THE INFLUENCE OF INTERFACIAL TURBULENCE ON THE RATE OF OXIDATION AND DEOXIDATION OF MOLTEN COPPER AND SILVER USING LOW-MOMENTUM VERTICAL GAS JETS

by

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We accept this thesis as conforming to the required standard

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ABSTRACT

The rate of oxidation of 99.99% and 99.999% pure copper samples at 1220°C by low-momentum jets of pure oxygen has been studied at gas flow rates of from 500 to 2000 cm³ min⁻¹. Oxidation rates at a given gas flow rate were found to be constant and were governed by starvation mass transfer kinetics. Factors studied for the reaction include: effect of lance height, effect of small additions of silicon and sulphur to the melt prior to oxidation, and effect of oxide patch area. Interfacial tension-generated flow, radially outward from the point of jet impingement, was observed during oxidation and surface velocity studies showed that such flow had a mean value of 26.1 ± 5.5 cm sec⁻¹ for all of the experiments and was independent of oxygen gas flow rate and copper bath oxygen concentration. Surface-blockage studies indicated that the bulk of the oxygen transfer to the copper occurred over the area described by the oxide patch. Liquid-phase oxygen mass transfer coefficients were calculated using the oxidation rates and oxide patch areas, and a mean value was found to be 0.104 ± 0.012 cm sec⁻¹, independent of oxygen flow rate, bath oxygen content, and dissolved sulphur and silicon contents.

The rate of oxidation of 99.995% pure silver at 1100°C was studied using low-momentum jets of pure oxygen at flow rates of 1500 and 2000 cm³ min⁻¹, and was found not to be governed by starvation mass transfer kinetics.
The oxidation rate was not dependent on oxygen gas flow rate and was found to be a factor of about 50 times less than those observed for copper. No spontaneous interfacial tension-generated flow was observed during oxidation of the molten silver and a possible explanation was postulated. Liquid-phase oxygen mass transfer coefficients were found to have a mean value of $2.88 \pm 0.41 \times 10^{-3}$ cm sec$^{-1}$, independent of gas flow rate and bath oxygen content.

The effect of interfacial turbulence on liquid-phase oxygen mass transfer coefficients in molten copper was to enhance the value by about 40 times over that observed in molten silver, where interfacial turbulence does not occur on oxidation.

Copper deoxidation at 1220°C using low-momentum jets of pure hydrogen at flow rates of 1500 and 3000 cm$^3$ min$^{-1}$ was studied, and was found not to depend on hydrogen flow rate, lance height, and starting oxygen concentration. The rate-controlling step was found to be the gas-phase mass transfer of hydrogen to the liquid surface for the first 3000 sec. of deoxidation. After this, liquid-phase oxygen mass transport control predominated.

Dissolved silicon was found to retard the deoxidation rate, while dissolved sulphur was found to enhance the deoxidation rate through continued SO$_2$ elimination. Interfacial tension-generated flow was observed during deoxidation and approximate surface velocities of 10 to 15 cm sec$^{-1}$ towards the point of jet impingement were observed. A mechanism for this flow was postulated. The gas-phase mass transfer coefficient was found to be $1.28 \pm 0.25$ cm sec$^{-1}$ for copper-oxygen alloys, and was $0.89$ cm sec$^{-1}$ in the presence of dissolved silicon and $2.68$ cm sec$^{-1}$ in the presence of dissolved
sulphur. An approximate value for the liquid-phase oxygen mass transfer coefficient in the liquid-phase control region was found to be $4.9 \times 10^{-3}$ cm sec$^{-1}$, and was found to be influenced by the presence of bubbling during this phase of deoxidation.

The rate of deoxidation of molten silver at 1100°C by low-momentum hydrogen jets was studied at hydrogen flow rates of 1500 and 2000 cm$^3$ min$^{-1}$. The rate was found not to depend upon hydrogen flow rate, but was found to decrease with decreasing starting bath oxygen concentration. Interfacial tension-generated flow was observed, during silver deoxidation, with approximate surface velocities of 10 to 15 cm sec$^{-1}$ towards the point of jet impingement. The rate-controlling step was found to be liquid-phase mass transfer of oxygen, and liquid-phase oxygen mass transfer coefficients were found to decrease with decreasing initial oxygen content. These values were enhanced by the presence of bubbling during deoxidation.

Interfacial turbulence during the dissolution of solid Cu$_2$S, Cu$_2$O, Se, and Te in molten copper was shown to occur. Values calculated for the spreading coefficient $S$, indicated that the spreading of these materials on molten copper was predictable.
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<tr>
<td>A</td>
<td>interfacial area for mass transfer, cm²</td>
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<td>B</td>
<td>constant.</td>
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<td>Cᵢ, Cᵢᵇ, Cᵣᵢᵇ</td>
<td>solute concentration; at the interface and in the bulk phase respectively, wt % or moles cm⁻³ where indicated.</td>
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<td>Dₛ/ₘ</td>
<td>diffusion coefficient for species s in metal m, cm² sec⁻¹.</td>
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<td>K</td>
<td>equilibrium constant.</td>
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<td>kₛ, kₒ, kₕ₂, kₕ₂₀</td>
<td>mass transfer coefficient for species s, oxygen, hydrogen, and water, respectively, cm sec⁻¹.</td>
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<tr>
<td>kₒᵥ</td>
<td>overall mass transfer coefficient, cm sec⁻¹.</td>
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<td>nₛ, nₒ, nₕ₂, nₕ₂₀</td>
<td>mass flux of species s, oxygen, hydrogen, and water respectively, moles sec⁻¹.</td>
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<td>[0]</td>
<td>concentration of oxygen in the liquid phase, wt % or moles cm⁻³ where indicated.</td>
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<td>Pₒ², Pₕ₂, Pₕ₂₀</td>
<td>partial pressure of oxygen, hydrogen, and water respectively, at the interface or in the bulk gas phase, atm.</td>
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<td>R</td>
<td>gas constant, 81.94 cm³ atm⁻¹ mole⁻¹.</td>
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<td>r</td>
<td>bath radius, cm.</td>
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<tr>
<td>s, sᵣ, sₙ</td>
<td>solute species; transferring across the interface, and non-transferring, respectively.</td>
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S spreading coefficient, dynes cm\(^{-1}\)

t\(_e\) surface renewal time, sec.

t time, sec.

T temperature, °C or °K where indicated.

U\(_r\) interfacial velocity of spreading, cm sec\(^{-1}\).

\(\gamma_O\) activity coefficient of oxygen.

V volume of metal bath, cm\(^3\).

\(T_s\) surface excess of solute species s at the interface, molecules cm\(^{-2}\).

\(\sigma_m, \sigma_{Cu}, \sigma_{Ag}, \sigma_{mo}\) surface tension for a metal, copper, silver and metal oxide, respectively, dynes cm\(^{-1}\).
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1. INTRODUCTION

1.1. GENERAL

Spontaneous interfacial turbulence has long been of interest to the surface chemist and chemical engineer. Pioneering work by Thompson in 1855, in alcohol-water systems, and later by Marangoni in 1871, established that local imbalances in interfacial tension could result in interfacial motions. Studies since this time have shown that such spontaneous interfacial motions occur for a wide variety of aqueous and organic phases, and that these motions profoundly affect mass transfer in fluid phase-separation processes, often increasing rates by an order of magnitude.

In the field of process metallurgy, the observance of any spontaneous interfacial motions has been hampered by experimental difficulties related to the opacity of the fluids involved and the high temperature encountered. Attempts to use predictions based on low temperature aqueous-organic systems for liquid metals have been unsuccessful owing to the vast differences in density, interfacial tension, and adsorption effects. Despite these problems, it is evident that interfacial turbulence could be very important in liquid metal systems because most metallurgical reactions occur at interfaces and, at high temperature, tend to be controlled by transport processes. Thus, the extra degree of mixing provided by spontaneous turbulence and any resulting increase in interfacial area could significantly accelerate reaction rates.
The present investigation was undertaken to determine the effects of interfacial turbulence on the rates of liquid-phase mass transfer during the oxidation of molten copper and silver using low-momentum (< 24 dynes) vertical pure gas jets.

1.2. SPONTANEOUS INTERFACIAL MOTION

1.2.1. SOLUTE EFFECTS ON INTERFACIAL TENSION

The works of Thompson and Marangoni established that imbalances in interfacial tension across an interface can lead to surface flow directed towards regions of highest interfacial tension. Local changes in the concentration of a surface-active solute residing at the interface, or changes in temperature can cause such imbalances in interfacial tension. Unless a large thermal gradient exists, however, it is generally considered that temperature effects are negligible.

Depending upon the exact nature of solute adsorption, a surface-active solute can either raise or lower the liquid metal interfacial tension. The relationship between interfacial tension $\sigma$, and solute concentration $C_s$, for both cases can be expressed as follows:

$$\left( \frac{\partial \sigma}{\partial C_s} \right)_{T,P} = -\Gamma_s \cdot \frac{RT}{C_s}$$

which is derived from the Gibb's adsorption equation. Values for the excess solute concentration at the interface, $\Gamma_s$, are positive if $\left( \frac{\partial \sigma}{\partial C_s} \right) < 0$ and negative if $\left( \frac{\partial \sigma}{\partial C_s} \right) > 0$. Most surface-active solutes in liquid metals are positively adsorbed; some of the experimentally observed effects on $\sigma_{\text{metal}}$ are given in Figs. 1.1 to 1.4 for Fe$^9$, Al$^{10}$, Cu - O$^{11}$ and Cu - S$^{11}$. Values
FIGURE 1.1 Surface Tensions for Solutions of C, P, N, O, S, and Se in liquid iron at 1550°C (Kozakeuitch⁹).
FIGURE 1-2 Surface tensions for Aluminum containing various solute metals at 50° to 80° above the liquidus (Korol'Kov10).
FIGURE 1-3  Effect of dissolved oxygen on the surface tension of molten copper (Monma and Suto).
FIGURE 1.4  
Effect of dissolved sulphur on the surface tension of molten copper (Monma and Suto\textsuperscript{11}).
of $\sigma_{\text{Cu}}$ in the presence of as much as 0.88 weight-% oxygen, reported by Eremenko et al.\textsuperscript{12}, agree well with those of Monma and Suto\textsuperscript{11}, where a lowering of $\sigma_{\text{Cu}}$ by 50% in the presence of oxygen was observed. Bernard and Lupis\textsuperscript{13} report that dissolved oxygen lowers the surface tension of liquid silver by 20%.

Generally speaking, the effect of solute metals is less than for solute non-metals. Those solutes exhibiting the highest degree of surface activity in liquid metals are oxygen, sulfur, selenium and tellurium.

1.2.2. MECHANISM FOR SPONTANEOUS MOTION

The cause of spontaneous interfacial motion has been established as being interfacial tension gradients, along the interface, due to non-uniform solute concentrations at the interface. Such differences in solute concentration are usually the result of non-uniform mass transport of solute across the interface on a micro- or macro-scale.

In a liquid system having a well-stirred bulk phase, micro-scale concentration fluctuations can occur as random solute-rich eddies penetrate to the interface, which is shown schematically in Fig. 1.5. Because the bulk solute concentration, $C_s^b$, is larger than the interfacial solute concentration, $C_s^i$, the eddy, on penetrating to the interface, will establish a concentration, and hence, interfacial tension gradient at the interface. Surface flow will be directed away from the region of the eddy, and the magnitude of such a flow will depend upon the rate of arrival of eddies at the interface, and the degree to which the interfacial tension is lowered by the eddies.
Transference of solute rich eddy penetrates to the interface and causes spreading.

**FIGURE 1.5**

Interfacial motion generated on a micro-scale due to eddy penetration.
On a macro-scale, concentration imbalances can occur as a result of the presence of a source or sink of a surface active solute, such as a partially immersed solid. For purposes of illustration, consider the case of a partially immersed solid, shown in Fig. 1.6. If the solid is soluble in the liquid, then concentration gradients will be established within the liquid phase as solute collects near the interface. Thus, a longitudinal surface tension gradient will be set up, and, for a positively adsorbed solute, flow will be directed along the interface away from the solid.

This mechanism has been used to explain the preferential attack of refractory bricks at the surface line of steel- and glass-making furnaces. Brimacombe and Weinberg have shown that a low-momentum (< 6 dynes) vertical oxygen jet impinging on the surface of a liquid metal is yet another example of a macro-sized local source of solute which can initiate spontaneous interfacial motion.

A surface-active species can also serve to block spontaneous surface motion. Up to now the transferring solute species has been considered as being the only surface active element present in the system. However, if another solute is present that is surface active but non-transferring, the situation may change considerably. According to Gibb's theory, a solute which depresses the interfacial tension must adsorb at the interface. As the amount of solute adsorbed in this Gibbs layer increases, the surface can become immobile so that it is effectively solid in that eddies rich in the transferring solute, \( s_t \), will be unable to spread as they penetrate to the interface, as in Fig. 1.7. This blocking action will likely retard the transfer of \( s_t \), and may serve to explain the effect of silicon on the rate of oxygen absorption by levitated copper drops observed by Glen and Richardson.
Interfacial motion generated on a macro scale by the presence of a partially immersed solid.
FIGURE 1.7 Effect of the presence of a non-transferring surface-active solute in an interface.
1.2.3. MASS TRANSFER COEFFICIENT

To measure the influence of interfacial turbulence on the rates of mass transfer in the liquid phase, a knowledge of the flux of the transferring specie(s) between adjacent fluid phases is necessary. In principle the molar flux can be related to the solute concentration profile by Fick's first law, but in the case of liquids this is very difficult, owing to convection effects. Thus, the normal method of evaluating the molar flux is empirical in nature.

The molar flux can be related to the concentration of a specie(s) by the following equation:

\[ \dot{n}_s = k_s \cdot A (C^i_s - C^b_s) \]  

(2)

where \( C^i_s \) and \( C^b_s \) are the concentrations of the transferring specie(s) at the interface and in the bulk phase, respectively, and \( k_s \) is the liquid phase mass transfer coefficient. This equation defines the mass transfer coefficient. Values for the mass transfer coefficient depend upon the geometry of the system, the position on the interface, the fluid velocity, and the bulk fluid properties. Because \( k_s \) is normally independent of solute concentration, it, rather than the molar flux, is usually derived from experimental data.

The mass transfer coefficient need not always be evaluated from experimental data, but also may be estimated from one of several mathematical models that have been developed in recent years\(^{19,20,21,22}\). These models are based on an idealized concept of the behaviour of stirred fluids and are derived from the diffusion equations. Perhaps the most realistic of
these is the Surface Renewal Model proposed by Higbie\textsuperscript{22}. In this model, for a system having a well-stirred bulk phase, a solute-rich eddy penetrates to the interface and remains in contact for a time, $t_e$, during which solute transfer to or from the eddy occurs by unsteady-state diffusion. At the end of this time period, the eddy is swept away from the interface and replaced by a new one.

By assuming that $t_e$ is so short that the concentration gradient in the eddy does not reach its rear boundary (i.e. the eddy is semi-infinite in thickness), the equations for this model can be easily stated\textsuperscript{23}. The solution of the unsteady state diffusion equation then leads to an expression for the mean value of the molar flux over the time interval $t_e$, as

$$\bar{n}_s(\text{avg}) = \frac{1}{t_e} \int_0^{t_e} \dot{n}_s \cdot dt = \frac{2\sqrt{D_{ss}/m}}{\pi t_e} \cdot (C_s^i - C_s^b)$$

from which the mass transfer coefficient is found to be

$$k_s = \frac{2\sqrt{D_{ss}/m}}{\pi t_e}$$

Values for $t_e$ are often difficult to obtain, but for particular stirring conditions such as involving rising bubbles, falling drops or impinging vertical gas jets, values for $t_e$ can be more easily estimated.

