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PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

Kinetics of Wetting for MgO, CaO, and BeO by Pd, Pt, and Rh Melts

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Abstract—The wetting of magnesium, calcium, and beryllium oxides (MgO, CaO, and BeO) is considered, depending on the ratios of the surface tensions of the oxides to the melts at inequality $\sigma_{sg}/\sigma_{lg} < 1$ characteristic of metallophobic solid surfaces. It is shown that the changes in the wetting angle with temperature during isothermal exposure are determined by the ratio of the surface tensions of the phases σ_{MgO}/σ_{Me}. It is found that the wetting angle moves down or up when the ratios of the surface tensions increase or decrease, respectively, depending on the values of σ_{sg} and σ_{lg}.

Keywords: surface tension, wetting angle, interphase energy, oxide, melt, phase, interphase boundary.

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INTRODUCTION

The subject of this study is associated with the continuously growing demand for the production of quality metal products during the melt stage and the crystallization of cast sections. Certain difficulties are encountered in studying the wetting of surfaces of solid oxides with high-temperature metal melts, especially with melts of platinum group metals (PGMs).

In practice, different meanings are often assigned to the concepts of wetting and unwettability, depending on the desired effect. In our case, however, wetting normally means that the wetting angle between the liquid and the solid body is less than 90°, while it is more than 90° for unwettability and the liquid tends to leave the surface and organize itself into a globe. This definition of the type of interaction does not offer a clear understanding of the effect the parameters of interphase interaction have on the wetting angle, as it does not consider the overall effect from the surface tensions of the contact phases. Experimental results from studying the wetting of magnesium, calcium, and beryllium oxides (MgO, CaO, and BeO) using melts of PGMs are considered by analyzing the character of interaction as it depends on the $\sigma_{MgO}/\sigma_{Me} < 1$ ratio of tensions at the MPG melt–solid-oxide–gas interphase boundary [1].

EXPERIMENTAL

Wetting was studied using the sessile drop method from the melting point (m.p.) to 2350 K in a staged heating and cooling mode with isothermal exposures for 0.5 h at five temperatures until equilibration of the actual angles. The equilibrium wetting angles were attained within 8 min after changing the temperature and isothermal exposures. Reagent grade oxide powders of the following granulometric composition were used: 0.060 mm (10–15%), 0.80 mm (50–60%), and 1.2 mm (40–25%). The supports were pressed with a force of 1–1.5 kbar, dried at 600 K, sintered at 1700 K, and annealed at 2273 K. The surfaces of the pellets were ground and polished with subsequent cleaning and determination of porosity (8–14%). The optimum topology of the surface of the oxide supports at the initial temperatures of each experiment was ensured by the preliminary sintering of the supports at the maximum experimental temperature. Each sample of metal was loaded onto a support and the experiment was conducted in the staged mode of temperature rise and fall at five temperatures and isothermal exposures of up to 0.5 h with continuous measuring of the wetting angles. This allowed us to track the changes in the wetting angle during the isothermal exposures and rise and fall of the temperatures. Wetting with melts (Pd, Pt, and Rh) was characterized by the high melting points (1828–2239 K) of the metals, accompanied by the formation of stable gaseous oxides of PGMs [2]. When the wetting of oxide supports with the same chemical formula and prepared under the same conditions was conducted with melts having different surface tensions, the change in the wetting angle was determined mainly by the tension of the liquid surface.

