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**ION-INDUCED CO ADSORPTION ON POLYCRYSTALLINE NICKEL.
SECONDARY ION MASS SPECTROMETRY STUDY**

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In the process of ion-induced CO adsorption (Ar^+ , 4 keV, $4 \mu\text{A}/\text{cm}^2$) on polycrystalline Ni at room temperature and $P = (1-40) \times 10^{-6}$ Pa the emission of Ni^+ , NiCO^+ , CO^+ , NiO^+ and C^+ ions is observed. The emission of the last three ions is due to the ion-stimulated dissociation of weakly bound CO state and NiO formation. The weakly bound state is formed owing to surface defects produced by ion bombardment. The cross sections of the ion-induced desorption are 1.8 and $0.8 \times 10^{-14} \text{ cm}^2$, respectively, for weakly bound and strongly bound states.

A broad spectrum of easily controlled and efficient effects of ion bombardment on the state of the surface of solid materials and on processes of adsorption and catalysis, as well as on the interaction of gases with these surfaces encourages the research in this field [1-3]. However, studies on ion-induced adsorption of gases on metal surfaces, in particular on nickel, are not numerous as yet, and the concrete data are scarce. Actually, the dependence of the cross section of ion-induced desorption on the energy of bombarding ions (He,

Ne, Ar and Kr) up to 500 eV for CO adsorbed on nickel (100) face has been measured [4]. Experiments on CO adsorption on Ni (100) face bombarded with ions revealed an increase of the amount of adsorbed CO caused by the developed surface roughness and increased number of surface centers upon bombardment [5]. It was shown that CO is adsorbed selectively on defect sites produced by the ion bombardment of Ni (111) [6]. Ion-induced surface defects accelerate dissociative CO desorption from nickel (100) face at 500 K, increasing the sticking coefficient from 0.02 to 0.4 [7].

In the present work, CO adsorption on polycrystalline nickel upon simultaneous surface bombardment with argon ions was studied using the method of secondary ion mass spectrometry (SIMS).

EXPERIMENTAL

The experiments were carried out using a secondary ion mass spectrometer MS 7201 with a monofield mass analyzer. The mass spectrometer is equipped with an automatic system for measurement control and data collecting and processing, designed at Boreskov Institute of Catalysis, based on DVK-3 computer and "CAMAC" interface. The software complex provides a survey and analysis of the total mass spectrum in the range of 1-250 a.m.u and measurement of ion currents for selected 8 masses in the process of bombardment, with simultaneous visualization of peak shapes and diagrams of peak heights vs. time.

The bombardment was performed by argon ion beam with an energy of 4 keV and a current density of $J = 4 \mu\text{A}/\text{cm}^2$. The beam diameter was 2 mm and the incident angle 45° . The pressure of residual gases in the mass spectrometer chamber did not exceed $P_{\text{O}_2} = 7 \times 10^{-7}$ Pa, thus providing the experimental conditions of "dynamically pure surface", $P_{\text{CO}} \ll 10^{-6}$ J [8].

Polycrystalline samples of 99.9% purity nickel were in the form of 30 μm thick foils. Foil bands with a size of 5x60 mm were cleaned in a special high-vacuum setup by long annealing

at 1100 K with brief flashes up to 1300 K. The bands were cut to pieces of 4x5 mm in size, and 6 pieces were placed into the mass spectrometer. All experiments were carried out at ambient temperature. It was found that some tens of seconds are sufficient for removal of the major part of surface impurities. However, Na^+ , Mg^+ , Al^+ , Si^+ , K^+ and Ca^+ ions were registered in the mass spectra. The concentrations of these impurities were estimated not to exceed 0.01%, with the exception of Mg, whose concentration was of the order of 0.1%.

The introduction of CO was performed using a piezoelectric valve SNA-2. Time constant of the evacuation of the mass spectrometer vacuum chamber was 0.05 s (volume 6 L, evacuation rate 150 L/s), permitting the introduction and evacuation of CO in the period of 1 s.

