



Fig. 2. Cross-section of the surface of a machined rotating-cantilever specimen of copper, showing short fatigue cracks running along striations. Specimen had fractured completely some 3 mm. from this point at 18,000 lb./sq. in. after 476,000 cycles at 170 c./min. Specimen axis horizontal. Etched with acid ferric chloride. $\times 370$

occurred in the fatigue specimens in a different mode from that in tension and compression.

The striations are not produced by the sectioning technique, since they may also be readily developed on the polished surface of a similar fatigue specimen, free of striations before the fatigue test. Neither are the striations produced by gradual application of the stress during loading, since they do not develop until a later stage in the fatigue life.

Fig. 2 shows small cracks in a surface crystal of a low-stress rotating-cantilever specimen. The cracks run along the striations revealed by etching, indicating that these, or the mode of deformation which results in their development, may play an important part in the formation of fatigue cracks. Similar striations have also been observed in fractured low-stress push-pull specimens of copper. Thus, they appear to be characteristic of low-stress fatigue-deformation in copper. Experiments concerning the variations in intensity of the striations due to stress and to testing frequency are to be described shortly. Also, the nature of the markings is being investigated by annealing experiments and by electron microscope investigations.

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¹ Wadsworth, N. J., and Thompson, N., *Phil. Mag.*, **45** (7), 223 (1954).

² Samuels, L. E., *J. Inst. Metals*, **83**, 359 (1955).

Mechanism of the Electrolytic Deposition of Titanium

ONE of the commercial methods of manufacturing pure titanium metal involves the high-temperature electrolysis of either K_2TiF_6 , $TiCl_4$ or $TiCl_3$ in a molten alkali halide eutectic. Several such processes have been in operation for some time, and certain

details of the preparative techniques have been published¹. The mechanism of these electrolytic methods has, however, remained in doubt. Of the two possibilities, (1) primary deposition of a titanium ion, complex or otherwise, on to a suitable cathode, or (2) secondary deposition where the titanium species are reduced by electrolytically produced alkali metal, the latter has seemed more probable because of the amorphous nature of the resultant titanium. It is true that fairly large dendritic crystals of titanium are produced during the electrolysis, but such dendrites are also found in the commercial preparation of titanium where $TiCl_4$ is reduced with liquid sodium. The current-voltage relations observed during electrolysis are also in keeping with a predominantly secondary process.

Recently, we have obtained direct evidence that the metal is finally produced by a secondary process; but, depending on the starting materials, this can be preceded by one or more primary steps. Using the gas-flushed tungsten micro-electrode, recently developed by Inman², polarographic analyses have been made of solutions of K_2TiF_6 , $TiCl_4$, $TiCl_3$ and $TiCl_2$ in the LiCl-KCl eutectic at temperatures between 380° and 550° C. Excellent reversible polarograms have been obtained for the primary reduction of $TiCl_3$ to $TiCl_2$, the half-wave potential with respect to platinum being -2.58 V. at 400° C., that for the decomposition of the eutectic being -2.79 V. The wave-height is strictly proportional to the concentration of $TiCl_3$ up to 0.01 weight per cent corresponding to ~ 200 μ amp., the highest current measurable with the recorder. The $\log i/i_d - i$ against E relation indicates a one-electron reduction step. That the reduction is to $TiCl_2$ and not to titanium metal is also evident when, after complete reduction, the reverse process is clearly indicated from the corresponding anodic polarogram.

$TiCl_4$ gives a cathodic wave at $E_{1/2} = -1.4$ V. at 400° C., although its form is distorted because of the difficulty in maintaining any concentration of $TiCl_4$ in the melt.

Neither $TiCl_3$ nor K_2TiF_6 gives a detectable cathodic wave or limiting current. A finite current only flows when the applied voltage exceeds -2.79 at 400° C., that is, the decomposition potential of the pure eutectic. It is therefore clear that K_2TiF_6 and $TiCl_2$, in this melt at least, can only be secondarily reduced to titanium by chemical reaction with alkali metal.

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² Hills and Inman (in preparation).