

Influence of copper substrate treatments on properties of niobium coatings

S. Calatroni, J.P. Bacher, C. Benvenuti, R. Cosso, J.M. Dalin, J. Guérin, D. Lacarrère, A. Lasserre, G. Orlandi, E. Radicioni, F. Scalambri, M. Taufer
CERN, 1211 Geneva 23, Switzerland

Abstract

The chemical treatment of copper cavities carried out prior to cavity coating has been studied in detail.

Electropolished and/or chemically polished copper samples have been analysed in terms of the achieved surface morphology, surface cleanliness and RRR value of sputter-deposited niobium films.

On the ground of the results obtained, and of the practical constraints of the envisaged application, it is concluded that about 120 μm of copper surface should be removed by electropolishing of half-cells, and that a further layer about 20 μm thick should be removed chemically after cavity assembly.

1. Introduction

To upgrade the energy of the LEP beams at CERN [1] from 55 to about 90 GeV, 192 four-cell 352 MHz superconducting accelerating cavities will be installed in the machine. About 170 of these cavities will be made of copper internally coated with a thin layer of niobium deposited by sputtering [2].

The fabrication of the Nb-coated copper cavities, presently carried out by three European manufacturers, starts from 3 mm thick sheets of OFHC copper which are lathe spun to form half-cells. The half-cells are then electropolished and electron beam welded to obtain a complete cavity, which after final chemical polishing is rinsed with ultra-pure demineralised water, dried with ethanol, pumped, baked at 200 °C and sputter-coated.

Some lack of reproducibility of the RF performance of the industrially produced cavities, together with very reproducible residual resistivity ratio RRR values obtained by all manufacturers on Nb-coated quartz samples, renewed CERN interest in the chemical treatments applied to copper prior to coating. The study carried out on this subject and the conclusions reached so far are reported below.

2. Apparatus and procedures

Electropolishing is carried out in a solution of orthophosphoric acid (H_3PO_4) and n-butanol ($\text{C}_4\text{H}_{10}\text{O}$) at volume concentrations of 55% and 45% respectively. The chosen current density is $6\text{A}/\text{dm}^2$ and the working temperature $20\text{-}25\text{ }^\circ\text{C}$.

The chemical polishing solution consists of sulfamic acid ($\text{H}_3\text{NO}_3\text{S}$) 5 grams per litre, hydrogen peroxide (H_2O_2) 5% in volume, n-butanol 5% in volume, ammonium citrate ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_7$) 1 gram per litre. Chemical polishing is carried out at $72\text{ }^\circ\text{C}$ and is preceded and followed by washing with sulfamic acid [3].

The $100 \times 100\text{ mm}^2$ samples used for the present study were cut from OFHC copper sheets obtained from the three cavity manufacturers. After chemical treatment, a strip 10 mm wide was systematically removed all around the perimeter of the sample to avoid edge effects. The remaining surface was cut into smaller samples according to the needs of the various analytical tools subsequently used, namely Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES) and Scanning Auger Mapping (SAM).

Differently polished samples were also coated with Nb films inside stainless steel cavities of LEP geometry. For this study the Nb coating was uniformized to the industrially adopted procedure with the samples lying on the lower halves of cavity cells. With each batch of samples, quartz samples have also been coated to ascertain that standard quality of the coating had been obtained.

Since the copper substrate does not allow resistive measurement of the niobium film RRR, a procedure has been developed consisting in dissolving the copper substrate in nitric acid and glueing the bare thin niobium film on a kapton adhesive ribbon. This same procedure was also carried out on Nb-coated quartz samples after measuring their RRR value. The reproducibility of the results obtained before and after this treatment may be taken, at least in first approximation, as proof that the adopted procedure does not alter the characteristics of the Nb film.

3. Results and discussion

The surface morphology as observed by SEM on copper samples after electrochemical removal of surface layers of different thickness is shown in Fig. 1. Surface pitting is generally observed on all samples inspected, which tends to increase up to a maximum at about 80 to 100 μm depth and then decreases resulting in a smooth, defect free surface. After removal of a thickness of the order of 200 μm or more, grain boundaries are revealed. A similar increase of defect density up to 100 μm depth is also displayed by chemically polished samples, which however present more pronounced pitting and smooth grain boundaries even for large surface thickness removal (Fig. 2).

