ADSORPTION OF OXYGEN ON SOLID AND LIQUID GALLIUM

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The cathodic charging curves previously recorded [1] on cleavage faces of single crystals of antimony and bismuth in 0.1 N KOH after potentiostatic residence at potentials more negative than the equilibrium potential of phase oxide formation have a distinct desorption region,* to which a specific quantity of electricity (q) corresponds. The φ—q dependence (the oxygen adsorption isotherm) has a stagewise character, which indicates the energy nonuniformity of the solid surface [1]. It was therefore of interest to investigate adsorption on a metal which can be in either the liquid or solid state at low temperatures.

For this investigation we choose Ga-000 gallium (mp 29.7°C). The amount of oxygen sorbed at constant potential (φ_{an}) was determined from the cathodic charging curves by finding the quantity of electricity consumed on desorption. The method was described in detail in [1]. The experiments were performed in 0.01 N KOH in argon, the reference electrode was a mercury oxide electrode in the same solution, the potentials are given with respect to a normal hydrogen electrode. The electrodes (area 0.35 cm^2) were anodically polarized for 10 sec under potentiostatic conditions. The cathodic charging curves ($i = 45 \cdot 10^{-4}$ A/cm^2) were recorded on a loop oscillograph. The anode polarization potential (φ_{an}) was varied abruptly at 10 mV intervals. The series of recordings was begun at a potential φ_{an} 10 mV more positive than the hydrogen evolution potential at this current density, and was ended at the onset potentials of gallium oxide formation. According to thermodynamic data [2], gallium oxides can be formed at potentials more positive than —1.2 V.

Figure 1 shows the isotherms of oxygen adsorption on gallium at different temperatures. Curve 1 relates to adsorption on a solid surface (20°C) and is similar to the curves obtained for bismuth and antimony [1]. As in [1], the number of steps on the curve, characterizing the number of active sites on the solid surface, is small — six. Adsorption of oxygen begins on the most active surface sites at a potential of 1.576 V (60 mV more positive than the hydrogen evolution potential). The potential at which the step on the curve begins characterizes the energy of adsorption on curve sectors of specific type, and the height of the step is related to the surface area which is occupies. The region of more negative potentials (from —1.576 to —1.230 V) is characterized by a weak increase in the amount of adsorbate and corresponds to the more active sectors, which apparently occupy a relatively small part of the surface. The region from —1.230 to —1.113 corresponds to the more rapid increase in the amount of adsorbate with an increase in φ_{an}.

An increase in temperature to 32°C, which leads to melting of gallium, shifts the φ, q curves (curve 2, Fig. 1) toward more positive potentials, and the number of steps decreases to three. The potential range of the remaining steps coincides with the potentials of the less active sectors of the solid surface. Fusion therefore leads to the disappearance of the more active sectors. Owing to the fact that in this experiment the residence time at 32°C was only 10 min, the metal clearly retained certain features of the solid surface relief, namely the less active sectors. Such a possibility was indicated by Frenkel' [3]. If gallium is first kept for 2 h at 32°C or superheated to 52°C followed by cooling to 32°C, the isotherm

*The processes corresponding to the potentials of this region will be examined in greater detail in subsequent communications.

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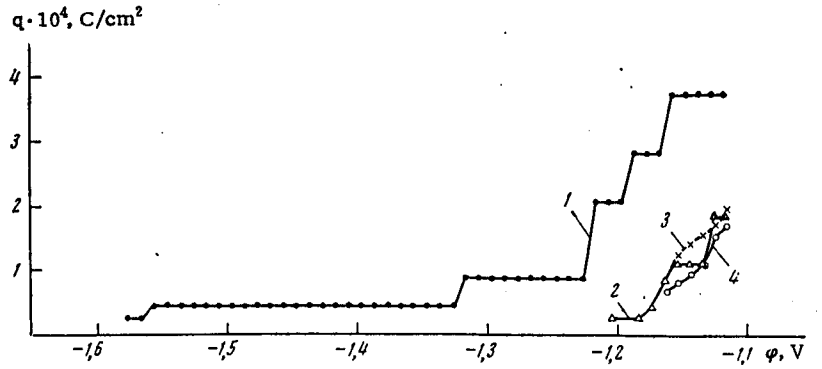

Fig. 1. Isotherms of oxygen adsorption on gallium at temperatures (°C): 1) 20; 2) 32 (residence time 10 min); 3) 32 (after superheating to 52°C with a residence of 30 min); 4) 52°; curve 2 at (—1.18)-(—1.15 V) coincides with curve 3).

(3, Fig. 1) does not have steps and begins at potentials more positive than curve 2. Adsorption of oxygen at 52° begins at the most positive potentials and gives a smooth isotherm (4, Fig. 1).

Assuming that at 52°C the surface roughness factor (f) of liquid gallium is equal to unity, we can assess the roughness of solid gallium by comparing the quantity of electricity consumed on desorption of oxygen at the most positive potentials (φ_{an} = 1.113 V), corresponding to maximum surface coverage. The corresponding values are $3.75 \cdot 10^{-4}$ and $1.79 \cdot 10^{-4}$ C/cm^2, hence f = 2.1.

Calculations showed that if oxygen is sorbed as O^{2-} anions with radius 1.76 Å [4] and occupies the area of a square in which a circle of given radius is inscribed, the maximum surface coverage at φ_{an} = —1.113 V and f = 2.1 is 35.4%. The more active sites, filled at potentials in the range from —1.576 to —1.230 V, occupy only 8% of the surface.

With an increase in temperature, the onset potential of adsorption becomes increasingly positive: —1.576, —1.24, and —1.163 V at 20, 32, and 52°C respectively.

In going from solid gallium at 20°C to liquid gallium at 32°C, the hydrogen evolution overvoltage decreases markedly (by 30.3 mV/deg). Further heating of liquid gallium reduces this overvoltage only by 2.7 mV/deg, which coincides with the data for lead [5].

Our data confirm the previous [1] assumption that the stagewise character of the isotherms of oxygen adsorption on a solid surface is due to its energy nonuniformity, and enable us to use the proposed method to get a picture of the relief of the solid metal surface. This is of great importance in the interpretation of corrosion problems.

LITERATURE CITED

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