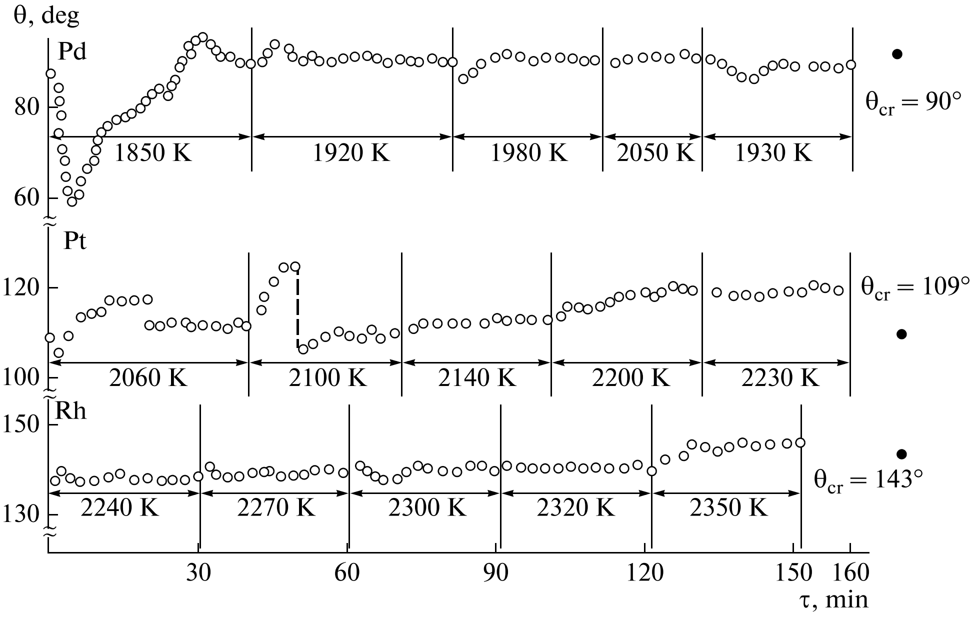

Fig. 1. Kinetics of wetting for MgO using melts of Pd, Pt, and Rh.

The resulting values of the metals' surface tensions were approximated by the equations

$$\begin{aligned} \sigma_{Pd} &= 1430 - 0.260(t - 1825\text{ K}), \\ \sigma_{Pt} &= 1746 - 0.156(t - 2047\text{ K}), \\ \sigma_{Rh} &= 1915 - 0.664(t - 2239\text{ K}) \end{aligned} \qquad (1)$$

and were in good agreement with the data of [1, 2]. The surface tension of the oxides was estimated using the equations of [2]:

$$\begin{aligned} \sigma_{MgO} &= 630 - 0.150(t - 3073\text{ K}), \\ \sigma_{CaO} &= 530 - 0.100(t - 2900\text{ K}), \\ \sigma_{BeO} &= 475 - 0.340(t - 2840\text{ K}). \end{aligned} \qquad (2)$$

RESULTS AND DISCUSSION

Wetting of Magnesium Oxide

The kinetics of wetting for MgO using melts of Pd, Pt, and Rh in the staged heating mode with isothermal exposure is presented in Fig. 1. The surface tensions of the melts decline as the temperature rises with the coefficient $d\sigma_{Me}/_{dT}$ = 0.260, 0.156, and 0.664 mJ/(m^2 K) when heated over the m.p. by 220, 140, and 110 K for Pd, Pt, and Rh, respectively. The surface tension of MgO in the range of 1825–2370 K fell from 817.2 to 735.5 mJ/m^2 with coefficient $d\sigma_{MgO}/dT$ = 0.150 mJ/(m^2 K), thus determining the ratios of the phases σ_{MgO}/σ_{Me} = 0.571, 0.451–0.437, and 0.396–0.400 for Pd, Pt, and Rh, respectively, upon the specified overheating.

A sharp reduction in the wetting angle (from 91° to 60°) with a subsequent increase to the initial values of 91° within 6 min was detected at the initial time at 1850 K upon wetting with Pd. When $\sigma_{MgO}/\sigma_{Pd} < 1$, the reduction in the wetting angle from 92° to 60° at the initial moment of wetting was due to the nonequilibrium topology of the oxide surface at $\sigma_{sl} \approx 0$ [3]. When equilibrium was attained, the wetting angle grew to its initial value of $\theta = 91°$, did not change with temperature, and was determined by the fixed ratio σ_{MgO}/σ_{Pd} = 0.571 in the temperature range of overheating.

