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FEATURES OF HIGH-TEMPERATURE OXIDATION IN AIR OF SILVER AND ALLOY Ag – Cu, AND ADSORPTION OF OXYGEN ON SILVER

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Thermodynamic calculations are provided for equilibrium in the system Ag $-$ O_2*. Kinetics of high-temperature (up to 900°C) oxidation in air of plates made from pure silver (99.99 mass% Ag) and jewellery alloy 84 at.% Ag – 16 at.% Cu are studied by nonisothermal thermogravimetry, and differential and petrographic analyses of the reaction products. Mechanisms are established for the corresponding oxidation reactions confirming the absence of chemical reaction for pure silver with oxygen at* $T > 422$ *K. The Wagner theory for oxidation of alloys containing precious metals is confirmed by the results. The temperature ranges are determined for van de Waals adsorption and chemisorption of oxygen at the surface of very pure silver powder with a specific surface area* $S = 0.4$ m^2/g*.*

Keywords*: silver, silver-copper alloy, high-temperature oxidation, adsorption, process mechanism.*

The properties of silver, including some data relating to its oxidation, in particular at high pressure, have been aired in a review [1], and in a monograph [2]. In dry air at room temperature silver is coated with a layer of oxide whose thickness does not exceed 100 nm. At 200°C the layer of oxide is somewhat thicker, at 300°C and a pressure of 2 MPa oxidation may be complete [2]. In order to measure the small thickness of the Ag_2O layer Davies [3] used an electrometric method. Benton and Drake [4] studied silver oxidation kinetics at 168°C and different oxygen pressures. They established that the rate of oxide formation is directly proportional to oxygen pressure, and the activation energy in the range 100-170°C is 92.2 kJ/mole. Menzel and Menzel-Kopp [5] carried out a crystallographic study of the Ag_2O layer obtained on a silver single crystal at 900°C and a pressure of 10 MPa; in these case oxidation occurs through a process of nucleus formation. Watanabe [2] studied single-crystal silver, heated in oxygen, by an electron diffraction method; in ozone oxidation is only possible in the presence of moisture. Dankov and co-authors [6] showed that the Ag_2O oxide lattice obtained at a silver anode is deformed.

The aim of this work is to study oxidation features in air for a plates of pure silver (99.99 mass% Ag) and jewellery alloy 84 at.% Ag – 16 at.% Cu up to 900°C, and also the mechanism of desoprtion-adsorption of oxygen at the surface of Ag (99.99 mass%) powder on heating it in an air up to 900°C. High-temperature oxidation of both compacted specimens was studied by thermogravimetry (TG) and differential thermal analysis (DTA) in a Q-1500 derivatograph in a nonisothermal regime with a rate of change in temperature of 10 deg/min. In order to determine the composition of oxidation products for Ag – Cu jewellery alloy at different stages of oxidation (at 650, 750 and 900°C) more prolonged (180 min) isothermal oxidation was performed in the same device. Oxide layers that formed on the plates were removed in the form of powder particles with a scalpel and analyzed in a mineralogical microscope MIN-8 using standard liquids with a known refractive index (petrographic analysis).

The specific surface area of high purity silver powder was determined by the BET (Brunauer, Emmett, Teller) method by low-temperature adsorption of nitrogen (in our case $S = 0.4$ m^2/g).

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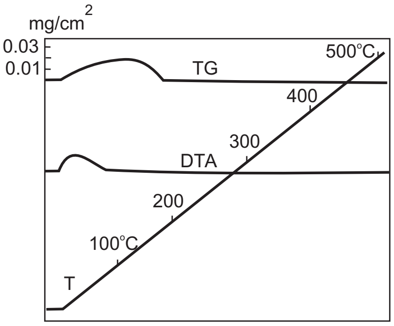

Fig. 1. TG- and DTA-curves for oxidation of a pure silver plate

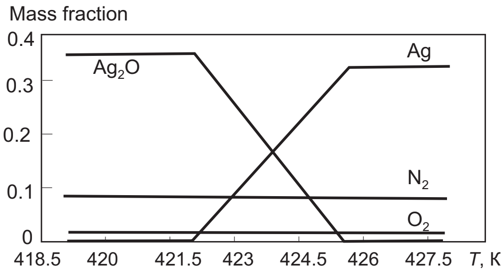

Fig. 2. Equilibrium composition of the system Ag – air (1:2 by mass) with pressure $P = 0.1$ MPa

Desorption-adsorption equilibrium Ag – $O_{2(ads)}$ in the range 20-900°C was also studied by the TG and DTA methods; the rate of change in temperature for a sample of a specimen (1.470 g) was 5 deg/min.