1.3. REVIEW OF PREVIOUS WORK

1.3.1. OBSERVATIONS OF SPONTANEOUS INTERFACIAL MOTION

In recent years, both Schlieren photography and high-speed motion picture photography have been used to study interfacial turbulence in liquid
metal systems, both at room temperature and at high temperature. Brimacombe and Richardson observed interfacial turbulence, using Schlieren photography, in their experiments with aqueous phases and mercury amalgams. In one such study, a mercury-indium amalgam was placed in a container and covered with a dilute solution of ferric chloride. Concentrated ferric chloride solutions were then introduced to the amalgam by means of a syringe, and the ensuing turbulence was photographed, as shown in Fig. 1.8(a) and (b). In Fig. 1.8(a) the amalgam (dark)-ferric chloride (light) interface is shown prior to introduction of the concentrated solution. There is no detectable interfacial motion. Figure 1.8(b) shows the same interface immediately after introduction of the concentrated solution. This Schlieren photography shows that the interface has become very highly agitated. The transfer of indium is from the amalgam to the ferric chloride solution. Surface velocities of up to 30 cm·sec$^{-1}$ were observed as was a three-fold increase in the aqueous-phase mass transfer coefficient. For this system, Brimacombe has shown that the observed turbulence is accompanied by a fluctuation in the electrical potential across the interface and so the effect may be electrocapillary in nature.

More recently, Brimacombe and Weinberg observed interfacial turbulence in high-temperature liquid metal systems where oxygen gas was jetted vertically onto the liquid metal surface. A bright oxide patch was observed to form directly beneath the jet and to spread rapidly over the liquid surface. Analysis of high-speed motion pictures of iron, tin and copper melts gave the following velocities:
FIGURE 1-8 Schlieren photographs of interfacial turbulence induced by a stream of 492 m MFe$^{3+}$ solution from a syringe onto a 0.1% In amalgam. The bulk aqueous phase is 50 m MFe$^{3+}$. Width of field 11 mm.

(a) ferric ion solution falls from syringe onto interface

(b) interface twitches, spreads rapidly from point of ferric ion impingement. (Brimacombe and Richardson$^{24}$).
(i) iron (1600°C): \( U_{Fe} = 25 \text{ cm/sec} \)
(ii) tin (1100°C): \( U_{Sn} = 80-150 \text{ cm/sec} \)
(iii) copper (1100°C): \( U_{Cu} = 50-100 \text{ cm/sec} \)

The oxide patches for iron and tin are shown in Fig. 1.9.

Momentum transfer from the jet (< 6 dynes) was eliminated as a possible source of interfacial motion by observing the effect of an argon jet, of 6 dynes momentum, on alumina particles on the liquid surfaces. Observed motions were less than 5 cm·sec\(^{-1}\). They proposed the following mechanism for the process:

(a) the oxygen concentration at the point of jet contact is at the saturation value;
(b) at the walls, the oxygen concentration is less;
(c) this concentration imbalance leads to changes in \( \sigma_{Cu} \), resulting in surface spreading towards regions of high \( \sigma_{Cu} \).

For a metal surface to spread in the presence of a metal oxide, the value of the initial surface tension of the metal, \( \sigma_m \), must be larger than the sum of the metal oxide surface tension, \( \sigma_{mo} \), and the interfacial tension between the metal and metal oxide, \( \sigma_{m/mo} \). This difference is termed the Spreading Coefficient, \( S \), and is defined as

\[
S = \sigma_m - (\sigma_{mo} + \sigma_{m/mo})
\]  

which must be positive for spreading to occur. Thus, the systems observed by Brimacombe and Weinberg\(^{15} \) all have positive values of \( S \) because the oxide patches are observed to spread over the melt surface during an experiment.
Interfacial turbulence on liquid tin and iron during blowing with pure oxygen gas at a flow rate of 120 cm$^3$ min$^{-1}$.

(a) bright oxide patch on surface of liquid tin vibrates and spreads rapidly over the surface. Velocity of the oxide pieces was estimated to be 80 to 150 cm sec$^{-1}$. (Brimacombe and Weinberg$^{15}$).

(b) spreading of oxide patch on liquid iron. The patch was observed to pulsate and then spread over the surface at a rate of 25 to 50 cm sec$^{-1}$. (Brimacombe$^{28}$).
As oxidation continues, the value of $\sigma_m$ will decrease, and so $S$ will decrease during an experiment. The interfacial motions observed by these workers have not been mentioned in other similar oxidation studies$^{27}$.

1.3.2. GAS JETS IMPINGING ON LIQUIDS

Because use is made of low-momentum gas jets in the present study, the literature of gas jets impinging vertically onto liquid surfaces is reviewed briefly here. All previous work has dealt with high-momentum gas jets due to their use in metallurgical processes such as the BOF and TBRC. The action of such jets is to vigorously stir the metal bath which, in turn, speeds the refining process. Several studies on the behaviour of these jets include the basic stirring patterns$^{19,20}$, fluid dynamics$^{29}$, circulation and penetration depths$^{26,30,31,32}$ and mathematical model descriptions for fluid flow patterns$^{33}$ and liquid-and gas-phase mass transfer coefficients$^{34,40}$.

The most relevant of these studies is that of Davenport et al$^{34}$ on the mass transfer rates across gas-liquid interfaces using jets impinging normal to the liquid surface. Liquid phase mixing was caused by the jet force, and for high jet momenta (e.g. 56,000 dynes) the bulk liquid appeared to be well stirred.

Water model studies, using hollow plastic beads to show both flow patterns and fluid velocities, indicated that the surface motion due to jet force was in a direction away from the point of jet impingement and was found to vary with jet momentum and lance height above the bath surface. Observed surface velocities ranged from 12 to 25 cm sec$^{-1}$, and it is of interest to note that jet velocities used were all significantly greater than 3000
cm sec^{-1} - some even reaching as high as Mach 2.

Mass transfer rates for gas jets soluble in the liquid phase were measured experimentally, and from these rates liquid-phase mass transfer coefficients were derived. These values were then compared to values calculated from an equation based on the Higbie Surface Renewal model. In this case, the eddies were assumed to contact the surface of the liquid at the point of impingement of the gas jet, and then proceed to traverse the surface as described before in section 1.2.3. Then, on solving the unsteady state diffusion equations, a relationship for the mean mass transfer coefficient, $\bar{k}_s$, is found to be

$$\bar{k}_s = B \left( \frac{U_r x D_s}{r} \right)^{\frac{1}{3}}$$

where $U_r$ is the surface velocity, $r$ is the bath radius, and $D_s$ is the diffusion coefficient for the solute species in the liquid phase. Values for the constant, $B$, in Eq. (6) are as follows:

(i) $B = \frac{2}{\sqrt{\pi}}$ if $U_r \cdot r$ is constant,

and (ii) $B = \frac{4}{\sqrt{3\pi}}$ if $U_r$ is constant.

The residence time for an eddy in the interface is given by $\frac{U_r}{r} = t_e$ (see sec. 1.2.3.).

Based on experiments for CO$_2$ jets impinging on water, they used Eq. (6) to calculate values for $\bar{k}_s$. For a surface velocity of 25 cm sec$^{-1}$, they calculated the following values:

(i) if $U_r \cdot r$ is constant, $\bar{k}_s = 3.1 \times 10^{-3}$ cm sec$^{-1}$;

(ii) if $U_r$ is constant, $\bar{k}_s = 3.4 \times 10^{-3}$ cm sec$^{-1}$.
The experimental value was $k_s = 1.8 \times 10^{-3} \text{ cm sec}^{-1}$, and they felt the agreement between theoretical and experimental values was reasonable. In this instance, there is no clear preference for either value of $B$.

In a similar study for CO$_2$ jets impinging on water, Bradshaw and Chatterjee obtained good agreement between theoretical and experimental results for $k_s$ using $Ur \cdot r$ as a constant value. They note that $k_s$ values increase with increasing jet momentum or decreasing jet height.

### 1.3.3. Kinetics of Molten Copper Oxidation and Deoxidation

During the oxidation and deoxidation of molten copper, mass transfer rates for oxygen can be controlled by transport in the gas and/or liquid phases as well as by the rate of chemical reactions at the surface. Thus, to correctly interpret mass transfer rate data, it is necessary to establish which of these processes controls the rate of transport.

Most laboratory-scale kinetic studies of copper oxidation have involved CO/CO$_2$ mixtures flowing over levitated pure copper droplets, where the partial pressure of oxygen in the gas phase was determined by the CO/CO$_2$ ratio used. In their study, Toop and Richardson found that, at 1400°C, the observed rates of approach to equilibrium indicated that the kinetics of oxygen transfer were chemically controlled for the reaction

$$\text{CO}_2 + \text{Cu} \rightarrow \text{CO} + [0]_\text{Cu} \quad (7)$$

In Fig. 1.10, the observed rates of oxygen uptake show that a constant value is reached quickly and that, at a fixed $P_{O_2}$, temperature controls the maximum amount absorbed.
Results for a 0.5-0.54 gm. droplet of copper levitated in a gas stream of CO:CO₂ ratio of 1:25 at 4160 ml.min⁻¹. (a) oxidation; (b) deoxidation (Toop and Richardson).
As these rate-controlling reactions occur at the interface, they felt that surface films could adversely affect the oxidation rates, but the exact effect was not known.

In a later study on levitated copper droplets of 99.999% purity, Glen and Richardson observed the same type of oxidation ratio as in Fig. 1.10 for the temperature range 1400°C to 1600°C. Their results are presented in Fig. 1.11. Electron Microprobe analysis of a cooled droplet indicated that a thin surface film of silica was present. (NOTE: Spec. pure copper has a silicon content < 2 ppm). To determine the effect of these films, levitated droplets were cleaned with HF solutions, dried, and relevitated for oxidation. The upper curve in Fig. 1.11 gives the results for cleaned droplets. From this study, it is evident that a very thin film of silica on the surface of molten copper droplets can reduce the oxidation rate by from 50 to 80%.

Analysis of the results indicated that, for the temperature range and gas pressures used, oxygen mass transport was gas-phase controlled. However, at temperature less than 1400°C, the equations for gas-phase control no longer appeared to apply. The exact reason for this discrepancy was not known, and they indicate that chemical kinetics were unlikely to be responsible. Nevertheless, the role of silica films in inhibiting the rate of copper oxidation has been established.

In a more industrial approach, Gerlach et al studied the rates of oxidation of a molten copper bath at 1300°C using high-momentum vertical gas jets with gas mixtures of 0.72 to 21% oxygen. The Surface Renewal model was applied to calculate values for the mass flux, and, on comparison with their
FIGURE 1.11  The uptake of oxygen from mixtures of $O_2 + N_2$ at 1400°C, by both desiliconized $\Delta$, and untreated, $\bigtriangleup$, copper drops. $P_{O_2} = 1.11 \times 10^{-4}$ atm. (Glen and Richardson 18).
experimental data, they found that mass transport control resided in the gas phase.

Frohme et al.\textsuperscript{38}, in similar experiments with oxidizing gas mixtures and molten copper at 1200°C, found that the mass transport rate for oxygen was gas-phase controlled. Furthermore, their values of gas phase mass transfer coefficient agree well with the results of Gerlach. They also studied the oxidation rates of copper containing 0.8 wt % sulphur, and found that the liquid-phase mass transfer coefficient for sulphur removal was 0.09 cm sec\(^{-1}\).

Based on these studies it appears that the oxidation rate of molten copper by dilute mixtures of oxygen gas is controlled by oxygen mass transport in the gas phase, and it is unlikely that chemical reactions influence this control. For jets of pure oxygen, mass transport control of oxygen in the gas phase is, of course, impossible, so control should reside in the liquid phase.

The deoxidation of molten copper has been studied by Themelis and Schmidt\textsuperscript{39} using a submerged vertical jet of pure CO at flow rates from 5 to 100 litres - min\(^{-1}\). Over the bath oxygen concentration range of 1.0 to 0.1 wt %, they found that the rate of reduction was unaffected by the changing oxygen content. For oxygen concentrations less than 0.1 %, the rate of reduction decreased on decreasing oxygen content. Thus, they concluded that the rate of deoxidation of molten copper (0.1 % < % O < 1 %) by a submerged vertical jet of CO is controlled by mass transfer of CO in the gas phase. For oxygen contents of < 0.1 %, a transition to liquid-film control was observed.
In a later study on mass transfer between a submerged horizontal gas jet and a liquid, Brimacombe et al.\textsuperscript{40} analysed the kinetic data of Themelis and Schmidt\textsuperscript{39} in terms of mass transport theory, and showed that the deoxidation of molten copper by a submerged jet of deoxidizing gas was transport controlled. Nanda and Geiger\textsuperscript{36} also studied the deoxidation of molten copper in this manner.

On the basis of these studies, it appears certain that the deoxidation of molten copper, by submerged jets of CO or H\textsubscript{2}, is mass-transport controlled.

1.3.4. KINETICS OF MOLTEN SILVER OXIDATION AND DEOXIDATION

Oxidation rates for molten silver have been investigated using high-momentum vertical gas jets. Chatterjee et al.\textsuperscript{41} have found that the oxygen mass transfer rates increased on increasing jet momentum and decreasing interfacial area, and decreased with increasing lance height. The mass transfer relationships were developed in a manner similar to those for Davenport et al.\textsuperscript{34}, and the experimental values for the mean liquid-phase mass transfer coefficient range from 0.001 to 0.015 cm sec\textsuperscript{-1}, depending upon the above conditions, for a bath temperature of 1000\textdegree{}C. Though surface velocities were not measured, they felt that since mass transfer was related to jet momentum, a correlation between mass transfer and surface velocity ought to exist.

In a later study, Chatterjee and Bradshaw\textsuperscript{42} measured the gas-phase resistance to mass transfer for high-momentum gas jets having P\textsubscript{O\textsubscript{2}} = 0.1 to 0.2 atm. Values for k\textsubscript{g} were found to vary from 1.4 to 4.8 cm sec\textsuperscript{-1},
depending on flow rate. On comparison with their prior data for pure oxygen gas jets, the values for $k_s$ were found to be 20\% less for air and 30\% less for other gas mixtures, indicating that the presence of a gas phase resistance to mass transfer can lower the liquid-phase mass transfer rate by as much as 30\%.

Sano and Mori\textsuperscript{43} studied the rates of absorption and desorption of oxygen in molten silver, at 1000°C using low flow rate gas mixtures (≈ 1000 cc min$^{-1}$). During the degassing of oxygen, surface motion was observed, and this motion appeared to decrease with decreasing oxygen concentration. The liquid-phase mass transfer coefficient obtained for pure oxygen and argon-oxygen mixtures range from 0.013 to 0.019 cm sec$^{-1}$. It is of interest to note that these values are similar to those for Chatterjee et al\textsuperscript{41}, who used high-momentum gas jets in their studies. It is not clear whether or not Sano and Mori observed any turbulence during oxidation, but the above comparison seems to indicate that some form of large scale stirring did exist, either spontaneous or mechanical in nature.

Based on the stirring effect of jets of pure oxygen on molten silver, oxygen mass transport is liquid-phase controlled. This changes over to gas-phase control when gas mixtures are used during oxidation. During deoxidation, oxygen mass transport is likely controlled in the gas phase.

1.4. SCOPE OF THE PRESENT STUDY

Although much work has been done on the kinetics of oxidation and deoxidation of molten metals, little is known about the relationship between spontaneous interfacial turbulence and mass transfer rates. Also, few
pictorial observations of the liquid metal surface during both oxidation and deoxidation have been made. The effects of dissolved surface active impurities on the oxidation and deoxidation rates of molten copper have only recently been studied, along with their dissolution behaviour from the solid state.