The drop in the σ_{MgO}/σ_{Pt} ratio from 0.451 to 0.437 in the 140 K range of overheating is accompanied by a rise in θ with temperature and slight fluctuations during isothermal exposures (Fig. 2). The slight rise in the ratios σ_{MgO}/σ_{Rh} = 0.396–400 in the 110 K range of overheating signals a weak trend toward change in the wetting angle as the temperature rises (Fig. 2). The drop in the ratios of the phase tensions upon moving from Pd to Rh (Fig. 2) at $\sigma_{MgO}/\sigma_{Me} < 1$ results in greater unwettability ($\theta > 90°$) as the wetting angle grows. It follows from the above that the ratio of MgO surface tension to the tension of the liquid phase across the range of overheating temperatures for each metal characterize the metallophobicity of MgO quite clearly.

Low-energy solid surfaces are thus characterized by unwettability ($\theta > 90°$), while the changes in the wetting angle detected upon a rise in temperature are mostly due to the structural reorganization of the interphase solid–liquid boundary accompanied by changes in the ratios between the surface tensions of the contact phases [3].

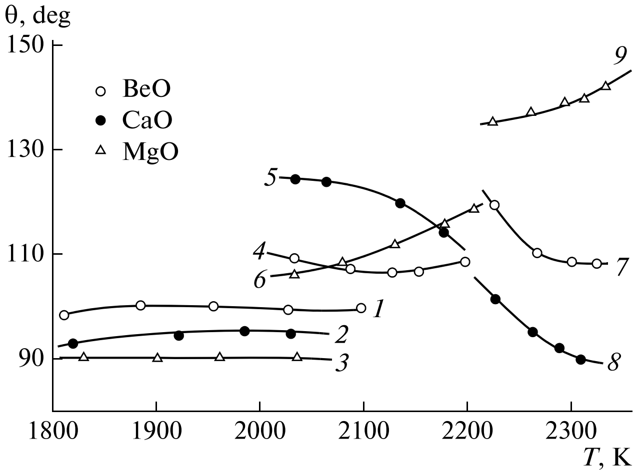

Fig. 2. Polytherms of the wetting angles of oxides (○) BeO, (●) CaO, and (△) MgO using melts of (*1*, *2*, *3*) Pd, (*4*, *5*, *6*) Pt, and (*7*, *8*, *9*) Rh.

Wetting of Beryllium Oxide

The kinetics of wetting during staged heating is presented in Fig. 3. Surface tensions for BeO (hexagonal lattice, $\sigma_{BeO} = 820–634$ mJ/m^2) and MgO (cubic lattice, $\sigma_{MgO} = 817.2–735.5$ mJ/m^2) are virtually the same within the range of 1825–2370 K, but the values of the temperature coefficients differ. Minimal changes in θ are detected in the unwettability area at the initial moment of wetting.

The wetting angle for Pd remains constant at 109° as the temperature rises, while the wetting angle for Rh shrinks from 120° to 110° and the wetting angle for Pt grows from 105° to 110° (Fig. 2). This behavior of the angle is due to the effect of the different temperature coefficients for the surface tensions of liquid metals Pd ($d\sigma/dT = -0.260$), Pt ($d\sigma/dT = -0.156$), and Rh ($d\sigma/dT = -0.644$) and the oxide ($d\sigma_{BeO}/dT = -0.340$ mJ/(m^2 K)) have on the change in the ratios between the tensions of the phases. Upon equal overheatings, the wetting angle grows following a drop in the ratios between the surface tensions of the phases. At the crystallization temperature of the metals, for example, the wetting angles change depending on the ratio between the tensions of the phases: $\theta_{Pd} = 90°$ ($\sigma_{BeO}/\sigma_{Pd} = 0.575$), $\theta_{Pt} = 110°$ ($\sigma_{BeO}/\sigma_{Pt} = 0.420$), and $\theta_{Rh} = 110°$ ($\sigma_{BeO}/\sigma_{Rh} = 0.355$), respectively.

The polytherms of the wetting angles demonstrate the improvement in unwettability in the order of the drop in the ratios $\sigma_{BeO}/\sigma_{Me} < 1$: Pd (0.510), Pt (0.385), and Rh (0.326) at $T = 2273$ K. Our experimental dependences confirm the conclusions of [3].

Wetting of Calcium Oxide

The kinetics of wetting during staged heating and the polytherms of the wetting angles are presented in Fig. 4. The similar character of the change in the wetting angle during isothermal exposure on CaO and MgO is apparently due to their identical cubic crystal lattice in the first approximation.

