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REPLICA ELECTRON MICROSCOPY OF IRRADIATED FUELS

Remarks on the Method

by

C. RONCHI, E. BAZIOR and H. KOSTECKA

1971

Joint Nuclear Research Centre
Karlsruhe Establishment - Germany
European Institute for Transuranium Elements

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ABSTRACT

The application of the replica technique and electron microscopy to the analysis of irradiated fuels is discussed with respect to the experimental technique. The most suitable replication methods for the various observable features are established on the basis of results obtained by the examination of irradiated fast reactor fuels.

KEYWORDS

REPLICA TECHNIQUES
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FAST REACTORS
INSPECTION
FOILS
ETCHING
GRAIN BOUNDARIES
BUBBLES
POROSITY
ACETYLACETONE

C O N T E N T S

INTRODUCTION *)

For a better understanding of the complex dynamics involved in the changes of the fuel structure during irradiations, features falling outside the field of resolution of the optical microscope, must be studied. Scanning electron microscopy (SEM) and replica transmission electron microscopy (REM) are the most direct ways to extend the surface analysis down to a resolution of about 100 Å.
The last method was largely used for the examination of irradiated fuel by several authors with different performances with somewhat different success.
The resolution obtainable by REM is indeed depending on the preparation methods of the replicas and on the state of the replicated surface. Hence the method must be adapted to the particular features one wants to observe. In the specific case of irradiated fuels, it is important to localise the highly magnified electron optical details on light optical micrographs of relatively low magnification, in order to establish precise correlation between the structural features and the properties deduced from the local analysis.

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*) Manuscript received on June 1, 1971

1. Experimental technique

Because of their high activity irradiated fuel specimens must be handled in shielded cells, where manipulation of thin films is impossible. Therefore, a two-stage replica technique was adopted.

1.1. 1st stage

Triafol foils(acetobutyrate) of o.ol to o.1 mm thickness are put on the specimen moistened with acetone and are allowed to dry. If the aceton is rightly dosed on the surface, the capillarity forces are large enough to establish a perfect contact between foil and specimen, without pressing. Depending on the configuration of the surface (i.e. its roughness) more or less acetone must be sprayed on to the surface. For instance, a surface containing deep cracks to be examined, must be replicated with a thick triafol foil with more acetone than in the case of a polished surface, where the use of thinner foils is more suitable.
Usually the first three or four strips serve only to clean the surface. These replicas are always very radioactive (at 5o cm distance more than 7o mrem.). Their examination shows that they usually contain some particles of the material to be replicated.
The fourth replica often shows a reduction in contamination of about a factor of ten with respect to the first one.
At a residual activity of about 5 mrem the specimen is checked for alpha activity and only replicas having less than looo alphas/cm^2 min. are brought into a glove box for a first decontamination. Here the replicas are washed in two steps ; firstly they are treated in two ultrasonic baths (with neutral solutions), then in a second glove box, a final ultrasonic bath sequence in water reduces their activity to less than 2oo alphas/cm^2min. At this moment the foil may be handled with a certain caution outside the boxes.

1.2. Shadowing and second replication stage

The triafol is shadowed with carbon or germanium at suitable angles, and then a supporting film of about 100 Å of carbon is deposited onto the replica . Later on the following operations are performed to remove the final replica from the triafol :

i) the triafol is coated on the shadowed side with molten sugar to avoid that the rapid dissolution of the foil curls up the carbon sheet.

ii) the triafol is then dissolved (in about twenty min.) and the remainder is rinsed in methylacetate.

iii) an electron microscope grid is placed on a fine net supported in a vessel containing water. The net is located close to the surface of the water in such a way that it is just moistened by the capillary forces

iv) the coated carbon film is put on the grid with the sugar bottom and the interesting part of the replica is centred on the grid with the help of a stereomicroscope.

v) the sugar is slowly dissolved by the water and the carbon replica finally lies on the grid.

The grid with the replica is photographed under transmitted light in a microscope. On the magnified light micrograph those parts of the replica are indicated, which contain the features to be studied in the electron microscope. Grids of particular shape are used to facilitate the determination of the position of the examined point.

2. Preparation of the specimen surface

The preparation of the specimen surface for replication is a delicate work, which, in our case, must be performed with very time-consuming remote manipulation techniques. Therefore, it is important to exploit the samples as much as possible.

