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SURFACE PROPERTIES OF HIGH PURITY ALUMINIUM POLISHED BY ANODIC AND CHEMICAL PROCESSES

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SURFACE PROPERTIES OF HIGH PURITY ALUMINIUM POLISHED BY ANODIC AND CHEMICAL PROCESSES

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The mechanical polishing of high purity aluminium presents special difficulties owing to its high plasticity. It is almost impossible to prevent elevations on the surfaces being pushed into the depressions, causing overlaps and deformation in lattice zones near the surface. The increased temperature caused by mechanical polishing is favourable to renewed formation of the oxide film immediately after processing. The polishing medium remains in the pores of this layer and in the overlap joints and cannot be removed entirely by the usual degreasing agents. If such a surface receives anodic treatment, a clouded oxide film appears. Even with high purity aluminium clear oxide films can only be obtained by a preliminary "polishing" by anodic or chemical means. Table 1* summarizes some of the familiar processes for anodic polishing.

In the last few years a number of processes for the chemical polishing of aluminium have become known. The principal constituent of most of the polishing solutions is phosphoric acid. For example, under the name "Alupol II - polishing bath" the following mixture of acids is given as being suitable for polishing:

80% phosphoric acid: 50% acetic acid: 5% nitric acid.

In addition to phosphoric acid and sulphuric acid other acid mixtures contain nitric acid as well as certain metallic salts, e.g. copper nitrate. A polishing solution was developed at the Vereinigte Aluminium Werke, Grevenbroich (VAW), consisting essentially of ammonium difluoride.

The effect of all polishing processes is the removal of the oxide film and impurities and also the smoothing of the surface. So far no details are known about the degree of smoothing resulting from the individual methods. However, in order to judge the quality of polishing processes, it is definitely necessary to know the degree of preliminary mechanical polishing required and also the state of the surface after polishing. The present work is therefore concerned with examining known methods of measurement and observation with regard to their suitability for indicating the state of the surface and also with determining approximately the polishing effect of certain processes which have different modes of operation.

In order to remove as far as possible the influence of the metallide on the measurement results, examinations were carried out exclusively on Raffinal and Reflectal of the following composition:

Raffinal:	Si	0.004 %	Reflectal:	Mg	0.5 %
	Fe	0.001 %		Fe	0.001 %
	Cu	0.0005 %		Si	0.0045 %
	Zn	0.002 %		Cu	0.001 %
	Remainder Al			Zn	0.002 %
				Remainder Al	

* For Tables, see end.

Some of the specimens were simply ground first with 6/0 emery, some were first ground and polished, followed by the Na_2SO_4/NaOH bath and subsequent anodic polishing after removal of the oxide film; others were chemically polished by the Erftwerk process. Reflection measurements were taken to determine the surface changes and photographs were made with the Panphot and the electron microscope (the electron microscope photographs were taken in Prof. V. Borries' Institute at Düsseldorf). Photographs were also produced by the microinterference process developed by Rühle.

REFLECTION MEASUREMENTS

Figure 1 illustrates the apparatus developed by J. Elze and Grüss (1)* for measuring the brightness of surfaces. It consists essentially of a double optical bench with a graduated circle; one of the arms remains fixed while the other can be rotated through any desired angle which can be read off. The fixed arm carries the light source and a condenser lens. During measurement these parts are housed in a container, closed on all sides, so as to avoid disturbance from stray light; in the front of the container there is an opening, serving as a stop, through which the beam of light passes. The rotating arm carries a second convergent lens, a shutter, and a photocell. All the sliding parts have a fine lateral adjustment. The slide which carries the stop in front of the photocell has in addition a fine adjustment for vertical movement so that the stop opening can be brought exactly into the path of the ray of light. The specimen holder is located on the goniometer axis. Figure 2 shows the path of the rays. The apparatus has an accuracy of 1%. The above-mentioned authors carried out an interesting experiment to determine the brightness of a surface from the measurement of scattering, using stops of varying diameter. At some future time we shall give an account of a comparison of these values, which are called the close-range scattering angle reflection, with the results of other measuring methods. We have been content, to start with, to measure the regular reflection as a standard for the surface brightness, under the conditions set out by the authors. These values are shown in Tables 2 and 3 and also accompany the photographs (Figures 4-17).

