This explanation seemed satisfactory until it was found that in fact it is the metal ion which is mobile in most oxide scales. Hence, the new oxide forms not at the oxide/metal interface but at the interface between the oxide and the corroding medium. In such circumstances there is no a priori reason for the generation of stress.

Rhines and Wolf [16] proposed that in metal/oxide systems, even where cation diffusion predominates, some anion diffusion occurs down the oxide grain boundaries and then a chemical reaction takes place with the outward moving cations forming new oxide within the scale, see Figure 8. Obviously, such a process would create a compressive stress in the oxide with a corresponding tensile stress in the metal substrate (incidentally the sign of the stress system would be the same were the PBR $< 1$). This explanation gained acceptance for some time until it was pointed out [17] that in order for new oxide to form at the old grain boundaries the boundaries would have to act simultaneously as anion vacancy and cation vacancy sources and this requirement violates the Shottky condition that the product of the defect concentrations should be a constant. Of course, there are circumstances where new oxide can form at grain boundaries, for example during diffusion creep deformation, but this is in response to an externally applied stress. In other words, the formation of new oxide at grain boundaries can relieve existing stress but it cannot, of itself, create new stress. It seems that if the source of stress is due to growth of new oxide within the scale, this must form in cracks and open pores.

It is possible that the commentators on oxide stretching may have been too cerebral, i.e., over concerned with trying to understand every aspect of the process even at the atomic level. It could be that it is extremely difficult for a new phase to form without generating internal stress, simply due to the manner of its formation as growth centers impinge on their neighbors. It has been known for almost a century that the simple process of salts coming out of solution can lead to the generation of stress, the so called crystallization force, which is sufficient to cause rocks to disintegrate. This occurs even where the overall crystallization processed lead to a net reduction in volume. Desch discovered in 1914 that Plaster of Paris may break a test tube as it sets even though there is an accompanying reduction in volume of about 7%. Perhaps in nature it is the formation of a new phase which is free of stress which is the truly unusual event.

## "GROWTH" OF CAST IRON

At the time that fin waving was first observed the most widely studied phenomenon in the field of oxidation deformation was the "growth" of cast iron. Countless cast iron components used as fire grates and in stoves had suffered distortion due to a combination of high temperatures and thermal cycling in oxidizing atmospheres. Interestingly enough, there were examples [18] of plane sheets of cast iron exhibiting tensile strain, see Figure 9. However, the microstructure of cast iron makes it a special case; during annealing, the subcritical cementite ($Fe_3C$) decomposes to ferrite and the latter frequently attaches itself to the original eutectic graphite flakes. The decomposition of cementite to graphite is accompanied by a large volume expansion and this will, of course, increase the external dimensions of the component. In addition to this, oxidation occurs preferentially along the metal/graphite flake interface so that the elongation process in this case is more of a "jacking" than a stretching action. This is a good illustration of how complex the elongation process can be. It emphasizes the potential importance of internal oxidation. Incidentally, it has been found recently that during the oxidation of stainless steel, silicon is preferentially oxidized close to the surface at the metal grain boundaries. The increase in volume associated with internal oxidation might account for at least part of the increase in length of the AGR pin described earlier.

## THE ROLE OF CARBON

Returning to the subject of oxide stretching of magnesium, the enhancement of strain when the corroding gas contains hydrocarbons is worth further consideration. Antill et al [11] suggested that magnesia may catalyze the breakdown of hydrocarbons and, in fact, small quantities of free carbon have been found in the corrosion product by other workers. Although Antill et al reject the suggestion, it seems possible that a process analogous to the Boudouard reaction could play a part in the deformation process.

## The Boudouard Reaction

The Boudouard reaction, which has a significant rate only upon a catalytic surface, leads to the deposition of elemental carbon:

$$2CO \rightarrow CO_2 + C$$

This deposited carbon can give rise to extensive deformation of the catalyzing surface. Two examples will be described. It is, of course, a process which is different in one important respect from oxide jacking -- the metal does not take part in a chemical change, it is simply a catalyst. Nevertheless, the end result is similar to that produced by oxide jacking.

Perhaps the best known example of the occurrence of the Boudouard reaction is the damage it causes in blast furnace fire bricks. It often leads to the production of carbon at iron spots in the bricks leading to expansion and disintegration. Carbon may also form by this process at iron bars used to reinforce the walls of the furnace. In one example quoted [19] a lump of carbon about 0.3 m in diameter formed around a reinforcing bar. The carbon grows as filaments and has been compared to various biological growths. Its formation can be so damaging as to require the complete replacement of a blast furnace lining within a year, whereas it should have lasted several years. So extensive has been the problem that a standard routine test has been derived to test the susceptibility of fire bricks to "carbon jacking".

Incidentally, there are a number of other volume-producing reactions which can cause damage to fire bricks. A classic oxide-jacking process occurs when molten iron penetrates the brick and subsequently oxidizes.

The Boudouard reaction can also cause damage to steel samples heated in carbon dioxide. This process, because of its potential importance in gas-cooled reactors, has been extensively studied by Pendlebury and his colleagues [20,21]. The result of one of their experiments is illustrated in Figure 10 where a mild steel specimen has had a pre-existing wedge shaped crack extended by the deposition of carbon after exposure to carbon monoxide gas for 200 hours at 500 C. Electron microscopy of the carbon deposit revealed that it consisted of an assembly of filaments. The geometry of these was quite complex. Figure 11 illustrates an array which had formed a double helix. The filaments took the form of thick walled tubes; the growth center was an iron-containing particle which remained in the filament tip. The fact that