

SURFACE TENSION OF SILVER IN DIFFERENT MEDIA

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(Received 30 November 1992; accepted in revised form 1 February 1993)

Abstract—By means of electron microscopy, the stability of silver particles in redox buffers has been studied and values of the surface tension of silver in aqueous solution of buffers and a gelatin medium have been determined to be 0.72 J m^{-2} and 0.68 J m^{-2} , respectively. Using calculations of the binding energy per atom in vacuum, an effective value of 0.86 J m^{-2} for the surface tension for silver clusters was determined.

Keywords: Silver clusters, surface tension, electron microscopy, redox potential.

1. INTRODUCTION

In recent years much attention has been paid to studies of small silver particles, which, for example, are produced by the photolysis of halogenides of the metal, electrochemical development and other processes, and numerous attempts have been made to determine the effective specific Gibbs free-surface energy (σ) in order to elucidate the mechanism of the processes going on in these phase conversions and solid state reactions.

Such determinations have been performed for massive silver by many workers. In the case of molten metal, it was shown that a temperature decrease caused a surface tension increase that varied over a wide range, from 0.78 to 1.3 J m^{-2} [1–3]. The results obtained for crystalline silver are not always in agreement with each other. According to the most reliable data, $\sigma = 0.8\text{--}1.1 \text{ J m}^{-2}$ [4–5], but as pointed out in [5], the introduction of a certain amount of oxygen (under a partial pressure of 0.2 atm) into pure helium reduces the surface tension of silver at 932°C from 1.15 to 0.4 J m^{-2} . The determination of the surface tension of silver particles in a colloidal degree of dispersivity is a more complex problem. An attempt was made in [6], and an effective value of 0.525 J m^{-2} was obtained. Other results were reported by the authors of [7] and [8], who gave σ values for silver particles sprayed on carbon or silver bromide with $\sigma = 0.92 \text{ J m}^{-2}$. According to these authors, coating of silver particles by a thin gelatin film decreases their surface tension to 0.4 J m^{-2} . Analysis of the surface tension values obtained from calculations based on different theoretical models for both liquid and solid silver suggests a wide spread in the data, from 0.7 to 2.2 J m^{-2} . Nevertheless

most of the estimates fall within the range of $0.8\text{--}0.9 \text{ J m}^{-2}$.

Experimental and theoretical values for the surface tension of silver are within the range $0.7\text{--}1.3 \text{ J m}^{-2}$, but differ greatly according to the method by which they were obtained. This contradiction in the data makes it difficult to choose the correct σ value for the metal and in its disperse and massive state, especially in the case of temperatures far from the melting point. An attempt to determine the specific free-surface energy of small silver particles has been made in the present paper in order to get more reliable data. Two approaches were used here, the first being based on the known Gibbs–Thompson equation. Here the experimental dependence of the critical sizes of silver particles in buffered redox solutions on their potential was determined, and from the slope of the curve obtained, the σ value was established. In the second approach a purely calculational technique was applied to determine this value, making use of the binding energy data for silver atoms in vacuum obtained via molecular orbitals [10–14]. Comparing values obtained on the basis of Baetzold's calculations [10] and Stranski–Kaishev's [15] results for the formation and new phase growth mechanism allowed σ to be determined for small silver clusters.

2. EXPERIMENTAL

By means of thermal evaporation in a vacuum of 10^{-3} Pa on the Formvar supporting films, silver particles were prepared for further investigation. Some of the silver-sprayed samples were coated by a film of a protective colloid of gelatin in a 0.1% water solution. Fe^{2+} and Fe^{3+} redox buffers were used to

determine the critical sizes of the particles as described in [16], where samples of sprayed silver were kept for 5–30 s. The salt concentrations in the buffer solutions were:

$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ —0.2 M,
citric acid—0.15 M,
 AgNO_3 —0.001 M,
 $\text{FeSO}_4(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ —0.01–0.15 M.

With changes in the latter salt concentration the necessary value for the redox system potential was achieved. Electron microscope examinations of silver particles treated in redox buffers were conducted on "Hitachi HU-12" and "JEOL JEM-100CX" electron microscopes with point-to-point resolution of real objects at least 0.5–0.7 nm. It should be noted that thickness of gelatin film for coating the silver particles was chosen so that it could be preserved during preparation while not influencing the quality for microscope viewing. The size of the critical silver center was determined by the location of the minimum on histograms of the size distribution. This particular minimum occurred due to the growth of some of the particles of critical size and the disintegration of other particles (when the probability of growth and disintegration of critical size particles is equal). Hewlett–Packard 9825 A software was used in the calculations.

