

CHEMISTRY AND SURFACE TREATMENT

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1. INTRODUCTION

What is new in surface treatment of Nb cavities since the last workshop in 1980? If one asks this question one has at first the impression that no real progress has been made. The recent increase in field obtained, is certainly not due to a better surface treatment, but to a better bulk material, that is, a higher thermal conductivity. The maximum obtained Q-value is not superior to what has already been published long time ago and there are very few new treatment methods: the abrasive tumbling at DESY and the ultraviolet light-oxygen treatment at Orsay. However, at a more detailed examination one discovers in fact quite a substantial improvement.

A few years ago, when a laboratory obtained good results, other laboratories just copied their treatment methods, assuming, that the key for the success must lie in those specific methods. Today one has much better understood what is necessary for obtaining adequate surfaces. Now laboratories develop all their own sequence of surface treatments, well optimized to their specific requirements, which depend on the means available, the frequency, the shape and the size of their cavities and the number of cavities to be built.

The results obtained a few years ago were in general at first rather moderate and improved only after a number of cycles of mechanical rework of bad spots, chemical treatment, and new measurement. Today, results are good typically already after the first cool-down.

It is especially this point that inspires confidence for big superconducting acceleration projects as for example what will be needed for LEP. Because for such a project, where at least one cavity has to be produced per week something like 90% of all cavities should reach specified field and Q after the first cool-down.

2. WHAT SURFACES DO WE NEED?

Of course, we need surfaces, that allow high fields, high Q-values and if possible, show little electron activity.

This leads to certain requirements of surface topology and surface composition.

2.1 Surface topology

From experience one knows how a surface should look like under a Scanning Electron Microscope. I want to illustrate this with a few examples. Fig. 1 shows a surface, which has been locally electropolished. This surface appears clean and very smooth. If a complete cavity is electropolished the surfaces look even smoother. However, one does not need surfaces that smooth. A chemically polished surface as shown in fig. 2, which is clean however not very smooths gives very similar results up to frequencies of at least 3 GHz. In fig. 3 a surface is presented, which has been obtained by a different chemical polishing mixture. This surface is probably quite adequate. However, all laboratories try to avoid such a surface, where an additional etching structure is superimposed over the grain structure.

Mechanical rework has been tried with different methods with the aim to find a way of rework that does not require another chemical polishing. A hard-metal cutting tool turning at slow speed cuts properly the niobium metal. The vibrations of the tool and the cavity on the other hand cause a rattling and pieces of niobium are torn out of the surface (fig. 4). Such a surface originating from a repair of a bad spot has at least once worked properly at CERN without a following CP or EP.

If one wants to take the bad point out in one piece with a chisel for further analysis one gets a surface which looks smoothly cut at first view (fig. 5). But at the edges of this groove niobium is smeared over the surface (fig. 6). This leads to a quench in CERN cavities at low fields (typ. 1-2 MeV/m). The same is true, if one uses a hard-metal hand-tool turning at high speed (dentist's turbine drill). In this case no rattling occurs, but the niobium is not cut properly and smeared over the surface.

Reworking done with emery paper leads to a very contaminated surface. Abrasive material is pushed into the niobium (fig. 7). Thus, a chemical or electrochemical polishing of at least 20 μm has to be done.

2.2 Surface composition

Many studies have been done on the influence of different surface compositions, especially oxide layers, on r.f. superconductivity. Unfortunately only very few observations of the surface composition of actual cavities have been done, and their correlation to cavity performance evaluated. What can be found on a surface is shown in tables 1 and 2.

Samples 1 and 2 have been obtained from the CERN 5-cell 500 MHz cavity, which has operated in PETRA at DESY. The reference sample has been treated separately in the CERN chemical laboratory. In all three cases analytical grade etching mixtures and high purity demineralized water have been used. Surface analysis with SIMS shows at a depth of 10 \AA an impressive number of foreign elements are found in considerable quantities (table 1). In table 2 one can see that lead further increases near the surface.

The origin of this contamination and its influence on cavity performance are unknown. It is also unknown whether these surfaces are "normal" in CERN cavities or whether this was an exceptional accident. More analytical studies will have to be done.