TABLE 1

FEATURES	MOST APPROPRIATE SURFACE FOR ANALYSIS
Small gas bubbles (up to 1000Å)	cut, polished and slightly
Small precipitates "	cath. vacuum etched surface.
Larger bubbles and pores (several microns)	inter or intragranular fracture, or cut polished
Large precipitates "	and deep etched surface.
Grain boundaries	intergranular fracture surface
Cracks	cut surface

Three types of surfaces can be prepared for replication :

a) fracture surfaces
b) polished surfaces
c) polished and etched surfaces

In an irradiated fuel the most interesting features, indicated in table 1, are more or less detectable depending on the way of surface preparation. Hence, the choise of the type of preparation of the surface is made on the basis of the features to be studied. In the next paragraphs a detailed discussion of the surface preparation techniques is made from this point of view.

3. Surface features and their replication

3.1. Fission gas bubbles and small precipitates.

3.1.1. Previous work.

The first electron micrographs of irradiated fuel showing gas bubbles were presented in 1960 by Bierlein et al. (1). Later on other results were published in the IAEA Symposium in Vienna (1963) (6,)7 ; Mikailoff and coworkers (2) tried to make a quantitative treatment of their replica micrographs, measuring swelling coefficient, bubble density and gas concentration. (+) Various methods of quantitative metallography were used to determine these parameters (1,3).

(+) The dimensions of the fission gas bubbles and solid fission product precipitates may fall down the limit of resolution allowed by the replica method, i.e. about 100 Å . The REM analysis of these defects is therefore incomplete, nevertheless for many purposes (e.g. swelling calculation, study of fission product kinetics etc.) the data recognizable with REM are largely sufficient.

Nevertheless a direct critical comparaison between the micrographs, obtained on the same specimen by REM and TEM, was made only in 1965 by Bainbridge and Hudson (4). These authors remarked that the bubbles observed on the replica were larger than those observed by direct transmission, in the same specimen, by about a factor of two. We shall examine in the next paragraphs the causes of this enlargement. In the same work it was pointed out that the cathodic vacuum etched surfaces were always the most suitable ones for the bubble replication.

More recently Ross (5) observed fission gas bubbles on fractured surfaces of irradiated fuels. The replication method was that of direct carbon deposition, however, the resulting resolution was not better than that obtained with the two-step methods ; Ross did observe indeed bubbles down to about 2oo Å diameter.

3.1.2. Adopted technique for revealing gas bubbles

After a large number of different attempts, we observed that the best resolution for bubbles and small precipitates is obtained by replicating polished and slightly cathodic vacuum etched surfaces. The specimens are prepared as follows :

prior to cutting, they are impregnated under vacuum with araldite to prevent fragments being dislodged and lost during subsequent processes. Cutting is effected by a diamond wheel.

After cutting the specimens are mounted in plastic and ground on a polishing machine with a "whirlemet" attachment for holding these specimens. Papers on which the specimens are ground are 32o, 4oo and 6oo grid. Polishing is effected using diamond pastes of 6,1 and 1/4 u grades. The lubricant used during polishing is a special oil for diamond paste AB Automet, from Bühler Ltd. Between each of the grinding and polishing steps the specimen is ultrasonically cleaned in CCl_4 and after the final polish is also rinsed in alcohol and dried in a stream of hot air.

The specimens are etched in a cathodic vacuum etching device, using an Argon beam accelerated at 8 Kev. During the bombardment the vacuum is lo^{-3}/lo^{-4} torr. The bombardment dosis is about $1,5mA/cm^2$ for forty minutes. The sample holder, inclined at an angle of 45^{o}, rotates during the etching to prevent the formation of pits. An exemple of surface with gas bubbles, prepared with this method is given in Fig. 1. Note that the shadowing angle must not necessarly be small to reveal small bubbles.
If the cathodic etching is too deep, the surface becomes so rough that it is spoiled for the observation of small features (see fig. 2).
On the other side, we remarked that the non-etched specimens give a poor resolution on the replica (see fig. 3). Probably the effect of the etching is to clean perfectly the surface and to improve the capillarity forces during the penetration of the plastic in the surface irregularities.

