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LIQUID WIRES AND THEIR SURFACE FILMS

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Abstract

Function of oxide films in supporting molten wires of Pb, Sn, Zn and Bi.—A wire of low melting point metal may be made to glow when freely suspended and heated in air or oxygen. This has been shown to be due to the formation of an oxide film of sufficient tensile strength to permit the molten metal to be sustained even though its melting point is much lower than the glowing temperature. It has been shown that the assumption of Damianos, that the oxide film serves only as a network in preventing a surface change of the liquid and that the tensile strength of the molten metal holds it together is not tenable.

Ability of sulphide, bromide and chloride films to support molten wires.—Wires with clean surfaces when heated in nitrogen break at the melting point of the metal. Experiments with sulphide, bromide, and chloride films reveal three facts, (1) if there is not a firm coat at the melting point of the metal the wire breaks at that temperature, (2) if the melting point of the coat is between the melting point of the metal and the glowing temperature, then the wire breaks at the melting point of the coat, (3) if the melting point of the film is above the glowing point, the wire can be made to glow when freely suspended.

Temperature coefficients of resistance.—The suspension of molten metals by their oxide films affords a unique method of measuring the temperature coefficients of resistance of low melting point metals through the solid and liquid states.

Introduction

IT WAS reported by D. Damianos[1] in a note entitled "Can a freely suspended lead wire glow?" that a lead wire through which an electric current was passed might be heated to the glowing temperature and still remain intact. By observing the change in resistance with current he concluded that the lead must be melted, and that an oxide film prevented a surface change of the liquid and enabled the tensile strength of the metal to hold the wire together. He further found that when the lead wire was heated in nitrogen, the wire broke without reaching the glowing temperature.

This somewhat unusual phenomenon led to our investigation of the surface films and their relation to the suspension of wires of molten metals. The metals selected for experimentation were lead, tin, zinc, and bismuth because their melting points are lower than the glowing temperature. Their respective melting points are: lead, 327; tin, 232; zinc, 419; and bismuth, 269°C. Since the temperature of a substance at the first visible red is about 525°C and at a dull red it is 700°C it is obvious that when a wire of the above type is made to glow, the metal itself must be in the molten state.

Apparatus and Method

Glass tubes were drawn out until practically uniform in bore. Lead, tin, zinc and bismuth metals were melted and drawn into these tubes, which

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[1] D. Damianos, Phys. Zeits. **27,** 289 (1926).

varied from 0.3 to 3 mm in diameter. After the metals had solidified they were placed in hydrofluoric acid, which removed the glass. This acid does not react readily with any of the metals except zinc. It was necessary in the case of zinc to give the minimum exposure to the acid. Great uniformity and various sizes of lead and tin wires were obtained by drawing them through a die. The dimensions of the wires that were ordinarily used were 0.8 mm in diameter and from 1 to 4 cms in length.

The wires were heated slowly to the glowing temperature, and a simple voltmeter-ammeter method was used in obtaining the relation between current and resistance. A special current breaking device was constructed to prevent the burning out of the voltmeter when the breaking points of the metallic wires were reached. The wires were soldered to heavy copper leads and electrically heated in air. Fig. 1 shows a representative series of current-resistance curves for lead. The break in the curve indicates the melting of the lead, and the slope of the curve above the melting point is greater than the slope below that point. A corresponding curve for tin is very similar in general to the one for lead. The slope is not as great either below or above the melting point, as it is in the case of lead. The current-resistance curve for zinc rises gradually up to the melting point, there the resistance practically doubles, and then the curve acquires a small negative slope which changes to a small positive one before the glowing temperature is reached. The curve for bismuth is less reproducible. The wire could be kept suspended at the glowing point for a long time, and a large number of curves were plotted, but a consistent type of curve could not be obtained.