These results confirm the presence on the copper sheet of a surface layer with a high density of crystallographic defects due to the lamination process which results in preferential chemical corrosion, i.e. pitting. This layer appears to be on the average about 100 μm thick, a depth at which the highest concentration of defects is present. In order to be safely outside this damaged layer, at least 140 μm should be removed. In the light of the reported evidence, electropolishing seems to provide a better surface than chemical polishing, but its application is not straightforward in an almost closed vessel such as cavities.

Therefore it has been decided to electropolish the cavity half-cells prior to welding them together. Since welding implies a further risk of contamination, chemical polishing is applied after cavity assembly.

This final chemical treatment may also be beneficial in removing the uppermost part of the surface which might be enriched by H₂ during electropolishing. Direct evidence of a higher surface concentration of H₂ and of its deleterious effects on the properties of the Nb coating is not available at present. A further study will be devoted to this subject.

An elemental surface analysis carried out by AES shows the existence of a strong correlation between pitting and the presence of carbon on the copper surface (see Fig. 3). More precisely, the carbon concentration presents a broad maximum corresponding to a removed surface thickness in the range 80 to 100 μm, where the highest pitting density was observed.

The results shown in Fig. 3 are average values from measurements taken at various locations of the same sample, and therefore they are not very explicit on the microscopic nature of the contamination. This aspect has been investigated by SAM, showing that contamination is the result of retention in the pits of the chemicals used for surface polishing (see Fig. 4). Obviously, the importance of this effect depends on the effectiveness of surface rinsing, which may be quite different for cavities with respect to the analysed samples. The reported evidence is in any case an explicit indication of the potential risk inherent in the presence of the pits, which therefore should be minimized.

In order to ascertain if the Cu surface contamination could be transferred to the Nb film and reduce its purity, the RRR values of Nb films deposited on samples which had undergone different chemical treatments have been measured. Since, in the real case of cavities, electropolishing is applied first, the samples used for this study have been electropolished and then polished chemically. The results, shown in Fig. 5, indicate that for any given surface thickness dissolved by electropolishing, the RRR values decrease monotonically when increasing the thickness of the chemically removed layer. Furthermore, the stronger is the initial electropolishing, the higher are the RRR values obtained.

It is worth noting that the RRR values measured on copper samples are slightly higher than those reproducibly obtained on quartz samples produced during the same coating processes, indicating that the growth of the niobium film is influenced by the morphology of the underlying substrate.

4. Conclusions

This study confirms the presence on OFHC copper sheets of a surface layer damaged by lamination and its detrimental influence on the quality of the niobium coatings applied to LEP accelerating cavities. This layer seems to be thicker than that previously estimated (about 80 μm) on the grounds of reduced sampling statistics. However the reported data indicate that sufficiently high RRR values may be obtained (about 20) even if a copper surface thickness of 80 μm is dissolved, provided however that the surface be properly rinsed after polishing. The inherent risks of insufficient rinsing may be reduced by increasing the dissolved copper thickness to at least 140 μm.

5. Acknowledgements

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References

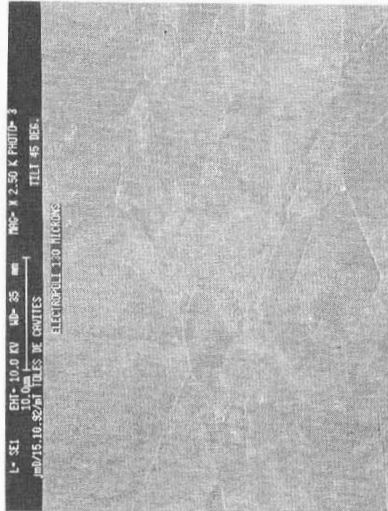
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Figure Captions