3.1.3. Etching effect on the sizes of the small defects.

It is necessary for quantitative measurements to know the effect of the etching on the dimensions of the sections of bubbles and precipitates in a given cut surface.

a) Bubbles

Both chemical and vacuum cathodic etching were checked on the irradiated fuel specimens.
The shape of the bubbles etched with nitric acid is shown in fig.4. One sees that the attack changes the spherical shape of the bubbles and prevents the determination of their size.

The cathodic vacuum etching on the contrary seems to preserve the spherical shape of the bubbles, but since the sheet of material removed by the ion bombardment is much larger than the diameter of the etched features, a sensible enlargement of their sizes is to be expected. This effect is discussed in detail in Appendix 1. An average statistical enlargement factor of 1.3 is deduced for all the bubbles having sizes under about o.5 microns, that represents the estimated layer depth removed during etching. For larger cavities this factor drops.
Because of the thickness of the shadowing film, which falls in the dimension range of the smallest observable defects, their shadows are not well defined, but are contoured by a half light zone having a depth comparable with the foil thickness. That makes difficult the measurement of the actual shadow wideness and tends to involve a systematic over-estimation of the sizes. Measuring the external size of the bubble contours is not advisable because in this use the over-estimation factor is a function both of the sheet thickness and of the bubble size. However, if the internal sizes of the shadows are measured at large magnification (e.g. by optical lo x projection of a lo.ooo x migrograph) the involved systematic error is not larger than 15 % for bubbles of some hundred angstroms. Finally, for practical purposes a correction factor is assumed, taking into account the above mentioned etching enlargement, obtaining a value of about 1.5 (if the cross section radii are measured the factor becomes 1.77).

3.2. Large pores and precipitates

In nuclear fuels the state of the residual porosity and the larger intergranular fission gas bubbles are the most important features related to the in-pile behavior. Only electron microscopy allows to investigate the internal structure of the pores.
(e.g. in $UPuO_2$ fuels, already after 1 % burn-up nearly all pores

in the temperature zones above 13oo ^{o}C are partially filled with solid fission products. To observe this particularity with the replicas, it is necessary to etch the surface more than in the preceding case, so that the different phases are well displayed by their different etching features. Examples of pores containing precipitates are given in fig. 6 (as comparaison the image of a clean pore in now irradiated material is given in fig. 7). Sometimes the solid contaminant presents a very coarse surface structure, and its presence can be detected also without etching (fig. 8), but elsewhere the nature of the contaminant appears only after a strong etching (fig. 9 and 1o). In all cases it is possible to distinguish the precipitates lying directly in the matrix and the precipitates in pores. In the first case they are indeed subjected to the polishing and their structure after etching appears more regular (fig.11).

3.3. Grain boundaries and cracks

For most purposes the replication of a polished and etched surface gives enough information about the morphology of the grain boundaries, concerning their porosity and precipitate content. Fig. 12 shows an example of modification of the grain boundary-structure at different radial temperatures in an irradiated oxide fuel. The micrographs enable an estimation of the intergranular porosity with a precision of about 3o %.
When more precise measurements are required, the direct analysis of the grain boundary interface by fractography is necessary. Fig. 13 presents a fractomicrograph of an oxide fuel before irradiation. Here the shape and the size of the pores are measurable with better precision and if the specific surface of the specimen is known, the local porosity coefficient may be evaluated with an error lower than 2o %.

In fractured surface replicas, the shadow angle is not determined, therefore this method is not indicated for stereographic measurements and particularly for measuring small defect sizes.
Of most interest is the observation of the cracks produced in the irradiated fuel. The biggest ones are normally filled by the impregnating substance, but the smaller ones are often large enough for their structure being replicated to a good extent, even on polished surfaces. From the observation of the cracks it is sometimes possible to get an idea of their nature and of the stress state of the surrounding region (see.fig. 14).

4. Artifacts

The surface replicas, expecially those obtained with a two-stage technique, sometimes present artifacts due to different causes. Their identification is often more difficult than that of the structural features. Only a large experience on the applied preparation method enables the sources of an artifact to be determined and then avoided.
Some of the most frequent artifacts are shown here and their causes if known, indicated in the captions.

Notice : All the examples given in the pictures are taken from Fast Breader Fuels ($U_{0.8}Pu_{0.2}O_2$) irradiated in the Dounreay Fast Reactor.