RESULTS AND DISCUSSION

During CO adsorption the following ions are observed in the mass spectra of secondary ion emission: Ni^+ , NiCO^+ , CO^+ , NiO^+ , C^+ . Their peak intensities vs dose are presented in Figs 1 and 2. Three sets of experiments on CO adsorption were carried out. In the first set the introduction of CO was performed prior to the bombardment; in the second and third one CO was introduced in 100 and 200 s after the bombardment. The pressure of CO was varied from 1 to 40×10^{-5} Pa. The differences between these sets of experiments are manifested in different kinetic dependences caused by development of the surface upon the bombardment. The interruption of CO introduction in the gas phase leads to the fall-off of all ion currents due to the ion-stimulated desorption of adsorbed CO.

Figure 3 gives the dose dependences of ion currents of NiCO^+ and $\text{NiCO}^+/\text{Ni}^+$. It should be noted that in these experiments the ion currents for peaks with $m/z=86$ (NiCO^+) and 58 (Ni^+) were measured alternately for ca. 1.5 s, but for collecting the data represented by curve 1 the sample was removed several times from the beam for 10 s and then again

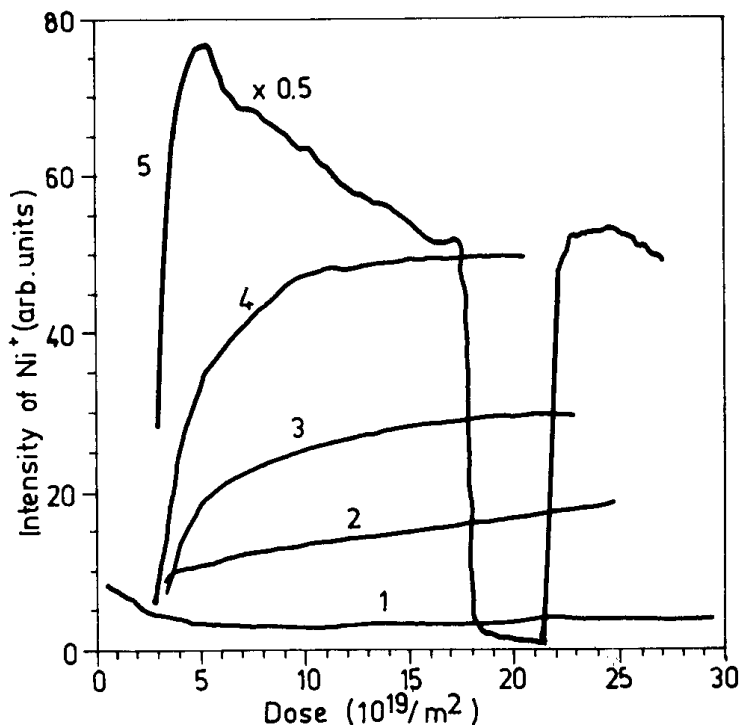


Fig. 1. Ni⁺ ion emission intensity vs. the dose of ion bombardment at different CO pressures (Pa):
 1 - background level 5×10^{-7} ; 2 - 1.5×10^{-5} ; 3 - 4.0×10^{-5} ; 4 - 10×10^{-5} ; 5 - 40×10^{-5} .

The sharp rise and fall of curve 5 is due to the interruption of CO introduction

bombarded. As the CO pressure in these experiments was varied in the range of $(1-10) \times 10^{-5}$ Pa such long exposures (3 L) were sufficient to achieve a steady-state coverage. The data represented by curve 2 were obtained under conditions when the CO pressure was cut off several times. In addition, Fig. 3 also shows the values for NiCO⁺ (curve 3) obtained under the same conditions as for curve 2.