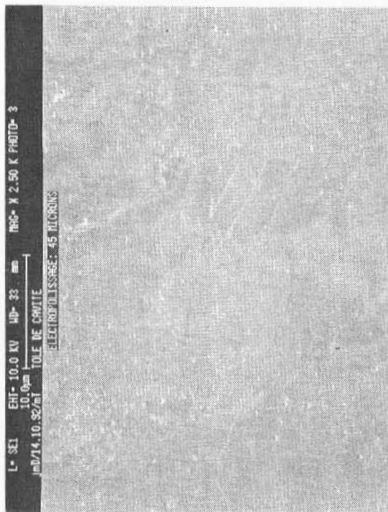
- Fig. 1 Copper surface morphology after removal by electropolishing of :
A) 45 μm ; B) 130 μm ; C) 230 μm .
- Fig. 2 Copper surface morphology after removal by chemical polishing of :
A) 60 μm ; B) 80 μm ; C) 100 μm ; D) 120 μm ; E) 200 μm .
- Fig. 3 Elemental composition by Auger Spectroscopy of the surface of copper as a function of the surface thickness removal by chemical polishing.
- Fig. 4 Scanning Auger mapping of the chemical composition inside and around a pit. A) Cu map; B) C map; C) Cl map; D) N map.
The analysis indicates the presence of chemical residues in the pit.
- Fig. 5 Dependence of Nb film RRR on chemical treatments applied to the copper surface. The lower values have been measured on samples produced under "standard" conditions (400 V, 6.3 kW, 6×10^{-4} mbar, 200 °C and film thickness 1.2 μm). The upper (black) values are obtained on samples 3.6 μm thick coated at 550 °C making use of the new optimised parameters, i.e. 400 V, 11 kW, and 6×10^{-3} mbar. The arrows indicate the values obtained on quartz samples coated during the same processes.



