
STRUCTURE OF MATTER
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Surface Properties of Sodium, Potassium, and Their Binary Alloys in the Liquid State

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Abstract—The results from investigating the surface characteristics of liquid sodium, potassium, and four potassium–sodium alloys are considered. The Auger spectra and profiles of metal droplets with atomically pure surfaces in the solid and liquid state are studied under the same experimental conditions. It is shown that potassium is a surfactant with respect to sodium at the temperature of an experiment in the investigated range of volume concentrations. It is noted that the obtained values of surface tension are 15% higher than the reference values.

Keywords: surface, liquid, vacuum, tension, concentration, droplet, spectrum, isotherm, electrons

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INTRODUCTION

Most of our information on surface layers of metals in the liquid state is currently obtained by measuring density and surface tension. The parameters of adsorption, the mutual positions of separating surfaces, excess energy, transition layer thickness, and a number of other surface characteristics in different phase states are determined using the concentration and temperature dependences of surface tension and the coefficients of activity in the volume of a solution. Such algorithms have disadvantages, so it is better to measure these parameters directly. This became possible with the emergence of electron spectroscopic means of surface analysis, which are mainly used for diagnostics of solid surfaces, while there are no fundamental prohibitions on similar experiments with liquids. The literature contains results from investigating the surfaces of a set of low-melting metals (e.g., In, Sn, and Pb) in the solid and liquid states by means of Auger spectroscopy and the lying droplet technique [1]. There are no analogous articles devoted to alkali metals.

Meanwhile, similar investigations for alkali metals and their alloys would allow us to study the effect oxygen and the residual gas of ultra-high vacuum chambers have on the characteristics of surfaces, and to clarify the role of the phase state of the mechanisms of such phenomena as surface segregation and adsorption. It would also allow us to correctly calculate a surface's set of thermodynamic parameters, providing information on the activity of components in the volume and on the surface, on the short-range order in the surface layers of liquid solutions, and so on.

EXPERIMENTAL

Features of setup used in this work include the possibility of analyzing surfaces in the solid and liquid states [2]. Two sample holders are used for this purpose: the first is used for solid samples of the same type as in [3]; the second is used to analyze samples in the solid and liquid states that serve as supports for samples heated by a molybdenum foil furnace. Such a holder allows us to deform liquid droplets with the greatest possible diameter, which in turn enables us to use the lying droplet technique [4] with the corresponding adjustments. The holder was used in this work to study the concentration dependences of surface tension and surface concentrations simultaneously. Substrates made of 12Kh18N10T steel that were mounted on the furnace fastened on the manipulator were used. Each sample was heated by radiation. The temperatures of both type samples were controlled using a PP-1 Pt/Pt-Rh thermocouple, calibrated for the melting points of sodium, potassium, and cesium.

Surfaces of sodium, potassium, and surface segregation under the conditions of atomically pure surfaces in liquid sodium–potassium alloys were investigated via Auger spectroscopy with simultaneous measurements of surface tension using the lying droplet technique. The measurements were performed in an ultra-high vacuum setup (the highest vacuum was 10^{-8} Pa), pumped by zeolite and ion sputter pumps. Prior to each experiment, the working chamber was degassed by heating it to 573 K. A cylindrical mirror energy analyzer of charged particles with an axis–axis optical system was used to register the Auger spectra.

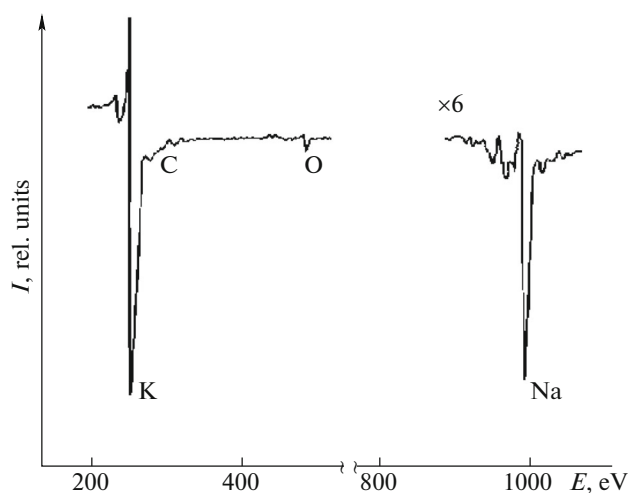


Fig. 1. Auger spectra of sodium and potassium at 373 K after surface cleansing by an electron beam.

The diameter of the incident electron beam with maximum energy $E = 2$ keV was 0.5 mm at a current of $I_p = 0.5$ – 3 μ A.

The purity of initial metals was no less than 99.95 at %. All of the main operations of opening the ampoule with metal, cutting the samples for investigation from the bulk sample, and weighing them were conducted in liquid nitrogen to slow the oxidation reaction and isolate the samples from the atmosphere. Samples were loaded using a lock chamber in which an inert atmosphere was maintained by a flow of purified and cooled argon.

After loading the main metal into the working chamber and forming droplets, a metal additive was introduced if necessary. At the temperature of experiment (373 K), the solutions were mixed by a manipulator. The droplets were then adjusted with subsequent surface cleansing. The Auger spectra were measured, and droplet profiles were registered for samples with atomically pure surfaces.