Therefore, the aims of the present study were to:

(a) attempt to correlate mass transfer and interfacial turbulence data for both copper and silver, through the use of high speed cine photography;

(b) to study the effect of dissolved sulphur on both the oxidation and deoxidation rates for molten copper;

(c) to observe photographically the dissolution behaviour of solid Cu$_2$S, Cu$_2$O, Se and Te.
2. EXPERIMENTAL

2.1. APPARATUS

All experiments were performed in the apparatus shown in Fig. 1.12. The main body was fabricated from transite, with exterior dimensions of 32.5 x 32.5 x 52.5 cm. The assembled furnace was lined, to a height of 27.5 cm with porcelain wool insulation. A 17.5 cm dia. copper induction coil was centred in the apparatus, provision having been made for cooling water inlet and outlet.

Graphite susceptors were fabricated from a 10 cm dia. graphite rod. Each finished susceptor was 5 cm thick and had a centred 5 cm hole for crucible placement. To support the graphite, a 6.25 cm thick refractory brick was shaped to fit inside the induction coil.

When the graphite susceptor was centred and placed so that it extended slightly above the top level of the induction coil, fine powdered alumina was added to this level. A final piece of porcelain wool was placed over the alumina, with a hole left for installation of the crucibles. Molten copper and silver samples were held in recrystallized alumina crucibles, of 100 cm$^3$ and 50 cm$^3$ capacity respectively, supplied by McDaniel Corp.

To allow for gas jet positioning, thermocouple installation, and sample withdrawal, a 12.5 cm dia. hole was bored in the top place of the furnace. A circular plate, 17.5 cm dia. and 1 cm thick, was fabricated from
FIGURE 1-12  Cross-sectional view of experimental apparatus.
316 stainless steel, and installed over the opening.

A 1.6 cm dia. hole was bored in the centre of the steel plate for the lance guide. The lance guide was fabricated from 316 stainless steel rod, and had the final dimensions of 4.7 cm long, 1.4 cm dia., and 0.7 cm bore. The lance was held firmly in place by means of a Wilson seal. In all, five 1.6 cm dia. threaded holes, spaced 55° apart on a circle of 3.2 cm radius, were placed in the steel plate. For all experiments, the lance used was a 0.2 cm i.d. by 7.6 cm long mullite tube which was fitted into a 0.6 cm o.d. by 0.3 cm i.d. alumina lance 30 cm long.

Fused quartz sample tubes, 0.3 cm o.d., 0.2 cm i.d. and 90 cm long, were used to withdraw from 1 to 2 gm metal samples from the crucibles. As cuprous oxide attacks quartz, that part of the sample tube in contact with the molten copper was coated with Alcoa XA-17 reactive alumina, dried, and fired at 1200°C for two hours, to provide an inert protective coating for the tubes.

Temperatures were measured by two Pt - Pt - 10% Rh thermocouples held in alumina protective sheaths. The thermocouples were connected to two calibrated Honeywell chart recorders through a cold junction.

Surface observations were made through a 10 x 10 x 0.5 cm quartz window, centred 37 cm from the bottom of the apparatus. During filming, additional observations were made through a 2.5 cm dia. quartz sight glass held in a removable stainless steel tube inclined 10° from the vertical in the top plate. Two copper tubes were attached to this assembly to provide for argon gas shielding.

A Hycam high-speed cine camera was used to photograph the liquid metal surfaces in both black and white and colour.
Gas flow rates were metered by calibrated Gilmont flow meters. All gases were dried with silica gel.

2.2. MATERIALS

2.2.1. COPPER

The copper used was supplied in two forms, cathode sheets and rod. The cathode sheets, supplied by NORANDA, were of 99.99% purity, and the rod stock, supplied by ASARCO, was of 99.999% purity. Spectroscopic analyses (TABLE I) give the impurity levels for each.

2.2.2. SILVER

Fine silver was supplied by ENGELHARD INDUSTRIES, and was of 99.995% purity. The spectroscopic analysis (TABLE I) gives the impurity level.

2.2.3. SELENIUM AND TELLURIUM

Both the selenium and tellurium samples used were supplied by the FAIRMONT CO., and were of 99.99% and 99.8% purity respectively.

2.2.4. REAGENTS

The copper sulfide (Cu$_2$S) and copper oxide (Cu$_2$O) powders used were of reagent grade. All acid solutions were made from distilled water and reagent grade acids. The argon, oxygen, and hydrogen gases, supplied by CANADIAN LIQUID AIR, were all of commercial purity. Gases were used direct from cylinders but were dried by passing through silica gel. All graphite used was reagent grade.
TABLE I
SPECTROSCOPIC ANALYSIS OF COPPER
AND SILVER SAMPLES

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>ELEMENT</th>
<th>NORANDA</th>
<th>ASARCO</th>
<th>ENCELHARD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>COPPER</td>
<td>SILVER</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>&lt; 10 ppm</td>
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<td>Cu</td>
<td>MATRIX</td>
<td>MATRIX</td>
<td>ND</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>10 ppm</td>
<td>&lt; 0.7 ppm</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Pb</td>
<td>ND</td>
<td>&lt; 1 ppm</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Mg</td>
<td>1 ppm</td>
<td>ND</td>
<td>&lt; 1 ppm</td>
<td>&lt; 10 ppm</td>
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<td>Ni</td>
<td>ND</td>
<td>&lt; 1 ppm</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Se</td>
<td>ND</td>
<td>&lt; 1 ppm</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Si</td>
<td>10 ppm</td>
<td>&lt; 1 ppm</td>
<td>&lt; 1 ppm</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Ag</td>
<td>10 ppm</td>
<td>&lt; 0.3 ppm</td>
<td>MATRIX</td>
<td>ND</td>
</tr>
<tr>
<td>S</td>
<td>ND</td>
<td>&lt; 1 ppm</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Sn</td>
<td>ND</td>
<td>&lt; 1 ppm</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ti</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>&lt; 10 ppm</td>
</tr>
</tbody>
</table>

NOT DETECTED: Sb, As, Ba, Be, Bi, B, C, Ca, Cr, Co, Ga, Au, Mn, Mo, Nd, K, Na, Sr, Ta, Th, W, U, V, Zn.
2.3. PREPARATION

2.3.1. COPPER

Cathode sheets were cut up and induction melted, in 6000 gm lots, in a graphite crucible. During melting, argon gas was passed over the melt surface to retard oxide formation. The copper was then cast in small cylindrical graphite crucibles, of 750 gm capacity. The average solidified billet measured 3.5 x 8.2 cm. A similar procedure was used for the high-purity rod stock.

The solidified billets were then cleaned to remove surface oxides, particularly silica, as follows:

(a) immersed in 50% HNO₃ for 15 min.;
(b) washed in water for 5 min.;
(c) washed in 5% HF for 2 hrs.;
(d) washed in water for 30 min.;
(e) dried with ethyl alcohol and stored in a dessicator.

The samples were weighed prior to use in an experiment.

2.3.2. SILVER

Fine silver, of 2000 gm weight, was melted in a box furnace and cast into cylindrical graphite crucibles of 400 gm capacity. The solidified billet measured 2.5 x 7.5 cm on average. The cleaning procedure was the same as for copper, and samples were weighed prior to use in an experiment.
2.4. PROCEDURE

2.4.1. COPPER EXPERIMENTS

For each experiment a clean, weighed copper billet was placed in the alumina crucible and positioned in the susceptor. The top plate was then installed and secured. Each thermocouple was positioned, and connected to the strip-chart recorders. The lance was then lowered to within 5 cm of the crucible, and argon flushing at 1500 cm$^3$ min$^{-1}$ was begun, 30 minutes prior to heating the copper.

The induction power was then switched on and set at 5KW during the melting process. When the copper had melted, after $\approx$ 90 min., the power was reduced to 2KW to achieve the experimental bath temperature.

An initial oxygen sample was withdrawn from the melt and logged in the record book. The lance was then lowered to $\approx$ 0.1 cm from the liquid surface. Gas flow was changed over to oxygen at a desired flow rate and, as soon as the oxide patch appeared on the bath surface, a timer was started. Samples were withdrawn at convenient time intervals, over the course of an experiment and quenched in water.

For surface velocity studies, fine alumina chips ($\approx$ 0.15 cm long) were added to the melt, through a quartz tube, at the point of jet impingement. High speed motion pictures (300 frames·sec$^{-1}$) were made of the spreading of these particles for later analysis. The average time for an oxidation experiment was 350 sec.

At the end of an oxidation experiment, the oxygen was switched off, and argon at a rate of 2 litres · min$^{-1}$ was passed over the melt in
preparation for deoxidation with hydrogen. After purging for 10 min., an
initial sample was taken. Then, with the timer zeroed, hydrogen at a desired
flow rate was passed over the melt. Filming and sampling techniques were
as before, except that no alumina chips were added. Degassing experiments
lasted, on average, 1000 sec.

2.4.2. SILVER EXPERIMENTS

Clean, weighed, silver billets, of ~ 400 gm mass, were placed in
50 cm³ capacity alumina crucibles, and positioned in the susceptor. Oxidation
and deoxidation experiments were performed in the same fashion as
for copper. Motion pictures (32 frames • sec⁻¹) were made during a run at
timed intervals, as before. There were no surface velocity studies performed.

2.4.3. EXPERIMENTS WITH SULPHUR

Powdered cuprous sulphide, of 99.9% purity, was added in weighed
proportions to molten copper to give starting compositions of 0.01%, 0.05%,
0.1% and 0.5% by weight sulphur. Oxidation, deoxidation and surface velocity
studies were then conducted as for pure copper. Samples were analysed for
both oxygen and sulphur.

2.4.4. EXPERIMENTS WITH Se, Te, Cu₂S and Cu₂O SOLIDS

Weighed samples of Se, Te, Cu₂S and Cu₂O were held in baskets fabri-
cated from pure copper wire, and these baskets were suspended over molten
pure copper. When partially immersed, their dissolution behaviour was
recorded by high speed photography. No samples were taken.

2.5. ANALYSIS

2.5.1. SAMPLE PREPARATION

Quenched samples of both copper and silver were first filed to remove any adherent alumina or silica pieces from the sample tubes. Then, the samples were cleaned with 50% HNO₃ for 15 minutes, followed by a water and ethyl alcohol wash.

Each 1 to 2 gm sample was trimmed to be approximately 0.06 gm for oxygen analysis and ≥ 1 gm for sulphur analysis, because of limitations imposed by the upper detectable limits of the LECO analyses.

2.5.2. OXYGEN AND SULPHUR

Weighed samples were analysed using LECO oxygen and sulphur analysers, having accuracies of ± 10 ppm and ≈ ± 2% respectively. The small oxygen samples used were found to be reproducible within the larger initial samples taken.

2.5.3. OXIDE PATCH SIZE AND SURFACE VELOCITY

The high-speed motion pictures obtained during experiments were analysed using a Model 900-B MOTION ANALYSER from Photographic Analysis Ltd. This consisted of a 16 mm variable speed movie projector and magnifying screen, with an X-Y calibrating recorder having digital display.
For surface velocity studies, the X-Y recorder was first calibrated for the crucible diameter at the liquid surface. Then, the X-Y coordinates for a given pellets' trajectory were recorded, from which surface velocities could be determined.

Oxide patch surface areas were based on a statistical analysis of patch diameters, measured by the recorder, for a given sequence of frames in a film. The oxide patch, as observed from above, appeared uniformly circular.
3. RESULTS

3.1. COPPER OXIDATION

3.1.1. OBSERVATIONS

When oxygen was blown onto the molten copper surface, a circular oxide patch was observed to form instantaneously on the liquid at the point of jet impingement, and this patch was seen to increase in area during an experiment. Figure 3.1 shows the liquid copper surface both before and after oxygen is introduced; the growth of the oxide patch with time is shown in Fig. 3.2. Surface motions were identified both through ripple formation on the clear portion of the surface (away from the patch) and tongues of oxide spreading radially outward from the oxide patch, as can be seen in Fig. 3.2.

The thickness of the oxide patch could not be measured, but it should not be more than 1 to 2 mm, as this was the approximate distance of the lance tip above the liquid surface.

During preliminary tests, it was noted that the bulk temperature of the molten copper rose approximately 25°C during oxidation. Taking this into account, the temperature for each experiment was controlled so that the average temperature during oxidation was 1220°C ± 10°C, a reference temperature for which the interfacial oxygen concentration is known. In Fig. 3.3 a typical time-temperature curve is presented, showing the rise in temperature during oxidation.
FIGURE 3-1 Interfacial turbulence during oxygen absorption by molten copper.
(a) copper surface prior to oxygen introduction; (b) copper surface during oxidation. Note distortion of crucible rim reflection. Gas flow rate is 1500 cm$^3$ min$^{-1}$. 
FIGURE 3.2 Growth of oxide patch on molten copper during an experiment. (a) $t = 40$ sec., oxide patch area = 2.02 cm$^2$; (b) $t = 183$ sec., oxide patch area = 3.21 cm$^2$. Note tongues of oxide spreading from edge of patch. Gas flow rate is 1500 cm$^3$ min$^{-1}$. 
FIGURE 3-3

Temperature-time plot for Run 41, showing temperature rise during oxidation. All other runs exhibited similar behaviour.
Early in the molten stage prior to each experiment, the surface of the molten copper was seen to twitch, in a random fashion, for approximately ten minutes. On attaining thermal equilibrium, the surface twitching ceased, leaving the molten copper surface clean and smooth. The cause of this twitching is not known, but it could likely be due to the evaporation of a surface film or the desorption of a surface-active species from the bulk of the liquid.

3.1.2. OXIDATION RATES

Oxidation experiments were performed on molten copper samples using pure oxygen jets with flow rates of 500, 1000, 1500, and 2000 cm$^3$ min$^{-1}$. Other variables considered were changes in lance height and presence of dissolved silicon and sulphur. The experiments were not continued to the oxygen saturation point of 2.1 wt % because as saturation was approached, the oxide patch shape became markedly irregular, making area measurements difficult. Also, it was found that the lance tended to become plugged with solid copper oxide as the saturation value was approached. Typical experimental rates of oxygen absorption are shown in Figs. 3.4 and 3.5. In Fig. 3.5 the reproducibility of oxidation experiments at an oxygen flow rate of 1500 cm$^3$ min$^{-1}$ is shown. Similar behaviour was observed at other oxygen flow rates. From the slopes of the lines in Figs. 3.4 and 3.5, the oxidation rates for all copper experiments were calculated (moles oxygen per sec.), and are presented in Table II, together with the maximum possible oxygen absorption rates based on the flow rate of oxygen through the lance.
FIGURE 3.4  Concentration of oxygen in copper as a function of time for four different oxygen blowing rates.
FIGURE 3.5 Oxidation-time relationship for pure copper experiments at 1500 cm$^3$ min$^{-1}$ oxygen blowing rate.
<table>
<thead>
<tr>
<th>Run Number</th>
<th>Oxygen Flow Rate (cc/min)</th>
<th>Approximate Lance Height (mm)</th>
<th>Flux of Oxygen to surface ( F_1 ) x 10^4 moles 0 sec</th>
<th>Flux of Oxygen Absorbed by Cu ( F_2 ) x 10^4 moles 0 sec</th>
<th>Difference ( (F_1 - F_2) ) x 10^4 moles 0 sec</th>
<th>Impurity Added (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>500</td>
<td>1</td>
<td>7.44</td>
<td>5.36</td>
<td>2.08</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>1000</td>
<td>1</td>
<td>14.89</td>
<td>12.82</td>
<td>2.07</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>19.7</td>
<td>2.62</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>20.04</td>
<td>2.28</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>2000</td>
<td>1</td>
<td>29.76</td>
<td>25.2</td>
<td>4.56</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>2000</td>
<td>1</td>
<td>29.76</td>
<td>24.8</td>
<td>4.96</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>1500</td>
<td>10</td>
<td>22.32</td>
<td>18.9</td>
<td>3.42</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>1500</td>
<td>20</td>
<td>22.32</td>
<td>17.88</td>
<td>4.34</td>
<td>-</td>
</tr>
<tr>
<td>37</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>17.68</td>
<td>4.64</td>
<td>-</td>
</tr>
<tr>
<td>41</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>19.38</td>
<td>2.94</td>
<td>0.002% Si</td>
</tr>
<tr>
<td>43</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>15.53</td>
<td>*6.79</td>
<td>0.1% S</td>
</tr>
<tr>
<td>44</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>11.37</td>
<td>*10.95</td>
<td>0.5% S</td>
</tr>
<tr>
<td>45</td>
<td>1500</td>
<td>1</td>
<td>22.32</td>
<td>20.99</td>
<td>+1.33</td>
<td>0.01% S</td>
</tr>
<tr>
<td>51</td>
<td>1500</td>
<td>~1</td>
<td>22.32</td>
<td>20.46</td>
<td>+1.26</td>
<td>0.05% S</td>
</tr>
</tbody>
</table>

* not considering \( O_2 \) lost as \( SO_2 \)

+ considering \( O_2 \) lost as \( SO_2 \)
3.1.2.1. BULK-PHASE MIXING

Mixing of the bulk copper phase was provided by both the inductive field and the spontaneous turbulence generated during oxidation. To determine if the bulk copper phase was well-stirred, and hence if the bath oxygen concentration was homogeneous, the oxygen supply was turned off after 256 sec. during an experiment, and sampling was continued to determine both the change in oxygen concentration and the time taken to reach constant composition. The results are shown in Fig. 3.6.