APPENDIX 1

The bubbles cut by the external surface are represented by bowl shaped cavities with a basic circle size depending on the depth of their centers. The ion beam impinges their surface with variable angles, but the rotation of the specimen during the bombardment gives a cylindric symmetry to the etching. Part of the sputtered material is actually set free, but part is re-deposed on the bubble surface. The situation may be simplified considering a beam which enters a sphere and sputters the material off its surface.
In this geometry one finds (8) that the sputtered material covers the sphere unformly. Therefore, in our case the amount actually escaped is given by the fraction of the free bowl to the total surface of the sphere :

$$f^{I} = \frac{2\pi R(R-z)}{4\pi R^2} = \frac{R-z}{2R}$$

where z is depth of the bubble center and R its radius.
In a first approximation, if the plane surface receives X ions per square centimeter, the dose on the bubble surface is given by :

$$X \; f^{II} = X \frac{(R^2-z^2)\pi}{4\pi R^2 - 2\pi(R-z)R} = X.\frac{R-z}{2R}$$

Therefore, if the etching advances on the plane surface with a velocity A, one may expect that the radius of the bubble grows with a velocity given by $A\, f^{I} f^{II}$ On the statistical distribution of the bubbles cross-sections appearing on the etched surface, an average "enlargement factor" can be calculated, assuming the value of

$$F = \frac{1}{2R} \int_{-R}^{+R} \left(\frac{R-z}{2R} \right)^2 dz = 1,33....$$

It is worth remarking that the enlargement of the bubble radius involves a change of the cross section radii depending on the position of the cut. A statistical treatment of the problem gives the average enlargement factor F' for the radii of the cross sections , which are measured on the replicas. This factor is given by,

$$F' = (F)^{3/2}$$

i.e. in our specific case F' = 1.54.

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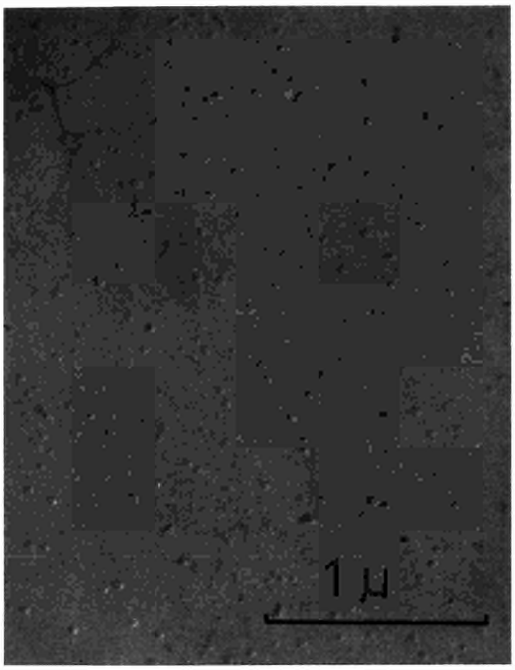