RESULTS AND DISCUSSION

According to our results, it may be argued that cleansing surfaces of liquid alkali metals and alloys of surface-active oxygen-containing impurities via argon ion bombardment (500 eV, 5 μ A/mm²) is not effective enough. The best results were achieved using an electron beam, based on the mechanism of electron-stimulated desorption [5, 6]. Here, the electron excitation caused by the inelastic interaction between primary electrons and adsorbed particles, leading to interatomic and intraatomic Auger transitions, are of primary importance. As a result, the multiple ionization of the anionic components occurs, with their subsequent emission from a material's surface. Desorption by similar Auger decay on the main levels of cations

can occur only for compounds with maximal valence [6], which corresponds to our case on surfaces of alkali metals. Electron beam parameter E_p was 1000–2000 eV at a current density of 50 μ A/mm². In this method of cleansing the surfaces of liquid metals and alloys, no Auger peaks were detected after 5–10 s, and the concentration of oxygen atoms was <1 at % for all of the investigated samples (Fig. 1).

Quantitative interpretation of Auger spectroscopy results, performed with allowance for matrix effects using the scheme described in [6], assumes that we know the relative sensitivity factors of Auger lines in the liquid state. For pure sodium and potassium in the liquid state (373 K), the intensity of the main Auger lines obtained under the same experimental conditions is 1.31 and 1.14 times higher than the intensity of the Auger peaks of these elements in the solid state, respectively. The ratio of the peak–peak amplitudes of the 253 eV $L_2M_{23}M_{23}$ potassium line and the 990 eV $KL_{23}L_{23}$ sodium line was 14.2 (Fig. 1). A comparison of the Auger spectra of pure metals shows that the shape and energetic position of Auger lines of pure metals at $T = 373$ K did not change upon transitioning to alloys. Our results from calculating the surface concentrations of Na–K alloys in the liquid state ($T = 373$ K) are presented in Fig. 2 (curve 1).

The values of surface tension obtained for pure sodium and potassium at their melting temperatures were 243 and 126 mN/m, respectively; these differ from the reference values by approximately 15%. One reason for these differences is apparently that many researchers assumed their investigated surfaces were free of surface active impurities after vacuum distillation when measuring surface tension. In all cases, the pressure of residual gas in the measuring cells was 10^{-6} – 10^{-7} Pa, at which the time needed for the adsorption of a monolayer from the residual gas at accommodation coefficients close to unity was 1–2 h, while preparations for an experiment after pumping and measurement usually require several tens of hours in glass cells soldered off from the vacuum stations. We may conclude that the big droplet technique was used to investigate surfaces with impurity atoms taken from the residual media, which can strongly influence the measured characteristics.

Our isotherm of surface tension $\sigma(x)$ of sodium–potassium alloys with atomically pure surfaces at a temperature of 373 K is shown in Fig. 2 (curve 2). The data on $\sigma(x)$ obtained by our group using the big droplet technique (curve 3) [7], and by the authors of [8] (curve 4), are presented for comparison. We can see that the values of $\sigma(x)$ obtained using the big droplet technique lie below those obtained in this work.

A comparison of the theoretically calculated isotherms of surface tension for Na–K [9, 10] and our data showed satisfactory agreement with the results obtained by our group using the big droplet technique

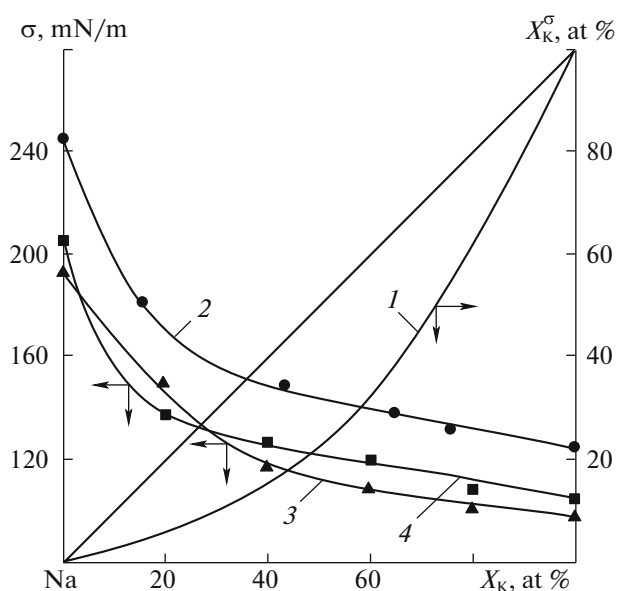


Fig. 2. Isotherms of (1) surface concentration and (2) surface tension from this work, (3) [7], and (4) [8] for sodium–potassium at $T = 373$ K.

(Fig. 2, curve 3). If we employed our experimental data on σ for an atomically pure surface in calculating its isotherm using the two-parameter equation from [9], agreement with the isotherm presented in Fig. 2 (curve 2) was also observed.

As was shown in earlier works devoted to studying Na–K alloys, concentration dependence $\sigma(x)$ at 373 K indicated surface activity by potassium in alloys with sodium: adding several percents of potassium lowered surface tension to 20 mN/m. Neither the eutectic point on the Na–K phase diagram nor the compound KNa_2 were reflected on the isotherm of surface tension in the form of an extreme shape of the curve.

CONCLUSIONS

A procedure for loading and preparing alloys, obtaining atomically pure surfaces, and performing *in situ* experiments to measure the surface characteristics of alkali metals was developed. Na and K samples with atomically pure surfaces and Na–K alloys were analyzed via Auger spectroscopy with the simultaneous registration of liquid droplet profiles. Isotherms (373 K) of the surface concentrations and surface tensions for Na–K binary systems were plotted according to the obtained data. Our experimental data on the $\sigma(x)$ of investigated metals were higher than the data reported by other authors.

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