Maximum fluctuations of θ are also detected in the initial period of wetting until equilibrium is reached. The wetting angle for Pd remains constant at 94° as the temperature of overheating rises to 220 K, while it shrinks from 102° to 94° and 124° to 118° for Rh at 110 K and Pt at 140 K, respectively. The growth in the wetting angle is easily tracked for Pd, Pt, and Rh in the order of the drop in the ratios between the tensions of the phases, σ_{CaO}/σ_{Me} (0.446, 0.353, and 0.311), at both the m.p. and the maximum overheating of the

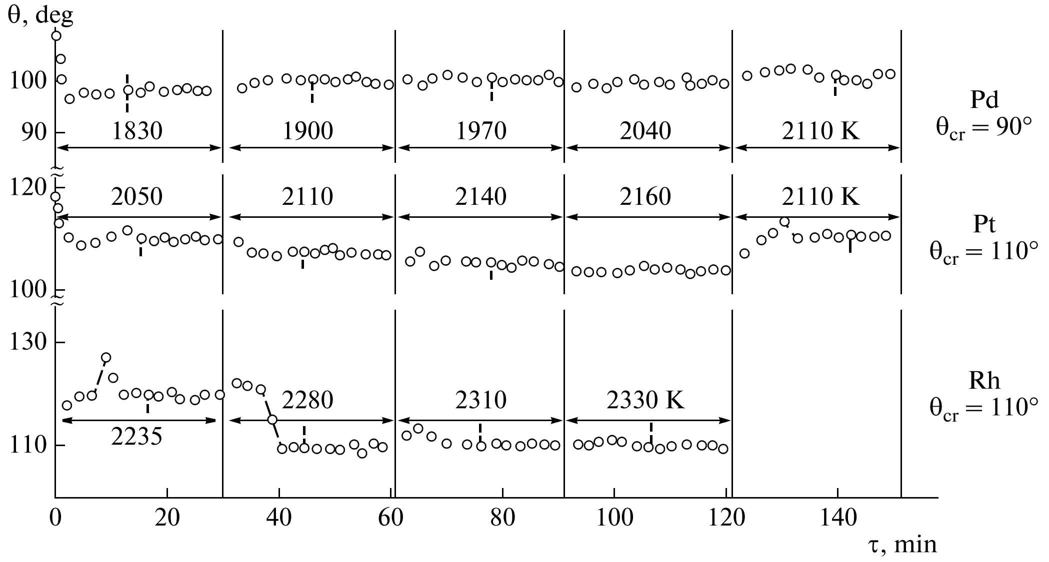

Fig. 3. Kinetics of wetting for BeO during the heating stage.

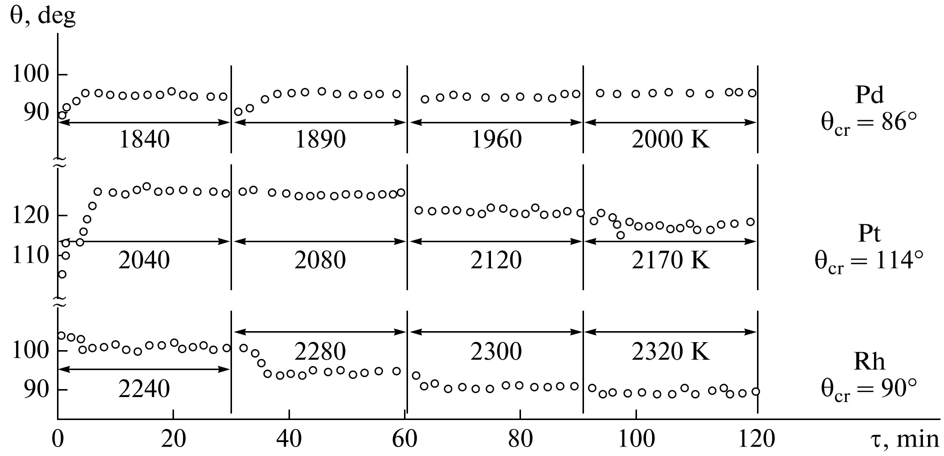

Fig. 4. Kinetics of wetting for CaO.