The cross sections of ion-stimulated desorption σ were calculated from the fall-off of ion currents of NiCO⁺ upon the interruption of bombardment and cut-off of CO introduction

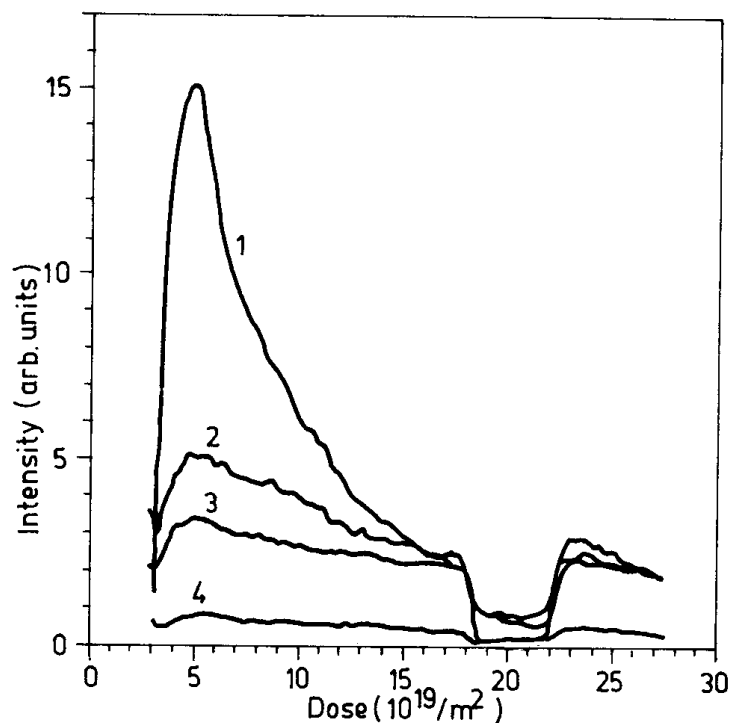


Fig. 2. Dependences of Ni^+ , CO^+ , NiO^+ and C^+ ion currents on the dose of ion bombardment at $P_{\text{CO}} = 40 \times 10^{-5}$ Pa (curves 1-4, respectively)

(curves 1 and 3, respectively) according to the formula: $I = II e^{-\sigma Jt}$. The value of σ for case 3 was found to be $0.8 \times 10^{-14} \text{ cm}^2$ and that of I varied from 1.5 to $1.8 \times 10^{-14} \text{ cm}^2$, in accordance with the increase of the dose.

Figure 4 presents dose dependences of ion currents for NiO^+ normalized to the current of NiCO^+ . A similar behavior is exhibited also from the time dependences of C^+ current. The presence of C^+ and NiO^+ ions in the spectra points to the dissociative nature of adsorption. Its contribution is increased with increasing CO pressure, and accompanied by NiO formation on the surface. The formation of NiO phase follows from the observation that the interruption of CO introduction leads to increase of the ratio of $\text{NiO}^+/\text{NiCO}^+$ ion currents (Fig. 4). In addition, at CO pressure above 10^{-4} Pa the formation of