3.1.2.2. SILICON EXPERIMENTS

The role of interfacial silicon in reducing the oxidation rate of molten copper was clearly shown by Glen and Richardson\(^{18}\). To minimize any possible effects due to silicon contamination, the copper billets used in these experiments were treated with a 10% HF solution prior to use, as described in sec. 2.3.1. The silicon content of the as-cast material was found to be 0.001%\(^{44}\). To prevent contamination from the silica sampling tubes, that portion of the tube in contact with the molten copper was coated with alumina, as described in sec. 2.1. This film was found to be adherent and protective.

To determine the effect of dissolved silicon on the oxidation of copper in the present experiments, 0.002% silicon was added to 99.999% pure copper (Table I) in Run 41. The results are given in Fig. 3.7 and Table II.
FIGURE 3.6 Oxidation-time plot for Run 28 at 1500 cc min\(^{-1}\) O\(_2\). Oxygen shut off at 256 sec. to check on bulk stirring properties.
FIGURE 3.7 Comparison of the oxidation-time relationship for Run 25 (no Si added) and Run 41 (20 ppm Si added); both at 1500 cc min⁻¹ oxygen flow rate.
FIGURE 3.8 Oxidation-time relationship for copper containing dissolved sulphur at 1500 cc min$^{-1}$ oxygen flow rate.
3.1.2.3. SULPHUR EXPERIMENTS

Four experiments were performed with varying initial sulphur contents of 0.5%, 0.1%, 0.05%, and 0.01% to determine the effect of dissolved sulphur on the oxidation rate for molten copper. The chosen oxygen flow rate was 1500 cm$^3$ min$^{-1}$, and both oxygen and sulphur analyses were performed. In Fig. 3.8 the results of these experiments are presented, together with an average oxidation rate for sulphur-free copper.

3.1.3. SURFACE VELOCITY STUDIES

During oxidation of the copper samples, alumina particles were dropped onto the bath surface near the point of jet impingement to permit rough measurements of surface velocity. These particles were observed to spread radially outward at a very rapid rate. Analysis of motion picture films showed that the particles moved with a reasonably constant velocity across the bath surface until they approached the crucible rim, where the velocity rapidly decreased. At no time did the trajectory of the particles vary from a straight-line path radially across the surface. Those particles collecting near the rim of the crucible were seen to move only in small, tight circles at very slow rates. Results of these surface velocity studies are presented in Figs. 3.9 through 3.12, showing surface velocity as a function of radial distance from the lance. In all cases the lance position is at zero cm and the crucible rim is at roughly 2.8 cm.
FIGURE 3·9 Surface velocity as a function of Radial distance from lance. Runs 22 and 23. Vertical lines show edge of oxide patch.
FIGURE 3.10  Surface velocity as a function of Radial distance from lance. Runs 24 and 26. Vertical lines show edge of oxide patch.
FIGURE 3.11 Surface velocity as a function of Radial distance from lance. Runs 27 and 29. Vertical lines show edge of oxide patch.
FIGURE 3.12 Surface velocity as a function of Radial distance from lance. Runs 30 and 41. Vertical lines show edge of oxide patch.
3.1.4. OXIDE PATCH AREAS

Oxide patch areas were measured from the same sequence of motion picture film used to determine surface velocities. For bath oxygen contents up to approximately 1.5 wt %, the oxide patch was uniformly circular in appearance, as seen in Fig. 3.1. Sections of the patch were observed to become detached and to dissolve as they spread across the surface. At bath oxygen contents of more than 1.5 wt %, tongues of oxide were seen to spread out from the patch across the bath surface, making patch area measurements uncertain. All areas were measured at fifteen time intervals during a given film sequence, and these results were statistically analysed. The measured areas had a standard deviation of less than 10% within each group. Results for these area measurements are presented graphically in Figs. 3.13 and 3.14.

3.1.5. SURFACE BLOCKAGE STUDIES

Experiments were performed to determine the area through which the majority of oxygen mass-transfer occurs, so that the surface area term in the mass transfer equation could be correctly evaluated. A centred 2.75 cm dia. hole was bored in a 5.0 cm dia. alumina disc, and this disc was carefully placed on the molten copper surface as shown in Fig. 3.15. Oxygen was then jetted onto the open surface in the centre, and the rate of oxygen absorption from jets of 1000 and 1500 cm$^3$ min$^{-1}$ oxygen flow was measured as before. The results are given in Table III.
FIGURE 3.13 Oxide patch area as a function of copper bath oxygen concentration for four oxygen flow rates.
FIGURE 3.14 Oxide patch area as a function of copper bath oxygen concentration for four initial sulphur concentrations at 1500 cm$^3$ min$^{-1}$ oxygen flow rate.
FIGURE 3-15  Top view of apparatus for reduced surface area experiments, showing configuration of the alumina disc.
### TABLE III

**EXPERIMENTAL RESULTS FOR OXYGEN UPTAKE RATES OVER REDUCED SURFACE AREA**

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Oxygen Flow Rate (cm³/min)</th>
<th>Surface Area (cm²)</th>
<th>Oxygen Uptake Rate (moles O/sec) × 10⁻⁴</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1000</td>
<td>25</td>
<td>12.82</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>1000</td>
<td>5.94</td>
<td>10.74</td>
<td>16.2</td>
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<tr>
<td>24</td>
<td>1500</td>
<td>25</td>
<td>19.7</td>
<td></td>
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<td>25</td>
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</tr>
<tr>
<td>36</td>
<td>1500</td>
<td>5.94</td>
<td>17.87</td>
<td>10.0</td>
</tr>
</tbody>
</table>
3.2. SILVER OXIDATION

3.2.1. OBSERVATIONS

Unlike the oxidation of molten copper, virtually no surface motions were observed to occur during the oxidation of the molten silver samples. The only detectable surface motions were the slight twitchings and circular stirrings of less than 5 cm sec\(^{-1}\) velocity, as was observed for copper, just after melting had occurred. On attaining thermal equilibrium the bulk of these motions disappeared, leaving the surface clean and mirror smooth. Figure 3.16 shows the liquid silver surface both before and after oxidation had begun.

All experiments were performed at a controlled temperature of 1100°C ± 10°, and a typical heating curve is shown in Fig. 3.17. As molten silver does not have a stable oxide at this temperature, an oxide patch similar to that for molten copper, was not expected to form during the oxidation stage. Discrete surface patches, however, were observed to form on some of the molten silver samples. These patches were likely composed of oxidized impurities that are insoluble in the molten silver, but, as the level of contamination of the silver was small\(^4\), the patches should not have contained much material. In any event, these patches were easily cleared to the edge of the liquid surface using a probe, and, because the general surface motions were slight, patches tended to remain at the edge of the liquid surface.
FIGURE 3.16  Surface of molten silver during oxidation. (a) Argas only; (b) oxygen gas at 1500 cm³ min⁻¹ flow. Note absence of interfacial motions as seen in crucible rim reflection.
FIGURE 3.17 Time-temperature plot for Silver Run 4 showing experimental temperature. All other silver runs give similar results.
FIGURE 3.18

Oxidation time relationship for silver experiments for two oxygen flow rates.
TABLE IV

ABSORPTION AND MASS TRANSFER
DATA FOR LIQUID Ag OXIDATION

<table>
<thead>
<tr>
<th>Run Number</th>
<th>$c_o^b$ (moles)</th>
<th>$\dot{n}$ Delivered moles 0/sec $\times 10^4$</th>
<th>$\dot{n}$ Absorbed moles 0/sec $\times 10^4$</th>
<th>$k_o \times 10^3$ cm/sec</th>
</tr>
</thead>
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<tr>
<td>4</td>
<td>0.0075</td>
<td>22.32</td>
<td>0.388</td>
<td>4.02</td>
</tr>
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<td></td>
<td>0.0167</td>
<td>22.32</td>
<td>0.388</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>0.0162</td>
<td>22.32</td>
<td>0.388</td>
<td>3.53</td>
</tr>
<tr>
<td></td>
<td>0.0227</td>
<td>22.32</td>
<td>0.388</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>0.0206</td>
<td>22.32</td>
<td>0.388</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>29.76</td>
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<td></td>
</tr>
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<td></td>
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<td>7.43</td>
</tr>
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<td>29.76</td>
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</tr>
<tr>
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<td>0.0117</td>
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<td>0.408</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>0.0118</td>
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<td>0.408</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>0.0139</td>
<td>29.76</td>
<td>0.408</td>
<td>2.77</td>
</tr>
<tr>
<td>7</td>
<td>0.001</td>
<td>22.32</td>
<td>0.423</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>22.32</td>
<td>0.423</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>0.007</td>
<td>22.32</td>
<td>0.423</td>
<td>2.64</td>
</tr>
<tr>
<td></td>
<td>0.009</td>
<td>22.32</td>
<td>0.423</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>22.32</td>
<td>0.423</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>22.32</td>
<td>0.423</td>
<td>3.36</td>
</tr>
</tbody>
</table>
3.2.2. OXIDATION RATES

Oxidation experiments were performed on molten silver baths using pure oxygen jets having flow rates of 1500 and 2000 cm$^3$ min$^{-1}$. Experiments were continued for approximately 350 sec. in each case. Owing to difficulties encountered during the analysis of the samples, only four of the eight experiments attempted proved to be reasonably successful.

Oxygen uptake rates for the silver experiments are shown in Fig. 3.18. Oxidation rates were determined from the slopes of the lines in Fig. 3.18 and are presented in Table IV, together with the total flux of oxygen delivered to the bath surface.

3.3. COPPER DEOXIDATION

3.3.1. OBSERVATIONS

In preparation for deoxidation experiments, each sample was first oxidized using an oxygen jet of 1500 cm$^3$ min$^{-1}$ flow for a period of approximately 350 seconds. Then, the apparatus was purged with argon gas at 1500 cm$^3$ min$^{-1}$ for approximately 800 sec. to remove excess oxygen from the furnace atmosphere before introducing the hydrogen gas. During the inert gas purge, only minor stirring motions were observed which were likely due to the stirring effect of the inductive field.

When hydrogen was jetted onto the liquid copper surface, instantaneous surface flow directed to the point of jet impingement was observed. Pieces of debris were seen to collect beneath the lance and to spin around rapidly. For the most part, these surface motions appeared to be highly disorganized,
Interfacial turbulence during the deoxidation of molten copper with hydrogen. (a) copper surface before deoxidation started; (b) copper surface after deoxidation started. Note distortion of crucible rim reflection.
as opposed to the radial flow outward seen in copper oxidation. These same random motions were observed by Small and coworkers\textsuperscript{55} in their study of hydrogen absorption by copper baths containing dissolved oxygen. Because of the randomness of these surface motions, surface velocity measurements were not attempted. However, the velocities did appear to be in the range of 10 to 15 cm sec\textsuperscript{-1}.

The pieces of debris collecting beneath the lance were of irregular shape and did not appear to change in size during an experiment. These pieces are likely composed of non-reducible oxides such as silica and alumina. When these pieces were pushed from beneath the lance by a probe, they were observed to recollect quickly at the point of jet impingement. As this patch tended to obscure most of the surface motions near the lance, the only evidence of surface stirring was seen as swirls of lighter coloured liquid in the clear portion of the liquid surface. The liquid copper surface both before and after deoxidation had begun is shown in Fig. 3.19; distortion of the crucible rim reflection is evidence of surface motion. For all deoxidation experiments, the bath temperature was maintained at 1220°C ± 10°, as in sec. 3.1.1., and no temperature change during deoxidation was observed.

3.3.2. DEOXIDATION RATES

Using jets of pure hydrogen at flow rates of 1000, 1500, and 3000 cm\textsuperscript{3} min\textsuperscript{-1}, deoxidation experiments were performed on molten copper samples containing varying amounts of dissolved oxygen. The average duration of an experiment was 1200 sec, with one lasting for 5400 sec. to essentially zero
FIGURE 3.20 Deoxidation-time relationship for copper Runs 31 and 32.
FIGURE 3.21

Deoxidation-time relationship for copper experiments at two hydrogen flow rates.
FIGURE 3-22 Deoxidation-time relationship for copper Run 50, showing regions of gas-phase and liquid-phase control.
TABLE V
EXPERIMENTAL RESULTS FOR OXYGEN FLUXES DURING DEOXIDATION OF COPPER

<table>
<thead>
<tr>
<th>Run Number</th>
<th>H₂ Flow Rate (cm³/min)</th>
<th>Approximate Lance Height (cm)</th>
<th>Flux of H₂ to Surface (moles/sec) × 10⁴</th>
<th>Flux of O from (moles/sec) × 10⁴</th>
<th>Run Duration (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>Ar Only</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1200</td>
</tr>
<tr>
<td>32</td>
<td>1000</td>
<td>1</td>
<td>7.44</td>
<td>1.80</td>
<td>1200</td>
</tr>
<tr>
<td>33</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>2.20</td>
<td>1000</td>
</tr>
<tr>
<td>37</td>
<td>3000</td>
<td>1</td>
<td>22.32</td>
<td>2.09</td>
<td>1200</td>
</tr>
<tr>
<td>38</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>1.99</td>
<td>2010</td>
</tr>
<tr>
<td>39</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>2.14</td>
<td>800</td>
</tr>
<tr>
<td>40</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>2.68</td>
<td>1000</td>
</tr>
<tr>
<td>41</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>1.42</td>
<td>1000</td>
</tr>
<tr>
<td>* 43</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>4.3</td>
<td>1000</td>
</tr>
<tr>
<td>* 45</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>1.63</td>
<td>800</td>
</tr>
<tr>
<td>50</td>
<td>1500</td>
<td>1</td>
<td>11.16</td>
<td>1.7</td>
<td>3000</td>
</tr>
</tbody>
</table>

* OXYGEN ALSO LEAVING AS SO₂ BUT IN AN UNKNOWN AMOUNT BECAUSE SULPHUR ANALYSIS NOT POSSIBLE.
oxygen content. In each case the lance height was maintained at approximately 10 mm above the liquid surface. The observed deoxidation rates are presented graphically in Figs. 3.20 to 3.22 as a function of experimental time, and from the slopes of these lines, the deoxidation rates (moles O per sec.) as presented in Table V were calculated.

