ADSORPTION OF OXYGEN AND CARBON MONOXIDE ON Dy_mCu_n BIMETALLIC SURFACES AT ROOM TEMPERATURE

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The adsorption of oxygen and carbon monoxide on surfaces of dysprosium, copper, and their bimetallic "alloys" Dy_mCu_n was studied by work function measurements. In the starting stage of adsorption of oxygen, copper surfaces are more reactive than dysprosium surfaces, and bulk oxide appears in the sub-surface copper layers at room temperature; this was also observed for the bimetallic surfaces, where the starting adsorption of oxygen took place nearly exclusively on copper. With dysprosium, the bulk oxide did not form at room temperature; instead, oxygen was adsorbed on the surface to form a layer consisting of species of two kinds with substantially different dipole moments. Carbon monoxide practically did not adsorb on copper at 25°C, whereas on dysprosium it exhibited dissociative adsorption. On the bimetallic surfaces (DyCu and $DyCu_6$) the amount of adsorbed CO decreased proportionally to the increasing Cu content of the alloy. Segregation of copper in the surface layer, observed for the bimetallic Dy_mCu_n "alloys", resulted in an additional decrease in the amount of adsorbed CO.

Rare earth metals, alloys and compounds and their interactions with gases have been subject to extensive investigations both in pure and applied research. In addition to their basic physical and chemical properties[1-11], their surface behaviour, formation of hydrides, chemisorption and catalytic properties have attracted interest[1,12-20]. The ever-increasing interest in these substances is due particularly to their ability to dissolve high volumes of hydrogen in their bulk, owing to which they can serve as convenient materials for economical hydrogen storage. Another important reason for the study of these substances is their high catalyst activity in a number of reactions such as oxidation of CO and hydrocarbons, hydrogenation and isomerization of olefins, dehydration of alcohols, *etc.* Among the most serious requirements placed on them for practical use are those of structural stability, acceptable thermal conductivity and, in particular, resistance to common poisons such as O_2, H_2O or CO for the whole catalyst lifetime. Some of these problems, particularly the structure stability and desired thermal conductivity, are conveniently solved by using the substances in the form of binary or more complex alloy systems where one of the constituents is copper[21].

The objective of the present work was investigation of the properties of Dy_mCu_n bimetallic systems in relation to their interaction with oxygen and carbon monoxide.

EXPERIMENTAL

The apparatus was as used previously[22,23]. The gas adsorption was examined *via* work function measurements, performed using a Kelvin's vibrational capacitor[24] with phase-sensitive detection of the signal (Figs 1a—c). The reference electrode was a surface-oxidized tantalum plate 5 × × 10 × 0·25 mm³ dimensions. The diode method[24] was also used for determining the work function values in dependence on the Dy_mCu_n alloy composition; the voltage shift in the volt––ampere characteristics at a constant current was measured. A thermionic tungsten cathode was used, the film coatings were the anode (Fig. 1d). The work function value for polycrystalline copper, $\varphi = 4·65 \pm 0·05$ eV, was taken from ref.[24]. Changes in the work function $\Delta\varphi$ are defined in this paper as $\Delta\varphi = \varphi_a - \varphi_b$, where the subscripts a and b refer to the state of the surface after and before the interaction, respectively. All work function data are in eV.

The metal surfaces were prepared by vacuum deposition of Dy, Cu, and Dy_mCu_n alloys of known bulk composition on the walls of a spherical glass adsorption cell held at a temperature of approximately 20°C during the process. The mass of the films was about 7 mg, their geometrical surface area about 100 cm². The residual gas pressure during the coating was on the order of 10^{-7} Pa. The two metals and their alloys in a purity better than 99·96% were obtained from the Mendeleev Institute of Technology in Moscow. Prior to their vacuum deposition from an electrically heated tungsten carrier both the metals and the carrier were degassed perfectly in an ultrahigh vacuum. The deposited films were stabilized at approximately 90°C for a minimum of 15 minutes. The average time of deposition was about 60 min, and after the deposition, the adsorbate was admitted in a time shorter than 90 min.

Carbon monoxide of research grade purity was supplied by Matheson; it was used as received and admitted *via* two freezing traps cooled with liquid nitrogen. Oxygen, obtained by thermal decomposition of potassium permanganate *p.p.* (Lachema, Brno), was admitted likewise.

The gas pressure was measured with a Pirani vacuum gauge. The adsorbed amounts of the gases, N_a, were determined volumetrically and converted to the degrees of coverage Θ defined[22] as $\Theta = N_a/N_a^*$, where N_a^* corresponds to the equilibrium pressure of the gas above the adsorbing layer, which was about $3 . 10^{-3}$ Pa (roughly the threshold value for the thermal conductivity vacuum gauge used).