3. HOW TO OBTAIN RELIABLY GOOD SURFACES

In general there are always the same procedures, with a different emphasis though, at each step during production: inspection, mechanical rework, chemical or electrochemical polishing and rising.

3.1 Inspection

Especially large low frequency cavities ask for meticulous inspection of squaremetres of surface and metres of welds. Defects bigger than, say 10 μm , which are not detected can produce bad performance of a cavity.

Up till now no automatic instrument has been developed to help in this difficult task. Everybody is relying on the skill of a well-trained technician, scanning the surfaces with their eyes and finding with their finger tips welding beads or sharp edges on the welds. Suspected areas are then looked at with a magnifying glass or a telescope.

A microscope at the end of a manipulator arm approached to the surface can reveal topological details, which are lost if one is using a telescope. For this reason the development of such a device has been started at CERN. Smooth mirrorlike surfaces and welds allow a more efficient inspection than the "orange skin" surface obtained with chemical polishing.

3.2 Rework

Depending on the size and nature of the defect, rework is done either with a hard-metal tool (dentist's drill) or/and with emery paper.

For multicell cavities the access to all parts of the cavity becomes impossible. Therefore, one is developing at Cornell [1] and at CERN a numerical controlled manipulator, which allows a tool to be brought to the region of the defect. Because of vibrations of the manipulator arm and cavity, it is however not easy to produce a smooth milling or grinding of the defect area.

Successful tests have been done at CERN with a local electropolishing. A jet of a modified electropolishing mixture (hydrofluoric acid, sulfuric acid and phosphoric acid) is directed through a niobium nozzle on to the defect [2]. The nozzle is connected as cathode and the cavity as anode. Up till now, however, it was not possible to avoid some hydrogen of reaching the cavity surface. Despite this hydrogen contamination an acceleration field of 8 MeV/m has been reached in one of our 500 MHz cavities and the locally electropolished spots (one at the equator and one near the iris) did not show up on the temperature map.

Clean surfaces are obtained by chemical or electro-chemical polishing. Niobium is not a very noble metal and the freshly polished surface is highly reactive. It is therefore important to use high purity analytical grade chemicals and for the subsequent rinsing well demineralized high resistivity water. Otherwise more noble metal ions can be chemically deposited on the surface. This is not possible with electro-chemical polishing as long as current flows. But it should even be more pronounced once the current is being switched off.

3.3 Electropolishing (EP)

With EP one gets very smooth mirrorlike surfaces [3]. These surfaces were expected:

- (a) To produce less field emission. Comparing the results of different laboratories, this effect is doubtful [4], [15].
- (b) To have a higher Q because the surface is smaller. Evaluating the test results with a 350 MHz cavity at CERN, it is evident that the difference between a CP surface and an ideal (EP) surface is rather small [16].
- (c) To facilitate recognition of defects on the surface. To my opinion this is the most important advantage of EP.
- (d) To avoid a chemical run-away reaction, which is the big danger of CP.

But EP has a number of disadvantages, which has led more and more laboratories to abandon this method:

- (a) EP is slow. The 40 $\mu\text{m}/\text{h}$ given by Siemens is even optimistic, because the process has frequently to be stopped, the mixture pumped and the hydrogen gas removed. At Saclay one needs 48 h for the polishing of one of their helix-type cavities [14].
- (b) The niobium surfaces have to be protected from the developing hydrogen gas. At KEK this is accomplished with a porous teflon membrane around the cathode [4]. Dornier in Germany announced that they have developed a new electrolyte, which works without the development of hydrogen gas. However, no details were given.
- (c) A current density of $\sim 10^3 \text{ A}/\text{m}^2$ must be maintained over the entire surface in order to have good electropolishing. This is difficult or even impossible for complicated cavity shapes [14]. This current at a voltage of 10-15 V dissipates 10-15 kW/m^2 , which has to be cooled away.
- (d) The surface gets contaminated with the reduction products (H_2S and S) of sulfuric acid and has to be cleaned with a hydrogen peroxide solution.

