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Cold Fusion at ENEA Frascati: Progress Report

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Abstract

The resources dedicated by ENEA to Cold Fusion research in the last two years have been strongly reduced. Nevertheless, fruitful activity has been performed following two main lines.

The first line attains to the effort for reaching high values of D/Pd ratio in Pd in order to obtain the best conditions for cold fusion phenomena, in particular power excess production in electrolytic cells. The outcome of this research is the definition of the starting characteristic of Pd (metallurgy), and the procedure for its loading with Deuterium. The calorimetry by now assessed at ENEA Frascati has been used for the detection of power excess.

The second line concerns the attempt to detect in a clear way the production of ^4He during the power excess episodes. A system aimed to the analysis of the gases evolving from the electrolytic cell is being realised and will be briefly described.

Introduction

The literature on cold fusion has indicated the existence of a threshold in the concentration of Deuterium in Palladium, above which it is possible to observe an anomalous heat released from deuterated samples (1,2). Therefore, research in Cold Fusion at the ENEA Frascati laboratory in recent years has focused on studies of material science aimed to qualify Pd samples to be used in the electrolytic experiments. The main goal was to find those characteristics that lead to high loading ratios ($x > 0.9$ D/Pd) with a high grade of reproducibility. The flow mass calorimetry discussed in previous papers (3) could then be used to look for the heat excess produced during electrolysis with a precision of 20 mW in a range from 0 to 20 W.

It is well known that hydrogen dissolves in many metals and occupies interstitial sites in the host lattice. It expands the Pd lattice parameter up to 10%: this process generates stress fields when substantial concentration differences (strong gradients or coexistence of different phases) are created. The stress field can inhibit the hydrogen (deuterium) diffusion process (4). In order to overcome such limitations two strategies can be tested: first, to modify the loading dynamics avoiding the growth of high gradients; second, to prepare a material with a suitable microstructure to minimise the solute concentration gradient. Therefore, we studied the influence of dynamics on the loading process and found that different mechanisms of loading can be activated according to the sequence of thermodynamic states of the system during the loading itself. Moreover we tested the relevance of the material microstructure (i.e., grain size, dislocations) on the capability of the lattice to absorb hydrogen (and deuterium) and came to the definition of a grain size range in which the maximum loading ratio achievable is reproducibly greater than 0.9 D/Pd. Such studies and the analysis of the modifications induced by the loading on the Pd lattice showed that the sequence of steps leading to the transformation from Pd to high concentration PdH(D) is very complex and can easily explain the lack of reproducibility that commonly occurs in cold fusion experiments.

We also studied thin films of Pd, deposited on both metallic and polymeric substrates, to obtain a uniform distribution of solute into the lattice. The Pd films have been characterised via

Scanning Electron Microscopy and X-Ray Diffraction. Several configurations, such as Pd on Ni, Pd-Ni multilayer, Pd on polymers have been tested to optimise the deuterium absorption. The substrates were chosen in order to minimise the mechanical stress due to lattice expansion during the hydride/deuteride formation.

We are interested as well to investigate the nature of the heat excess produced in deuteride samples. The most common idea is that a ^4He atom formation from the D+D reaction releases about 24 MeV to the lattice and is responsible for the excess heat measured. We designed and built a system able to detect ^4He atoms present in the gases evolving from an electrolytic cell. The system is based on high resolution mass spectroscopy. However, because of the intrinsic difficulty due to the high level of ^4He contamination in the normal air (5 ppm), we built a system in which all gases except the nobles are pumped out before reaching the mass spectroscope quadrupole. This feature together with a static mode of operation in which gases evolving from the cell are accumulated and analysed once per day, will allow us to make an estimate of the ^4He atoms contained in each sample and to correlate that with the heat excess measured.

Experimental Procedure

We envisaged two possible approaches to avoid inhibiting the diffusion process. First, concentration gradients (and adverse stresses) can be minimised during the loading sequence. During the hydride formation the higher concentration β phase ($\text{D/Pd} > 0.67$ at 20°C) grows into a lattice together with a very dispersed concentration of H(D) atoms called α phase. This corresponds to regions with a very different lattice parameter (from 3.894 Å to 4.025 Å). At the borders of the different phases a very high strain is accumulated, its intensity comparable with the yield stress of the material. Thus, samples loaded passing through or avoiding the two phase coexistence region show very different metallurgical properties, i.e., the yield stress can be reduced of about 50% if $\alpha+\beta$ region is skipped during the loading (4). The second approach is to relieve the stresses generated in the metal through dislocation slipping, i.e., anodic stripping during electrolysis. Both procedures lead to a small increase in concentration (5).