RESULTS AND DISCUSSION

Composition of Bimetallic Film Surfaces

Films of dysprosium and its alloys with copper exhibited pronounced gettering effects: The pressure of the residual atmosphere decreased during their deposition, giving evidence of their high reactivity.

A serious problem with bimetallic films is that of the composition of their surface layers. Not infrequently, the surface layers are richer in one of the components, which results in different physical properties of the surfaces[25]. A quantity dependent on the surface properties solely is the work function. In the case of uncontaminated polycrystalline films prepared by a standard procedure the work function of the surface should depend nearly solely on their composition. The experimental values of the work function φ for the deposited films of Dy_mCu_n alloys are plotted in dependence on the composition of the starting alloys used in Fig. 2. The observed
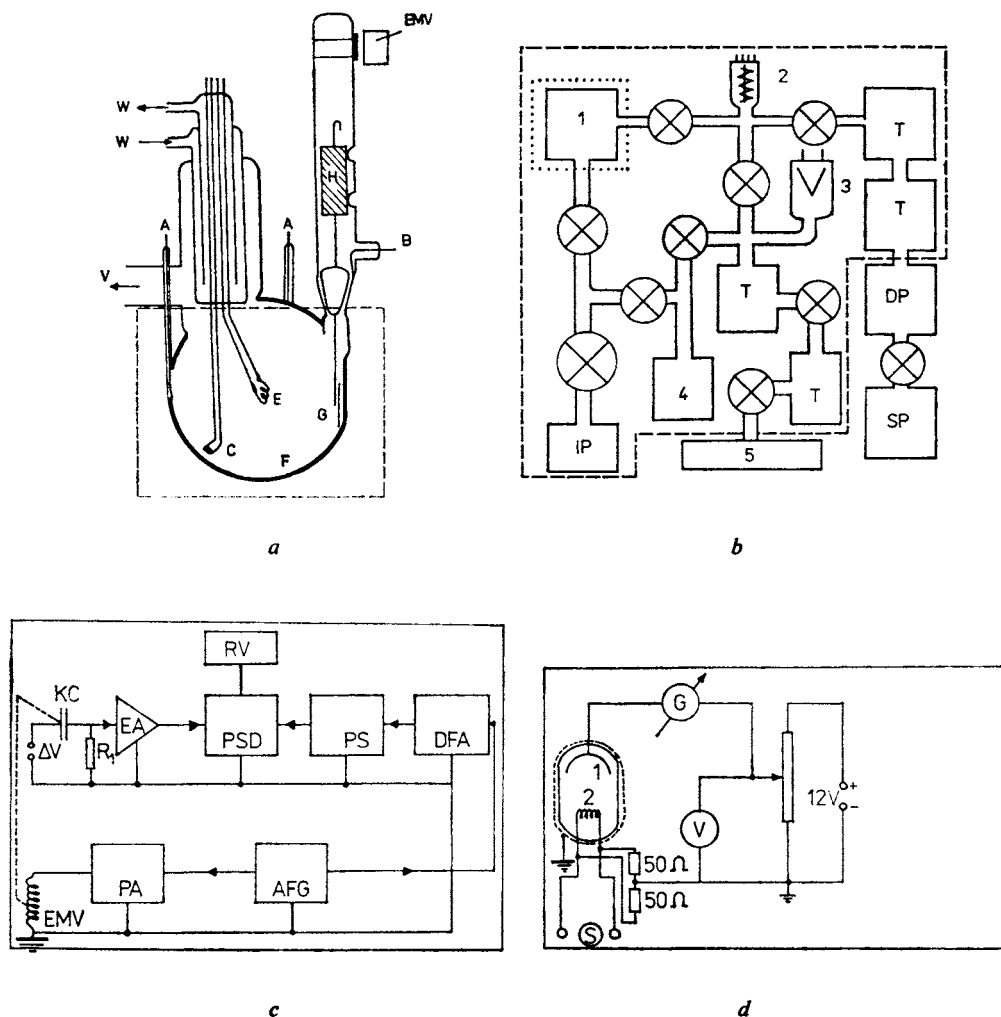
a