3.4 Chemical polishing (CP)

Also with CP one can obtain very smooth surfaces by using a mixture of concentrated hydrofluoric acid and nitric acid in a ratio of 1:1. The speed of this reaction is very fast (30 s for 60 μm). Therefore, it can only be used for small cavities. Slowing down of the reaction can be done by the addition of phosphoric acid. The most frequently used mixture (standard mixture) consists of equal volumes of hydrofluoric acid (48%), nitric acid (65%) and phosphoric acid ($d = 1.7$). At a temperature of 25°C this mixture dissolves 4-6 $\mu\text{m}/\text{min}$ of niobium from the surface. However:

- (a) The surface is not very smooth (orange skin). This does not strongly influence the performance of the cavity, but it is definitively an obstacle for the detection of defects.
- (b) Despite the slowing down of the reaction, it is still strongly positively temperature dependent and exothermic, which means it has the tendency of run-away. Therefore, great care has to be taken in the design of the CP equipment. It must be possible under all circumstances to drain rapidly the acid mixture from the cavity, especially if great volumes of acid are used.

- (c) The phosphoric acid has the property of forming water unsolvable niobium phosphates on the surface of the cavity. This happens, when the mixture, charged with niobium ions leaves a film on the warm cavity surface, from which hydrofluoric and nitric acid evaporate rapidly. Depending on the specific conditions 1-5 min. are sufficient to precipitate the phosphate, which adheres strongly to the surface. Even with a high pressure (200 bar) water, jet it was not possible to remove these stains. These phosphates can be dissolved by hydrogen peroxyde, transforming the phosphates in some places into insoluble niobium oxyde, or by concentrated hydrofluoric acid. Using diluted hydrofluoric acid the phosphates also dissolved but we observed surface corrosion.

One can in most cases avoid phosphate stains by using fresh acid mixtures for the last CP with as low a phosphoric acid content as possible, by externally cooling the cavity during draining of the mixture and by rinsing thereafter rapidly with plenty of water.

At the CERN chemical laboratory a number of experiments with CP have been done [5] in order to obtain smoother surfaces at slower speeds:

- (a) The speed of CP increases with temperature (factor 2 between 16°C and 35°C), with the addition of water (bad surfaces), more hydrofluoric acid, and by stirring (irregular surface).
- (b) The speed of CP decreases by addition of more nitric acid, more phosphoric acid, higher viscosity (one of the effects of phosphoric acid but can be achieved by other additives) or by cooling of the mixture and/or the cavity surface. In all cases some increase of surface profile has been observed.
- (c) Substitution of phosphoric acid by sulfuric acid. In this case the mixture also works when stirred. The reaction is faster than with phosphoric acid, and can not be slowed down with more sulfuric acid. This mixture has to be prepared with care and is hygroscopic.
- (d) The substitution of phosphoric acid by acetic acid yield very bad surfaces.

- (e) The substitution of nitric acid by hydrogen peroxyde (nitric acid is problematic for waste treatment). This mixture is unstable and the surfaces obtained were bad probably due to the higher water content.
- (f) Other additives like methyl-cellulose, polyelectrolyte, aluminium phosphate etc. have been tried, but no improvement has been observed.
- (g) A "chemical tumbling" has been tested. An inert material (Ba SO_4) and some acid mixture has been filled into the cavity and the cavity turned around its axis. Although we have not yet obtained an improvement, we have the impression that this approach is promising.

Hence, up till now the "standard mixture" is a good compromise. The mixture is stable and the surface does not deteriorate up to 16-20 g/l of niobium dissolved. The speed can be reduced with little effect on the surface profile by cooling down to $\geq 5^\circ\text{C}$ and/or by adding phosphoric acid up to 3 parts if not stirred or to 6 parts if stirred (as used at DESY [6]).

3.5 Rinsing

At least the rinsing after the final EP or CP should be done with high quality demineralized water. Distilled water is of poorer quality. It seems reasonable to use water of the same quality as used for semiconductor fabrication. For the last rinse a membrane filter of 0.1 to 0.2 μm pore size is necessary. Organic contamination must be removed by a carbon adsorption filter upstream of the membrane filter. For more details see the paper of P. Kneisel [7].

Let me now comment on the different steps of the fabrication.

3.6 Sheet material

The incoming niobium sheets are visually inspected for inclusions, deep scratches and waviness of the sheet. Sometimes a chemical analysis and/or a heat conductivity measurement are made and the grain size evaluated.