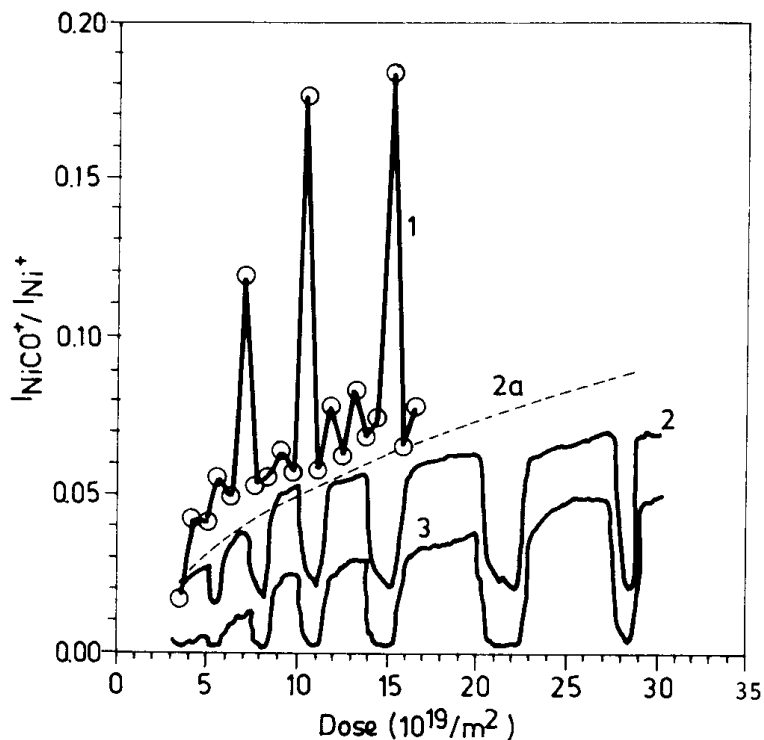


Fig. 3. Ratio of $\text{NiCO}^+/\text{Ni}^+$ ion currents (curves 1 and 2) and ion current of NiCO^+ (curve 3) as functions of the dose of ion bombardment. Curve 1 is obtained with the interruption of the bombardment, and curves 2 and 3 with the interruption of CO supply into gas phase

NiO noticeably affects the emission of secondary ions, which is exhibited by the drop in ion intensity already at a CO pressure of 40×10^{-5} Pa after 100 s (Figs 1, 2).

Some admixture of oxygen (4%) to CO results in a similar effect at lower pressures. However, at a mixture pressure of 10×10^{-5} Pa the opposite phenomenon takes place, *viz.* the maximum ion intensity of peaks shifts in the direction of larger doses. This appears to be due to the interaction of oxygen with CO.

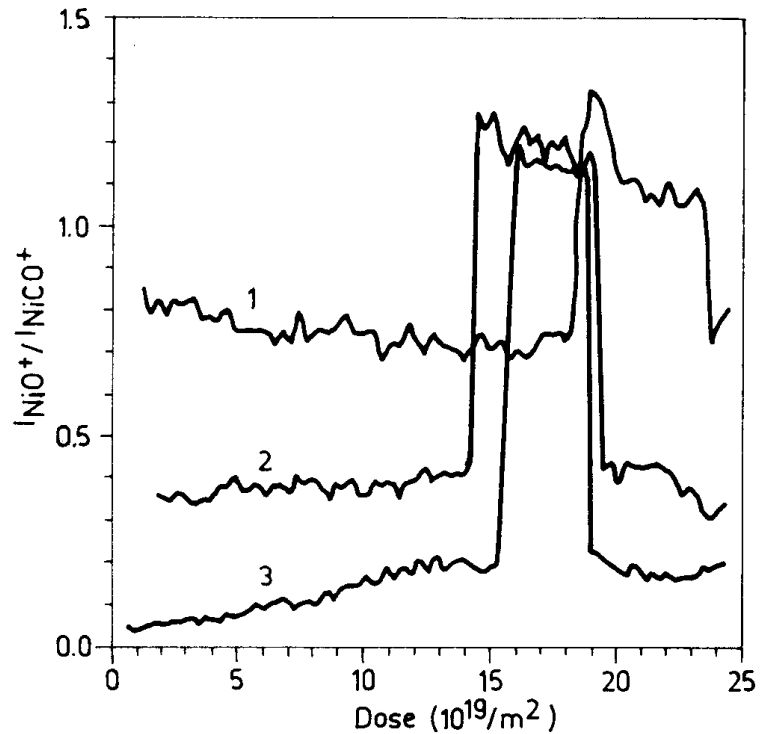


Fig. 4. Ratio of $\text{NiO}^+/\text{NiCO}^+$ ion currents vs. the dose of ion bombardment at different CO pressures (10^{-5}Pa): 1 - 1.5; 2 - 10; 3 - 40.

The fall and rise of signals are caused by the interruption of CO supply

First and foremost, it should be noted that, in contrast to SIMS studies of CO layers adsorbed on particular nickel planes (in the absence of CO in the gas phase) [5, 9-11], under the conditions of this study the emission of C^+ , NiO^+ , CO^+ was observed. The emission of the first two ions is certainly due to CO dissociation. The latter process can be caused by defect formation upon bombardment and by the action of the ion beam. In fact, the defects were found to increase CO dissociation, but this effect became noticeable only at 500 K [7]. In addition, under the conditions of this study the bombardment

changes the surface topography, while the concentration of defects of the "vacancy" type does not change considerably. Indeed, it was previously shown that the dependence of the concentration of vacancies on the dose upon the bombardment is expressed as follows: $n = n_0 [1 - \exp(-D/D_0)]$, where n_0 and D_0 are the defect concentration and dose upon saturation [12], respectively. Using the data of [12] obtained for argon, we found that in our conditions the defect concentrations calculated, e.g. for 100 and 1000 s of bombardment differ by less than 15%. On the other hand, the bombardment of adsorbed CO layers was not found to result in the emission of C^+ and NiO^+ ions [9-11].

