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A Theoretical Analysis of the Stability of Surface Oxides During Diffusion Welding of Metals

The dependence of dissolution time on oxide thickness and temperature is determined for selected metals

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ABSTRACT. The effect of surface oxide layers on the diffusion welding of metals is considered in terms of the stability of the oxide phase. For oxides that do not evaporate or dissociate to gaseous products at the welding temperature, an analytical method is presented through which calculations of the times necessary for oxygen dissolution are possible for plane (sheet), cylinder, and sphere geometries. The dependence of the dissolution time on oxide thickness and temperature is calculated for selected metals.

Introduction

It is generally accepted that short range interatomic forces must be brought into play before a solid state weld can be established between faying surfaces (Ref. 1). Thus the generally observed poor weldability of contaminated surfaces is attributed to the failure of establishing these forces as a consequence of the existence of an intervening layer. In such cases, welding can be accomplished, at least locally, if the contaminant layer is broken through the application of pressure, as in the case of hot pressure welding.

Numerous publications have dealt with the role of surface contaminants, notably oxide layers, in the welding of metals

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(Refs. 2, 3). These are thoroughly discussed in a recent review by Jellison (Ref. 4). In general, the presence of surface oxide layers hinders metal-to-metal welding. However, there are experimental indications (Refs. 5, 6) of welding between oxidized surfaces. In such a case it is believed that oxide sintering or the formation of a multi-oxide compound (Ref. 7) is a requirement for the establishment of a good joint.

In a relatively recent paper, Bryant (Ref. 8) proposed an empirical method for the determination of the minimum pressure and temperature required for the hot isostatic pressure welding of metals. In this approach metals are categorized according to the thermodynamic stability of their oxides and the solubility of oxygen in the metals. Metals with low oxide stability or high oxygen solubility can be diffusion welded even if they are initially coated with an oxide.

Jellison (Ref. 4) stated that the principal mechanism of destruction of oxide films is the assimilation of the oxide into the metal, presumably through the diffusion of the oxygen resulting from the decomposition of the oxide at the metal-oxide interface. Metals such as copper, iron, and titanium possess high oxygen solubilities and thus are believed to weld following the assimilation of the oxide by the dissolution of oxygen in the metal.

Along with these solubility criteria are considerations associated with relative interfacial stabilities. In the case of copper, for example, experimental evidence

(Ref. 9) clearly shows that these considerations are important. When oxidized copper spheres were placed on copper foil and heated at 1123 K (1396°C or 2545°F), the surface oxide layer was observed to break up into clusters following the sintering of the spheres to the foil. The process is preceded by the diffusion of copper through the oxide layer to establish metal-metal contacts by sintering (Ref. 9). In this case, the metal-metal interface is energetically more favorable than the metal-oxide interface.

Karlinski (Ref. 10) has proposed that diffusion welding is a manifestation of sintering and explained his results on the welding of nickel, chromium, and a stainless steel on this basis. In a recent paper (Ref. 11) the author has proposed an analytical model for the determination of the role of surface oxide films in the sintering of metals. This approach is extended here to the diffusion welding of metals.

Classification of Oxides

In order to assess their effect on the diffusion welding process of metals, oxides are classified into three categories or cases:

1. Oxides which are unstable with respect to evaporation or dissociation to gaseous species.

2. Oxides which are unstable with respect to dissolution (as dissolved oxygen in the metal).

3. Stable oxides.

Table 1—Thermally Unstable Metal Oxides

Oxide	T_h[a]
Ag_2O	0.38
IrO_2	0.50
MoO_2	0.44
OsO_4	0.14
PdO	0.63
RuO_2	0.11

(a) T_h is defined as the homologous temperature of instability with reference to the absolute melting point of the metal.

Examples of oxides representing the first category are listed in Table 1 along with the homologous temperature of the metal at which each becomes unstable in air. As indicated in Table 1, instability includes sublimation as well as decomposition. Thus diffusion welding of any of these metals will take place between oxide-free surfaces if the temperature is higher than the indicated homologous value and if the welding is carried out in air.

Oxides can, of course, be made unstable at lower temperatures if the partial pressure of oxygen is lowered. For example, nickel oxide is thermodynamically unstable with respect to dissociation if it is heated to 1150 K (1423°C or 2593°F) under an oxygen partial pressure, P_{O_2}, of 10^{-9} atm. Under the same condition of P_{O_2}, however, chromium oxide is stable to within 10 K (10°C or 18°F) of the melting point of chromium.

Now we shall consider the case where the oxide becomes unstable with respect to dissolution (case no. 2 above). Here, the oxide is less stable as a phase than a solid solution of oxygen in the metal. This is represented by the equations:

$$MO \rightarrow M + O \qquad (1)$$
$$O \rightarrow O(sln) \qquad (2)$$

where MO is the oxide, M is the metal, and O(sln) represents dissolved oxygen in the metal.