For the discovery of iron inclusions the sheets are put for one day in water perhaps a bit acidified with hydrochloric acid. Iron inclusions show up as rusty spots. Although iron inclusions will disappear in the further steps of fabrication, they are a good indication for the cleanliness during lamination. The side on which one finds inclusions or scratches is put to the outside of the cavity.

Normally rework (grinding) of defective regions is already done at the suppliers place. The supplier prefers to deliver the sheets with a brushed surface. This not only contaminates the surface with the brush material, but it also hides more serious defects. Therefore, most laboratories specify today expressively non-brushed surfaces. The grain size should be in the 50 μm range (ASTM 6) in order to allow proper deep drawing or spinning. Fine grain < 10 μm is frequently an indication of low purity niobium. In this case one should do a chemical analysis, a heat conductivity measurement at low temperatures or an RRR measurement.

Material has been rejected at different laboratories mainly for inclusions (Al, Ti, Ta, Fe), for contamination of the surface (with Au, Ag) from improperly cleaned lamination cylinders, for deep scratches or marks on both sides, and for strong waviness, which indicates thickness variations and creates problems for deep-drawing and spinning.

3.7 Formed cavity parts (e.g. half-shells)

Inspection now concentrates on marks and scratches or foreign material (abrasives) pushed into the surface during forming. These defects are reworked as described earlier.

After this operation at DESY [8] the entire surface is ground. This has to be done at low speed and possibly with an appropriate lubricant, otherwise one smears the niobium over marks and scratches and the surface only appears to be clean and smooth.

Then after the damage layer (30-100 μm depending on the forming operation) is removed by EP or CP.

After this step a thorough inspection takes place, because this is the last stage with an easy access to the entire surface. It is helpful at this point to make a diagnostic anodization [9], i.e the surface is anodized in diluted NH_4OH to 100V (2000 Å thickness). Certain inclusions are more easily detected on this golden-greenish surface. If a rework has to be done, another CP or EP is necessary.

3.8 Welded cavity

Now inspection and mechanical rework is concentrated on the welds. At DESY [6] most of these defects are removed by an integral tumbling (of course not holes and fissures). The cavity is partially filled with abrasive stones and water and then turned around its axis for one week. The surface is smooth after this operation but has a dark grey colour due to the pollution with the abrasive material. It is astonishing how easily this surface can be cleaned with two rather mild CP's.

It is recommended to degrease the cavity before the last CP or EP with a normal industrial degreasing sequence (warm detergent-water-freon). The last EP or CP is made to remove 10 to 20 μm .

In a few laboratories 2-5 oxypolishing cycles [10] follow. The cavity is anodized as for the diagnostic anodization and subsequently the oxide layer dissolved with hydrofluoric acid. This operation is expected to reduce field emission. At CERN we were not able to see any difference with and without oxypolishing. This operation has therefore been discontinued.

The same is observed with a subsequent treatment with hydrogen peroxyde. This treatment is still done in most laboratories. If EP is used hydrogen peroxyde is necessary for removing breakdown products of the sulfuric acid.

An interesting cleaning operation has been tried at Orsay [11] by irradiating the cavity surface in the presence of oxygen.

3.9 Final rinsing and drying

From here onwards all laboratories observe highest possible cleanliness. The rinsing is done with large amounts of well demineralized and filtered water in front of a laminar air-flow filter of class 100 (per cubic foot < 100 particles in the range between 0.5 μm and 5 μm , and 0 particles above).

In some places an additional rinsing with alcohol after the water rinse is done. This was given up at CERN for safety reasons (inflammability and toxicity of the methanol being used). If alcohol rinsing is done the cavity can be immediately connected to the vacuum system, reducing the exposure of the cavity to air and dust. It is very difficult to inspect the cavity without contamination. If an inspection is wanted another rinsing has to follow.

3.10 Heat treatment

A heat treatment has been shown to substantially reduce the residual resistance. The best R_s of a CP treated cavity at Wuppertal was 33 n Ω , whereas at the same place an R_s of 4 n Ω was obtained after heat treatment of 1 h at 1900°C and a vacuum better than 10^{-6} mb. A 1 h heat treatment at 850°C still brought a twofold improvement. A CP thereafter increased the R_s to similar values as before the heat treatment [12].