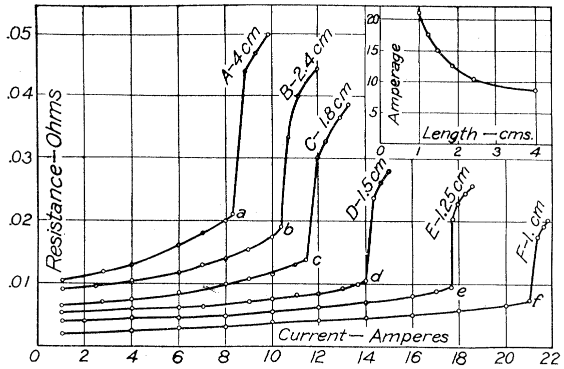

Fig. 1. Comparison of current and resistance at melting point with the length of the wire.

The curves in Fig. 1 show the variation of current and resistance of wires of uniform cross-section with length. The wires were 0.8 mm in diameter and the lengths varied from 1 to 4 cms. The currents (indicated by the points *a*, *b*, *c*, *d*, *e* and *f*) where the wires began to melt, are plotted against length in the upper right-hand corner. This curve shows that the current carrying capacity of a wire does not remain constant but increases with decrease in length, because of the greater percentage of heat carried away by conduction to the end leads as the length is decreased.

A lead wire was kept glowing for an hour and then cooled, and its characteristics noted. The displacement of the curve showed that the resistance of the wire had greatly increased. This was shown to be largely due to change of shape. The wires sag when melted, thicken in the middle, and get smaller near the ends. Wires supported on asbestos showed a very small increase in resistance when heated a second time. When a wire was cooled before it reached the melting point, and the characteristics noted a second time, the increase in resistance was inappreciable. These results indicate that the thickness of the oxide coating was not changed appreciably even when heated for a considerable period in air.

Wires Heated in Nitrogen

An apparatus was constructed which permitted the heating of wires in an atmosphere of nitrogen. An absorber for oxygen (potassium hydroxide with pyrogallol) was placed between the nitrogen generator and the apparatus. The lead, tin and zinc wires, that had been sand-papered after soldering and just before inserting into the nitrogen, broke when heated, at a current strength that corresponded with the point on the characteristic curve in air where the resistance practically doubled. Before sulphuric acid and calcium chloride were placed between the oxygen absorber and the apparatus (for the absorption of water vapor) the lead wires broke at a point which was later shown to be the melting point of the metal. The tin and zinc wires, however, oxidized enough from the water vapor to remain coherent until the glowing point was reached. When borax was put on the surface of the tin and zinc wires, in order to remove any oxide that might be on the surface and to keep any new oxide from forming, the wires broke at the melting points. These points were indicated by a sudden increase in the resistance of the wires, and at these temperatures droplets of unoxidized metal fell in the tube. When precautions were taken to remove all water vapor, wires of the different metals broke at their respective melting points. The fact that lead was not oxidized by the water vapor enough to remain suspended is probably due to its greater weight, and to the fact that it does not oxidize as quickly.

When a lead wire was sand-papered before soldering and heated in nitrogen it remained intact until the glowing temperature was reached, but when sand-papered after soldering it broke at the melting point. This showed that the heat of soldering was sufficient to form an oxide film that would support the wire. When newly drawn lead wires were scraped with a knife and left exposed to the air for a day, it was found that the oxide film was sufficient to keep the wire suspended to the glowing temperature. For these experiments small clamps were used instead of soldering. In every case where a thin oxide film was formed on the surface, the glowing point could be reached, while if the necessary precautions were taken to prevent or remove the film the wires would break down into droplets at the supposed melting points of the metals.

Wires Heated in Oxygen

The characteristics of the three kinds of wires were noted when heated in oxygen, and found to be identical with those noted in air. From the experiments in nitrogen and oxygen it may be concluded that the suspension of the low melting point metals to the glowing point is due to an oxide coat or film on the surface.