OBSERVATION OF THE SURFACE

The resolving power of the optical microscope is limited, owing to the undulatory nature of light; where white light is used it is about 0.4 μ for good immersion systems. The necessary magnification, appropriate to this resolving power, is then about 1000:1.

On the other hand, the electron microscope has a much higher resolving power - it can resolve down to 1-2 mμ - so that 150,000 magnifications of a surface are possible. Such high magnifications were not required for these investigations. The highest were a tenth power lower. The electron microscope is also greatly superior to the optical microscope as regards definition in depth. If, in spite of all these advantages, the electron microscope photographs produced during our investigations gave to some extent incorrect information on the effect of the various polishing processes - as could be proved by comparison with the light-optical photographs of the same surfaces - this was entirely due to the photographic technique. A plexiglass replica of each surface to be studied was obtained and then obliquely shadowed with silicon

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* For references see end.

monoxide vaporised in a vacuum. The vapour-deposited film was removed from the plexiglass and irradiated in the electron microscope. Since the photographs obtained in this way showed no structure at all for polished test pieces it can be suspected that after the polishing process a transparent film of aluminium oxide having a smooth surface is formed and the plexiglass replica was formed from this. It is advisable therefore to employ a different method of making replicas in which an artificial oxide film is produced on the aluminium surface and is then irradiated in the electron microscope after the aluminium has been dissolved by concentrated sublimate solution. There are no photographs in existence, produced by this process, so there is no possibility of making comparisons.

Another very simple method of surface testing is the micro-interference process developed by Rühle. This is based in principle on the phenomenon of interference of equal thicknesses. A semi-transparent plane-parallel glass slip, vapour-coated with aluminium, is laid on the experimental surface. The air gap between the surface of the specimen and the glass slip is made into the shape of a wedge by introducing a thin aluminium foil between the upper end of the glass slip and the experimental surface. Care must be taken here to ensure that the glass slip, with the coated side turned towards the surface of the specimen, is firmly attached at the upper and lower ends. A ray of light falling vertically on to the semi-transparent layer is partly reflected, partly transmitted and then reflected at the surface under examination. This results in a difference in the length of the light path, giving rise to interference phenomena. If both faces of the wedge are perfectly level it is possible to observe dark bands parallel to the edge of the wedge at those points where the thickness of the wedge measures an odd multiple of a quarter wave-length of the light employed. If, however, the lower wedge face, in our case the experimental surface, is rough, the bands are no longer straight but more or less irregular lines can be observed which nevertheless follow the points of equal thickness of the wedge. Thus we obtain a contour pattern, similar to those known in cartography, which is shown in Figure 3.

Figure 4 shows a Reflectal surface re-treated by grinding with 6/0 emery and polishing; quite distinct grinding marks can be recognized.

Figure 5 shows, magnified 100 times, a photograph obtained by the microinterference process of the same surface. A scratch can be distinguished on the left hand side. Since the convexity of the lines at any time extends to the next line, the depth of the scratch is about half the length of a light wave, so that with the sodium light employed in this case it is 0.3 μ. Another noteworthy point is the serration of the lines, which can be seen even more distinctly in Figure 5. Figure 6 is also a 100 x magnification of the same surface, but so as to obtain a greater distance between the lines, the angle of the wedge was made about 10 times as small as in Figure 5. This serration is a consequence of the grinding marks which, accordingly, have a depth of about 1/10 wave-length.

Figure 7 shows for comparison an electron microscope photograph of the same surface 15,000 x. Here, too, the much higher resolving power of the electron microscope is demonstrated.