3. RESULTS AND DISCUSSION

3.1. Silver surface tension in water solution of redox buffers with and without a gelatin coating it

Figure 1 shows the dependence of the critical size of silver particles d_{cr} vs the overvoltage value of the redox buffer systems ΔE , with and without a gelatin

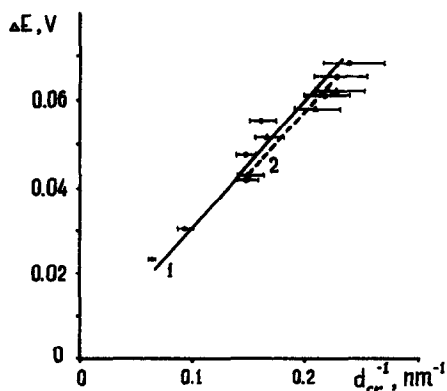


Fig. 1. Dependence between redox potential (ΔE) of buffer solution and inverse value of critical center diameter ($1/d_{\text{cr}}$), formed in them: 1—for silver particles without gelatin coating, 2—for silver particles in a gelatin medium.

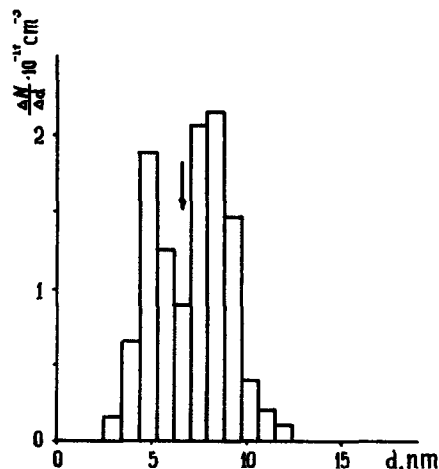


Fig. 2. Histogram of silver particles treated 30 s in a redox solution having $\Delta E = 0.042$ V. The arrow indicates the position of the class containing the particles of critical size.

film. The method for the determination of d_{cr} for silver particles in aqueous solution of redox buffers is shown in Fig. 2. Analysis of the results showed that ΔE and d_{cr} satisfied the equation $\Delta E = \text{const}/d_{\text{cr}}$, with a rather high correlation coefficient of 0.969 for uncoated particles and 0.953 for gelatin-coated particles. This confirmed the applicability of the Gibbs–Thompson equation for particle sizes from 0.4 nm to determine σ from the relationship:

$$\Delta E = \frac{4\sigma V_m}{Fd_{\text{cr}}}, \quad (1)$$

where V_m is the molar volume of silver ($V_m = 17.06 \times 10^{-30} \text{ m}^3$) and F is the Faraday constant. For silver particles without a gelatin coating, $\sigma = 0.72 \pm 0.06 \text{ J m}^{-2}$ and for particles in a gelatin medium, $\sigma = 0.67 \pm 0.02 \text{ J m}^{-2}$.

The similarity of values for silver particles with and without a gelatin coating within the accuracy of experimental error does not agree with the results obtained in [8]. This might be connected with the fact that in [8], the gelatin layer was removed after buffer treatment. Such a procedure would lead to a change in the sizes of the silver particles and a drift in d_{cr} . In addition, silver particles may have adsorbed a large amount of oxygen when the protective coating was applied. According to [5] this leads to a decrease in σ of up to 0.4 J m^{-2} .

The values determined for σ are in accordance with those described in the literature. They are obtained for colloidal particles of sizes from 2000 to 15,000 atoms and probably can be used in calculations of up to 300 atoms, i.e. when the metallic properties are still preserved [17].

3.2. Surface tension of small silver particles

As initial values, data for the binding energy φ_i per silver atom [10] for different size aggregates (see Table 1) were used. The values φ_2 , φ_3 and φ_4 for linear, ringlike and massive aggregates, respectively, are given in the table, as well as values of the formation energy of aggregates $i\varphi_i$ as a whole.