Function of the Oxide Coat

Wires of nickel-copper, nickel-chromium, German silver, copper, lead, tin, zinc and bismuth, about no. 20 B. & S. in size, were mounted at the same time on a thin asbestos support, which was heated uniformly by means of bunsen flames. The wires all glowed almost simultaneously. When the source of heat was removed they ceased glowing at practically the same instant. This indicates that the temperature reached is more than 525°C and that the low melting point metals are in a molten state. When lead, tin, and bismuth wires were dropped on the asbestos after it had reached a temperature above 400°C the metals would melt so quickly that the expansion would cause a disruption of the oxide coat in a number of places, especially along the upper surface, and small droplets of the liquid would protrude through the openings. When the wires were heated slowly this did not occur. Two possible explanations were offered at the time. It was thought that either the oxide coat would adjust itself to the expansion of the liquid by stretching, or that when the surface film broke, a new film would quickly form to cover and withhold the exposed metal. The latter idea was abandoned when the experiment was performed in nitrogen, in which the film remained intact but which gave no chance for new oxide seals to be formed. G. Vicentini and D. Omodei[2] give 0.003076 cc per gram or 0.03488 cc per cc as the value for the change in volume of lead when it melts. The thermal coefficient of expansion (cubic) of lead is[3] 0.0000882. L. Playfair and J. P. Joule[4] give 0.0000795 for the coefficient of thermal expansion (cubic) of lead oxide. When a lead wire was heated in nitrogen and transformed from room temperature to the molten state, say from 27°C to 327°C, the expansion of a unit volume of the lead was $300 \times 0.0000882 + 0.03488 = 0.06134$. The expansion of a unit volume of the lead oxide was $300 \times 0.0000795 = 0.02385$. This shows that the expansion of lead is 0.03749 cc per unit volume more than the lead oxide. The fact that the lead expanded 2.57 times as much as the lead oxide indicates that the coat really stretches and is possibly under tension.

Reference has been made to the work of Damianos[1] in which he regards the liquid lead filament as flexible, hanging in the form of a catenary, with individual parts actually in tension. He further states that, "Since the lead oxide film is exceptionally thin and its tensile strength correspondingly small one cannot assume that it functions as a sort of tube which carries the liquid

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[2] G. Vicentini and D. Omodei, Atti. Acad. Torino, **23**, 38 (1888).

[3] Hodgman and Lange, Handbook of Physics and Chem., 10th Edition, 468.

[4] L. Playfair and J. P. Joule, Journ. Chem. Soc., **1**, 137 (1849).

lead, but rather one must assume that it is the tensile strength of the liquid which holds it together." That this is not the correct explanation has been shown experimentally. Oxidized lead wires were bent in the middle in the shape of a hairpin and supported in a vertical position by means of a horizontal copper wire. These were inserted in an electric furnace at a temperature above the melting point of lead. Frequently, the molten lead would flow within the oxide coat to the ends of the wire where the oxide films, very much expanded, would sustain large globules of the molten metal. Thus a thin, collapsed, and tubular film was left to uphold the entire weight of the lead wire, and it was obvious that the oxide coat had considerable strength.

To determine more exactly the function of the oxide film a new method was adopted. A heavy brass bar was designed to hold one end of an oxidized lead wire so that it could be suspended vertically. The wire was then lowered into an electric furnace through an opening in the top in such a way that the lower part first reached the melting temperature. The melting of the wire would progress upward very quickly and as soon as the melted portion of the wire reached a length where its weight was sufficient to break the oxide film, that part of the wire would fall. This length will hereafter be referred to as the breaking length. By measuring the length of the wire before and after the experiment, the breaking length and hence the volume and force necessary to break the wire could be determined. The oxidation was the same in every case as the time taken for the breaking length to be reached was almost instantaneous. For wires of a given diameter the breaking lengths could be checked with a surprising degree of accuracy and the simplicity of the experiment made it possible to take, as the accepted value, the average of a large number of determinations. The breaking force was determined for a number of wires of different diameters and the results are given in Fig. 2. Since the breaking force is proportional to the volume and the circumference of the oxide film is proportional to the radius of the wire, the breaking volume is plotted against the radius. The fact that this is a linear relation, shows that the oxide coat serves wholly in supporting the liquid wire. The cross-section