In the case of chemical polishing the grinding marks disappear completely after a polishing period of 10 sec. as is shown in Fig.8. Consequently the appropriate interference photograph, Fig.9, also shows no serration of the lines. Polishing for 15 sec. brings no fundamental change, which of course, to judge from the results of the reflection measurements, was only to be expected (Fig.10).

It is interesting to see that the electron microscope photograph of the same surface (Fig.11) shows a considerably better polishing effect than Fig.10, particularly when it is remembered that the magnification in Fig.11 is twice as great as in Fig.10, viz. X = 2200 as against X = 1000. The reason for this surprising fact would seem to lie in the fact mentioned earlier that in photographs taken with the electron microscope it is the surface of the oxide film which forms after polishing which is photographed, while with the light-optical photographs, owing to the transparence of the oxide film the aluminium surface is visible.

All the photographs shown until now were of specimens which had not been anodised. It appears, however, that conditions are quite similar in the case of anodised specimens.

The course of events in the removal of the oxide film differs from that in chemical polishing. Thus, Fig. 12 shows the Panphoto reproduction M = 1000:1 of a Raffinal surface after one removal operation. As a result of the moderate attack in this process the grinding marks are still clearly visible although not so definitely marked as in Fig.4.

Similarly the interference photograph, Fig.13, still shows the serrations which have been described. After three removal operations the grinding marks have disappeared (Fig.14) and the illustration of the surface now resembles Fig.8 with the exception of the grain boundaries which can be seen there. Of course the same effect can be established by means of the reflection measurements. The corresponding interference photograph (Fig.15) is now to a certain extent like Fig.9 and no serrations can be seen.

Figures 16 and 17 illustrate Raffinal specimens polished in the Na_2SO_4/NaOH electrolyte after preliminary polishing and fine grinding as well as preliminary chemical polishing. It can be seen from these photographs and also from the reflection values that the surface has greater reflectivity than after treatment with the other polishing processes. The difference is most marked in the interference photographs and the values for the regular reflection. In the Erftwerk polishing process preliminary grinding with 6/0 emery is in general sufficient. Experience has shown that in many cases even this can be dispensed with. Fig.18 illustrates how widely the surfaces can differ after mechanical, chemical and anodic polishing. Comparison with the values for regular reflection shows that this is definitely influenced not only by the depth of the grooves but also by their frequency. Further study will be devoted to experiments for determining and examing this relationship.

SUMMARY

In order to study the polishing effect of anodic and chemical polishing processes observations of high-purity aluminium surfaces were

made by optical microscope, electron microscope, and by the multiple interference process. The regular reflection was also measured by means of the gloss-meter developed by Elze and Grüss. Irregularities in the surface were measured by means of interference photographs and compared with the values for regular reflection. Comparison of all the photographs and figures yields a good picture of the change in the surface of high-purity aluminium brought about by anodic and chemical polishing.

This work deals solely with the measurement and representation of the effects of the polishing process. It does not deal with the limits of anodic and chemical polishing. Development of chemical polishing is still in full course. There is good reason to hope that the polishing effect of this process can be increased considerably. An account will be given later of the limits of anodic and chemical polishing processes.

References.

Elze and Grüss "Metalloberfläche" 6 (1952), A 17-23.