Fig. 1 : Bubbles revealed on a polished and slightly CV etched surface

Fig. 2 · With a deeper etching the bubbles are hardly revealed

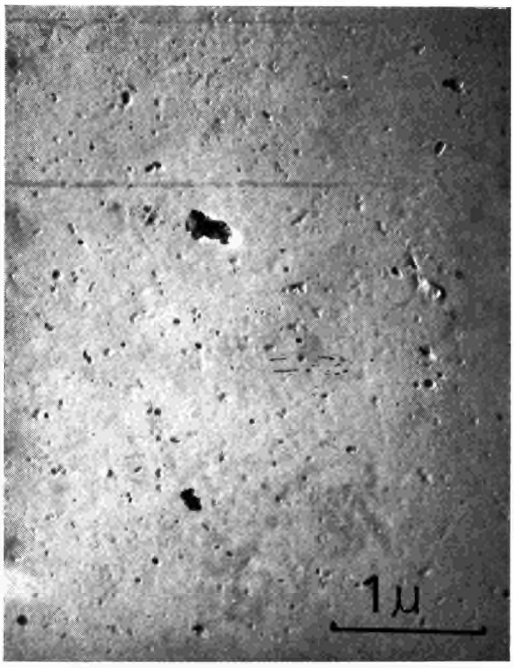

Fig. 3 : Bubbles replicated on a polished and washed surface

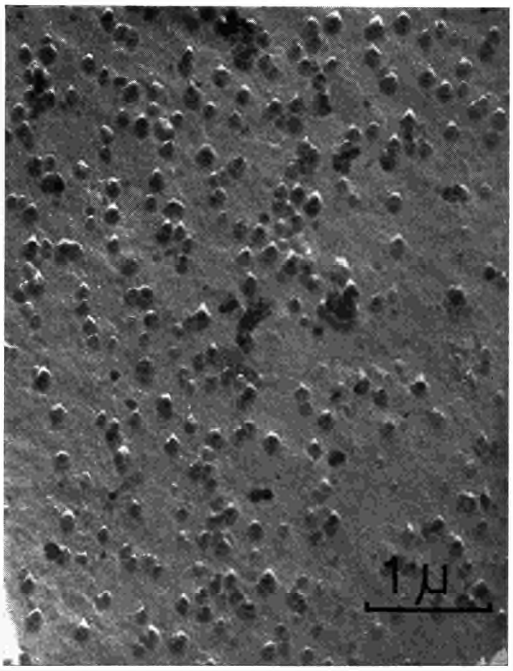

Fig. 4 : Bubbles etched with nitric acid

Fig. 5 : Small precipitates revealed by slight CV etching. Their contrast is here reversed, compared with that of the bubbles

Fig. 6 : Pore containing solid fission products

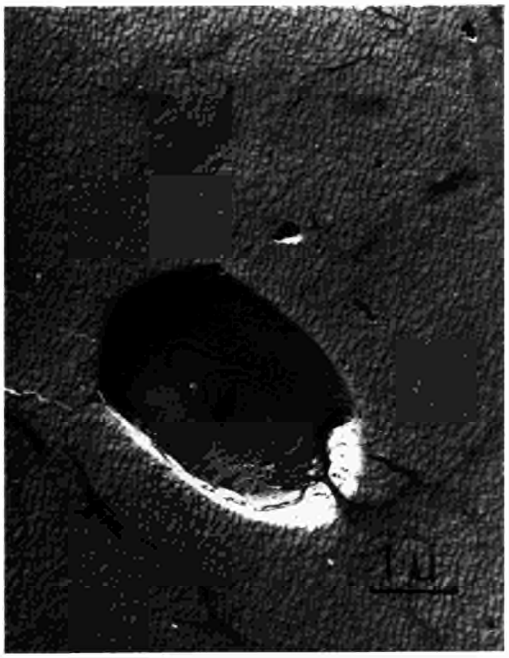

Fig. 7 : Clean pore

Fig. 8 : Contaminated pores on a polished surface

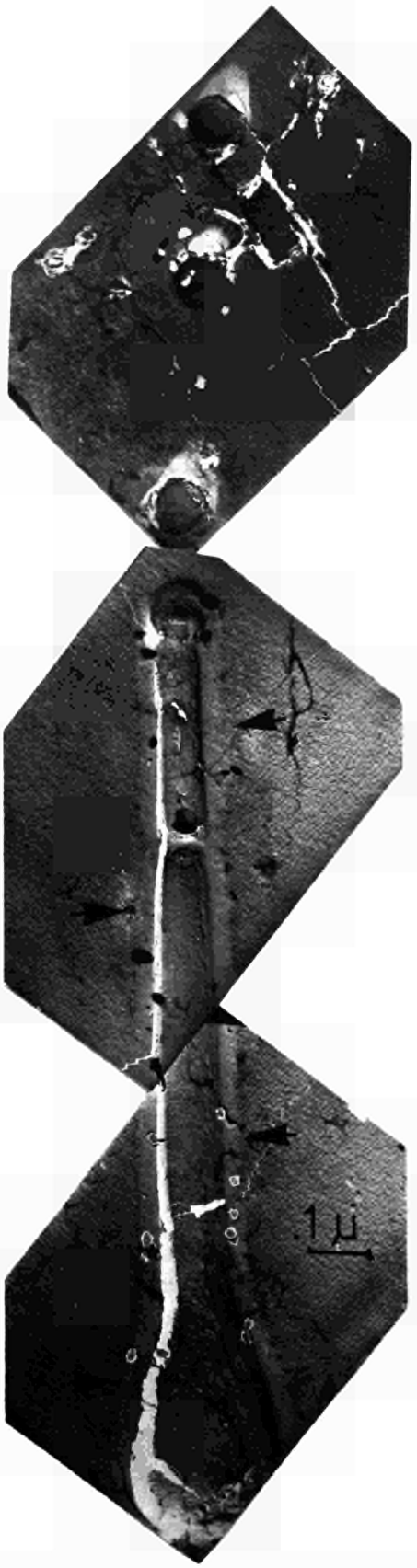

Fig. 9 : Scission
of a pipe-shaped pore under surface tension forces. The etching reveals the presence of contaminants on its surface (arrows)