3.4. SILVER DEOXIDATION

3.4.1. OBSERVATIONS

Deoxidation of molten silver samples was performed in a manner similar to that described for molten copper in sec. 3.3.1. During the inert gas purge only slight stirring motions were observed and were presumably due to the stirring effect of the inductive field. As described in sec. 3.2.1., some surface patches were observed during oxidation, but these were quickly removed (v 40 sec.) during deoxidation. When hydrogen gas was jetted onto the molten silver bath, surface flow directed from the edge of the crucible towards the point of jet impingement was observed to occur. This flow was punctuated by rapid, randomly directed twitchings of the whole surface, making velocity measurements difficult, much the same as was observed for copper. Rough estimates indicate that average velocities were in the range of 10 to 15 cm sec\(^{-1}\). After about 90 sec., a film of what appeared to be very fine bubbles formed on the surface and disappeared from the centre radially outwards. On removal of this film, the surface appeared clean and bright and motions ceased. It is not known of what this film was composed. Throughout the deoxidation some gas bubbling in the liquid was observed to
FIGURE 3.23 Interfacial turbulence during the deoxidation of molten silver with hydrogen. (a) molten silver surface before deoxidation started; (b) molten silver surface after deoxidation had begun. Note distortions in the crucible rim reflection and the lance tip reflection.
FIGURE 3.24 Deoxidation-time relationship for liquid silver experiments at two hydrogen flow rates.
occur, and that by single, random bubbles, with only slight surface disruptions. In Fig. 3.23, the molten silver surface both before and after deoxidation has begun is shown.

3.4.2. DEOXIDATION RATES

Using jets of pure hydrogen at flow rates of 1500 and 3000 cm sec\(^{-1}\) the deoxidation rates for molten silver were measured. The lance height was maintained at 10 mm throughout each experiment, and the bath temperature was controlled at 1100°C, with no observable fluctuations during deoxidation. Experiments were continued for up to 500 sec. and none went to complete deoxidation. Owing to difficulties encountered in analysis, only four of the eight experiments attempted provided satisfactory results. The observed deoxidation rates are presented graphically in Fig. 3.24, and the approximate rates (moles O per sec.) were calculated from the slopes of the lines in Fig. 3.24 and are presented in Table IX.

3.5. SOLID DISSOLUTION EXPERIMENTS

3.5.1. OBSERVATIONS

Weighed samples of commercially pure Cu\(_2\)O, Cu\(_2\)S, selenium, and tellurium were suspended in pure copper baskets, and lowered to the molten copper surface by means of a copper wire. The ensuing events were observed and photographed through the viewing port using a high-speed camera at 200 frames per second. A piece of Cu\(_2\)S suspended above the bath surface can be seen in
FIGURE 3.25 Interfacial turbulence during the dissolution of solid Cu₂S (a) before contacting surface; (b) ~ 2 sec. after contacting surface. Note distortions in crucible rim reflection.
FIGURE 3.26 Interfacial turbulence during the dissolution of solid surface active agents. (a) Cu₂O; (b) Se; (c) Te. Note distortions in the crucible rim reflection.
Fig. 3.25(a). This photo also shows the relative quiescent nature of the molten copper just prior to introducing the Cu$_2$S sample, as witnessed by the reflection of the crucible rim.

When contact with the copper was initiated, the surface of the bath was observed to become highly agitated as shown in Fig. 3.25(b). The reflection of the crucible rim was distorted by the presence of ripples and waves formed as a result of surface motion, directed radially away from the solid Cu$_2$S, induced by the dissolution of the Cu$_2$S solid. White patches visible on the bath surface are areas of molten Cu$_2$S (mp. 1130°C), which are spreading away from the solid and dissolving in the copper. Complete dissolution of a 4 gm piece of Cu$_2$S required only about 8 seconds. No surface velocities were measured due to experimental difficulties. Based upon the previous values obtained during copper oxidation (sec. 3.1.3.), however, the velocities encountered during Cu$_2$S dissolution appear to be in the range of 20 to 40 cm sec$^{-1}$. Similar experiments were conducted for Cu$_2$O, selenium and tellurium solid additions, since these materials are known to lower the surface tension of molten copper$^{11}$, as discussed in sec. 1.2.1. The pictorial results of these experiments are shown in Fig. 3.26. All solids melted and spread rapidly across the surface, but, in the case of selenium and tellurium, the surface was quickly covered with a film of the molten metal, obscuring further surface motions. Fume formation was also a problem, and so these latter experiments were less satisfactory.
4. DISCUSSION

4.1. COPPER OXIDATION

4.1.1. OXIDATION RATES

As seen in Figs. 3.4 and 3.5, the oxidation rates for molten copper are constant at all the flow rates studied. The reproducibility of oxidation rates at the oxygen flow rate of 1500 cm$^3$ min$^{-1}$ is shown in Fig. 3.5, and these results indicate good agreement among the various experiments. Changes in the flow rate of oxygen delivered to the bath surface are seen to be matched by identical changes in the oxygen absorption rate, as is evident in Table II. Also, the rates of oxygen delivery to the bath surface and that absorbed by the copper are seen to be similar. Thus, the oxygen absorption rate for molten copper, using a low-momentum oxygen jet, varies directly with the input oxygen flow rate for the experimental conditions described. This is an effect indicative of starvation mass transfer.

In Runs 29 and 30, the lance height above the surface was increased by a factor of 10 and 20 respectively to determine the effect of increased lance height on oxygen absorption rates. From a comparison of the above rates to that of Run 25 in Table II, the observed differences are only 5 and 10 respectively, clearly not a major effect. These small differences in absorption rate on increasing lance height are most likely due to oxygen losses to the freeboard. Thus, the effect of changes in lance height, over the range studied, is small.
4.1.1.1. BULK-PHASE MIXING

From Fig. 3.6, it can be seen that only 25 sec. are needed, from the time of oxygen shut off, to reach constant bath composition. The slight increase in oxygen concentration observed, amounting to only 7.3% of the value prior to shut-off, is probably due to continued oxygen absorption from the freeboard as well as to departures from perfect mixing in the bulk liquid phase. Since only 0.06% oxygen is absorbed after oxygen shut-off, it is clear there are no gross errors in assuming the bulk copper phase to be well-stirred.

4.1.1.2. SILICON EXPERIMENTS

The experiments of Glen and Richardson\textsuperscript{18} clearly demonstrated the severe retardation in oxygen absorption rates due to blockage of adsorption-reaction sites by interfacial films of silica. This is an effect that would apply especially to their experiments, where small droplets of molten copper were levitated in a slowly flowing gas stream of low oxygen partial pressure. Being surface active, a few p.p.m. of dissolved silicon would naturally concentrate in mono-layer proportions over the whole surface, and present a layer of silicon to the oxidizing gas. Thus a coherent network of silica is easily formed which prevents further oxidation, as shown in Fig. 1.11. Because of the dynamic nature of the present experiments, where oxidation occurs at a point source resulting in rapid surface spreading away from the point of jet impingement and in a high degree of surface agitation, it seems unlikely that such interfacial silica films could exist and retard the
oxidation rate. The results given in Fig. 3.7 and Table II show that added silicon does not in fact retard the oxidation rate of molten copper in the present experiments. Further to this, a recent paper by Forster and Richardson mentions that interfacial silica films can be removed from the surface of molten copper by molten Cu₂O, which forms a soluble product with the silica. Since molten Cu₂O is present in our experiments, it is unlikely that any coherent silica films could exist at the interface and adversely affect the copper oxidation rates. The above results indicate that small amounts of dissolved silicon have little effect on the oxidation of molten copper when large-scale surface spreading occurs. Thus, the procedures taken to ensure a low silicon content in the melt may have been unnecessary.

4.1.1.3. SULPHUR EXPERIMENTS

Dissolved sulphur is another surface-active solute which has much the same effect on the interfacial tension of molten copper as does oxygen. These experiments were undertaken to determine if the oxidation rate of molten copper could be altered by the presence of dissolved sulphur in a manner similar to the effect of dissolved oxygen on nitrogen absorption rates in molten iron. From Fig. 3.8 and Table VI it can be seen that as the initial sulphur content increases, the corresponding copper oxidation rate decreases. It is worthy of note that the oxidation rates show the same constant behaviour as those for pure copper. Moreover, the rates of sulphur loss due to oxidation are also linear. By comparison with the oxidation results for sulphur-free copper in Table II, one can see that a large difference between delivered oxygen flux and absorbed oxygen flux exists for
<table>
<thead>
<tr>
<th>Run Number</th>
<th>% S Added as Cu₂S</th>
<th>Delivered oxygen x 10⁴ moles O₂/sec</th>
<th>Absorbed oxygen x 10⁴ moles O₂/sec</th>
<th>Difference [Deliv.-Abs.] x 10⁴ moles O₂/sec</th>
<th>Oxygen Lost as SO₂ x 10⁴ moles O₂/sec</th>
<th>Corrected Absorbed oxygen rate x 10⁴ moles O₂/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>0.1</td>
<td>22.32</td>
<td>15.58</td>
<td>6.79</td>
<td>1.27</td>
<td>16.85</td>
</tr>
<tr>
<td>*44</td>
<td>0.5</td>
<td>22.32</td>
<td>11.37</td>
<td>10.95</td>
<td>9.62</td>
<td>21.99</td>
</tr>
<tr>
<td>45</td>
<td>0.01</td>
<td>22.32</td>
<td>20.99</td>
<td>1.33</td>
<td>0.0746</td>
<td>21.065</td>
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<tr>
<td>51</td>
<td>0.05</td>
<td>22.32</td>
<td>20.46</td>
<td>1.86</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* SO₂ bubbling was observed during this experiment and may have affected the absorption rates indicated in this table.
initial sulphur contents of 0.5% and 0.1%, with only minor differences occurring for the lower sulphur contents. However, when the amount of oxygen lost as $\text{SO}_2$ gas is taken into account, as in Table VI, the discrepancies between delivered and absorbed oxygen fluxes are minimized for all but the 0.1% sulphur case. In this instance, the cause of the discrepancy is most likely due to errors in the sulphur analysis. Sulphur dioxide gas bubbling was observed at only the largest initial sulphur content of 0.5%.

Overall, the effect of small amounts of dissolved sulphur on the oxidation rate of molten copper is negligible. Discrepancies between the delivered and absorbed oxygen fluxes, when dissolved sulphur is present, are due to oxygen loss as $\text{SO}_2$ gas from the interfacial regions of the copper bath.

4.1.2. SURFACE VELOCITY STUDIES

On examination of Figs. 3.9 through 3.12 it can be seen that velocity profiles for the particles can be divided into three regions:

(a) Oxide patch region - particle velocities are low in this region likely because the particles are accelerating and may be hampered by oxide viscosity effects. Near the edge of the oxide patch, the particles accelerate to the observed velocity maxima. The velocity of the liquid copper beneath the oxide is unknown, but is likely the same as for the clear surface region.

(b) Clear surface region - particles move at constant velocity through this region up to a radial position of 1.4 to 1.8 cm, where deceleration
FIGURE 4.1  Flow pattern in liquid caused by an impinging gas jet. Note stagnant areas, labelled S. (Davenport et al.)
This same type of flow pattern should exist for the interfacial turbulence caused by low momentum oxygen jet impinging on liquid Cu, Sn, and Fe.
begins. This region experiences some rippling, which may affect the observed velocities.

(c) Crucible rim region - here particles experience rapid deceleration to near zero velocity. Minor random stirring motions of less than 5 cm sec\(^{-1}\) were observed. Apparently this region is stagnant, and it extends outwards from the crucible rim for approximately 0.8 cm. The existence of this stagnant region is likely a manifestation of the stirring pattern in the liquid, which is probably the same as that shown schematically in Fig. 4.1 (where stagnant areas are labelled S). Higher values of \(\sigma_{\text{Cu}}\) in the stagnant region may also contribute to the deceleration of the particles.

Recorded velocity maxima range from 20 to about 35 cm sec\(^{-1}\) for all the experiments. For the low momentum jets employed, observed surface velocities do not appear to vary with either oxygen flow rate or lance height. Though particle motions were too erratic for any degree of precision to be obtained, it is felt that the above velocity range is representative for all experiments.

Velocity maxima were plotted against bath oxygen concentration and are shown in Fig. 4.2. From this it appears that the surface velocity decreases slightly on increasing bath oxygen content, as is also seen in Figs. 3.9 to 3.12. This decrease in velocity is likely due to decreases in the size of the clear surface region for unimpeded particle acceleration, caused by increases in oxide patch area on increasing bath oxygen content (see sec. 4.1.3.). Also, decreases in the interfacial tension driving force for surface spreading (sec. 1.2.2.) on increasing bath oxygen content could account for the observed decrease in velocity maximum on increasing bath
FIGURE 4·2 Maximum surface velocity as a function of copper bath oxygen concentration.
oxygen content. The mean velocity maximum was found to be 26.1 cm/sec, with a standard deviation of 21.1%. The straight line in Fig. 4.2. is obtained from a linear regression analysis of the data.

Brimacombe and Weinberg observed spreading velocities for oxide particles on molten copper ranging from 50 to 100 cm sec$^{-1}$. These values are 50% larger than velocities observed in the present experiments, but as the earlier measurements were more crude in nature, having been made without the aid of the equipment described in sec. 2.5.3, this discrepancy may not be surprising.

4.1.3. OXIDE PATCH AREAS

Oxide patch areas were measured so as to characterize the area involved in oxygen transport to the bulk copper phase. As seen in Figs. 3.13 and 3.14, values of oxide patch area generally increase on increasing oxygen flow rate. With the exception of experiments at an oxygen flow rate of 2000 cm$^3$ sec$^{-1}$, where problems in area measurement arose, oxide patch areas also appear to increase with increasing bath oxygen content in a linear fashion.

Figure 3.14 shows the effect of dissolved sulphur on the oxide patch areas. The observed areas are all less than those for sulphur-free copper at the same oxygen flow rate. At an initial sulphur content of 0.5%, the bath surface was disrupted by SO$_2$ gas bubbling, and so oxide patch areas here cannot be correlated to the sulphur-free cases. In these experiments with sulphur, a reduction in oxide patch area due to the presence of dissolved sulphur is not a surprising development owing to SO$_2$ elimination.
from the bath. Under these conditions, the surface regions of the copper are unable to saturate in oxygen, especially at the edge of the oxide patch, allowing for a lesser degree of surface coverage.

4.1.4. SURFACE BLOCKAGE STUDIES

From the results presented in Table III, it is clear that only slight differences in oxygen absorption rate occur when the bath surface area is reduced by about 76%. As a result, oxygen transport to the bulk copper phase can be considered to occur predominantly in the area described by the oxide patch. This area will be used to calculate liquid-phase mass transport coefficients for oxygen.

4.1.5. MASS TRANSFER COEFFICIENTS

Using oxygen uptake rates and oxide patch areas previously determined, mass transfer coefficients for oxygen in the molten copper were calculated from Eq. 2, as

\[ \dot{n}_o = k_o A(C_o^i - C_o^b) \quad (2) \]

The rate of oxygen absorption by copper was shown in sec. 1.3.3. to be controlled by liquid-phase oxygen mass transfer.

The interfacial oxygen concentration, \( C_o^i \), was taken from the phase diagram of Johnson 49 at 1220 °C, and was found to be 2.1 wt %. Values of \( k_o \) from Eq. 2 are presented graphically in Figs. 4.3 to 4.5 as a function of bath oxygen content; all exhibit little change in \( k_o \) on increasing bath
FIGURE 4.3  Liquid-phase oxygen mass transfer coefficient as a function of copper bath oxygen concentration. Horizontal line is mean $k_o$ for pure copper experiments using oxygen gas at 1500 cm$^3$/min.
FIGURE 4.4  Liquid-phase mass transfer coefficient ($k_o$) as a function of bath oxygen concentration. The mean value is $k_o = 0.104$ cm/sec, and the straight line is from a linear regression analysis of the data.
FIGURE 4-5 Liquid-phase oxygen mass transfer coefficient as a function of copper bath oxygen concentration showing the effect of dissolved silicon and sulphur. Horizontal solid line is mean \( k_o \) for pure copper experiments using oxygen gas at 1500 \( \text{cm}^3/\text{min} \); horizontal dashed line is from a linear regression analysis of the data for sulphur-bearing copper.
oxygen content. Since the surface velocity decreases by only about 18% during an experiment (sec. 4.1.2.), it is reasonable to assume that the degree of stirring of the copper remains constant during an experiment, and so the constancy of $k_Q$ values is to be expected.