These results can't be considered conclusive, but they show that the stress field inside the Pd lattice is largely responsible for the inhibition of the diffusion process.

We then went on to study the influence of the concentration of short circuit paths (dislocations and grain boundaries) on the diffusive process. The hydrogen diffusion coefficient is an order of magnitude higher in the grain boundaries than in the bulk. Thus, by increasing the grain boundary density (i.e., small average grain size) the diffusive process may take place in two steps: first, hydrogen is incorporated in the grain boundary network where the diffusivity is higher, permeating the material bulk without generating substantial strain, owing to the small volume fraction involved. In a second step it can be incorporated into the grain bulk by a diffusion process where the grain boundary acts as a source.

A maximum loading ratio is observed in a certain range of the grain size, around 50-60 microns. We attribute this effect to the presence of two factors that enhance the H diffusion into the material and show an opposite trend with grain size: a smaller grain size reduces the strength of the stress field at the sample surface since the grain boundary network plays a leading role as a fast H (D) transporter through the sample bulk; the softening of the mechanical properties induced by a larger grain size can activate stress relief mechanisms based on plastic deformation. Traces of this effect can be found in the morphology of the sample surface after the H (D) charging procedure.

Even though the statistics are quite poor, there is an increase of the successful experiments if the correct grain size of the Palladium is selected (see Fig. 1). The effect observed was very

small, but it is quite clear and outside the error of the calorimeter.

Electrodes prepared in Frascati have operated in an SRI calorimeter following the above-described loading protocols and results similar to ours have been obtained (6).

We then started an investigation of Pd thin films (1000-2000 Å), to test whether lower dimensions can help in relieving the stress. Nickel seems, at a glance, the best metallic substrate in Pd hydride preparation for the following reasons: Pd and Ni have both the fcc structure; they both expand their lattice by dissolving Hydrogen atoms in the volume; the difference between strains can help in reducing the stress at the boundary between film and substrate.

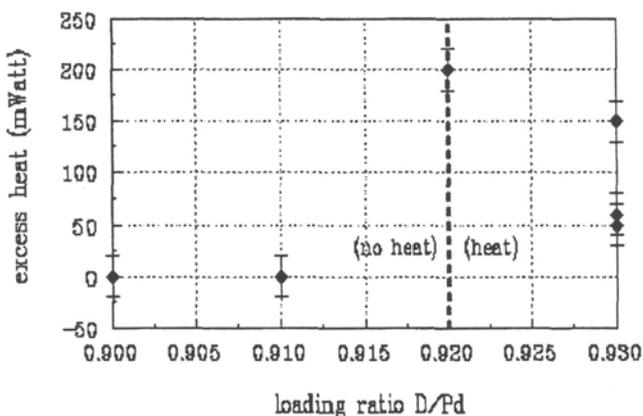


FIG. 1 Reproducibility of heat excess experiments for samples with average grain size 50-60 microns.

We also tested different substrates such as polymers, but the data interpretation is complicated in this case by the modification of the polymer physical-chemical characteristics during the electrolysis. Thus we will report only the results obtained on Nickel substrates.

We prepared Nickel plates (100 μm thick) coated with thin (1000-2000 Å) Palladium film by thermal deposition in vacuum. Because of the difference in the thickness of the two metals and their similar resistivity, it is impossible in this case to distinguish between the Pd and the Ni resistance and hence to monitor the loading ratio in real time during the experiment. However, it can be said that the presence of Pd on the Ni surface increases the Hydrogen absorption (see Fig.2).

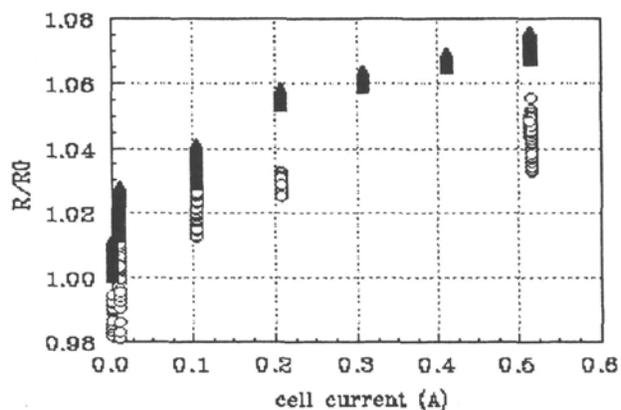


FIG. 2 Effect of deuterium loading on Pd-Ni. Black triangles Pd film on Ni. Open circles pure Ni.

We also measured the behaviour of heat excess versus the total R/R_0 and found always a similar trend in all the experiments done (see Fig.3). We always measured an exponential behaviour of the heat excess versus the R/R_0 parameter (i.e. the concentration).