Fig. 10 : Pore partially filled by solid fission products

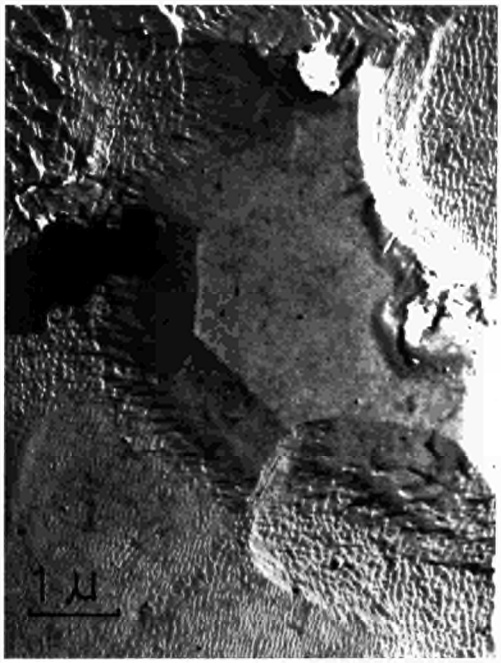

Fig. 11 : Large precipitate in the cold zone of the fuel

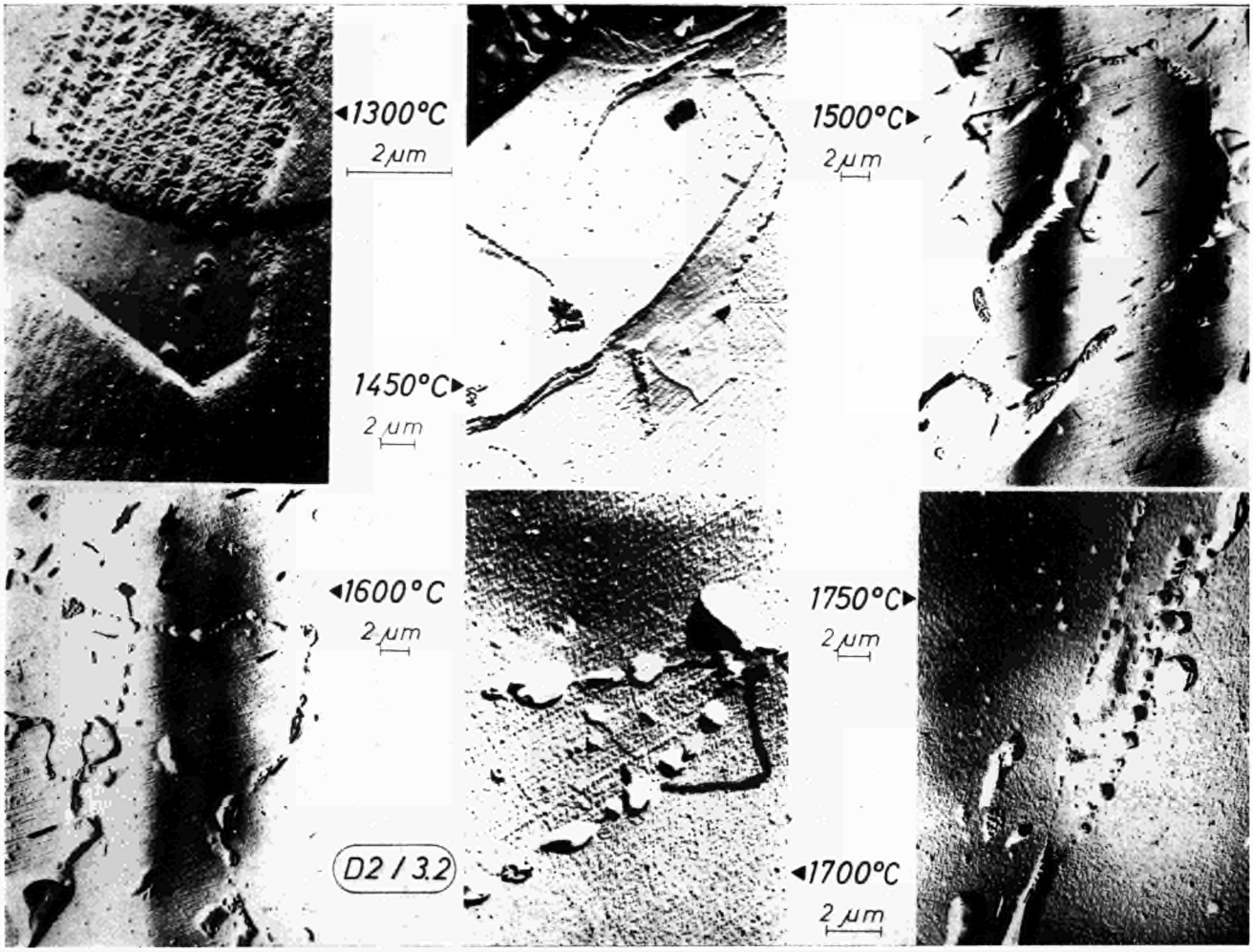

Fig. 12 : Intergranular porosity observed, in different recrystallization regions, on a polished and CV etched surface