A silver plate, as also for silver powder in the original condition, contained at the surface a very fine layer black in color (Ag_2S), and therefore before each test a specimen was washed in concentrated $AgNO_3$ solution. Dissolution of the film is due to formation of a complex compound $Ag_2S \cdot nAgNO_3$, within which the complex former is the sulfur atom. As is well known [7] gradual darkening of silver items is connected with formation of silver sulfide with action on metal silver of the impurity hydrogen sulfide contained in the air, and also oxygen:

$$4Ag + 2H_2S + O_2 = 2Ag_2S\downarrow + 2H_2O. \tag{1}$$

In our tests with nonisothermal heating of a plate of 99.99 mass% Ag in air a mass increase for a specimen was only observed at 150°C ($\Delta m/S \sim 0.02$ mg/cm^2), after which it remained equal to zero over the whole temperature range, i.e. up to 900°C (Fig. 1); the single peak of the DTA curve for heat release corresponded to 40°C. Thus at temperatures above 150°C and at atmospheric pressure the Ag_2O oxide formed at lower temperatures is entirely decomposed:

$$2Ag_2O_{(cr)} = 4Ag_{(cr)} + O_{2(g)}\uparrow. \tag{2}$$

On account of the one of the main principles of equilibrium in heterogeneous systems: the activity of any substance within the composition of a system in the form of a pure crystalline phase is constant at a constant temperature, it is possible to prescribe the equilibrium reaction constant, without indicating the substance comprising this phase. In particular, the equilibrium reaction constant (2) may be determined as

$$K_{eq} = \left(P_{O_2} \cdot P_{Ag}^4\right) / P_{Ag_2O}^2 . \tag{3}$$

Here P_{O2} is oxygen partial pressure in the system; P_{Ag} and P_{Ag_2O} are partial pressure of saturated vapor above silver crystals and silver oxide, respectively.

This expression is simplified due to the fact that P_{Ag} and P_{Ag_2O} are constant. Therefore it is possible to write

$$P_{O_2} = K. \tag{4}$$

It can be seen from the equation obtained that with equilibrium under conditions of constancy for temperature the partial pressure of oxygen, formed as a result of partial decomposition of silver oxide, is constant. For example, at 400 K the equilibrium constant for Ag_2O decomposition is 0.145 Pa. Whence it follows that at this temperature silver oxide will decompose until the partial pressure of oxygen in the gas in contact with the solid phase reaches 0.145 Pa. Considering that the partial pressure of oxygen in air is 0.21 Pa, a silver plate at 400 K will react with atmospheric oxygen forming oxide. However, at 426 K the dissociation pressure for Ag_2O reaches 0.21 Pa. Whence it follows that at a higher temperature silver will not oxidize in air.

This is also confirmed by direct thermodynamic calculations. In order to clarify the fundamental possibility of silver oxidation at different temperatures and oxygen partial pressures we performed calculations for the thermodynamically

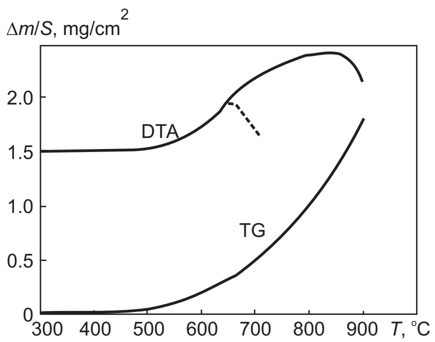

Fig. 3. TG- and DTA-curves for high-temperature oxidation of alloy 84 at.% Ag – 16 at.% Cu plate