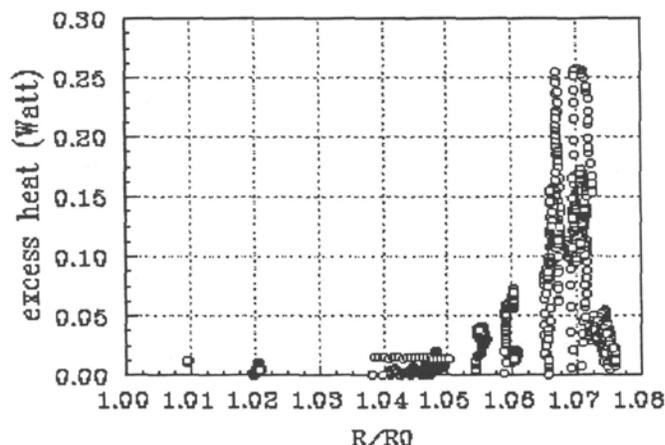


FIG. 3 Heat excess of a Pd film (1000 Å) on Ni plate.

A new test of thin film behaviour in electrolysis in heavy water has been done. We built a multiple cathode cell in order to test whether the excess power measured is a multiple of the one measured in a simple cell. The scale up of the system is probably the best way to persuade the skeptics of the reality of the heat excess production.

The first configuration used is a set of parallel electrodes: anode-cathode-anode-cathode-anode. This geometry is very complex from an electrochemical point of view, because we don't know exactly the primary current distribution, the electric field configuration and the boundary field effect. Further, there are still unsolved problems with the film adhesion on the substrates that limits the electrolysis time to few days.

At first glance parallel electrodes work in parallel with the same voltage and almost equal currents, but this is correct only if all electrodes behave the same way. The comparison between double and single cathode cells shows an increase of the excess heat measured (see Fig. 4).

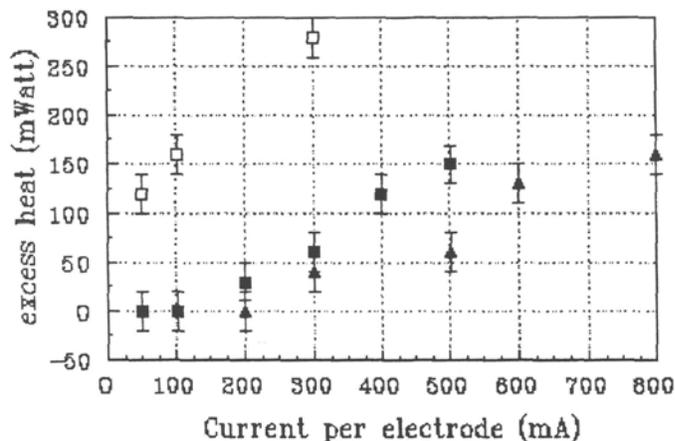


FIG. 4 Comparison between single and multiple electrode configuration. Open square: 2 cathodes, closed triangles and squares: 1 cathode.

Traces of ^4He are searched for in gases evolving from the electrochemical cell.

The method chosen consists in: accumulating the gases evolving from the cell in a small volume containing a catalyst for a time of the order of a day, expanding it into a volume containing activated charcoal at 77 K, thus eliminating water vapour, oxygen and other condensables, expanding once more the remaining gas in a stainless steel UHV chamber equipped with a high resolution mass spectrometer, pumping with a getter pump which eliminates all but noble gases. When steady state is reached, the signal of the spectrometer gives a measure of the number of ^4He atoms collected. The piping connecting the electrolytic cell and the detecting system has been tested against pollution from the ^4He contained in the atmosphere, giving an upper limit of 10^{13} atoms per sample due to air pollution. The first tests aimed to calibrate the system have been made, with satisfactory results.

The first measurements will be made on the gases evolving from the electrolytic cells; further developments will allow the detection of the gases embedded in the electrodes through the metal dissolution.

Conclusions

Summing up the results reported above, it is possible to state that there has been a steady, even if not fast, progress in pursuing the main aims of the ENEA-Frascati program, which are the realisation of reproducible experimental conditions for the production of heat excess and the subsequent search for nuclear ashes. The study of both the dynamic of the absorption and the metallurgy of Pd (4,5), has allowed the reaching of reproducible high loading (>0.9 D/Pd) and the quasi-reproducibility of heat excess production. The use of thin Pd films, just started, seems very promising both for obtaining high loading ratios and testing the scalability of the phenomenon. The use of a static measure of the possible presence of ^4He , intended as a nuclear ash of the D+D nuclear reaction, is in phase of assessment, and faces this problem in an original fashion, very promising for the neatness of its results.

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