D. G. Howitt

The Surface Analysis of Copper Arc Beads—A Critical Review

ABSTRACT: The chemical composition of arc beads has been purported to reflect the local atmospheric conditions at the precise moment when the arc occurs. It has further been claimed that Auger analyses, taken from beneath the surface contamination layers of an arc bead, can be used to distinguish whether the arcing was the cause of a fire. The hypothesis is that because atmospheric gases are trapped in the arc bead when it solidifies, the concentrations of gases inside the bead will reflect ambient conditions when the arc causes the fire, but rich concentrations of combustion gases when it does not. A review of the literature on the solubility of gases in liquid copper indicates that there is no scientific justification for this hypothesis.

KEYWORDS: forensic science, electrical fires, arc bead formation

In the last few years it has become a popular idea to invoke the Auger analysis of arced copper wiring in order to say something about the likelihood that a fire was caused by some sort of electrical fault. The justification for the technique, which is due to MacCleary and Thaman (1) and Anderson (2–4), is that atmospheric gases, telltale of the environment in which the arc occurs, are somehow trapped in the liquid metal at the moment of the bead formation. The results from the analyses of arc beads, in the original paper by Anderson (2), appear to indicate a substantial presence and meaningful variation of oxygen and other gases. Elemental concentrations in copper arc beads as high as 86 at % (8.6 × 10⁵ ppm) for carbon and 36 at % (3.6 × 10⁵ ppm) for oxygen are cited, as are the significant reductions to levels in the region of 3 at % (3 × 10⁴ ppm). Anderson's justification for the requisite gas solubility in liquid copper at the melting point is a general reference to Fast (5), which contains Butts' early phase diagram for the copper-oxygen system (6) and Seiverts' Law (7) which correlates the gas concentrations in the liquid metal to the square root of the partial pressures in the local atmosphere. The oxygen concentration in the liquid at the melting point in Butts' phase diagram is about 2 at % (2 × 10⁴ ppm), which is also about the limit for the detection of oxygen in copper by Auger analysis. Seiverts' Law is merely the correction for the dissociation of a diatomic molecule when it goes into solution as an atom, which is the same for both liquids and solids. In a second paper, published by Anderson (3), there are totally different results concerning carbon, chlorine, and calcium with a complete absence of oxygen, and in a subsequent letter (4) in response to criticism by Beland (8), a long list of marginally relevant references is provided. Unfortunately, there is no mention in any of the papers of the work that has actually

been done on the solubility of gases in copper, nor the extensive compilations of diffusion and solubility data for liquid and solid copper at high temperatures.

Discussion

There is a wealth of literature concerning the solubility and diffusion of oxygen in copper (5–16). What is probably most damning to the proposition that the arc bead composition is in any way significant is the fact that the solubility of oxygen in molten copper, when it is exposed to air, is well below the limit of detection by Auger analysis (9–13). This is apparent when you apply Seiverts' Law (7) to Butt's phase diagram (6), although there has been some refinement since then. There are several other problems, not the least of which is that oxygen is actually more soluble in solid copper at the melting point (1083°C) than it is in the liquid (13–16) and that the diffusion coefficients for oxygen are also higher in the solid phase (9,13,16). Thus, copper will actually be less likely to absorb oxygen during a fire when it is in the liquid state.

The maximum amount of oxygen that can dissolve in liquid copper when it is exposed to air, according to a compilation of all the available data, is less than 5 parts per million (Fig. 1). This is well below the minimum detectable limit for oxygen in copper using Auger analysis, which is of the order of one atomic percent (1 × 10⁴ ppm) at best. Clearly, the levels of gas solubility are contrary to Anderson's suggestion and the concentrations that are being measured cannot possibly be related to the concentrations of atmospheric gases.

The diffusion coefficients for oxygen in copper are also shown in Fig. 2 and, although there is an increase in the absorption rates with increasing temperature, the rate of oxygen absorption is very much faster in the solid phase. Indeed from the diffusion and solubility data that have been compiled, one might more reasonably expect to expel oxygen from the liquid metal, rather than absorb it, during the formation of an arc bead.