b

c

d

FIG. 1

Apparatus used. *a* Layout of the adsorption cell. A film contacts, B reference vibrational electrode contacts, C tungsten cathode for diode v–a characteristics measurement, E vacuum deposition source (tungsten carrier and metal to be deposited), EMV electromagnetic vibrator, F deposited film (anode for diode v–a characteristics measurement), G reference vibrational electrode for contact difference measurement with a vibrational (Kelvin's) capacitor, H glass-coated iron core for reference electrode manipulation, W thermostatting water feed. *b* Layout of vacuum apparatus. 1 adsorption cell, 2 ionization manometer, 3 Pirani thermal conductivity vacuum gauge, 4 quadrupole mass spectrometer (Centronic AIG 50), 5 gas tank, DP diffusion pump, IP ionic pump, SP sorption pump, X vacuum valves. The part heatable to 400°C is shown in a dashed line, the space that can be thermostatted at a desired temperature to within ±2°C is shown in a dotted line. *c* Block diagram of electronic circuits used for measurement of contact potential

dispersion of the φ values in the low Cu content region probably arises from segregation of copper in the surface layers of the alloy deposits, resulting in a composition different from that of the bulk. (It should be noted that similarly as for other systems, the $\varphi(Dy_mCu_n) = f(\% \, Cu)$ curve has a minimum[24] and the value for a zero copper content is identical with the work function of dysprosium.) Taking into account the fact that the copper content of the alloys used was never lower than 30%, the results shown in Fig. 2 can be so formulated that to a first approximation, the work function of the deposited films increases linearly with increasing copper content of the alloy bulk. As to the amount of copper atoms in the surface layers of the film, it can be deduced to the same approximation that this amount increases linearly with increasing amount of copper atoms in the alloy bulk, but no conclusions can be drawn as to whether the surface layers are enriched with either of the two components or not.

With the objective of gaining a deeper insight into the composition of the surfaces of the "alloy" deposits, particularly with respect to their possible enrichment, the adsorption of CO on them was investigated. Use was made of the fact that at relatively low pressures, CO adsorbs selectively on the dysprosium component of the Dy_mCu_n surfaces, the copper component only blocking the surface sites capable of adsorbing this gas[26,27]. In Fig. 3 the amounts of adsorbed CO at a constant pressure, about $3 \cdot 10^{-3}$ Pa, above the "alloy" films are shown and plotted in dependence on the composition of the bulk alloys used for the deposition. The adsorbed amount data are relative with respect to the value obtained for dysprosium surface (labelled A). The results confirm the conclusion that the dependence of the surface composition on the composition of the alloy bulk is linear, as was inferred from Fig. 2. Moreover, the results suggest that the surfaces of the deposited "alloys" are partly (about 10%) enriched with copper.

Interaction of Bimetallic Films with Oxygen

Chemisorption of oxygen on metals results largely in an increase in the work function of the metal. This is usually ascribed to the effect of the formed negatively oriented dipole layer constituted by the oxygen atoms (oxygen adsorbs dissociatively on the majority of metals at room temperature). Occasionally, a decrease in the work function has been observed, followed by an increase at higher amounts of interacting

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difference by Kelvin's vibrational capacitor method. KC Kelvin's capacitor (reference electrode: surface-oxidized tantalum), AFG broadband generator (Tesla BM 524), DFA frequency doubler, EA electrometric amplifier with an input resistance R_1, EMV electromagnetic vibrator, PA power amplifier, PS phase shift, PSD phase sensitive detector, RV recording voltmeter, ΔV compensating voltage. *d* Diagram of circuit for diode volt–ampere characteristics measurements. 1 deposited metal film (anode), 2 tungsten cathode, G galvanometer, S regulated stabilized a.c. supply 3V/5A. The measuring cell shielding is shown in a dashed line

oxygen; this has been related to the incorporation of oxygen atoms in the sub-surface layers and subsequent formation of oxide[14,15]. The observed work function changes for Dy, Cu, and DyCu films on their interaction with oxygen at room temperature are shown in Figs 4 and 5. From these results, in conjunction with published data, it can be inferred that oxygen does not form the bulk oxide with dysprosium at this temperature; the surface layer formed on the adsorption is constituted by two different types of surface species with different dipole moments (Fig. 4). For copper, on the other hand, the results give unambiguous evidence of the formation of bulk oxide even at room temperature (Fig. 5).