In addition to the relative thermodynamic stabilities of the phases on both sides of the equations, this process may also be kinetically controlled. The process may be controlled by the kinetics of the dissociation step, equation (1), or by the dissolution and diffusion step, equation (2).

In this paper we assume that the dissociation step is rapid relative to the second step and that the process is hence basical-ly controlled by the diffusion of the dissolved oxygen from the original oxide-metal interface into the bulk of the underlying metal. There is experimental evidence to support such an assumption (Ref. 12). Thus a finite time is required for an oxide with a given thickness to dissolve in the base metal. This time, represented as t_d, is the period necessary before the solubility process is complete and the metal surface is oxide free.

To calculate time t_d we consider the three geometries of a plane (sheet), a cylinder, and a sphere. Figure 1 shows the configuration of a plane. Here a sheet of metal with thickness of 2ℓ is covered by an oxide layer with a thickness of ξ on each surface. For the cases of cylindrical and spherical geometries, ℓ is the radius and ξ is the oxide thickness.

Since the time necessary for complete dissolution of the oxide depends on the ratio (ξ/ℓ), we first calculate the maximum value of (ξ/ℓ), i.e., the thickest oxide layer for any given ℓ. Since the total amount of oxygen must be conserved (i.e., the amount of oxygen in the oxide before decomposition and diffusion equals the amount of oxygen dissolved in the metal after the completion of the process),

$$C_oV_o = C_mV_m \qquad (3)$$

where C_o and C_m are the concentrations of oxygen in the oxide and metal, respectively, and V_o and V_m are the total volumes of the oxide layer and the metal, respectively. The maximum ratios for (ξ/ℓ) are:

Plane: $\qquad (\xi/\ell)_{max} = C_m/C_o \qquad (4)$

Cylinder: $(\xi/\ell)_{max} = \frac{1}{2}(C_m/C_o) \qquad (5)$

Sphere: $(\xi/\ell)_{max} = \frac{1}{3}(C_m/C_o). \qquad (6)$

Since C_o can be assumed to be independent of temperature, i.e., the oxide composition does not change significantly with temperature, we can express equations (4) to (6) as a function of temperature in the following general way:

$$(\xi/\ell)_{max} = K\frac{a}{C_o} \exp(-b/RT) \qquad (7)$$

where a exp (−b/RT) represent the

Fig. 1 — Geometric representation of an oxide coated plane sheet of a metal

Fig. 2 — The dependence of the maximum ratio of (ξ/ℓ) on temperature

Fig. 3—Dissolution times for 100 Å thick oxide layers for various metals

Fig. 4 (above right)—The effect of oxide thickness on the dissolution time $T_h = 0.5$

Fig. 5 (right)—The effect of oxide thickness on the dissolution time $T_h = 1.0$

expression for the temperature dependence of the solubility of oxygen in metals.

Values of the constants a and b are obtained from Ref. 12. In equation (7), K is a constant whose value is 1.0, 1/2, or 1/3 for the plane, cylinder, and sphere geometries, respectively.

The time required for the dissolution of the oxide at the maximum ratio can be calculated for the plane, cylinder, and sphere geometries from the following relationships, respectively (Ref. 13):

$$\frac{C - C_i}{C_s - C_i} = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{2n+1} \quad (8)$$

$$\exp\left[-D(2n+1)^2/4 \; \ell^2\right] \cdot \cos\frac{(2n+1)\pi x}{2}$$

$$\frac{C - C_i}{C_s - C_i} = 1 - \frac{2}{\ell} \sum_{n=1}^{\infty} \quad (9)$$

$$\exp\left[-D \; \alpha_n^2 t\right] \frac{J_o(x \; \alpha_n)}{J_1(\ell \; \alpha_n)}$$

$$\frac{C - C_i}{C_s - C_i} = 1 - \frac{2\ell}{\pi X} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \quad (10)$$

$$\sin\frac{n\pi x}{\ell} \exp\left[-D \; n^2\pi^2 t/\ell^2\right]$$

where C_i is the initial concentration of oxygen in the metal, C_s is the concentration of oxygen in the metal at the oxide-metal interface, C is the concentration in the metal at a distance x from the center line of the plane or the center of the cylinder and sphere, D is the diffusion coefficient of oxygen in the metal, and t is time.

The symbols J_0 and J_1 in equation (9) refer to the Bessel functions of the zeroth and first order, respectively, with α_n being the root of this function. We assume that $C_i = 0$ and $C_s = C_m$, i.e., that the metal is saturated with oxygen at the oxide-metal interface. This assumption is a consequence of the statement made earlier concerning the rate-controlling step.