Even without a knowledge of the levels of gas solubility in liquid copper, one should be suspicious of the idea, because of the nitrogen. Nitrogen, of course, accounts for approximately 80% of the atmosphere but is conspicuously absent from the Auger spectrum published in Anderson's first paper. The assumption that the layers of the bead can be peeled away to reveal the preserved concentrations of trapped atmospheric gases is naive and completely ignores the role of the surface oxide. A nitrogen signal is far less likely to appear in an Auger spectrum from copper because the nitride, unlike the oxides, is unstable above 800°C and so only grows at intermediate temperatures. The formation of oxide layers is clearly what is producing oxygen concentrations as high as 36 at % (3.6 × 10⁵ ppm) (2), bearing in mind the composition of cupric oxide (Cu_2O).
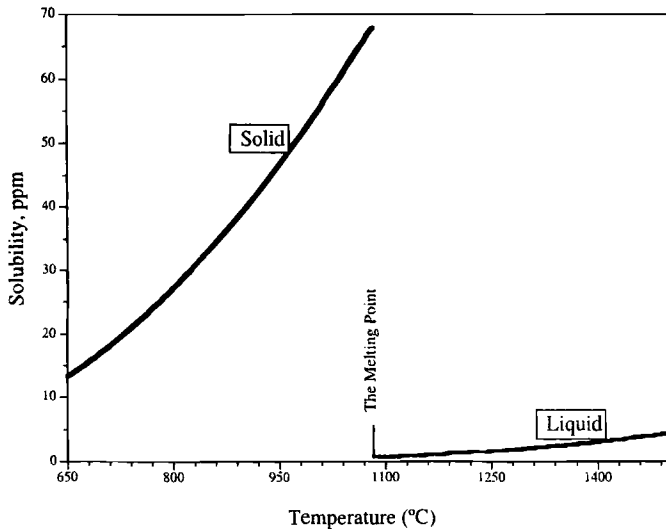
FIG. 1—*Oxygen solubilities in liquid and solid copper as a function of temperature, averaged from the compiled references in (13).*
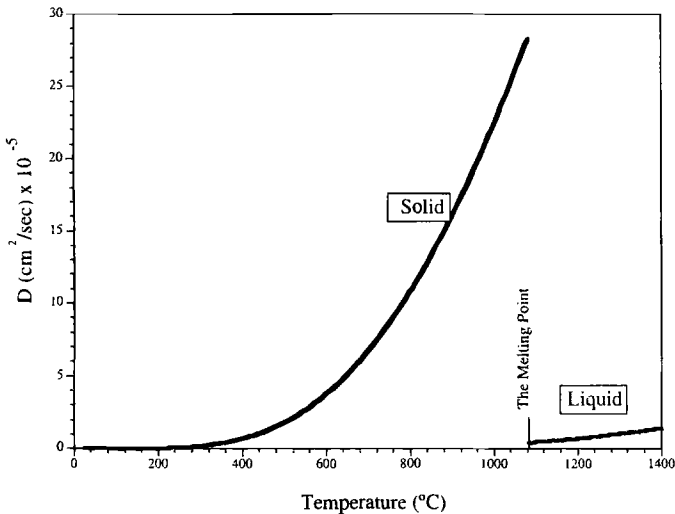

FIG. 2—*The temperature dependence of the diffusion coefficients for oxygen in copper, averaged from the compiled references in (13).*

Summary and Conclusions

It is clear from the extensive work that has been done on the solubility of gases in liquid copper that the Auger spectra, derived from arc beads, contain absolutely no information pertinent to the cause or origin of a fire. The levels of gas solubility in liquid copper, exemplified by oxygen, are several orders of magnitude below the minimum amounts that one could possibly hope to detect by Auger analysis. Furthermore, neither the solubility nor the rate of diffusion of atmospheric gases are expected to be any greater in liquid copper at high temperature than they are in the solid at much lower temperatures. Indeed, the premise that atmospheric gas concentrations are somehow trapped for posterity in a copper arc bead is totally wrong and based on a misunderstanding of the thermodynamic and kinetic behavior of this material.

References

1. MacCleary RC, Thaman RN. U.S. Patent 4,182,959, (1980).
2. Anderson RN. Surface analysis of electrical arc residues in fire investigation. J Forensic Sci 1989;34(3):633–7.
3. Anderson RN, Wolfe TA. Scientific examination of electrical arc residues to determine fire cause. Fire Arson Invest 1992; 42(3):58–9.
4. Anderson RN. Letter to the Editor, Fire Arson Invest 1994;45(2):44–5.
5. Fast JD. Interaction of metals and gases, Vol. 1, thermodynamics and phase relations. New York: Academic Press 1965.
6. Butts A. Copper. American Chemical Society Monograph Series, New York: Reinhold Publishing Corp., 1954.
7. Sieverts A, Krumbhaar W. Uber die löslichkeit von gasen in metallen und legierungen. Ber Dtsch Chem Ges 1910;43(I):893–900.
8. Beland B. Examination of arc beads. Fire Arson Invest 1994; 44(4):20–2.
9. Oberg KE, Friedman LM, Boorstein WM, Rapp RA. The diffusivity and solubility of oxygen in liquid copper and liquid silver from electrochemical measurements. Metallurg Trans 1973;4(1):61–7.
10. Kulkarni AD. The thermodynamic studies of liquid copper alloys by electromotive force method. Metallurg Trans 1973;4(7):1713–21.
11. Seow HP, Biswas AK. Thermodynamic properties of oxygen in liquid copper. Proc Australasian Inst Metals Mining 1973; 245:39–45.
12. Fitzner K, Moser Z. Activity of oxygen in dilute liquid Cu-O alloys. Metals Technol 1979;6(7):273–5.
13. Fromm E, Hehn W, Jehn H, Hörz G. Physik Daten—Gases and Carbon in Metals (Thermodynamics, Kinetics and Properties), Pt. XXI: Group 1B Metals (1) Copper (Cu). Stuttgart: Max-Planck-Institut fur Metalforschung, Institut fur Werkstaffwissenschaften, 1984.
14. Wada T, Fueki K, Mukaibo T. Determination of the solubility of oxygen in copper by the coulometric method. Bull Chem Soc Japan 1976;49(11):3317–8.
15. Horrigan VM. The solubility of oxygen in solid copper. Metallurg Trans A 1977;8A(5):785–7.
16. Otsuka S, Kozuka Z. The diffusivity of oxygen in liquid copper by electrochemical measurements. Metallurg Trans B 1976; 7B(3):147–9.

Additional information and reprint requests:
Dr. David G. Howitt
Department of Chemical Engineering and Materials Science
University of California
Davis, CA 95616