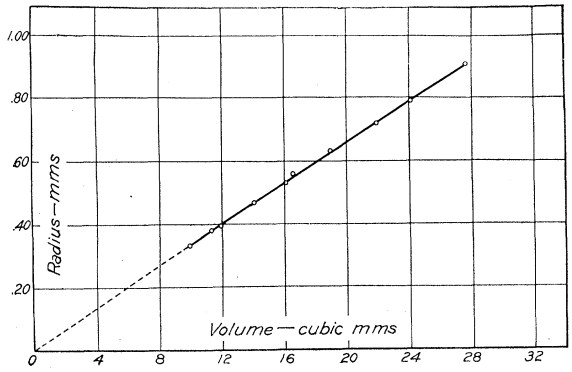

Fig. 2. Variation of breaking volume with radius of cross-section of molten lead wires.

of the oxide film varies with the circumference or the first power of the radius, while the cohesive or tensile forces in the molten lead vary with the area of the cross-section or the second power of the radius, and if any appreciable part in the supporting of the molten wires could be attributed to the latter the relation expressed in Fig. 2 could not result in a straight line. One might question the accuracy of this statement by assuming that the surface tension at the liquid-oxide surface is an appreciable factor, and therefore might exert a noticeable force which would vary as the first power of the radius. That this is not the case is indicated by the readiness with which molten lead will flow over the inner surface of an oxide film, thereby showing that the liquid lead wets the oxide surface and that no surface film of the liquid lead is formed to introduce the factor referred to as surface tension. Damianos' assumption therefore that the oxide film serves only as a network in preventing a surface change of the liquid and that the tensile strength of the liquid holds it together is not tenable, and it must be concluded that the surface films have considerable strength and serve in supporting the molten metal.

Effects of Other Inorganic Coats

An experiment was made to see what would be the effect of a lead sulphide coat on the suspension of a lead wire. When a scraped wire was heated in hydrogen sulphide, it held up to the glowing temperature as if it were in oxygen. A zinc wire remained suspended to the glowing point under the conditions of the experiment, but tin wires broke at the melting point in every case. The fact that tin wires when heated in hydrogen sulphide for fifteen minutes, almost at the melting point, broke down when the melting point was reached, led to the making of chemical tests which revealed no trace of a sulphide. It was however found that when heated in this way for an hour a sulphide coat was formed that would suspend the wire to the glowing temperature. A good check was later obtained from an article by A. Ditte[5] which stated that hydrogen sulphide does not act on tin at ordinary temperatures, but at 100°–400°C it forms stannous sulphide.

Further tests showing the suspension of molten metallic wires by surface films were made in an atmosphere of chlorine gas. The lead wires remained intact up to the glowing temperature, while the tin and zinc wires broke at their melting points. The effect of the lead chloride and zinc chloride coats were as expected from previous experimental results, but since the melting point of stannous chloride is a little above the melting point of tin it seemed that it should not break so suddenly at the melting point of tin. However, according to M. Berthelot,[6] chlorine converts stannous chloride into stannic chloride. Since the melting point of stannic chloride is below the corresponding point for tin this agrees with the experimental results.

To test the effect of bromide coats, the wires were scraped beneath the surface of bromine solution, removed after a short exposure, and the characteristics noted in nitrogen. The tin and zinc wires broke at their melting

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[5] A. Ditte, Ann. Chim. Phys. (6) **19,** 68 (1891).

[6] M. Berthelot, Thermochemie, Paris **2,** 154 (1897).

points, and the lead wire broke just past its melting point. Since the bromides of tin and zinc melt at a lower temperature than these metals and the melting point of lead bromide is just past the melting point of lead, the experimental results thus far indicate that the main requirement for a molten metallic wire to remain suspended is a surface coat that does not melt.

A summary of the effects of the different kinds of inorganic coats on the suspension of low-melting-point metals is given in Table I.

TABLE I

Summary of the effects of different inorganic coats on the suspension of metals of low melting point.