In Fig. 4.4, all the $k_Q$ values for experiments at an oxygen flow rate of $1500 \text{ cm}^3 \text{ min}^{-1}$ using pure copper are presented and show good reproducibility. The straight line is from a linear regression analysis of the data, and the mean $k_Q$ value was found to be $0.104 \text{ cm sec}^{-1}$ with a standard deviation of 11.6%. For comparison purposes, this $k_Q$ value was included in Fig. 4.3 and 4.5 as a horizontal line. With the exception of the experiment at $1000 \text{ cm}^3 \text{ min}^{-1}$ oxygen flow in Fig. 4.3, $k_Q$ values in pure liquid copper do not appear to vary with incident oxygen flow rate. As the surface velocity measurements also show no variation with oxygen flow rate, this fact is not surprising. The scatter shown for the experiments at $2000 \text{ cm}^3 \text{ min}^{-1}$ oxygen flow is a result of difficulties encountered in measuring oxide patch areas at this high flow rate. In Fig. 4.5, the $k_Q$ value for pure copper was found to compare favourably with those obtained from experiments involving dissolved sulphur and silicon, as

$$k_Q(S_i) = 0.099 \text{ cm sec}^{-1}$$

and

$$k_Q(S) = 0.112 \text{ cm sec}^{-1}$$

Since the observed deviation is only about 7% from the $k_Q$ for pure copper, it is apparent that, in a system displaying large-scale surface spreading, low levels of surface-active solute contamination have no discernable effect on oxygen mass transfer in liquid copper.
The relevant literature on copper oxidation, reviewed in sec. 1.3., indicated that the published works differ vastly from the present study in terms of jet flow rate, gas composition, and liquid metal bath size. On the basis of this, it is felt that a meaningful comparison of the results with those from the literature is not possible at this time.

4.2. SILVER OXIDATION

4.2.1. OXIDATION RATES

A small number of silver experiments were performed for comparison to the copper experiments, and these proved to be less satisfactory owing to the difficulties encountered in the analysis for oxygen. From Fig. 3.19, the oxidation of silver is seen to be approximately linear with time for each of the experiments. The oxidation rates (moles O per sec), calculated from the slopes of these lines, are presented in Table IV. Here it is seen that the oxidation rates for molten silver are all virtually the same despite the use of two different oxygen flow rates. On comparison with the oxygen flux to the bath surface, one can see that the oxidation rates are about a factor of 50 times less than the incident oxygen flux. This indicates that a surplus of oxygen is present and that starvation mass transfer does not apply to molten silver oxidation. The rate of oxygen absorption is controlled by transport in the liquid phase, as was the situation for copper.

As mentioned in sec. 3.2.1., some surface patches did appear on the molten silver during oxidation, but as these patches were easily swept away by a probe, it is felt that they did not hinder silver oxidation to any
measurable degree. Because the silver samples were pre-cleaned in the same manner as the copper samples (sec. 2.3.1.) and, since the initial silicon content was low (Table I), it is felt that interfacial silica films are unlikely to have occurred on the molten silver used here.

4.2.2. SURFACE MOTIONS

As mentioned previously, the oxidation of molten silver is not accompanied by any interfacial tension-induced surface flow, apart from the slight inductive field motions of less than 5 cm sec$^{-1}$. This is, at first, surprising since Buttner et al$^{52}$ and Bernard and Lupis$^{13}$ have shown that adsorbed oxygen does lower the interfacial tension of molten silver by as much as 300 dynes cm$^{-1}$ (33%)$^{13}$. Thus, it would appear that a driving force for surface spreading is present even though not of the magnitude observed for molten copper ($\Delta\sigma_{\text{Cu}} \approx 50\%$)$^{11}$. The explanation for the lack of surface spreading during the oxidation of molten silver may lie in the nature of oxygen absorption on molten silver. Richardson$^{8}$ has said that at elevated temperatures (> 900°C), adsorption kinetics are very rapid, and that the equilibrium solute excess at the interface, $\Gamma_s$, occurs virtually instantaneously. For the silver-oxygen system, Bernard and Lupis$^{13}$ have shown that the critical bulk silver-phase oxygen concentration for saturation of the interface with chemisorbed oxygen is only 0.004 wt %, and so can truly be considered an instantaneous process in the present case. Since silver oxide is not known to exist at these temperatures or pressures, it is reasonable to assume that the chemisorbed oxygen forms a monolayer covering the silver surface, and that the surface tension of the molten silver is
lowered uniformly across the surface. Without a local surface tension imbalance occurring, as was the case in the region of the oxide patch on molten copper, surface tension-induced flow will not occur. Even though pure silver eddies can (and likely do) penetrate to the interface, any resulting surface flow will be instantaneously damped out because there is a surplus of oxygen available for adsorption at any time. For molten copper, the oxygen also chemisorbs on the entire surface, but at the same time forms liquid copper oxide (Cu₂O) beneath the lance in a small confined patch. This patch does not cover the entire liquid surface because of constraints imposed by bath oxygen content, interfacial tension differences between the Cu₂O and the Cu (which are also controlled by the bath oxygen content), and oxygen jet flow rate, as discussed before. Thus, a point source of low surface tension exists, and surface flow radially outwards from this point occurs as the Cu₂O spreads and dissolves. The fact that the silver oxidation rates are roughly a factor of 50 times less than those observed for copper is almost certainly a direct result of the lack of interfacial tension-driven flow during molten silver oxidation.

4.2.3. MASS TRANSFER COEFFICIENTS

Because starvation mass transfer does not obtain during the oxidation of molten silver, the oxygen mass transfer coefficient in silver was calculated from Eq. (8), as

\[
\ln \left\{ \frac{c_i^o}{c_i^o - c_b^o} \right\} \frac{1}{c_i^o - c_b^o} \frac{t}{t=0} = -\frac{k_o A}{V} \cdot t
\]
Mass transfer from a pure oxygen jet to liquid silver. The straight line is from a linear regression analysis of the data.
The value for the interfacial oxygen content, $C^1_o$, was taken from the work of Mizikar et al$^{62}$ at 1100°C, and was found to be 0.28 wt %, which agrees with the results from other sources.$^{52,63-65}$ Unlike the situation for molten copper, the area for oxygen mass transfer in the silver experiments was considered to be the whole surface. The results of these calculations are presented in Table IV, and in Fig. 4.6 as a plot of $\ln X$ vs time. As can be seen, the points in Fig. 4.6 for the two flow rates show good agreement, and give an average value for the oxygen mass transfer coefficient of $2.88 \times 10^{-3}$ cm sec$^{-1}$. Because of the scatter of the data in Fig. 3.19 and thus also in Fig. 4.6, it was felt necessary to place error limits on the calculated $k_o$ values as shown by the dashed line in Fig. 4.6. The error in $k_o$ is then $\pm 0.41 \times 10^{-3}$ cm sec$^{-1}$. It is felt that the difficulties encountered in the analysis of the samples were responsible in part for the scatter observed in Figs. 3.19 and 4.6. Since $k_o$ for molten silver does not appear to vary greatly with gas flow rate in the present experiments, it is certain that control of oxygen transport resides in the liquid phase.

A comparison of the experimental oxygen $k_o$ values in silver with those available from the literature is given in Table VII. As was the case for copper, a direct comparison with the present experiments is not possible owing to the use of very high-momentum oxygen jets by the majority of other researchers. Chatterjee et al$^{41}$ used oxygen jets of from 3000 to 56,000 dynes force to achieve $k_o$ values in the range of 0.001 to 0.015 cm sec$^{-1}$. It is interesting to note, however, that the mean $k_o$ obtained here falls in the lower range of the above study. At the lowest jet force, momentum
TABLE VII
COMPARISON OF EXPERIMENTAL k_Q VALUES FOR MOLTEN SILVER
WITH THOSE FROM THE LITERATURE

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>P_0^2 (atm)</th>
<th>Jet force (dynes)</th>
<th>Observed mean k_Q (cm/sec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>1</td>
<td>18 and 24</td>
<td>.00288</td>
<td>Present Work</td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>-</td>
<td>.04 to .09</td>
<td>50</td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>20,000</td>
<td>.01 to .02</td>
<td>34</td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>3,000 to 56,000</td>
<td>.001 to .015</td>
<td>41</td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>~12</td>
<td>.014 to .019</td>
<td>43</td>
</tr>
</tbody>
</table>
transfer to the liquid silver is poor, and the effects of any bulk phase stirring – in Chatterjee's, the bulk phase was stirred by paddle stirrers at 50 rpm – become important in evaluating \( k_o \). Since there is virtually no momentum transfer from the jet in the present experiment, the fact that the observed \( k_o \) value agrees with the lowest obtained by Chatterjee is an indication that the bulk phase stirring is similar for both experimental conditions. Sano and Mori, on the other hand, achieved the same \( k_o \) values as their contemporaries using an oxygen jet of only 12 dynes force. Clearly this is an indication that their silver melt experienced a high degree of inductive stirring, resulting in the large \( k_o \) values they obtained.

4.2.4. INFLUENCE OF INTERFACIAL TURBULENCE ON LIQUID-PHASE MASS TRANSFER COEFFICIENTS

A comparison of \( k_o \) values for copper and silver is more meaningful than oxidation rates because this eliminates any differences in their respective driving forces. If the Surface Renewal Model of Higbie is assumed to hold for both copper and silver, then it would be expected that the ratio of values of \( k_o \) could be expressed as follows:

\[
\frac{k_{o,Ag}}{k_{o,Cu}} = \sqrt{\frac{D_{o,Ag}}{D_{o,Cu}}} = \sqrt{\frac{1.37 \times 10^{-4}}{1.03 \times 10^{-4}}} = 1.2 \frac{k_{o,Ag}}{k_{o,Cu}}
\]
However, the results of the present experiments indicate that the following result obtains:

\[ k_{Ag}^o = 0.03 k_{Cu}^o \]

This is a result of the lack of spontaneous interfacial turbulence during the oxidation of molten silver. Thus, it can be said that interfacial turbulence is capable of enhancing \( k_o \) in the liquid phase by a factor of 40.

To fully appreciate the effect of interfacial turbulence on \( k_o \) values in molten copper and silver, from a theoretical standpoint, the Higbie Surface Renewal Model, modified for a radial co-ordinate system, can be used to determine the effect of surface velocity on \( k_o \) for each metal. Such values can be readily calculated from Eq. (6), Chapter 1, and compared to the values obtained experimentally in this work. Calculated values of \( k_o \) are summarized for different surface velocities in Table VIII where one can see that the value in copper for a stagnant system \((U_r = 0.1 \text{ cm sec}^{-1})\) is about a factor of 17 times less than that observed in a fully turbulent system, while the observed \( k_o \) in silver appears to agree with that calculated for a stagnant system. The overall effect of surface tension-driven flow, then, is to enhance the mass transport of oxygen in the molten copper phase through vigorous stirring of the bulk metal phase.

In Table VIII, it can also be seen that the calculated and experimental \( k_o \) values for copper agree reasonably with each other, though the decrease in calculated \( k_o \) with increasing patch radius was not experimentally observed. The reason for this is not at all clear at this time. For silver, the experimental \( k_o \) agrees with that calculated for a stagnant system, and this
TABLE VIII

COMPARISON of CALCULATED and EXPERIMENTAL OXYGEN
MASS TRANSFER COEFFICIENTS FOR COPPER AND SILVER

\( T = 1220^\circ C \) (Cu); \( 1100^\circ C \) (Ag)
\( D_0/\text{Cu} = 1.029 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \); \( D_0/\text{Ag} = 1.37 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \)

\( \text{const (Eq.6)} = 1.303 \)

<table>
<thead>
<tr>
<th>Liquid Metal</th>
<th>Patch Radius (cm)</th>
<th>Surface Velocity (cm/sec)</th>
<th>Renewal Time (sec)</th>
<th>( k_0 ) (cm/sec)</th>
<th>( k_0 ) exptl. (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>0.1</td>
<td>5</td>
<td>0.0059</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>0.05</td>
<td>0.059</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>0.025</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
<td>0.019</td>
<td>0.095</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.0167</td>
<td>0.102</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.0</td>
<td>0.1</td>
<td>10</td>
<td>0.0042</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>0.1</td>
<td>0.042</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>0.05</td>
<td>0.059</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
<td>0.038</td>
<td>0.067</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.034</td>
<td>0.072</td>
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</tr>
<tr>
<td>Cu</td>
<td>1.5</td>
<td>0.1</td>
<td>15</td>
<td>0.0034</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
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<td>0.034</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
<td>0.057</td>
<td>0.055</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.05</td>
<td>0.059</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1.3</td>
<td>0.1</td>
<td>13</td>
<td>0.0042</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>1.3</td>
<td>0.0133</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>0.26</td>
<td>0.030</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>0.13</td>
<td>0.042</td>
<td>0.00288</td>
</tr>
</tbody>
</table>
appears consistent with the observed lack of radially-directed surface flow during oxidation. Since precise values for surface motions in molten silver are not presently available, however, the observed agreement may only be fortuitous.

In other molten metals, which have high-temperature stable oxides, it is possible that starvation mass transfer kinetics will obtain for oxidation with low-momentum gas jets. Because of the complexity of high-temperature reactions and of the number of variables involved, it is not possible at this time to develop equations for predicting $k_Q$ values using only the data from the present experiments. Further experiments on a wider range of liquid metals would be necessary before this is possible.

4.3. COPPER DEOXIDATION

4.3.1. DEOXIDATION RATES

The observed deoxidation/time plots in Figs. 3.20 and 3.21 appear linear in all cases for the time periods shown. From the results of pure argon degassing in Fig. 3.20, it is clear that oxygen will not desorb into an inert, oxygen-free atmosphere, despite the existence of a large concentration driving force. Thus, the observed deoxidation rates are due entirely to the effects of the hydrogen gas.

Changes in the flow rate of hydrogen to the copper surface do not appear to affect the deoxidation rates to any significant degree, as seen in Table V. For the low hydrogen flow rates used, the deoxidation rate is roughly constant, and, because a surplus of hydrogen gas is available for
reaction, starvation mass transfer kinetics do not obtain in these experiments. Variations in lance height were tried, but no change in the deoxidation rates was observed. Also, the variable starting oxygen concentration did not appear to affect the deoxidation rates.

From the extended duration experiment in Fig. 3.22, it can be seen that the constancy in deoxidation rate lasts for about 3000 sec (to \( \approx 0.55 \) wt. % oxygen), beyond which it decreases. This change indicates that a change is occurring in the deoxidation kinetics at this stage. A similar change was observed by Themelis and Schmidt\(^{39}\) for the deoxidation of copper using submerged jets of CO gas, and this indicated a changeover from gas-phase mass transport control (linear) to liquid-phase control (curved), as was discussed in sec. 1.3.3. Thus, the constant rate of deoxidation observed in Figs. 3.20 to 3.22 corresponds to gas-phase mass transport control (i.e. the transport of \( \text{H}_2\text{(g)} \) to the surface).

All experiments were not continued for the extended duration because, as the oxygen concentration becomes small (about 0.12 wt. %), hydrogen begins to dissolve in the copper at an appreciable rate, as discussed by Small et al.\(^{55}\). Under these conditions, water vapour will form within the bulk of the copper rather than at the interface, leading to bubble formation and subsequent enhancement of \( k_0 \) values.