TABLE 1 - Vocabulary

Process Designation	Patent	Electrolyte	Volt	Amp/dm^2	Temp.	Time	After-treatment	Literatur
Brytal Process	Br. Pat. 49 162	15% Na_2CO_3 + 5% Na_3PO_4	9-12	3.3-3.8	80° (±1%)	5-10 mins	Anodised 20% $NaHSO_4$, 35° 10 V 0,55 Amp/dm^2 12-15 min.	Schenk 1948 P.801
Alyak Process	USA Pat. 2 108 603	0.5-5% BF_3 (2.5%=;0.8%≃)	5-25 (8-12)	1.1-8.6 (2.15)	20-60° (30-33°)	5-15 mins	Anodised 7% H_2SO_4, 25° 20 V 1,3 Amp/dm^2 10 min.	Schenk 1948 P.803
"	USA Pat. 2 108 603	1.0-25% CrO_3 0.2-1.5% HF	16-22	2-15 (4.9-5.6)	30°-70° (50°)	5-30 (10) mins	" "	"
"	USA Pat. 2 040 618	1-60% H_2SO_4 0.2-1.5% HF	8-10 (= 8) (≃ 10)	1-11 (=10) (≃8.5)	30-70° (=60°) (≃35°)	3-30 (=10) (≃20) mins	" "	"
"	USA Pat. 2 045 286	" "	"	"	"	"	Film removal 1-8% Na_2CO_3 0.5-3% $Na_2Cr_2O_7$ 70-95° 0.25-3 min; Anodised as above.	"
French Method	Br. P. 618 120	40-90% H_3PO_4 >3% oxalic acid >1.5% boric acid 0.05-0.2% lead monoxide	50-25	4.5-200 (30)	20-90° (60°)	1-10 mins	Anodised 15% H_2SO_4 12V 10 mins. 20°.	Light Metals Bulletin 1949 Vol.11 No.9

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TABLE 1 - (continued)

Process Designation	Patent	Electrolyte	Volt	Amp/dm^2	Temp.	Time	After-treatment	Literature
Alcoa Method	Br. P. 613 887	30-50% H_3PO_4 25-55% glycerine remainder H_2O	20-60	5-10	70-80°	3-10 mins	Film removal H_3PO_3 + CrO_3 solution. Anodised 1.5% H_2SO_4	Light Metals Bulletin 1949 Nr.4
Phosphoric acid-Sulphuric acid method	French Pat. 708721	45-70 vol% H_2SO_4 5-15 vol% H_3PO_4 0.5-2 vol% HNO_3	12-14	10-15	75-100°	3-10 mins	Film removal Anodised in 15% H_2SO_4	Schenk 1948 P.805
"	Br. P. 612478	42 vol% H_3PO_4. 8 vol% H_2SO_4 17 vol% H_2O 33 vol% ethyl-monoethylester	1	3.5	40-90°			Patents of I.V. Westwood and United Anodising Ltd.
VAW - Polishing Process		10% Na_2SO_4 1% $NaOH$	10-8	10-15	90° (±3°)	10-8 mins	Rinse. Anodised in GS bath	
Film removal process	Patent applied for	7% oxalic acid (WGX treatment)	≃30-40V =50-60V	≃1.5 Amp =3.- "	20° (±2°)	≃10 =5 mins	Film removal in acid mixture Anodised in GS bath	

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TABLE 2.

Regular reflection in % compared with a silver mirror (with 97% regular absolute reflection)

Raffinal, mechanically ground and polished	47.6 %
(a) anodically polished and GS-anodised	84.0 %
(b) chemically and anodically polished GS-anodised	84.0 %
Reflectal (0.5% Mg), mechanically ground and polished:	
(a) 5sec. by Erftwerk-process chemical polishing, GS-anodised	81.6 %
(b) 10 sec. ditto	81.1 %
(c) 15 sec. ditto	81.6 %
Reflectal (0.5% Mg), mechanically ground and polished	
(a) 1 x WGX, GS-anodised	69.3 % (dull)
(b) 2 x WGX, GS-anodised	73.9 %
(c) 3 x WGX, GS-anodised	75.6 %

TABLE 3.