For DyCu films, the work function change patterns in the starting stage resemble closely those obtained with pure copper (see Fig. 5); this is true at degrees of coverage not exceeding values of $\Theta = 0.4 - 0.5$, which may approximately correspond to the amount of Cu atoms on the surfaces. This implies that interacting with surfaces of DyCu films, oxygen adsorbs first on copper and only then on dysprosium. In other words, in the starting stage of adsorption, Cu surfaces are more reactive with respect to oxygen than Dy surfaces. This may be in relation to the readiness of oxygen incorporation in Cu.
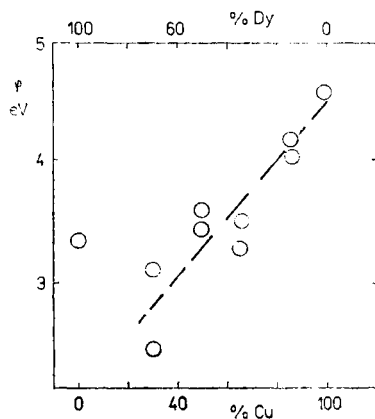

FIG. 2

Work function values φ (eV) for deposited films of Dy_mCu_n bimetallic alloys in dependence on the composition of the starting alloys used for deposition (% Cu or % Dy)
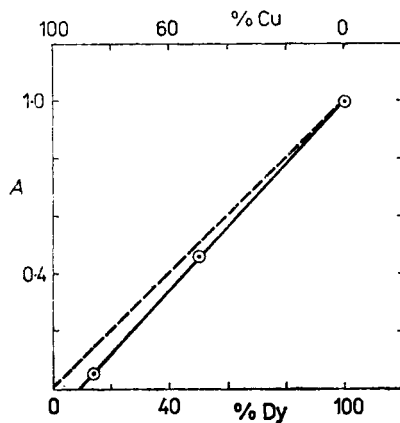

FIG. 3

Relative amount of CO adsorbed on surfaces of deposited films of Dy_mCu_n bimetallic alloys at a constant pressure, $p_{CO} \approx 3 . 10^{-3}$ Pa, in dependence on the composition of the starting alloys used for deposition (% Cu or % Dy). Dashed line corresponds to identical composition of alloy bulk and surface

After the $\Delta\varphi$ value has passed a maximum, the work function of the DyCu system exhibits an additional decrease at higher amounts of interacting oxygen, which may be associated with the formation of additional Cu and/or Dy oxides with a subsequent enhanced incorporation of oxygen in the sub-surface layers. This can be deduced from the fact that for some metals, oxygen chemisorption and its incorporation in the sub-surface layers have been observed to proceed simultaneously even at room temperature[28]. Moreover, the composition of the oxide layers formed depends heavily on the amount of interacting oxygen[29], different oxides and even different oxide mixtures being formed.

The Dy and DyCu surfaces covered with oxygen were exposed to hydrogen. For Dy, no measurable work function change or formation of a condensation product (water) was found in 24 h of interaction at a hydrogen pressure of the order of 10^2 Pa. In contrast to this, for the DyCu surfaces covered with oxygen, adsorption of hydrogen (or its interaction with the surface oxygen) followed by its absorption was observed. The results are shown in Fig. 6.

Interaction of Bimetallic Films with Carbon Monoxide

The results of investigation of interaction of CO with surfaces of rare earth elements can be interpreted assuming that dissociative adsorption associated with the formation of "carbonaceous" (probably "carbidic") or "oxidic" adsorption complexes takes place. Evidence for this has been derived from high resolution AES measure-
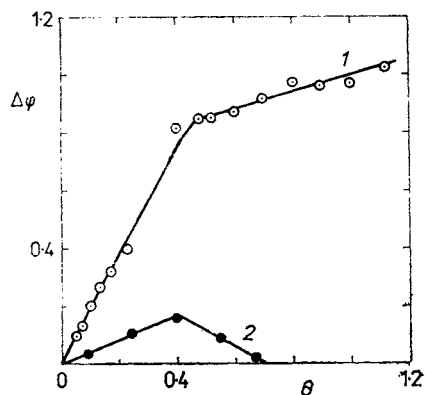

FIG. 4

Work function changes $\Delta\varphi$ (eV) for dysprosium films in dependence on the degree of coverage Θ during adsorption of oxygen (1) and carbon monoxide (2)
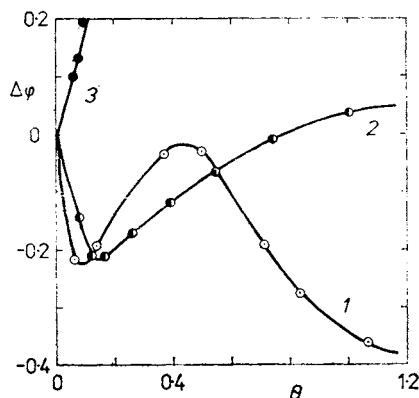
FIG. 5