Fig. 13 : Intergranular porosity observed in a fracture surface

Fig. 14 : Plastic crack replicated on a polished and CV etched surface

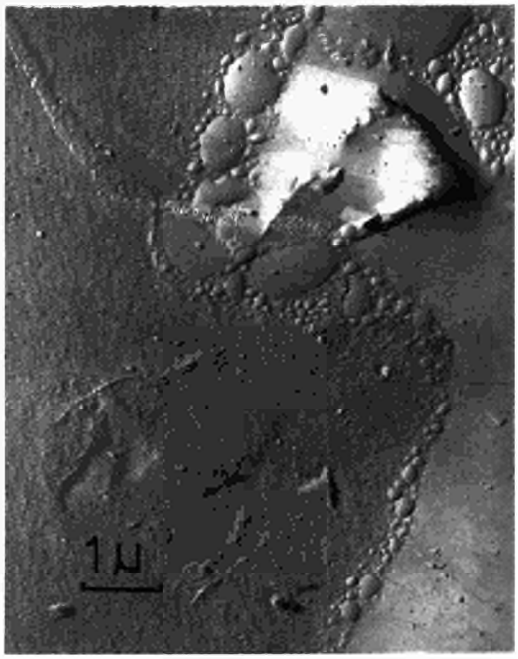

Fig. 15 : Artifacts due to failure of contact between triafol and surface

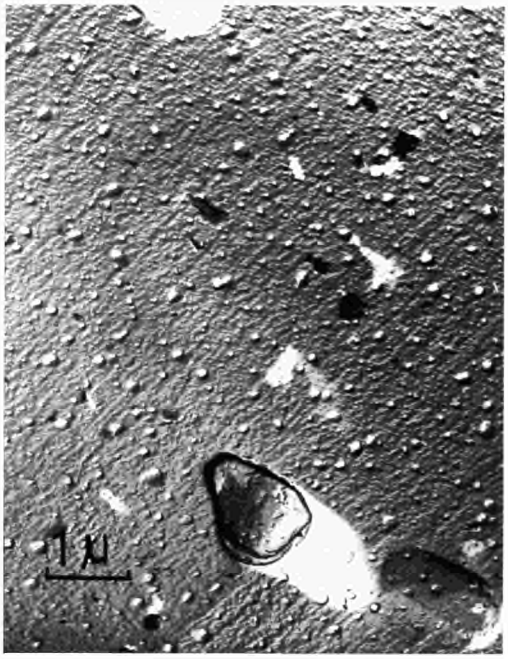

Fig. 16 : Artifacts due to non-dried triafol stripping

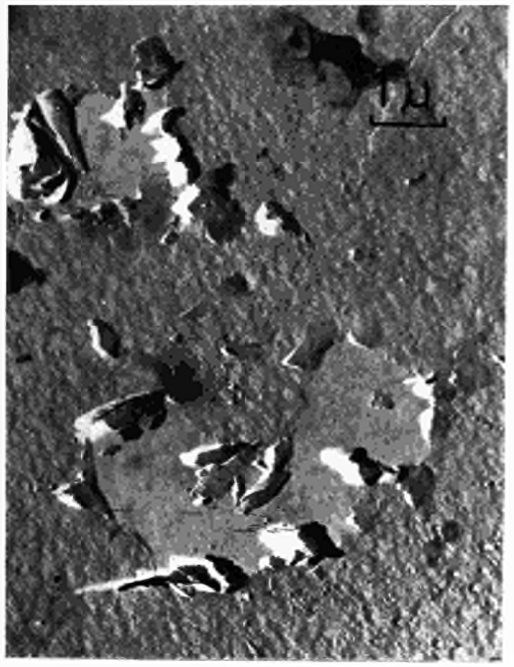

Fig. 17 :

Artifacts of unknown cause

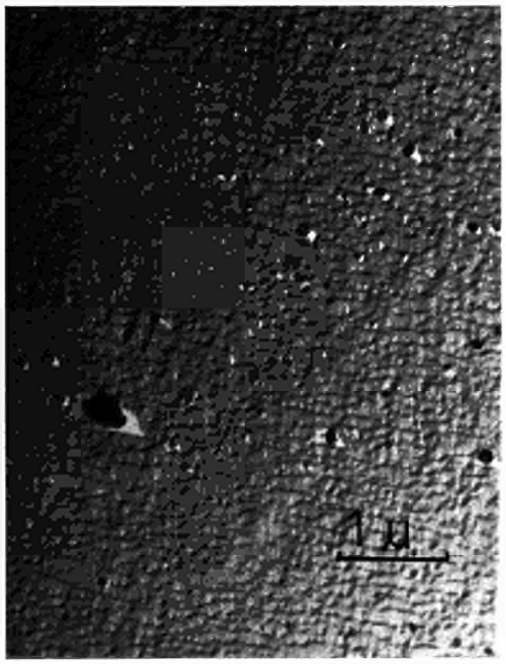

Fig. 18 :

Artifacts due to small carbon particles deposited during shadow casting. If this can not be prevented and if their presence may engender confusion in the