However, a heat treatment may not be possible or economically feasible for all cavities. Moreover, for big cavities it is very difficult to avoid mechanical deformations.

4. CONCLUSION

During the last years considerable progress has been achieved in niobium chemistry and surface treatment in all laboratories. Reliably surface fields of 15 to 20 MV/m have been reached already after first cool-down for single cell cavities. This is an important improvement

with respect to the situation a few years ago, when high fields were only obtained after a number of repair operations. However, for multicell cavities it is still difficult to reach the same fields. Residual resistances in the range of 30-50 n Ω are usually obtained. The beneficial effect of high temperature heat treatment on the residual resistance has been shown, although this process may be too expensive and too complicated for big cavities.

CP is more and more favoured, because the advantages of the smoother surfaces obtained with EP are smaller than expected, making the more complicated EP less attractive. Further development of CP, exploring the many possible niobium CP formulas [13], and which could eventually improve CP surface smoothness would be highly desirable.

High purity analytical grade chemicals, rinsing water and clean room laminar airflow techniques have proven their value and are used everywhere.

The composition of actual cavity surfaces and especially its effect on secondary electron emission should be studied further.

For large SC acceleration projects automatic surface inspection tools and numerically controlled rework manipulators will have to be developed.

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TABLE 1

Concentration of metals at a depth of ~ 10 Å

	Na	Mg	Al	K	Ca	Cr	Co	Sr	Nb	Rh	Ba	Ta	Pb
Reference	0.11	0.01	0.20	0.09	0.50	0.20	0.30	0.03	96.3	0.008	1.80	0.15	0.20
Sample 1	0.08	0.04	0.10	0.20	0.40	0.10	0.09	0.01	92.1	0.020	1.10	0.10	5.70
Sample 2	0.08	0.04	0.10	0.20	0.10	0.10	0.09	0.01	92.4	0.020	1.10	0.10	5.70

TABLE 2

Depth profile of NB and PB

	Sample 2		Sample 1		Reference	
	Nb	Pb	Nb	Pb	Nb	Pb
1	81.9	18.1	92.4	7.6	58.6	41.4
5	-	-	-	-	97.0	3.0
10	94.2	5.8	99.4	0.6	99.8	0.2
50	95.5	4.5	99.3	0.7	99.6	0.4
200	94.8	5.2	99.5	0.5	98.5	1.5
1000	98.7	1.3	99.3	0.7	99.8	0.2

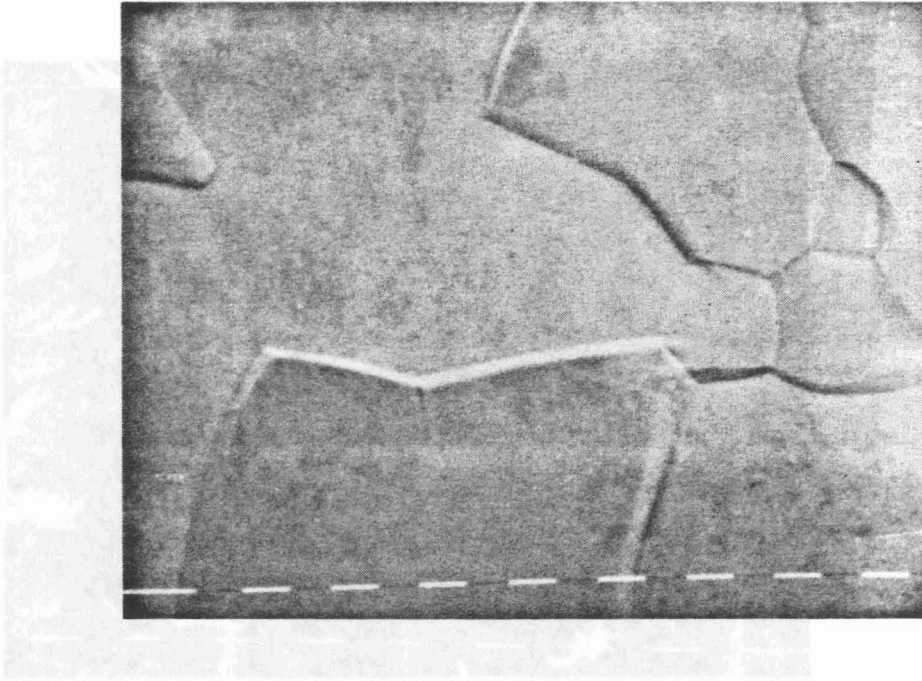


Fig. 1 - Locally electropolished surface (640X).