The possible explanation of both CO dissociation and the emission of CO^+ ions is the formation of a weakly bound CO state on the nickel surface subjected to ion bombardment. The bombardment of these species with ions can lead to the emission of CO^+ and $NiCO^+$. The formation of this state is confirmed by the jump of the σ value from 0.8 to 1.5×10^{-14} during CO adsorption with periodic interruption of the bombardment at low pressure - 1.5×10^{-5} Pa. Thus, it is the development of the surface and defects that cause the formation of such CO species. This is quite possible, because this is not a simple defective surface. As was shown in [13], the bombardment of Ni with argon with $E = 0.6$ keV at $T = 300$ K leads to the formation of crystal argon inclusions with an average size of 3 nm and a melting point above 575 K. It is worth mentioning that CO adsorption on polycrystalline films also results in the formation of a weakly bound CO state, but at higher pressures [14].

A relatively high value of the cross section of ion-stimulated desorption of CO_{ads} , obtained here, although exceeding considerably the size of the nickel unit cell, correlates satisfactorily with values given in other publications: $8 \times 10^{-15} \text{ cm}^2$ [4] and 10^{-14} cm^2 [15], obtained upon CO sputtering with argon with $E = 500$ eV and helium with $E = 2$ keV, respectively.

As the value of σ varies in inverse proportion to the bond energy [16], the heat of adsorption of weakly bound CO species should be approximately twice lower than that of strongly bound species: 125-105 kJ/mol [13, 16]. However, taking into account that the value of σ can be measured at room temperature, the life-time of the weakly bound state must be of the order of several seconds, and, consequently, the heat of adsorption should be ca. 75 kJ/mol.

A measure of surface roughness, according to [17], is the function Δz , defined as depth resolution upon ion sputtering. For polycrystalline metals the dependence of Δz on the depth of sputtering is expressed by the formula [17]:

$$\Delta z = (0.86 \pm 0.22) z$$

In the range of 15% accuracy the curves given in Fig. 3 can be linearized by plotting against \sqrt{t} . Therefore, they reflect the build-up of the coverage, as the concentration of adsorption sites increases, owing to surface development upon ion bombardment.

It was shown that the ratio of NiO^+/Ni^+ ion currents is proportional to the coverage (θ) [9, 10]. The kinetic equation for the adsorption accompanied with ion bombardment can be expressed as:

$$\frac{d\theta N_c}{dt} = kSP(1-\theta) - \sigma J\theta N_c, \quad (1)$$

where:

S is sticking coefficient, P - pressure (Pa),

$k = 4.6 \times 10^{20} / (mT)^{0.5} \text{ m}^{-2} \text{ s}^{-1}$, m - molecular mass,

T - temperature (K),

N_c - concentration of adsorption sites,

σ - cross section of ion-stimulated desorption.

For sputtering times over 500 s, one can take the value of $d\theta/dt = 0$ with sufficient accuracy. Then substituting the known value of N_c into eq. 1, it is possible to determine the

sticking coefficient. The limiting coverage of polycrystalline nickel films with adsorbed CO at room temperature and $P \leq 10^{-5}$ Pa, according to [14] is $0.7 \times 10^{19} \text{ m}^2$. If the concentration of adsorption sites at the beginning of the bombardment is taken as equal to the above value, and assuming that at $t > 500 \text{ s}$ it increases by a factor of 4, one can evaluate the sticking coefficient. The value obtained: 0.65 ± 0.25 correlates with values found by other authors, e.g. 0.9 in [16].

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