CARACTERISATION PHYSIQUE

N'ayant pu obtenir de monocristaux de la phase intermédiaire $Ag_3HgTl_3Te_4$, il n'a pas été possible de faire son étude structurale. Elle n'a pu etre caractérisée que par son diagramme de poudre X.

Du point de vue des propriétés electriques de cette phase, des mesures de conduction ont été effectuées, à titre exploratoire, sur des échantillons polycristallins par la technique de Van Der Pauw (4). On constate qu'elle est toujours de type p. La conductivité electrique est pratiquement constante de 100 à 400 K, ce qui correspond à un comportement dégénéré. A la température ambiante, elle est égale à 7 $(\Omega cm)^{-1}$.

A partir de la phase $Ag_3HgTl_3Te_4$, des compositions présentant un excés de mercure ont été préparées de manière à provoquer un phénomène de compensation dans le composé. Les mesures effectuées ont montré, dans ce cas, une forte diminution de la conductivité electrique et un comportement global de type n.

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INFLUENCE OF TEMPERATURE ON THE ELECTRONIC STRUCTURE OF PASSIVE FILMS ON AISI 304 STAINLESS STEEL PHOTOELECTROCHEMISTRY AND IMPEDANCE MEASUREMENTS.

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Previous studies (1,2) have shown that passive films on stainless stell show semiconductivity. However, little is still known about the effects of the conditions in which the films are formed on their electronic structure.

In this work the influence of temperature is shown. For that purpose, studies have been made with passive films formed at different temperatures (8-65°C) and an imposed potencial of 0.8V(SCE) in a borate-boric acid solution (pH 9.2). Photoelectrochemical and impedance techniques have been used, according to experimental procedure described elsewhere (2).

The results indicate an exponential increase of passive current with temperature (Fig.1), whereas the values of the band gap, E_g, obtained from the following equation (3):

$$(h\,\nu\,\eta)^{1/n} = B\,(E_g - h\,\nu) \qquad (1)$$

shown little dependence on temperature (Fig.2).

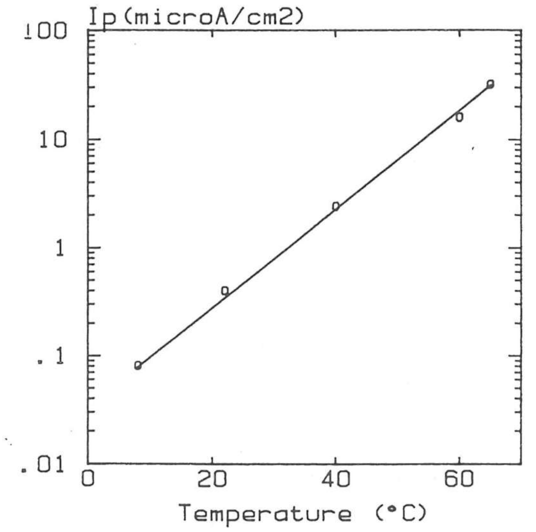

Fig.1 - Influence of temperature on passive current.

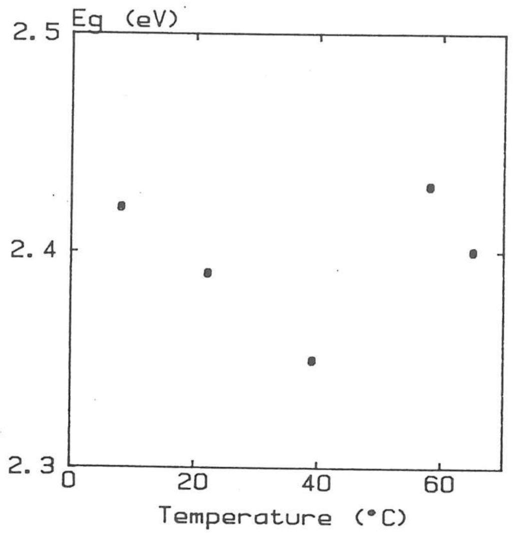

Fig.2 - Values of the band gap energy for the oxide
(assuming n=3 on equation 1) vs temperature.

Thus, although the kinetics of metallic dissolution through the passive film is strongly influenced by temperature, that does not seem to be a consequence of a major change on the electronic band structure of the oxide.

The oxides also show a high degree of disorder, since linear correlations are obtained for several values of n used in equation (1).

The differential capacitance of the film strongly increases with temperature (Fig.3), which could be indicative of a change either of the thickness of the film, of its structure (thickness of the space charge region) and/or of the species adsorbed.

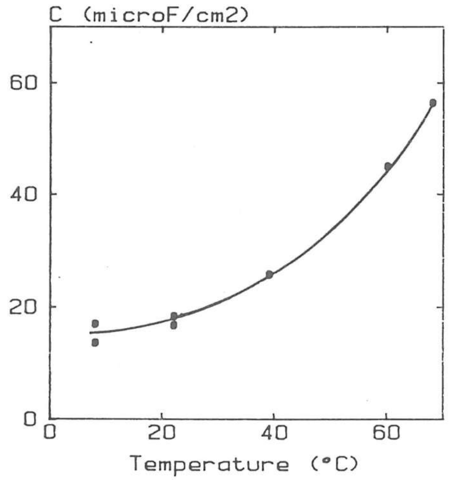

Fig.3 - Influence of temperature on the capacitance
measured at 1KHz.

The Mott-Schottky plots (Fig.4) confirm the increase of capacitance with temperature, but they also show a decrease in the slope of the linear part of the curve (approximately between -250mV and +250mV) with temperature. Since the concentration of donnors, N_D, varies reciprocally with that slope, then N_D increases with T. This correlation is of the Arrhenius type, i.e., the logarithm of N_D decreasing linearly with 1/T. Thus, assuming as valid the relation

$$N_D = A \cdot e^{-E_a/k_B T}$$

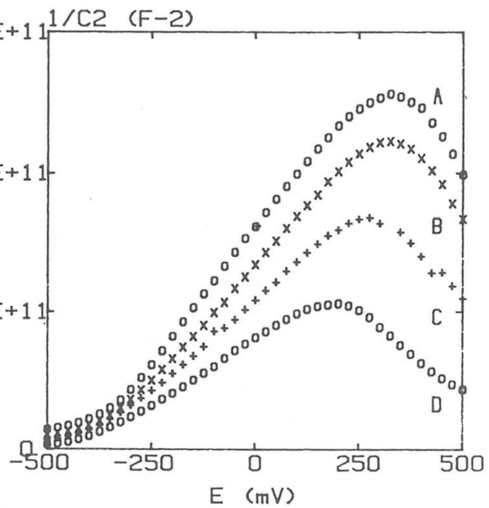

Fig.4 - Mott-Schottky plots for AISI 304 stainless steel at several temperatures
A:8°C; B:22°C; C:39°C; D:58°C
Electode area:0,125 cm^2

where:

E_a = activation energy
k_B = Boltzmann constant
A = constant

a value of 0.1 eV is obtained for the activation energy. This value corresponds, for a γ-Fe_2O_3 film, to the energy needed for the transition of an electron from the Fe^{2+} ion (dopant) in a tetrahedral position in a spinel type of structure to the conduction band.

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