The solutions to equations (8) to (10) for a saturated metal are (Ref. 14):

Plane: $t_d \simeq 1.7 \; (\ell^2/D)$ (11)
Cylinder: $t_d \simeq 1.0 \; (\ell^2/D)$ (12)
Sphere: $t_d \simeq 0.6 \; (\ell^2/D)$.   (13)

In these equations, ℓ is the half thickness or radius of the metal which corresponds to the maximum (ξ/ℓ) ratio. The time required for the complete dissolution of the oxide, t_d can be calculated from equations (11) to (13) if the diffusion coefficient D is known. Values of D were calculated from data obtained from Ref. 15.

Results and Discussion

As can be seen from equations (7) and (11) through (13), changing the metal geometry results only in a change in the constants. Consequently, the following discussion focuses, for convenience, on the plane sheet geometry.

Results of calculations of the maximum ratio of (ξ/ℓ) are shown in Fig. 2 as a function of the homologous temperature, T_h. For any given metal thickness, the results show that Ni can dissolve an oxide thickness which is about three orders of magnitude smaller than the corresponding value for Nb at the metals' respective melting points. Regardless of temperature, the metals Nb, Zr, and Ti can dissolve thicker oxides than can Ni, Co, Ta, and Cu. Metals with oxide surface layers thicker than the maximum will only partially dissolve this layer regardless of the annealing time. We return to this case at a later point in this paper.

The behavior of Fe in terms of the calculated variables of Fig. 2 is anomalous. The ratio $(\xi/\ell)_{max}$ has a much stronger dependence on temperature than all the other metals reported in Fig. 2. This behavior is the consequence of reported anomalous oxygen solubility data for this metal. The reported activation energy for oxygen solution in Fe, 56.6 kcal mol^{-1} (Ref. 12) is 6 to 13 times the corresponding values for the other metals. For example, nickel has a corresponding activation energy of 7.85 kcal mol^{-1}.

Values of the dissolution time t_d for various metals are plotted in Fig. 3 as a function of the homologous temperature for an oxide thickness of 100 Å. To cause such an oxide to dissolve immediately, e.g., $t_d = 1$ s, it is necessary to raise T_h to 0.925 for Ni. In contrast, a T_h value of only 0.2 is required to dissolve an oxide of the same thickness in the case of Ta. At $T_h = 0.6$, oxides of 100 Å thickness of such metals as Ti, Zr, and Cu dissolve instantly ($t_d \simeq 0.1$ s); however, it takes

4.4 hours (h) to accomplish the same result for Co and 11.6 days for Ni. The effect of oxide thickness on t_d is shown in Figs. 4 and 5 for T_h values of 0.5 and 1.0, respectively. Typically, the t_d increases by approximately three orders of magnitude as the oxide thickness increases from 50 to 1000 Å.

As stated previously, the results presented in Figs. 2 through 5 relate to the plane sheet geometry. Values of t_d for the cylinder and sphere geometries can be obtained from these figures and are related by the following ratios:

$$\frac{t_d \text{ (cylinder)}}{t_d \text{ (plane)}} = 2.35 \qquad (14)$$

$$\frac{t_d \text{ (sphere)}}{t_d \text{ (plane)}} = 3.18 \qquad (15)$$

The analysis thus far has considered oxides that are unstable with respect to evaporation or dissociation to the gas phase and dissolution into the base metal. There are cases, however, where the metal has a very limited solubility for oxygen and where the oxide is extremely stable. In such cases, as well as in cases where the oxide is too thick to dissolve completely in the metal, welding between clean metallic surfaces is not possible and other mechanisms have been proposed.

Compound formation between oxides has been suggested as one such mechanism (Ref. 7). In such a case, the welding process is dependent on the kinetics of nucleation and growth of the specific compound. The notion that welding can take place between oxidized surfaces through the sintering of the oxides has been proposed (Refs. 4, 5). This proposal, however, is generally not consistent with the temperature requirement for the sintering of metal oxides.

Typically, sintering (with densification) does not take place at temperatures below about half of the absolute melting point of the material. Since the melting points of oxides are much higher than the corresponding metal values, it is highly unlikely that oxide-to-oxide sintering can take place at normal welding temperatures. Although surface diffusion and evaporation-condensation mechanisms of sintering can operate at lower temperatures, these do not give rise to densification (Ref. 16), with the result that the structure remains porous and lacks strength.

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Stress Indices and Flexibility Factors for Concentric Reducers
by E. C. Rodabaugh and S. E. Moore

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Finite Element Analysis of Eccentric Reducers and Comparisons with Concentric Reducers
by R. R. Avent, M. H. Sadd, and E. C. Rodabaugh

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