Electropolishing 230 μm



Electropolishing 130 μm



Electropolishing 45 μm

Fig. 1 691

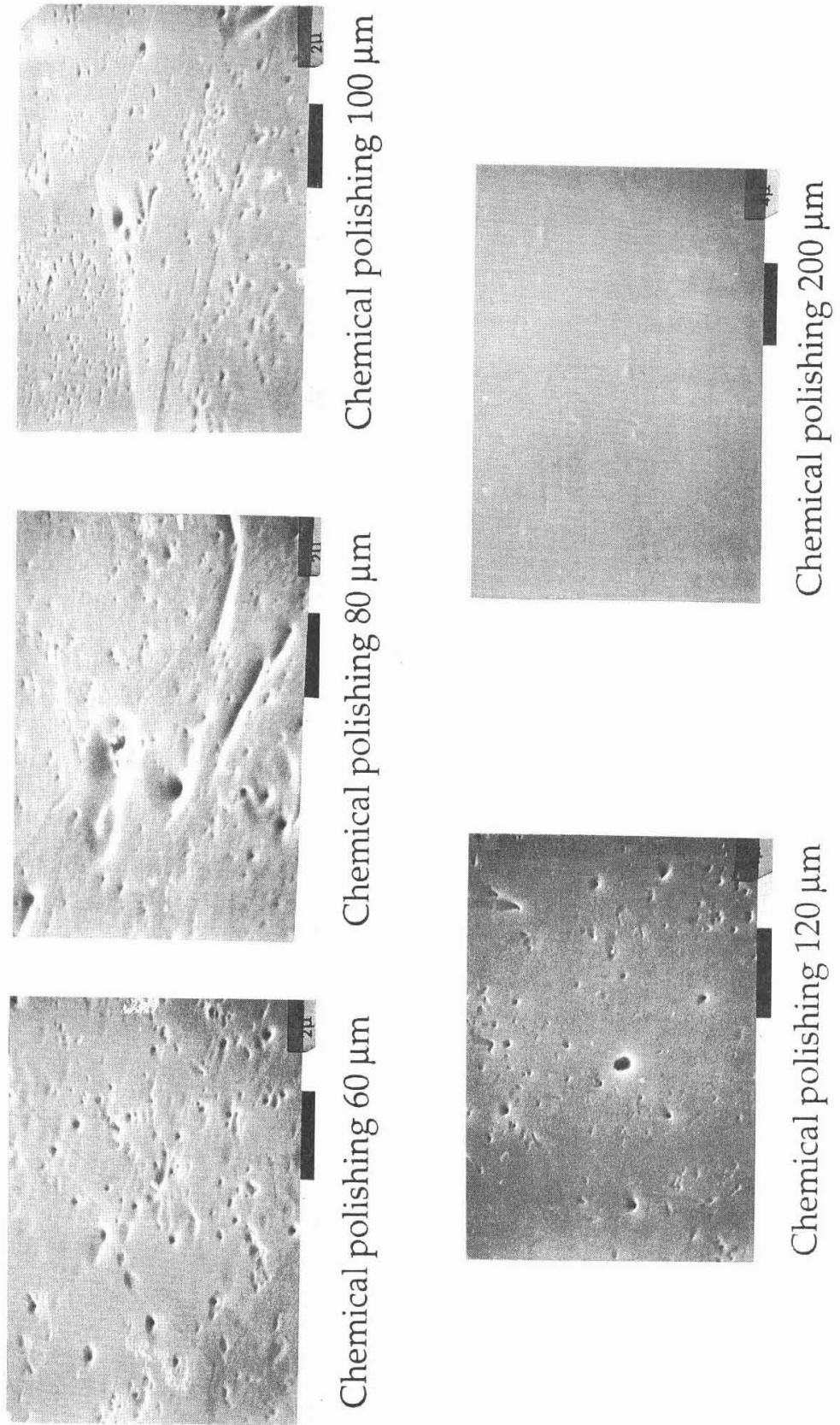