Regular reflection of ground and ground and polished sheet metal specimens of high-purity aluminium

	Ground	Ground and Polished
Raffinal, Anodically polished and GS-anodised	77.2%	83.9%
Chemically polished for 15 secs. GS-anodised		
Raffinal	81.0%	81.7%
Reflectal (0.5% Mg) soft	81.7%	81.3%

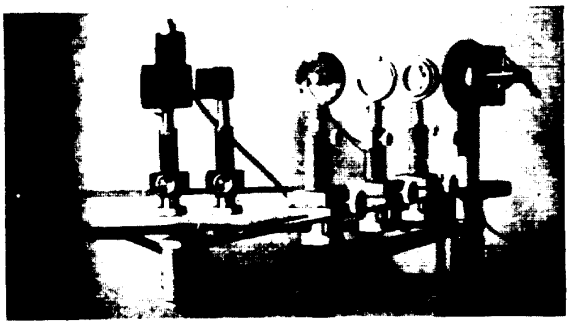

Fig.1: Optical bench for reflection measurement.

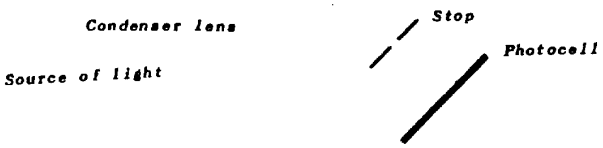

Fig.2: Ray paths in the optical bench

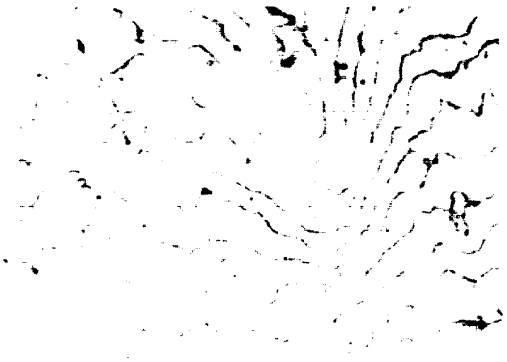

Fig. 3: Photograph of interference bands

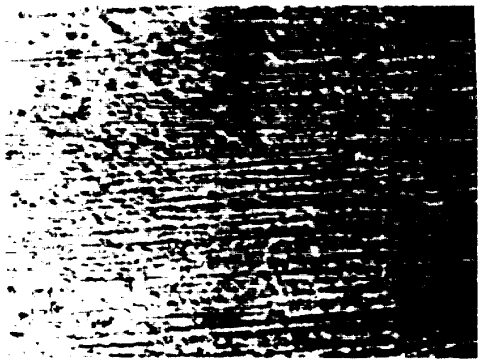

Fig. 4: Optical microscope photograph of a mechanically pre-polished reflectal specimen (0.5% Mg) M = 1000:1, 47.6% regular reflection (magnification).

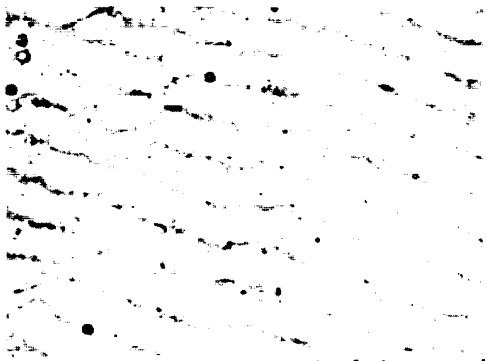

Fig. 5: Interference photograph of the pre-polished reflectal specimen (Figure 4). M = 100:1, 47.6% regular reflection.

Fig. 6: Interference photograph as in Figure 5 with magnified interference band interval, 47.6% regular reflection

Fig. 7: Electron microscope photograph of the same reflectal surface as in Figures 4 and 5, M = 15,000:1, 47.6% regular reflection.