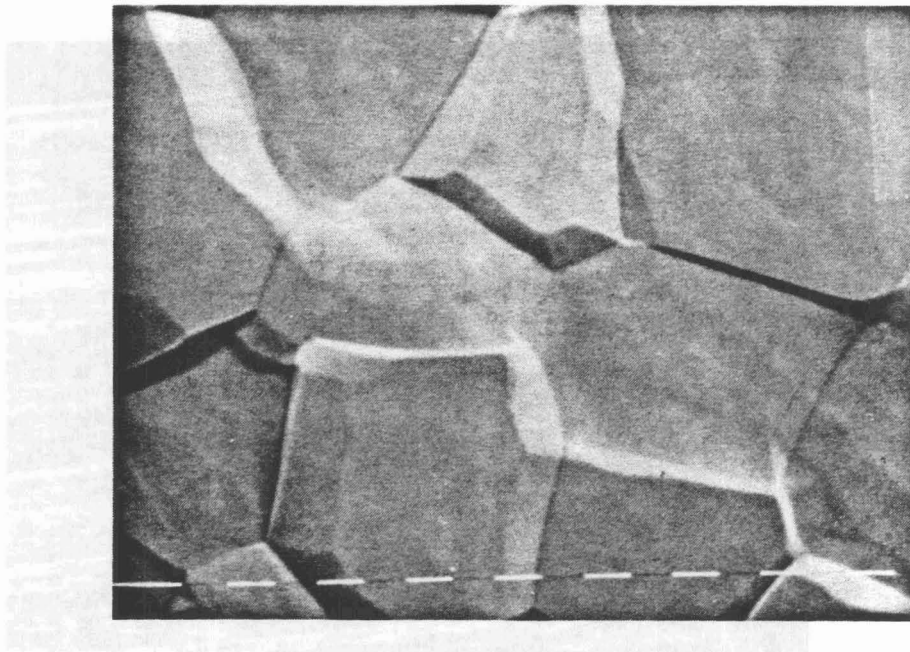


Fig. 2 Chemically polished surface with "standard mixture"(640X).

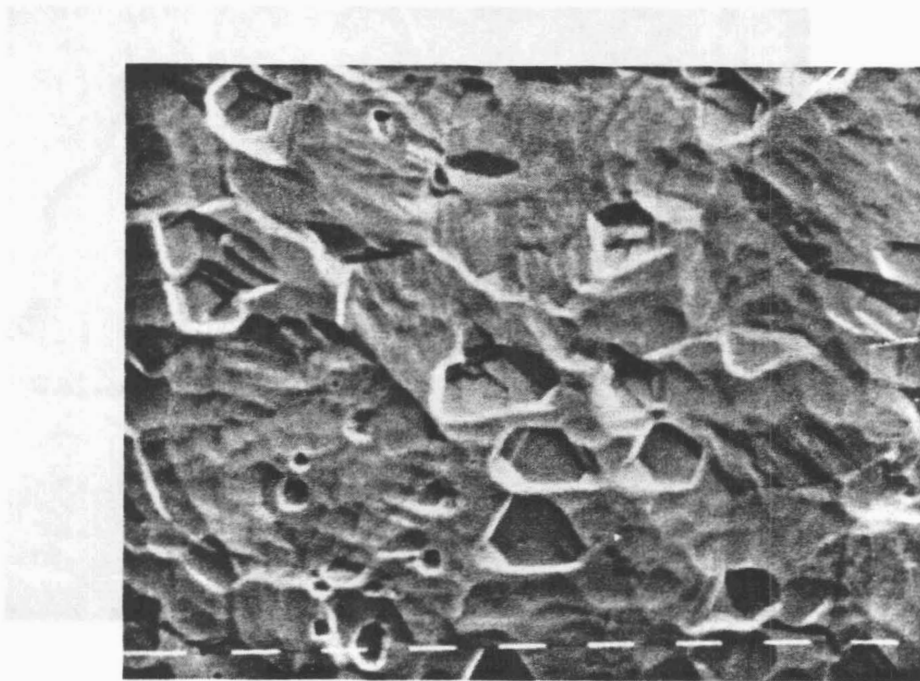


Fig. 3 - Chemically polished surface as in fig. 2 but mixture stirred and addition of water (640X).