4.3.1.1. EFFECT OF DISSOLVED SILICON AND SULPHUR

As discussed in sec. 4.1.1.2., silicon dissolved in copper does not exert any discernable effect on the rate of copper oxidation because it forms
a soluble compound with Cu₂O⁴⁺. However, when the Cu₂O content is reduced during deoxidation, the silica films could again reach the interface and perhaps have some influence on deoxidation rates through blockage of the interface to hydrogen gas. In Run 41, to which 20 ppm. of silicon had been added prior to oxidation, a large surface patch was observed to form during deoxidation. Analysis of this patch showed it to be composed of alumina and silica particles, and the analysis of the surfaces of the other deoxidation experiments showed no traces of either of these materials. As seen in Table V, the deoxidation rate of Run 41 is about 30% less than the average value, indicating that the observed traces of alumina and silica retarded the deoxidation rate.

In sec. 4.1.1.3., it was found that dissolved sulphur lowered the rate of copper oxidation by an amount roughly equal to the rate of SO₂ elimination. During deoxidation, if any sulphur is present, the deoxidation rates could continue to be enhanced by the removal of oxygen as SO₂. Because 0.004% sulphur remained in the bath of Run 43 at the start of deoxidation, the large rate observed in Table V is likely aided by SO₂ off-gassing. Sulphur contents were not measured, however, because of sample size restrictions.

4.3.2. SURFACE MOTIONS

The type of surface motions described in sec. 3.3.1. were difficult to analyse because of their randomness, and the reported values of surface velocity of 10 to 15 cm sec⁻¹ are only approximations. A detailed analysis of the surface flow is beyond the scope of the present study, however it is
useful to attempt an explanation of surface flow during the deoxidation of copper. Observations of surface flow during deoxidation have been reported in the literature. A schematic representation of the liquid copper interface during hydrogen deoxidation is seen in Fig. 4.7. From the data in Table V, it is clear that the bulk of the hydrogen flow to the interface remains unreacted, and so leaves the area as shown in the diagram. The major reaction site is at the point of jet impingement. When the hydrogen gas reaches the surface, it reacts immediately with the dissolved oxygen to form H\textsubscript{2}O vapour, and analysis of the equilibrium constant (Appendix I) has shown this reaction to proceed completely to H\textsubscript{2}O vapour. Because of this deoxidation, the copper immediately beneath the lance now has a larger interfacial tension than the remainder of the interface, and so inwardly-directed surface flow will result. In the initial stages of deoxidation, this surface flow was found to stop when the hydrogen was briefly turned off. The surface flow will decrease on increasing time because the surface tension driving force also decreases, and in the liquid-phase control region, no surface flow was observed.

4.3.3. MASS TRANSFER COEFFICIENTS

For the interfacial reaction

\[
\text{Cu} \quad K_{H_2O}
\]

\[
H_2(g) + [O]_{Cu} \rightarrow H_2O_v
\] (10)
FIGURE 4.7  Schematic representation of stirring pattern and surface flow conditions during deoxidation of molten copper and silver with H₂ gas.

INTERFACIAL REACTION:  \[ \text{H}_2(g) + [\text{O}]_l \overset{K_{\text{H}_2\text{O}}}{\rightarrow} \text{H}_2\text{O} (g) \]

\[ K_{\text{H}_2\text{O}} \text{ IS LARGE} \quad \sigma_2 > \sigma_1 \]
it can be seen from Fig. 4.7, that the majority of the deoxidation should occur at the point of jet impingement, and that since hydrogen is relatively insoluble in molten copper at these oxygen concentrations\textsuperscript{55-58}, no deoxidation occurs within the bulk, but is confined to the surface. In sec. 4.3.1. it was shown that the rate of copper deoxidation, during the first 3000 sec., is controlled in the gas phase, and so hydrogen mass transfer coefficients, $k_{H_2}$, can be calculated from the rate data in Table V using Eq. (11),

$$\dot{n}_{H_2} = \frac{k_{H_2}}{RT} \cdot A \left( P_{H_2}^b - P_{H_2}^i \right)$$

(11)

where $P_{H_2}^b$, $P_{H_2}^i$ refer to the bulk-phase and interfacial hydrogen gas pressures respectively, and $R$ is the gas constant. Because the equilibrium constant is large (see Appendix I), it is reasonable to assume that $P_{H_2}^i$ is zero. The value for the area $A$ was taken as the total surface area.

From Table IX, the mean value for $k_{H_2}$ at a hydrogen flow rate of 1500 cm\(^3\) min\(^{-1}\) was found to be 1.28 cm sec\(^{-1}\) with a standard deviation of 19.5\%, and this value agrees with the $k_{H_2}$ found for a hydrogen flow rate of 3000 cm\(^3\) min\(^{-1}\). For the low flow rate of 1000 cm\(^3\) min\(^{-1}\), the $k_{H_2}$ value was found to be about 30\% less than those observed at the higher flow rates, indicating that $k_{H_2}$ becomes dependent upon hydrogen flow rate at values less than 1500 cm\(^3\) min\(^{-1}\).

In Run 41, the presence of dissolved silicon reduced the $k_{H_2}$ value to 0.89 cm sec\(^{-1}\) through blockage of the interfacial regions to hydrogen. It is interesting to note that this value is similar to the $k_{H_2}$ obtained for the low hydrogen flow rate experiment. The presence of residual sulphur in Run 43
TABLE IX
MASS TRANSFER COEFFICIENTS FOR THE DEOXIDATION OF MOLTEN COPPER AND SILVER

<table>
<thead>
<tr>
<th>Run Number</th>
<th>H₂ Flow (cm³ min⁻¹)</th>
<th>( \dot{n}_{H₂} ) moles x 10⁴ sec TO SURFACE</th>
<th>( \dot{n}_{H₂} ) moles x 10⁴ sec REACTED</th>
<th>( A ) (cm²)</th>
<th>( k_{H₂} ) cm sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>1000</td>
<td>7.6</td>
<td>1.80</td>
<td>25</td>
<td>0.88</td>
</tr>
<tr>
<td>33</td>
<td>1500</td>
<td>11.2</td>
<td>2.20</td>
<td>25</td>
<td>1.08</td>
</tr>
<tr>
<td>37</td>
<td>3000</td>
<td>22.3</td>
<td>2.09</td>
<td>19.6</td>
<td>1.30</td>
</tr>
<tr>
<td>38</td>
<td>1500</td>
<td>11.2</td>
<td>2.19</td>
<td>19.6</td>
<td>1.34</td>
</tr>
<tr>
<td>39</td>
<td>1500</td>
<td>11.2</td>
<td>1.99</td>
<td>19.6</td>
<td>1.67</td>
</tr>
<tr>
<td>40</td>
<td>1500</td>
<td>11.2</td>
<td>2.68</td>
<td>19.6</td>
<td>0.89</td>
</tr>
<tr>
<td>41*</td>
<td>1500</td>
<td>11.2</td>
<td>1.42</td>
<td>19.6</td>
<td>2.68</td>
</tr>
<tr>
<td>43+</td>
<td>1500</td>
<td>11.2</td>
<td>4.30</td>
<td>19.6</td>
<td>0.5</td>
</tr>
<tr>
<td>45+</td>
<td>1500</td>
<td>11.2</td>
<td>1.63</td>
<td>19.6</td>
<td>0.2</td>
</tr>
<tr>
<td>50</td>
<td>1500</td>
<td>11.2</td>
<td>1.70</td>
<td>19.6</td>
<td>1.06</td>
</tr>
</tbody>
</table>

* contained dissolved Si
+ contained dissolved S

<table>
<thead>
<tr>
<th>Run Number</th>
<th>H₂ Flow (cm³ min⁻¹)</th>
<th>( \dot{n}_{H₂} ) moles 0² x 10⁴ sec TO SURFACE</th>
<th>( \dot{n}_{H₂} ) moles 0² x 10⁴ sec REACTED</th>
<th>( A ) (cm²)</th>
<th>( k_o ) cm sec⁻¹</th>
<th>( C_o ) cm⁻³ x 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1500</td>
<td>11.2</td>
<td>1.92</td>
<td>11.6</td>
<td>.146</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>1500</td>
<td>11.2</td>
<td>0.89</td>
<td>11.6</td>
<td>.063</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>1500</td>
<td>11.2</td>
<td>0.17</td>
<td>10.2</td>
<td>.010</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>3000</td>
<td>22.3</td>
<td>0.13</td>
<td>10.2</td>
<td>.025</td>
<td>0.2</td>
</tr>
</tbody>
</table>
enhanced the $k_{H_2}$ value to 2.68 cm sec$^{-1}$ through added oxygen loss as SO$_2$ gas. Thus, it appears that the presence of surface-active solutes other than oxygen can slightly influence the apparent rates of hydrogen mass transfer in the gas phase during copper deoxidation.

As mentioned previously, there is a changeover from gas-phase to liquid-phase control of deoxidation occurring at about 3000 sec. for the copper deoxidation experiments. Using this, it is possible to obtain an approximate value for the liquid-phase oxygen mass transport coefficient $k_o$, but owing to the increased solubility of hydrogen in the bulk of the copper, deoxidation can now occur within the bulk copper phase, so that the $k_o$ value can only be approximate. A plot of $\ln(C_o/\text{FINAL} / C_o \text{ INITIAL})$ vs. time in Fig. 4.8 shows the definite change in slope at 3000 sec, and the slope of the dashed line in the liquid-phase control region gave the $k_o$ value of $k_o = 4.9 \times 10^{-3}$ cm sec$^{-1}$ which is very much smaller than the value of $k_o$ determined for oxidation. Removal of the remaining oxygen is a slow process, which was also observed by Frohme et al$^{38}$ and Small and co-workers$^{55}$.

As a check on the deoxidation kinetics, we can calculate the bulk oxygen concentration at which changeover from gas-phase to liquid-phase mass transport control occurs using the following relationship:

$$C_o^b = \frac{k_{H_2}}{k_o} \cdot \frac{P_{H_2}^b}{RT}$$

where values for $k_{H_2}$ and $k_o$ are those determined in the present experiments.
FIGURE 4.8  Plot of $-\ln \frac{C_{\text{FINAL}}}{C_{\text{INITIAL}}}$ vs. time for copper deoxidation showing change from gas-phase to liquid phase mass transport control of deoxidation of about 3000 sec ($\sim 0.37$ wt % $\text{O}$ in the bath).
$C_o^b = \frac{1.28}{4.9 \times 10^{-3}} \cdot \frac{1}{(81.94)(1493)}$

$C_o^b = 2.14 \times 10^{-3}$ moles O $\cdot$ cm$^{-3}$

From Fig. 3.22, we can see that the observed changeover occurs at about 0.55 wt % O ($3 \times 10^{-3}$ moles O $\cdot$ cm$^{-3}$), and this agreed with the calculated value, confirming that gas-phase mass transport control obtains for the initial 3000 sec. of copper deoxidation.

4.4. SILVER DEOXIDATION

4.4.1. DEOXIDATION RATES

As observed for silver oxidation, the results for deoxidation proved to have considerable scatter among the three experiments at 1500 cm$^3$ min$^{-1}$ hydrogen flow (Fig. 3.24). Deoxidation experiments were carried out immediately following each oxidation experiment, but it was noticed that during the argon gas flushing, prior to hydrogen jetting, each sample would lose about 50% of its oxygen content. Thus, it would appear that oxygen dissolved in silver is unstable and requires an oxidizing atmosphere in order to remain in solution, unlike the situation observed for copper in sec. 4.3.1. This trend was also observed by Sano and Mori$^{43}$ in their study of oxygen desorption from molten silver to flowing argon gas.

In Fig. 3.24 and Table IX it can be seen that for the same gas flow rate, three different deoxidation rates were obtained. Also, though it is difficult to assess accurately for the two hydrogen flow rates employed, there appears to be little dependence of the deoxidation rate on hydrogen
flow rate. It is seen, however, that the deoxidation rate decreases on decreasing bath oxygen content with the exception of Run 6, where analytical errors are believed responsible for the different behaviour observed. Since gas bubbling was observed throughout silver deoxidation and because the deoxidation rate depends on bath oxygen concentration, it is clear that the rate-controlling step cannot be hydrogen transport to the bath surface, but is liquid-phase transport of oxygen. As for copper deoxidation, this can also be shown in the following manner. At the change from gas-phase to liquid-phase control, the respective mass transport rates are related as follows:

\[ k_o C_o^b = \frac{k_{H2}}{RT} \cdot P_{H2} \]

Since no value of \( C_o^b \) at the changeover point in liquid silver is available, it has to be estimated from the data. In sec. 4.2.4., it was shown that, in the absence of interfacial turbulence during oxidation, \( k_{Cu} = k_{Ag} \). This equality should also roughly hold for deoxidation since the degree of turbulent behaviour is similar in both metals. Also, because mixing in the gas phase should be the same for both metals under the same jet conditions, \( k_{H2}^{Cu} = k_{H2}^{Ag} \). Thus

\[ \frac{k_{Cu}}{k_{o}} \approx \frac{k_{Ag}}{k_{o}} \]

and, substituting into Eq. (9), the value for \( C_o^b \) at the change of control is found to be 2.3 \((10^{-3})\) moles 0 \cdot cm\(^{-3}\) in molten silver. From Table IX, it can be seen that the starting oxygen concentrations are all less than the above value, and so the rate-limiting step is oxygen transport in the liquid phase. Because bubbling was observed, it is likely
that some deoxidation is occurring within the liquid, and so subsequent \( k_{o}^{Ag} \) calculations can only be considered approximate due to the enhancement in mixing caused by water-vapour bubbling.

### 4.4.2. SURFACE MOTIONS

As observed for copper in sec. 4.3.2., the type of surface motions found for silver were difficult to analyse because of their randomness, and the reported values of 10 to 15 cm sec\(^{-1}\) are only approximations. Furthermore, because bubbling was observed during all silver deoxidation runs, the resulting surface motions become even more complicated. A schematic representation of the silver surface is shown in Fig. 4.7, and the flow description for copper in sec. 4.3.2. will also apply to silver deoxidation, with the added complication of bubbling. The surface flow will decrease with increasing time because the surface tension driving force also decreases with increasing time.

### 4.4.3. MASS TRANSFER COEFFICIENTS

As shown in the previous section, oxygen transfer in the bath is the rate-limiting step in the deoxidation of molten silver with hydrogen gas. Therefore, oxygen mass transfer coefficients, \( k_{o} \), can be calculated from Eq. (8),

\[
\ln \left\{ \frac{c_{o}^{i} - (c_{o}^{b})_{t}}{c_{o}^{i} - (c_{o}^{b})_{t=0}} \right\} = -\frac{k_{o} \cdot A}{V} \cdot t
\] (8)
FIGURE 4.9 Liquid-phase mass transfer coefficients for oxygen during the deoxidation of molten silver with hydrogen gas.
The value for the interfacial oxygen content, $C^1_o$, is zero in the region of liquid-phase mass transfer control, and the area $A$ was taken as being the whole interface. The results of these calculations are presented in Table IX and in Fig. 4.9, as a plot of $\ln x$ vs time. As can be seen in Table IX the values of $k_o$ decrease with decreasing oxygen concentration. This same dependence of both deoxidation rate and $k_o$ values on the initial silver bath oxygen content was also observed by Sano and Mori in their study of oxygen desorption rates from molten silver to flowing argon gas.

On comparison with the $k_o$ value determined for copper deoxidation, the values obtained for silver are about an order of magnitude larger. It is felt that this difference is due both to the bubbling observed during silver deoxidation and to the fact that silver deoxidation was accompanied by interfacial turbulence in the liquid-phase control region, and copper deoxidation was not. Because of the scatter observed in the present data, however, it is difficult to ascertain the value of this comparison.