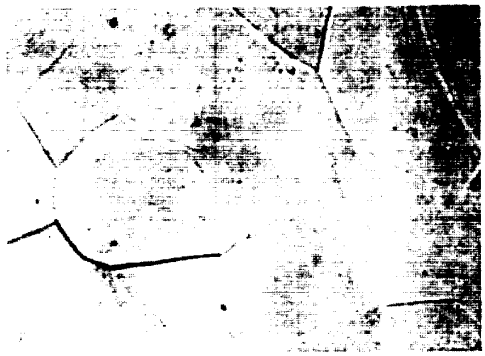

Fig. 8: Optical microscope photograph of a reflectal specimen polished chemically for 10 sec. M = 1000:1, 87.2% regular reflection.

Fig.9: Interference photograph of reflectal specimen (Figure 8). M = 100:1, 87.2% regular reflection.

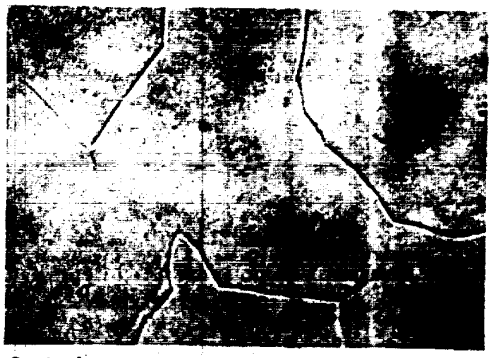

Fig.10: Optical microscope photograph of a reflectal specimen after 15 sec. chemical polishing. M = 1000:1, 88.6% regular reflection.

Fig.11: Electron microscope photograph of the chemically polished specimen in Figure 10. M = 2200:1, 88.6% regular reflection.

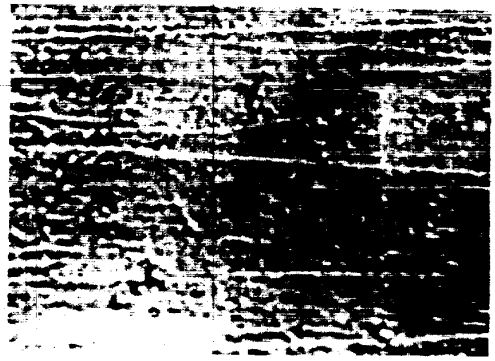

Fig.12: Optical microscope photograph of a Raffinal specimen once WGX-polished, GS-anodised. M = 1000:1, 64.4% regular reflection.

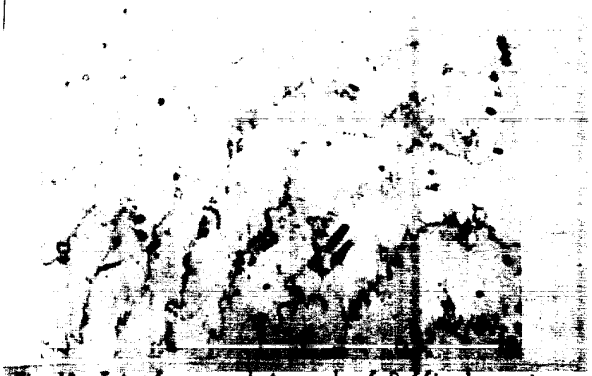

Fig.13: Interference photograph of Raffinal specimen in Figure 12. M = 100:1, 64.4% regular reflection.

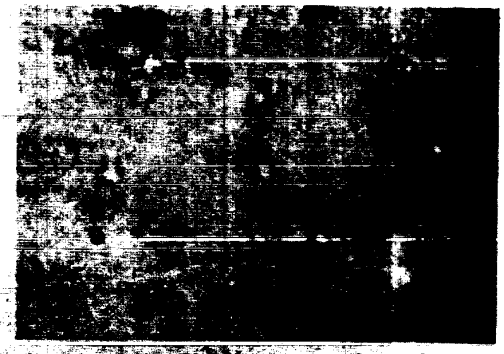

Fig.14: Optical microscope photograph of a Raffinal specimen, three times WGX-polished, GS-anodised. M = 1000:1, 79.4% regular reflection.