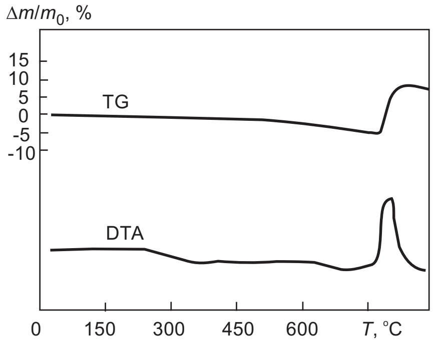

Fig. 4. TG- and DTA-curves for oxygen desorption-adsorption at pure silver powder

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equilibrium compositions in the systems silver – air and silver – oxygen at 298-1500 K and pressures of 0.05, 0.1, and 0.2 MPa. As is well known, the composition and other characteristics of a system in an equilibrium state, towards which spontaneous processes strive, is clearly determined by conditions for its existence. Generally a criterion for a system equilibrium is the extremum of any thermodynamic potential (minimum Gibbs free energy, entropy maximum, etc.).

In our calculations we found the entropy maximum for a multicomponent isolated system using an automatic system of thermodynamic calculations for equilibrium states ASTRA [8] with the corresponding approximations and algorithms. Marked approximations are the assumption about independence of substance thermodynamic properties in condensed phases on pressure and use for the gas phase of equation of state for ideal gases if there are reliable data for the thermodynamic properties of individual substances that may form from elements in the system being simulated.

In analyzing the equilibrium state in the silver – oxygen system, consideration is given to the possible existence of condensed Ag and Ag_2O phases; in the gas phase consideration was given to the possible existence, apart from O_2, N_2, CO_2, Ar, and Ag, other single and binary compounds (molecules) of the silver – oxygen system (it appeared that in a thermodynamically equilibrium system they are either not there or their content is negligibly small). Thermodynamic characteristics of substances from the ASTRA data base, formed from approved reference data, were used in the calculations.

As calculations (Fig. 2) have shown, solid silver oxide Ag_2O at atmospheric pressure is thermodynamically stable at up to 422 K, and above 426 K silver and its oxide are in an equilibrium state. If they form a solution, which is not considered in the calculations, this temperature range will be somewhat wider. Thus, silver may oxidize in air at below 422 K forming oxide Ag_2O that decomposes on heating above 426 K. An increase in temperature at a rate of $1.8 \cdot 10^{-4}$ K/Pa is caused by an increase in oxygen partial pressure.

Experimental data obtained in studying the high-temperature oxidation of jewellery alloy 84 at.% Ag – 16 at.% Cu (solid solution of copper in silver) by nonisothermal thermogravimetry and differential thermal analysis are provided in Fig. 3. The alloy exhibits very high corrosion resistance in air; at 900°C the maximum specific mass increase for a specimen $\Delta m/S = 1.78$ mg/cm^2. Oxidation of this alloy is two-stage. For the first stage of oxidation, characterized by an inverse parabolic dependence of specific mass increase on temperature, the DTA maximum corresponds to 650°C; for the second stage, characterized by linear dependence, it corresponds to ~850°C. Here in a quite narrow temperature range (700-750°C) there is a change-over from one mechanism to another, i.e. from a slower to a more rapid rate of alloy oxidation.

According to petrographic analysis data, the extremely thin heterogeneous film that forms during oxidation at 400-700°C on a specimen contains the lower oxide of copper Cu_2O of a red-brown color (refractive index $n = 2.67$) with inclusions of silver metal in the form of thin columns. At 500-700°C a thicker uniform layer forms of higher copper oxide CuO that is black with a refractive index $n = 2.91$, i.e. in total conformity with the known Wagner theory explaining the mechanism of oxidation for binary alloys containing precious metals [9].