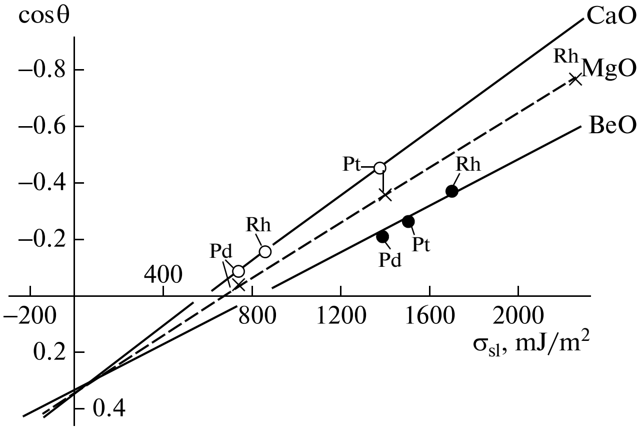

Fig. 5. Wetting angle as a function of the interphase energy at 2273 K.

metals, σ_{CaO}/σ_{Me} (0.449, 0.349, and 0.318), respectively. The experimental dependences are in accurate agreement with the theoretical conclusions of [3] for metallophobic solid oxide surfaces, the unwettability of which is determined by the ratio between the tensions of the oxides and the surface tension of the liquid metals at $\sigma_{CaO}/\sigma_{Me} < 1$.

We estimated the dependence of the wetting angle on the interphase surface energy (σ_{sl}) using the experimental data on the wetting of diatomic solid oxides and the Young equation

$$\sigma_{sl} = \sigma_{sg} - \sigma_{lgs}\cos\theta. \tag{3}$$

Functions $\theta = f(\sigma_{sl})$ of the wetting angles of each oxide are linear (Fig. 5) and their extrapolation to $\sigma_{sl} = 0$ yields angle $\theta \approx 74°$, which determines the lower boundary of the equilibrium limited wetting of low-energy solid surfaces [3]. The negative values of the interphase energy ($\sigma_{sl} < 0$) determine the nonequilibrium state of such systems [4, 5].

CONCLUSIONS

The theoretical and practical significance of considering the three-phase equilibrium of melts of PGMs with solid oxides upon wetting, based on the generally accepted classification of high-energy ($\sigma_{MeO}/\sigma_{Me} > 1$) and low-energy ($\sigma_{MeO}/\sigma_{Me} < 1$) solid surfaces was experimentally confirmed. The wetting of low-energy oxide surfaces is clearly determined by the ratios of the surface tensions of the phases, so long as inequality $\sigma_{MeO}/\sigma_{Me} < 1$ is satisfied. Solid-state diatomic oxides exhibit metallophobic properties upon wetting with melts of Pd, Pt, and Rh at temperatures of up to 2348 K. The wetting angles for Pd on MgO, CaO, and BeO remain constant with temperature at 91°, 94°, and 100°; they grow at the m.p. for Pt (110°, 110°, and 125°) and Rh (110°, 120°, and 140°), respectively. The dependences of the wetting angles on the interphase energy are linear at 2273 K, and their extrapolation to $\sigma_{sl} = 0$ yields wetting angle $\theta \approx 74°$.

REFERENCES

1. A. I. Timofeev, Russ. J. Inorg. Chem. **58**, 917 (2013).
2. A. I. Timofeev, Doctoral Dissertation in Technical Science (Sverdlovsk, 1990), p. 69.
3. N. A. Vatolin and A. I. Timofeev, Dokl. Akad. Nauk SSSR **302** (2), 358 (1988).
4. A. I. Timofeev, in *Proceedings of the 9th International Workshop on Physicochemical Analysis* (Perm, 2010), p. 80.
5. A. I. Timofeev, V. K. Lyalin, and V. P. Chentsov, in *Proceedings of the 13th International Interdiscipline Symposium on Order, Disorder and Oxide Properties ODRO-13, Rostov-on-Don, Loo, September 16–21, 2010*, Vol. 2, p. 161.

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