Substance	Gas	Coat	Melting Pt. of coat. °C	Temp. of metals reached. °C
Pb	N_2	None		327
Sn	"	"		232
Zn	"	"		419
Pb	O_2	PbO	888	Glowing point
Sn	"	SnO	dec. red ht.	" "
Zn	"	ZnO	1260	" "
Pb	H_2S	PbS	1112	Glowing point
Sn	"	SnS	882	" "
Zn	"	ZnS	1049	" "
Pb	Cl_2	$PbCl_2$	501	Faint glow
Sn	"	$SnCl_4$	−33	232
Zn	"	$ZnCl_2$	365	419
$PbBr_2$	N_2	$PbBr_2$	380	Just past m. p.
$SnBr_4$	"	$SnBr_4$	29.9	232
$ZnBr_2$	"	$ZnBr_2$	394	419

The effects of various inorganic coats on the suspension of low melting point metals reveal three facts: (1) if there is not a firm coat at the melting point of the metal the wire breaks at that temperature, (2) if the melting point of the coat is between the melting point of the metal and the glowing temperature, then the wire breaks at the melting point of the coat, (3) if the melting point of the film is above the glowing point, the wire can be made to glow when freely suspended.

RELATION BETWEEN RESISTANCE AND TEMPERATURE OF LEAD WIRES IN OXIDE FILMS

The curve in Fig. 3 is an accurate determination of the relation between resistance and temperature of an oxide coated lead wire when heated in an atmosphere of nitrogen. A special method of sealing a clean lead wire to brass blocks of considerable size was used. The wire was then coated with lead oxide by heating with an electric current in air. A sufficiently strong film was thus formed to hold the molten lead. The wire was then inserted in a specially constructed vessel which was filled with nitrogen and placed in an electric furnace. The temperature of the furnace was controlled and measured by means of a thermocouple. A constant small current of the order of 30 milliamperes was sent through the wire and the potential drop measured by means of a potentiometer. The change in resistance and temperature coefficients could thus be calculated.

This method of measuring the temperature coefficients of resistance of a metal as it slowly changes from the solid to the liquid state is unique in that the oxide film is used as a container for the molten metal. The nitrogen atmosphere prevents any further oxidation of the metal as the temperature is increased.

One noteworthy fact is that the change in resistance does not take place abruptly when the metal melts, at 327°C in the case of lead, but begins at about 320°C and continues at a rapid rate until about 340°C or above. The temperature control of the furnace and the reliability of the measurements may be judged by the fact that the time spent in changing the temperature from 320°C to 338°C was more than $1\frac{1}{2}$ hours.

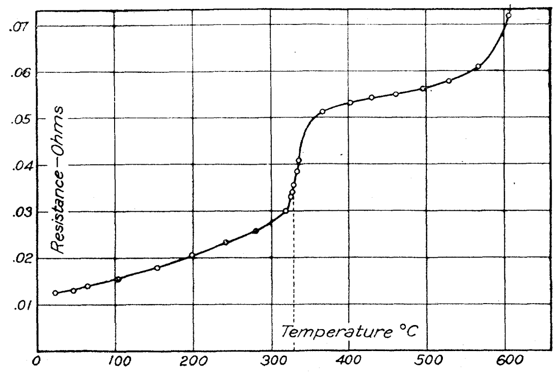

Fig. 3. Electrical resistance of lead at different temperatures.

Since in this experiment the oxide coated wire was supported by resting upon a porcelain plate it was first thought that the wire in the molten state might retain its form until above 800°C, the melting point of the oxide. The wire, however, broke at 650°C, and this is the temperature at which H. Roseti[7] and V. Kolhschutter[8] found that red oxide was changed to lemon yellow oxide. The formation of the yellow oxide was clearly evident when the wire was cooled. During the change there was apparently a weakening of the surface film, and this permitted the molten lead to lose its shape. By this method further work is being carried on in determining the temperature coefficients of low-melting-point metals at various temperatures in the solid and liquid states.

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[7] H. Roseti, Ber. **56 B,** 285 (1923).

[8] V. Kolhschutter, Zeits. Elektrochem. **16,** 356 (1910).