Work function changes $\Delta\varphi$ (eV) in dependence on the degree of coverage Θ during adsorption of oxygen. Film: 1 DyCu, 2 Cu, 3 Dy

ments[15], the high adsorption heat of CO on Dy and DyCu alloys[20] and also from the observed work function changes, particularly at low degrees of coverage. Our data for Dy, DyCu, and DyCu$_6$ films (Fig. 7) are consistent with the concept of dissociative chemisorption of CO (incorporation of undissociated adsorbed CO molecules is not feasible). "Adsorbed" carbon ("carbidic" or any other kind, *e.g.* "graphitic") on metals frequently induces lowering in their work function[30-32], which implies that the net result is electron charge transfer from the "carbonaceous" adsorption complex into the metal surface (the reverse would be observed if incorporation of this complex took place). Assume that this is also true of Dy and DyCu alloys. "Oxidic" surface complexes can behave in a very complex fashion, in dependence on whether the species are present on the surface or their incorporation takes place, and hence, work function increase or decrease can be observed. For Dy, formation of "carbidic" and "oxidic" complexes due to dissociative adsorption of CO in the starting stage of coating (up to $\Theta = 0.4$, Fig. 6) would result in a work function increase, which, however, would be considerably less marked than in the case of formation of the "oxidic" complexes solely (Fig. 4). This can be regarded as an evidence for the above assumption that the decrease in the work function of Dy is due to the formation of "carbonaceous" complexes on its surface (the formation of a half amount of "oxidic" complexes in the case of adsorption of CO as compared to O$_2$ was taken into account).

For both oxygen and carbon monoxide, the changes in the work function suggest that adsorption sites of two kinds exist on the surfaces of the films studied. The
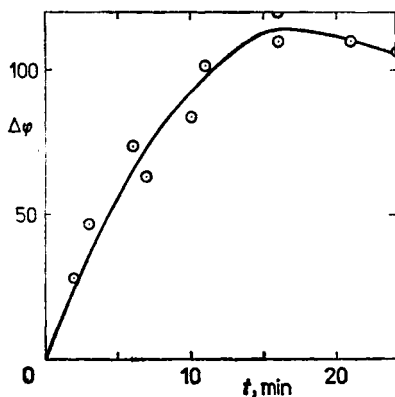

FIG. 6

Interaction with hydrogen for DyCu films covered with oxygen. Work function change $\Delta\varphi$ (meV), time t (min)
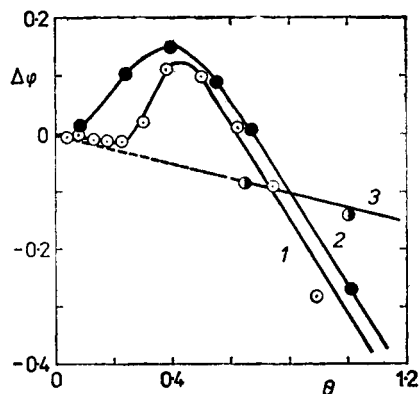
FIG. 7

Work function changes $\Delta\varphi$ (eV) in dependence on the degree of coverage Θ during adsorption of CO. Film: 1 DyCu, 2 Dy, 3 DyCu$_6$

"oxidic" and "carbonaceous" complexes, formed on them by dissociative adsorption, depend strongly on the degree of coverage. This applies particularly to the "oxidic" complexes where the ratio of dipole moments in the regions of lower and higher degrees of coverage is six (Fig. 4). Therefore, in the starting stage the effect of "oxidic" complexes prevails and the work function of Dy increases on the adsorption of CO, whereas at degrees of coverage higher than approximately 0·4, where "oxidic" complexes with a low dipole moment are formed (the slope of the tangent to the $\Delta\varphi = f(\Theta)$ curve is low), the effect of "carbonaceous" complexes on the work function predominates and a decrease in φ is observed.

For DyCu and $DyCu_6$, the effect of Cu atoms and aggregations in the surface layers must be taken into account, CO being virtually unadsorbed by them; this is also clear from Fig. 3, where the amount of adsorbed CO is seen to decrease linearly with increasing amount of Cu. The enrichment of the surface layers with copper, resulting in an additional decrease in the adsorption of CO, must also be considered. The small decrease in the work function in the starting stage of coating of these surfaces can be explained in terms of the possible incorporation of oxygen in the sub-surface layers.

At higher degrees of coverage, more complex surface interactions can be expected, associated with surface oxygen consumption or redistribution among the adsorption complexes resulting in the formation of new surface species or species desorbing into the gaseous phase.

The possible participation of other molecules in surface interactions with lanthanides, associated with catalytic effects of lanthanide compounds, lies beyond the scope of this treatment.

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