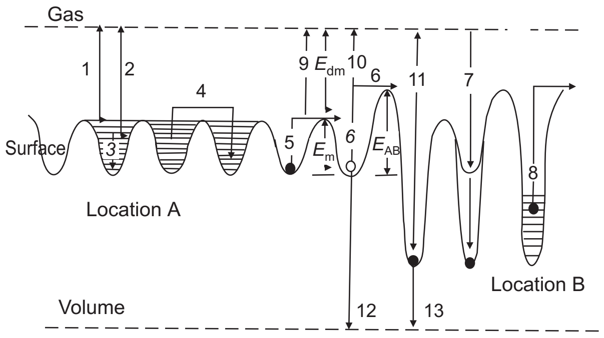

Fig. 5. Diagram of physical and chemical adsorption with interaction of oxygen molecules at the surface of pure silver powder

Processes of desorption-adsorption for oxygen on silver powder were studied by TG- and DTA-methods in relation to temperature in air since silver relates to the so-called group E of elements that do not adsorb nitrogen [10]. The data obtained (Fig. 4) point primarily to the fact that Ag powder with a specific surface $S = 0.4$ m^2/g at room temperature is a priori saturated with adsorbed oxygen (~5.4% of the powder sample mass) as a result of physical adsorption when in forming bonds individuality is retained for both the adsorbed gas molecules and silver atoms formed the specimen surface. As is well known [11], with physical adsorption a bond is accomplished by nonpolar van der Waals forces, dipolar interaction forces, and polarization forces.

On heating a specimen to 750°C there is almost total desorption of physically-adsorbed oxygen, and only at 780°C is oxygen chemisorption noted (~14.4% of the sample mass) accompanied by the release of heat when a gas molecule gives off or obtains an electron from the surface, is split into atoms that are bonded singly with the surface, share the electrons with one or several particles comprising the surface, etc.

In accordance with adsorption by the Lennard-Jones scheme [10], realized in our case, an O_2 molecule at the surface of silver may undergo elastic scattering and return to the gas phase (stage 1 in Fig. 5). As with elastic scattering of electrons this process may lead to diffraction. Normally O_2 molecules pass part of the kinetic energy to a solid and they are held at the surface by the center of weak (van der Waals) adsorption (stage 2). This state, labelled as A, corresponds to a small potential pit (physical adsorption).

The process of energy exchange between the solid and an oxygen molecule striking it (accommodation) at first leads to the situation that the O_2 molecule is held by the silver in state A, the bond between the gas molecule and the surface is vibration excited, but with further energy exchange the O_2 molecule may appear to be at the lower level of a potential pit A (stage 3). However, a molecule may fall into the lower level of a potential pit A and not at primary collision with surface, as in stage 3, but jumping to a neighboring adsorption center and losing excitation energy (stage 4 in Fig. 5). A molecule at the lower level of a potential pit A may move to a neighboring center A, obtaining thermal energy from the Ag crystal lattice sufficient in order to overcome the energy barrier E_m (stage 5). When at the surface there is a second state B with a higher bond energy (energy of chemisorption) an O_2 molecule of neighboring center A may move to state B, obtaining activation energy E_{AB} (stage 6). According the Lennard-Jones, in this case state A is a dynamic precursor of state B.

In our case states A and B are hypothetically placed at the same points of the silver surface (only temperature changes). Thus, an O_2 molecule, getting state A from the gas phase, passes into state B without moving over the surface (stage 7). In this case state A may be assumed to be a stationary precursor of state B.

In forming stable chemisorption bonds of O_2 molecules with the surface, i.e. in our case

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Ag Ag,

a comparatively large amount of energy is released (Fig. 4) that, as also in stage 4, is not entirely absorbed by that center B at which there was initial chemisorption. The molecule will diffuse from one state B into another until it does not pass to the crystal lattice sufficient energy in order to be held at a specific center (stage 8).

In conclusion it is noted that in dynamic equilibrium, established at a given temperature, an O_2 molecule can desorb from the silver surface at any instant of time. Here it is necessary to distinguish desorption in the course of diffusion (migration), requiring activation energy E_{dm} (stage 9), from desorption from states A and B with activation energies E_{dA} and E_{dB}, respectively (stages 10 and 11 in Fig. 5).

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