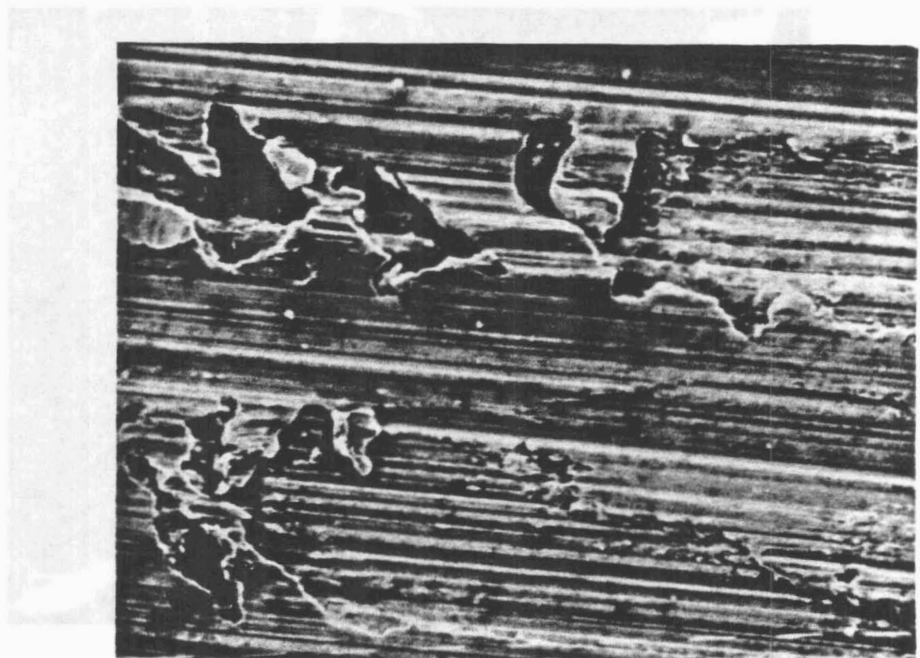


Fig. 4 - Surface cut with a hard-metal tool (dentist's drill at low speed) (640X).

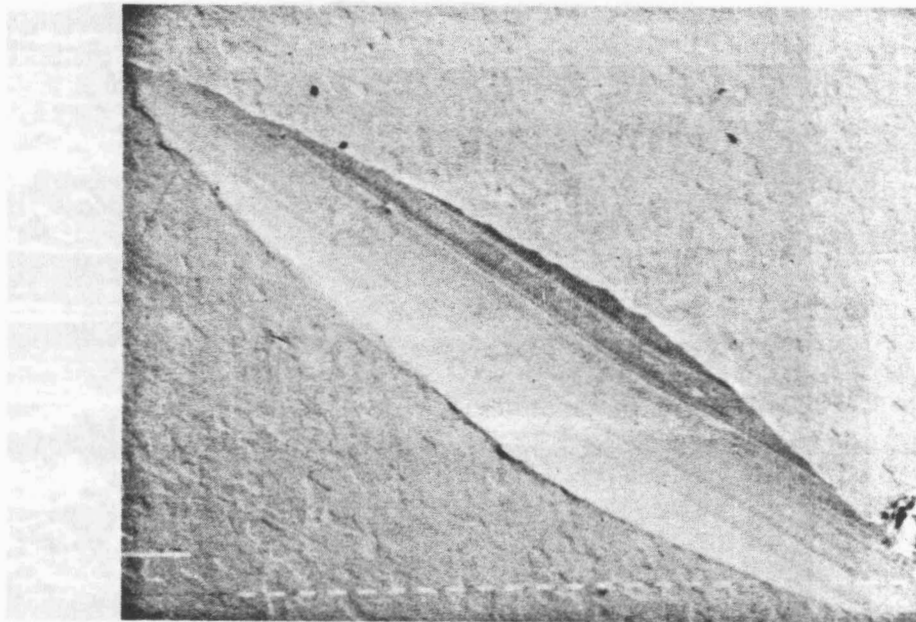


Fig. 5 - Surface cut with a chisel (20x).