bubble-counting, it is advisable to use a low melting shadowing material, and then evaporate the carbon sheet perpendicularly. In this case the particles do not show shadows and can easily be recognized among bubbles and precipitates having similar shapes

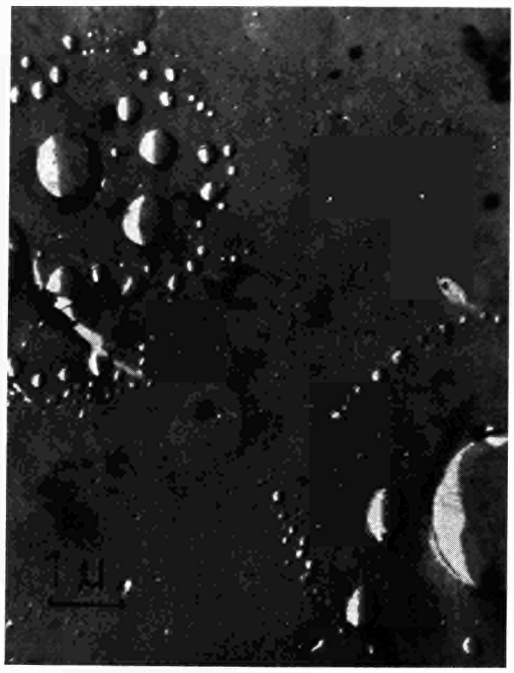

Fig. 19 - 20 : Artifacts due to air bubbles of different sizes formed between triafol and surface, which was not enough moisted with aceton

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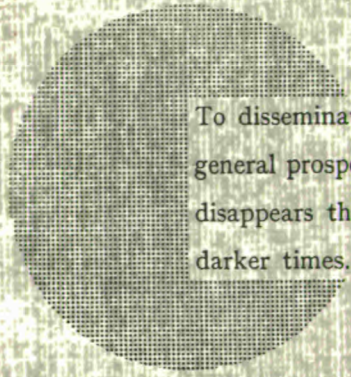

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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