According to the Stranski–Kaishev theory [15], the potential energy for cluster formation of size i , i.e. $\sum_{j=1}^i \psi_j$, is determined as:

$$\sum_{j=1}^i \psi_j = \sigma s, \quad (2)$$

Table 1. Binding energy per atom (φ_i) and formation energy ($i\varphi_i$) of silver aggregates of size i

i	Data from [10]		Data from [10] after approximation	
	φ_i (eV)	$i\varphi_i$ (eV)	φ_i (eV)	$i\varphi_i$ (eV)
1	0	0	0	0
2	0.91	2.76	0.35	0.70
3	0.92	0.82	0.53	1.58
4	0.63	2.52	0.64	2.55
5	0.95	4.40	0.71	3.57
6	0.88	5.28	0.77	4.64
7	1.06	7.42	0.82	5.76
8	1.18	9.44	0.86	6.88
9	1.13	10.2	0.89	8.04
10	1.16	11.6	0.92	9.22
11	1.12	12.3	0.95	10.4
12	1.13	13.6	0.97	11.6
13	1.11	14.4	0.99	12.9
14	—	—	1.01	14.1
15	—	—	1.02	15.3
16	1.10	17.6	1.04	16.6
17	—	—	1.05	17.9
18	—	—	1.06	19.1
19	1.12	21.3	1.08	20.4
20	—	—	1.09	21.7
21	—	—	1.10	23.0
22	—	—	1.11	24.3
23	—	—	1.12	25.6
24	—	—	1.12	27.0
25	1.13	28.3	1.13	28.3
26	—	—	1.14	29.6
27	—	—	1.15	31.0
28	—	—	1.15	32.3
29	—	—	1.16	33.6
30	—	—	1.17	35.0
31	1.17	36.3	1.17	36.3
32	—	—	1.18	37.7
33	—	—	1.18	39.1
34	—	—	1.19	40.4
35	—	—	1.19	41.8
36	—	—	1.20	43.2
37	—	—	1.20	44.5
38	—	—	1.21	45.9
39	1.14	44.5	1.21	47.3
40	—	—	1.22	48.7

where S is the centre of the surface. For a spherical aggregate, eqn (2) can be written as

$$\sum_{j=1}^i \psi_j = U\sigma i^{2/3}, \quad (3)$$

where U is a constant equal to $(4\pi)^{1/3}(3V_m)^{2/3} = 3.2048 \times 10^{-19} \text{ m}^2$.

Using the Stranski–Kaishev theory one should remember that σ for small particles has a physical analogy to surface tension and characterizes the number of disintegrated bonds on the particle surface [15].

The formation energy of aggregates of size i $i\psi_1 - \sum_{j=1}^i \psi_j$ can be equated to $i\varphi_i$, taken from the latest and most reliable data [10] obtained by calculation according to the Huckel method:

$$i\psi_1 - \sum_{j=1}^i \psi_j = i\varphi_i. \quad (4)$$

Substituting (3) into (4), we obtain:

$$i\varphi_i = \sigma U(i - i^{2/3}). \quad (5)$$

The possibility of transferring values obtained on the basis of quantum-mechanical calculations to the microscopic objects dealt with by classical thermodynamics must be qualified individually. This involves the concept of surface tension, the calculation of the number of atoms present in small silver particles, the determination of the sizes of development centers by the redox potential (ΔE) of the developers, the establishment of values of latent photographic image centers and too many other factors; the Gibbs–Thomson equation and the hypothesis of an unambiguous dependence between the particle size and the number of atoms is included as a part of these expressions. These dependences are used in the literature up to monoatomic formation; e.g. in [7] and [8], ΔE was extrapolated from massive silver to tens of atoms. A similar calculation is possible, for according to Stranski–Kaishev's theory [15] (almost all the crystallographic theory is based on this), the surface tension concept maintains its physical sense up to one atom. Furthermore, it is shown that σ is not changed when varying from massive aggregates to four-atom aggregates [18]. All this suggests rather a wide range for the application of thermodynamic formulas, from massive metal up to oligoatomic aggregates.

On this basis, it is possible to make a direct proportionality approximation of formula (5) using

φ_i values [10], to determine $\sigma = 0.86 \text{ J m}^{-2}$ (the correlation coefficient is 0.997). Thus, if we ignore the inevitable oscillations that are shown in [10], we may give the formation energy $i\varphi_i$ and the binding energy per atom φ_i in the form of functions whose values are given in the table.

As a result, we may conclude that the value of the surface free energy calculated theoretically on the basis of the latest data using the Huckel technique agree quite well with the known experimental data. This value is determined for aggregates containing tens of atoms, which suggests the existence of an "effective" surface tension analog for the molecular size particles. The value obtained characterizes the number of disintegrated bonds on the surface of the aggregates (according to Stranski-Kaishev's theory). It can be applied to the calculation of the energy characteristics, and serves as a link to the massive characteristics of samples as well as being useful in extrapolating the dependences (used for larger particles) on the areas of smaller particles.

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