Fig. 2

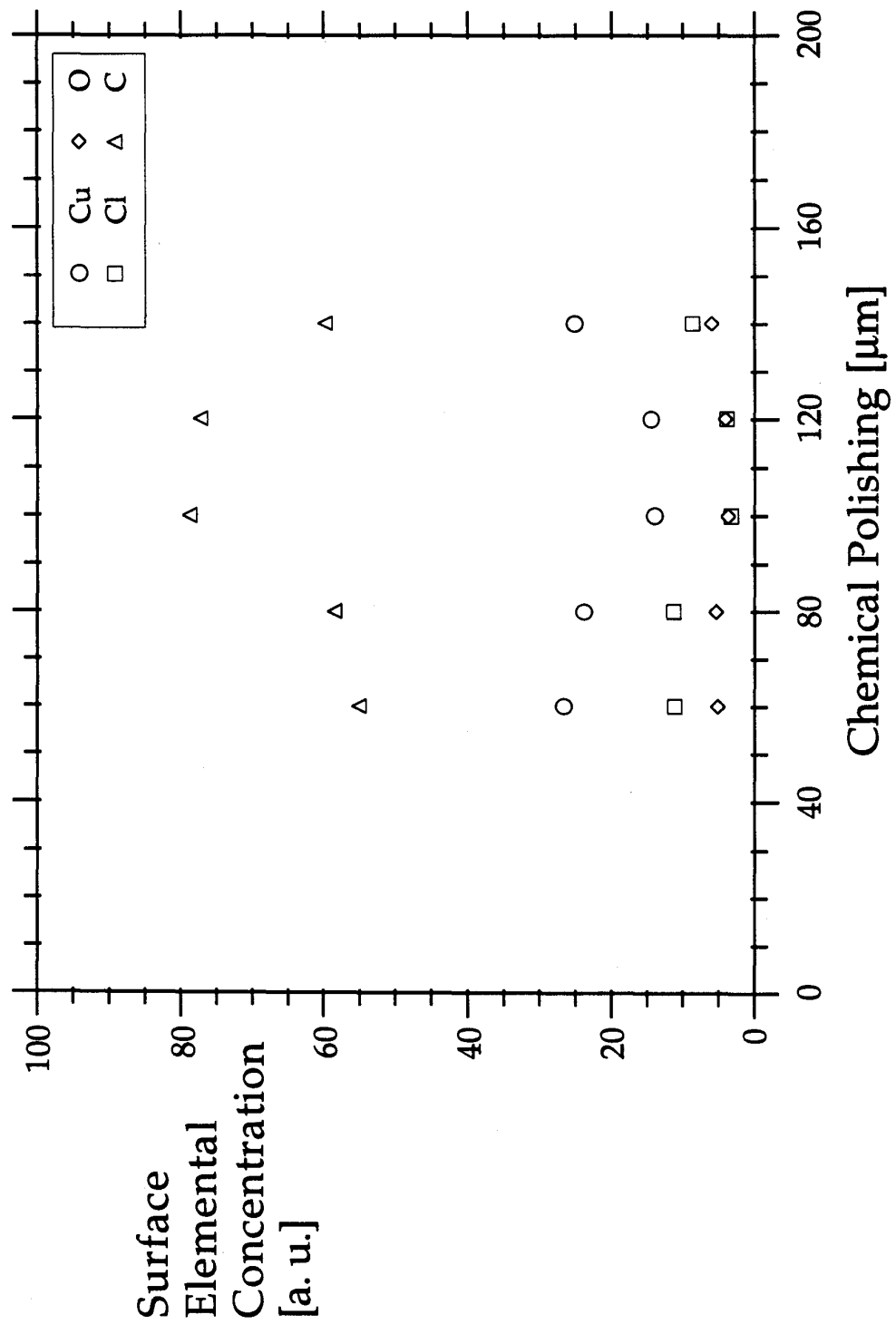
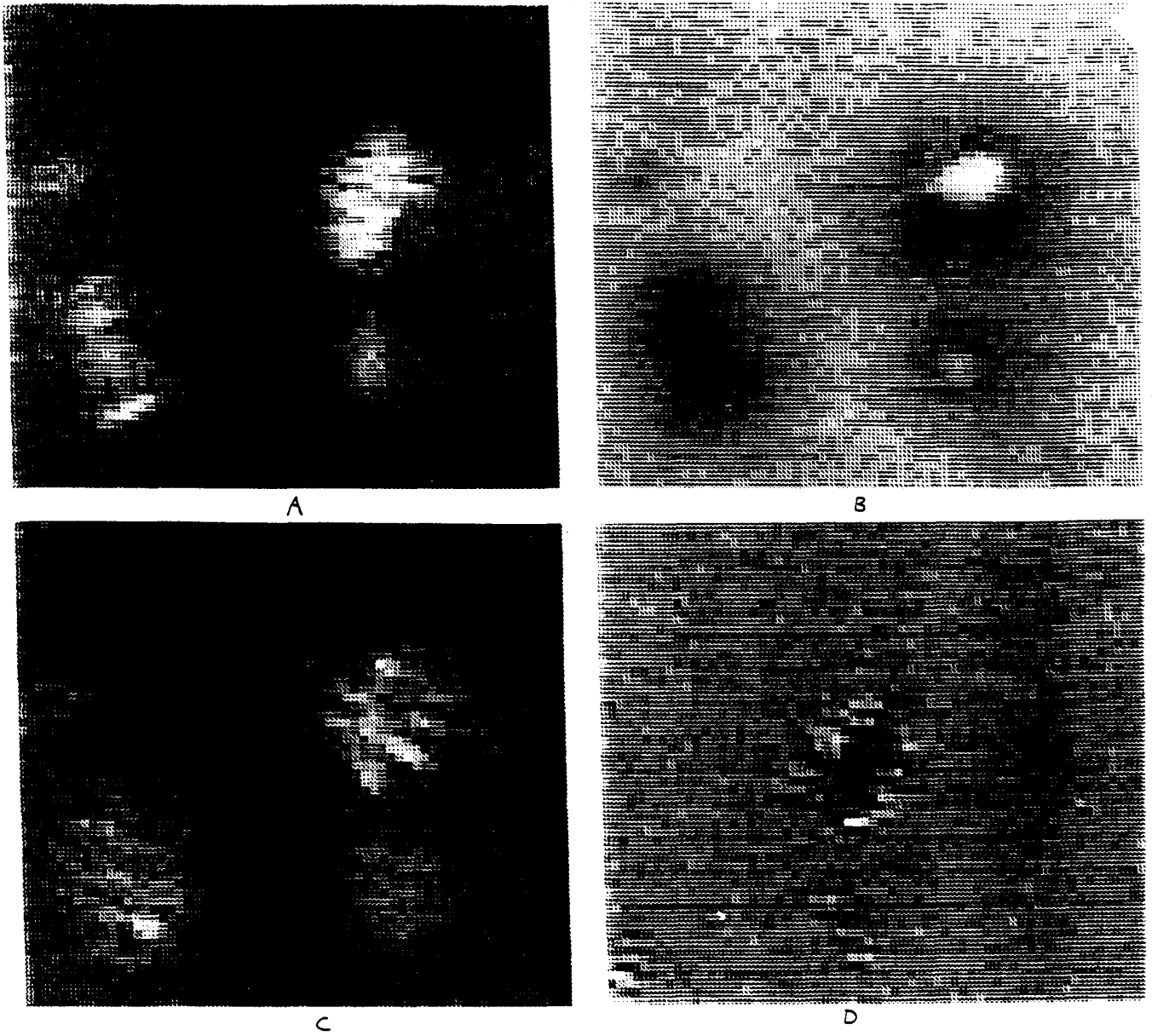