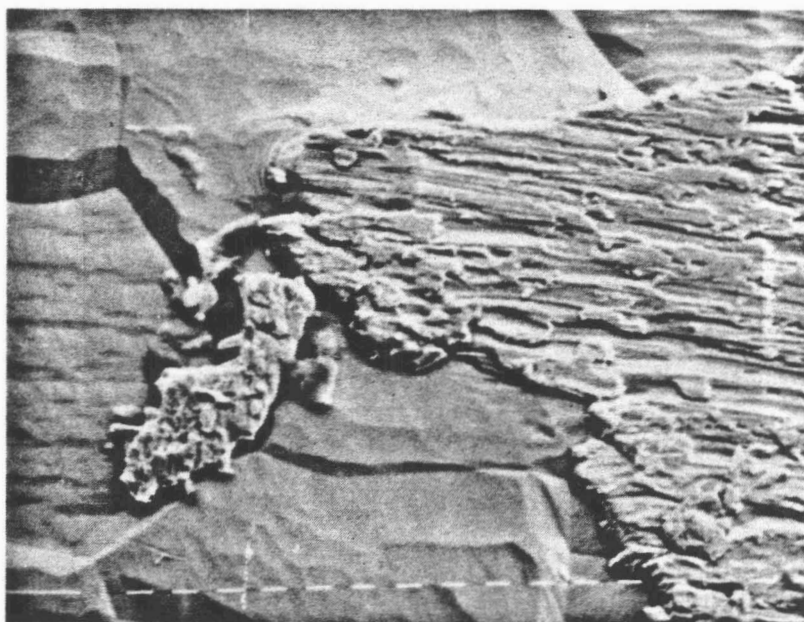


Fig. 6 - Same as fig. 5 at the end of the groove (320x).

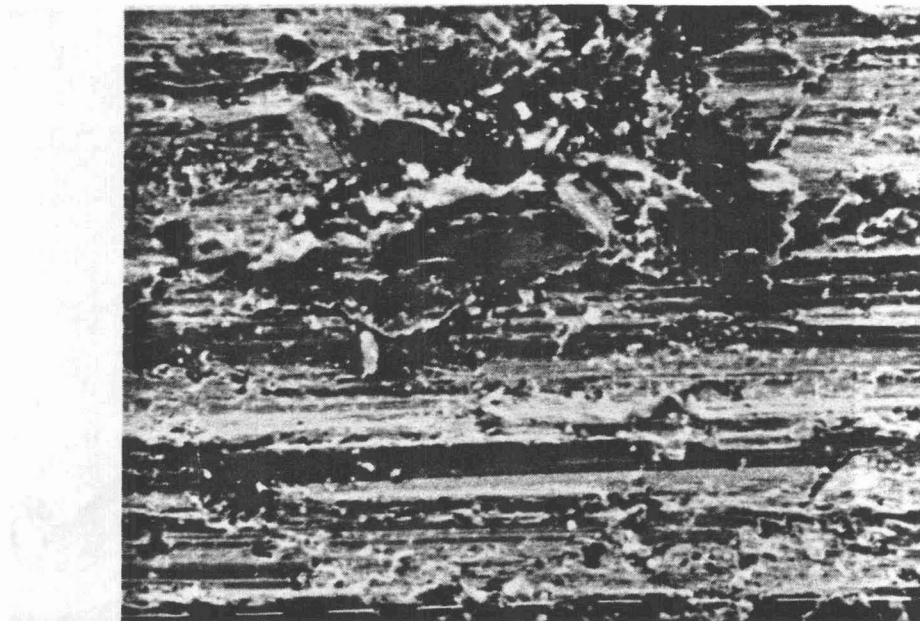


Fig. 7 - Surface ground with energy paper (640x).



Fig. 8 - Same as Fig. 7 at the end of the groove (110x)