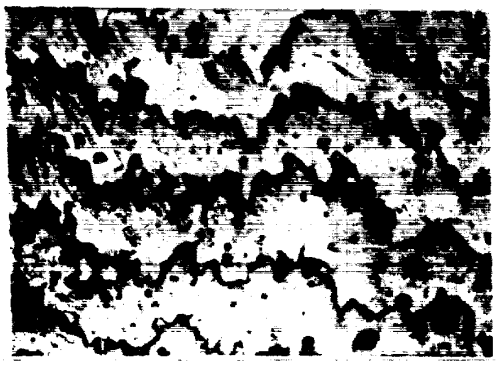

Fig.15: Interference photograph of the Raffinal specimen in Figure 14. M = 100:1, 79.4% regular reflection.

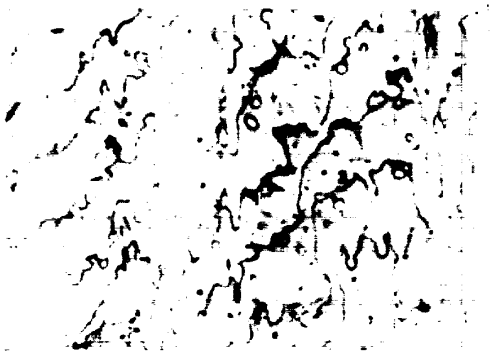

Fig.16: Interference photograph of a Raffinal specimen, mechanically pre-polished and anodically brightened, GS-anodised. M = 100:1, 79.2% regular reflection.

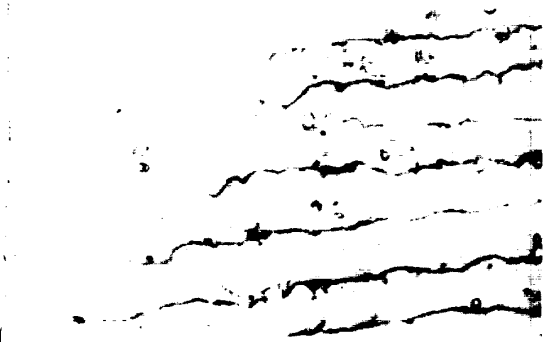

Fig.17: Interference photograph of a Raffinal specimen, mechanically pre-polished and anodized, GS-anodised. M = 100:1, 84.0% regular reflection.

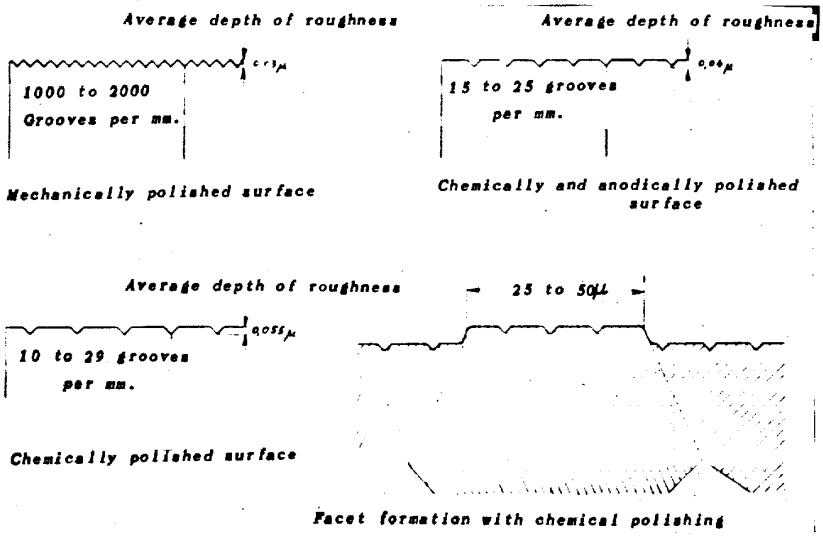

Fig.18: Diagrammatic representation of surface change due to various processes.