Fig. 3



- A) Cu map
- B) C map
- C) Cl map
- D) N map

Fig. 4

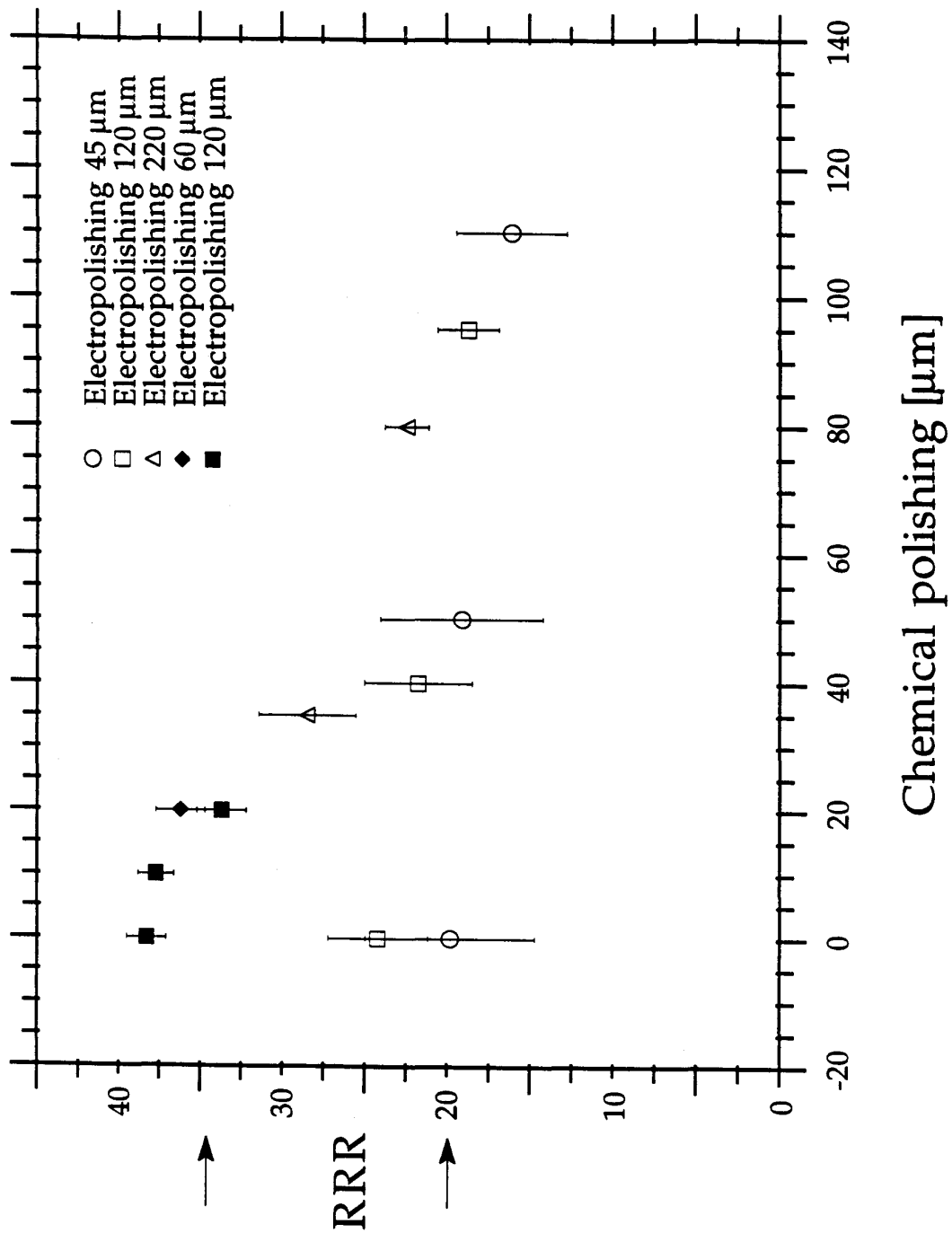


Fig. 5