4.5. SOLID DISSOLUTION EXPERIMENTS

4.5.1. SPREADING

The experimental observations of the spreading and turbulence generated during the dissolution of $Cu_2S$, $Cu_2O$, Se and Te are very similar to those made in sec. 3.1.1. during copper oxidation. Taking $Cu_2S$ as an example, the driving force for spreading of one liquid over another is the difference between the surface tension of pure copper, $\sigma_{Cu}$, and the sum of the surface tension of molten $Cu_2S$, $\sigma_{Cu_2S}^r$, and the interfacial tension along the
Cu₂S-Cu interface, σ_{Cu₂S/Cu}. This is often expressed as the initial spreading coefficient, S; as described by Eq. (5), sec. 1.3.1:

\[ S = \sigma_{Cu} - (\sigma_{Cu₂S} + \sigma_{Cu₂S/Cu}) \]  

(5)

Similar expressions can be obtained for the other three materials.

Naturally, spreading will only occur if S is positive. Some of the observed spreading and interfacial turbulence may also be due to a local reduction of the surface tension in the vicinity of the partially immersed solids (sec. 1.2.2.) where a higher solute concentration is likely, relative to the copper nearer the crucible walls. The surface would then also move spontaneously toward the region of higher σ_{Cu}.

As can be appreciated, the liquid-phase surface tensions for the four solids used in this test are rather difficult to obtain. Some tentative values have been located in the literature so that values of S can be roughly calculated from Eq. (5), and these are given in Table X.

The values of S in Table X are all very much larger than zero, as might be expected, because of the observed spreading behaviour of these four materials. Thus, this calculation could prove valuable for both industrial and laboratory experiments involving partially immersed solids in liquid metals.

Baes and Kellogg⁶¹ have reported observations of spontaneous surface motion during the dissolution of Cu₂S in partially molten copper in conjunction with their sessile drop study of the effect of sulphur on the surface tension of copper. They observed that small crystals of Cu₂S were thrown off the surface of the copper by surface eruptions and that during melting, samples
TABLE X
CALCULATED VALUES FOR THE SPREADING COEFFICIENT, S, FOR Cu₂S, Cu₂O, Se, AND Te

<table>
<thead>
<tr>
<th>Material (m)</th>
<th>Temperature (°C)</th>
<th>( \sigma_m ) (dynes/cm)</th>
<th>( \sigma_m/Cu ) (dynes/cm)</th>
<th>( S_m ) (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1200</td>
<td>1250^{58}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu₂S</td>
<td>1200</td>
<td>400^{59}</td>
<td>520^{59}</td>
<td>330</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>1200</td>
<td>500^{59}</td>
<td>\sim 700^{11}</td>
<td>\sim 50</td>
</tr>
<tr>
<td>Se</td>
<td>220</td>
<td>105.5^{58}</td>
<td>850^{11}</td>
<td>294.5</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>460</td>
<td>174.4^{58}</td>
<td>725^{11}</td>
<td>346.3</td>
</tr>
</tbody>
</table>
of Cu$_2$S + copper would often spontaneously fall off the sessile drop plaque. However they attributed these phenomena to melting effects rather than to spreading of the surface due to sulphur. Based on the present work, the latter effect is most likely to have been the driving force for the movements they observed as well.

4.5.2. SIGNIFICANCE

The finding that a macroscopic source of sulphur, selenium and tellurium, as well as of oxygen, can generate spontaneous surface motion is important since it shows that surface driven flow at high temperatures is not unique to the oxygen/metal system. This has implications that are worth considering when studies are undertaken of the kinetics of heterogeneous reactions in either the laboratory or in the metallurgical plant. In both cases due consideration should be given to the possibility of interfacial turbulence being present, since idealized hydrodynamic conditions can be fundamentally altered and reaction rates sharply accelerated. This consideration is especially important when the reaction involves a known surface-active agent. Certainly in the laboratory where experimental conditions are subject to careful control, the presence of interfacial turbulence should be checked whenever possible. For example, the mechanism outlined here and in sec. 1.2.2. has been used to explain the preferential attack of refractory bricks at the surface line of steel and glass-making furnaces. Many other metallurgical reactions yet to be examined in this way, such as re-oxidation of liquid metals during casting, are undoubtedly accompanied by interfacial turbulence.
5. CONCLUSIONS

1. The rate of oxidation of molten copper at 1220°C by low-momentum pure oxygen jets is governed by starvation mass transfer kinetics, and is not affected by changes in lance height or small additions of silicon. The effect of dissolved sulphur is to reduce the rate by an amount equal to the rate of sulphur elimination as \( \text{SO}_2 \) gas.

2. Surface velocity studies show that the interfacial tension-generated flow during copper oxidation has a mean value of 26.1 cm sec\(^{-1}\) (± 21%) and does not depend on oxygen gas flow rate or copper bath oxygen concentration.

3. Oxide patch areas are found to increase with both oxygen flow rate and increasing bath oxygen concentration. Surface blockage studies show that most of the oxygen transfer to the copper occurs in the area described by the oxide patch.

4. Oxygen mass transfer coefficients in the copper liquid phase are found to be 0.104 cm sec\(^{-1}\) (± 11.6%), and are independent of oxygen flow rate, bath oxygen content, and dissolved silicon and sulphur contents. Literature values are not available for comparison.
5. The rate of molten silver oxidation at 1100°C is not governed by starvation mass transfer kinetics, but is controlled by transport in the liquid phase. The oxidation rate is not dependent on oxygen gas flow rate and is seen to be a factor of 50 times less than that observed for copper.

6. No spontaneous interfacial tension-generated flow is observed during molten silver oxidation. The reason postulated for this observation is that oxygen absorption by silver occurs uniformly across the interface. Because silver has no stable oxide at the temperature studied, a point source of low \( \sigma_{Ag} \) from which spreading can occur is not able to exist at the point of jet impingement.

7. Oxygen mass transfer coefficients in the silver liquid phase are found to be \( 2.88 \times 10^{-3} \) cm sec\(^{-1} \), and are independent of oxygen flow rate and bath oxygen content. A direct comparison with the literature values is not possible due to experimental differences. However, it is shown that for non-turbulent systems, the degree of external bulk-phase mixing is important in evaluating \( k_o \) values.

8. The effect of interfacial turbulence on liquid-phase oxygen mass transfer coefficients in molten copper is to enhance the value by about 40 times over that observed in molten silver where interfacial turbulence does not occur on oxidation.

9. The rate of deoxidation of molten copper at 1220°C by low-momentum pure hydrogen jets does not depend upon hydrogen flow rate, lance height and
starting oxygen concentration, and is constant for the first 3000 seconds. The rate-controlling step is the gas-phase mass transfer of hydrogen to the liquid surface. Dissolved silicon retards the de-oxidation rate by blocking the interface to hydrogen gas, and dissolved sulphur enhances the rate through \( \text{SO}_2 \) elimination.

10. Surface velocities of 10 to 15 cm sec\(^{-1}\) towards the point of jet impingement are observed, but because of the randomness of these motions, a detailed analysis is not possible. The proposed mechanism for this flow is inward spreading to a region of higher \( \sigma_{\text{Cu}} \) directly beneath the hydrogen lance than at a point on the interface some distance from the lance. As the flow depends upon the bath oxygen concentration, it will decrease with time during refining.

11. The hydrogen mass transfer coefficient to molten copper at \( 1220^\circ \text{C} \) for a hydrogen flow rate of 1500 and 3000 cm\(^3\) min\(^{-1}\) is found to be 1.28 cm sec\(^{-1}\) (± 19.5\%). At a hydrogen flow rate of 1000 cm\(^3\) min\(^{-1}\), this value is reduced by about 30\%, indicating that a dependence on hydrogen flow rate occurs at values below 1500 cm\(^3\) min\(^{-1}\). The \( k_{\text{H}_2} \) values are reduced to 0.89 cm sec\(^{-1}\) in the presence of dissolved silicon, and enhanced to 2.68 cm sec\(^{-1}\) in the presence of dissolved sulphur. An approximate \( k_\theta \) value for the liquid-phase mass transfer control region is found to be 4.9 (10\(^{-3}\)) cm sec\(^{-1}\), and is influenced by the presence of bubbling during this phase of deoxidation. This \( k_\theta \) value is similar to that for a stagnant system.
12. The rate of deoxidation of molten silver at 1100°C by low-momentum pure hydrogen jets does not depend upon the hydrogen flow rate, but does depend upon the starting bath oxygen concentration, decreasing as the concentration decreases, and likely depends on the bubbling observed during deoxidation. The rate-controlling step is liquid-phase oxygen mass transfer.

13. Surface velocities of the same magnitude as seen for copper deoxidation are observed for molten silver deoxidation, and the proposed mechanism for this flow is identical to that for copper, with the added complication of gas bubbling.

14. Oxygen mass transfer coefficient in the liquid phase for hydrogen flow rates of 1500 and 3000 cm³ min⁻¹ are found to decrease with decreasing initial oxygen concentration. These values are enhanced by both the presence of bubbling and the interfacial tension-generated surface flow during the deoxidation of the silver, but it is impossible at this time to determine the degree of this enhancement.

15. Interfacial turbulence during the dissolution of solid Cu₂S, Cu₂O, Se and Te in molten copper is shown to occur. Values calculated for the spreading coefficient, S, indicate that spreading of these materials on molten copper, and the resulting turbulence, is a predictable effect.
6. SUGGESTIONS FOR FUTURE WORK

1. The oxidation of molten copper using jets of air at various flow rates could be studied to determine if interfacial turbulence will occur under these conditions.

2. Other metal systems having high-temperature stable oxides could be studied to determine if interfacial turbulence occurs during oxidation with low-momentum oxygen jets, and what effect this has on the oxidation rates. A partial list of such metals could include iron and nickel. It would also be of interest to study the oxidation of these metals using low-momentum jets of air.

3. It would be of interest to study the deoxidation of both molten copper and silver using low-momentum jets of CO. Because CO is insoluble in molten copper and silver, bubbling during deoxidation would not be a problem, and it would be interesting to compare the deoxidation rates with those obtained for hydrogen.

4. Surface blockage studies for molten silver could be performed to determine the effect of interfacial area on oxidation and deoxidation. This could also be studied for copper deoxidation.

5. Oxidation and deoxidation studies for molten copper, silver, iron and nickel could be performed over a range of temperatures to determine the effect of temperature on the oxidation/deoxidation rates and on the
magnitude of the interfacial turbulence in each case.

6. The influence of surface-active agents, such as silicon, sulphur, selenium and tellurium, on the oxidation rates of silver, iron and nickel, could also be studied.
BIBLIOGRAPHY


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APPENDIX I

CALCULATION OF THE EQUILIBRIUM CONSTANT $K_{H_2O}$

1. $K_{H_2O}$ FOR THE COPPER-OXYGEN-HYDROGEN SYSTEM

Hydrogen gas reacts with oxygen dissolved in copper, at the gas-liquid interface, to form $H_2O(g)$, as

$$H_2(g) + [\%0]_{Cu} \rightarrow H_2O(g)\quad (1)$$

and the equilibrium constant $K_{H_2O}$ is given as

$$K_{H_2O}^{Cu} = \frac{P_{H_2O}^i}{P_{H_2}^i \cdot \gamma_o \cdot [\%0]_{Cu}}$$

where $P_{H_2O}^i$ and $P_{H_2}^i$ are the interfacial concentrations of water and hydrogen gases. As these interfacial pressures are hard to evaluate, it is desirable to determine $K_{H_2O}^{Cu}$ from the free energy for reaction (1) by using the following expression:

$$\Delta G^o(1) = -RT \ln K_{H_2O}$$

Assuming that equation (1) is valid to the saturation limit, the free energy $\Delta G^o(1)$ was derived from the following equations:
\[
\begin{align*}
\text{Cu}_2\text{O}(s) & \rightarrow 2\text{Cu}(1) + \frac{1}{2} \text{O}_2(g) \quad (2) \\
+ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(g) & \quad (3) \\
\frac{\text{Cu}_2\text{O}(s) + \text{H}_2(g) \rightarrow 2\text{Cu}(1) + \text{H}_2\text{O}(g)}{} & \quad (4) \\
\Delta G^0 &= 46,700 + 3.92 T \log T - 34.1 \text{T} \quad \text{(Ref. 66)} \\
+ \Delta G^0 &= -57,250 + 4.48 T \log T - 2.21 \text{T} \quad \text{(Ref. 66)} \\
\Delta G^0 &= -10,550 + 8.40 T \log T - 36.31 \text{T} \quad (4) \\
\text{Cu}_2\text{O}(s) + \text{H}_2(g) & \rightarrow 2\text{Cu}(1) + \text{H}_2\text{O}(g) \quad (4) \\
- \frac{\text{Cu}_2\text{O}(s) \rightarrow [\%0]\text{Cu} + 2\text{Cu}(1)}{} & \quad (5) \\
\text{H}_2(g) + [\%0]\text{Cu} + \text{H}_2\text{O}(g) & \quad (6) \\
\Delta G^0 &= -10,550 + 8.40 T \log T - 36.31 \text{T} \quad (4) \\
- \Delta G^0 &= 22,003 + 3.92 T \log T - 27.82 \text{T} \quad \text{(Ref. 67,70)} \\
\Delta G^0 &= -32,553 + 4.48 T \log T - 8.49 \text{T} \quad (6)
\end{align*}
\]

At the experimental temperature of 1220°C (1493°K), the free energy value is

\[\Delta G^0 = -23,998 \text{ cal mole}^{-1} \text{ o}^{-1}\]

Thus, \(K_{\text{H}_2\text{O}}^\text{Cu}\) is

\[K_{\text{H}_2\text{O}}^\text{Cu} = 3354.7, \quad \text{and based on a 1 wt % standard-state oxygen concentration}\]

\[K_{\text{H}_2\text{O}}^\text{Cu} = 5.81 \times 10^5 \text{ cm}^3 \text{ mole}^{-1}\]
2. \( K_{\text{Ag}_2\text{O}} \) FOR THE SILVER-OXYGEN-HYDROGEN SYSTEM

As was the case for copper, \( K_{\text{Ag}_2\text{O}} \) was derived from the free energy \( \Delta G^o \) for the following equations:

\[
\begin{align*}
\text{Ag}_2\text{O}^\circ (s) &\rightarrow 2 \text{Ag}(1) + \frac{1}{2} \text{O}_2(g) \quad (7) \\
\text{Ag}_2\text{O}^\circ (s) + \text{H}_2(g) &\rightarrow 2 \text{Ag}(1) + \text{H}_2\text{O}(g) \quad (9)
\end{align*}
\]

\[
\begin{align*}
\Delta G^o(7) = 3,250 - 6.8 T & \quad \text{(Ref. 68)} \\
\Delta G^o(8) = -57,250 + 4.48 T \log T - 2.21 T & \quad \text{(Ref. 66)} \\
\Delta G^o(9) = -54,000 + 4.48 T \log T - 9.01 T
\end{align*}
\]

\[
\begin{align*}
\text{Ag}_2\text{O}^\circ (s) + \text{H}_2(g) &\rightarrow 2 \text{Ag}(1) + \text{H}_2\text{O}(g) \quad (9)
\end{align*}
\]

\[
\begin{align*}
\Delta G^o(10) = -54,000 + 4.48 T \log T - 9.01 T & \quad \text{(Ref. 69,70)} \\
\Delta G^o(11) = -53,319 + 4.48 T \log T - 9.01 T
\end{align*}
\]

At the experimental temperature of 1100°C (1373°K), the free energy value is

\[ \Delta G^o(11) = -46,390 \text{ cal mole}^{-1} \text{oK}^{-1}. \]

Thus, \( K_{\text{Ag}_2\text{O}} \) is

\[
K_{\text{Ag}_2\text{O}} = 2.58 \times 10^8,
\]

and based on a 0.1 wt % standard state oxygen concentration,

\[
K_{\text{Ag}_2\text{O}} = 4.5 \times 10^{11} \text{ cm}^3 \text{mole}^{-1}.
\]