CLAISSE

The First and Finest in Fusion

JEAN-PHILIPPE GAGNON

Preparing Borate Beads using Metal Fragments and Filings: Example of a Lead-Tin Alloy Fusion

Colloque Rayons X et Matières 2001

Corporation Scientifique Claisse Inc.
Parc Technologique de Québec
350 rue Franquet, suite 40
Sainte-Foy (Québec) G1P 4P3, Canada
Tel. : (418) 656 6453 • Fax : (418) 656 1169
www.claisse.com

ABSTRACT

Traditional fusion techniques make it possible to fuse oxidized compounds. However, new procedures allow us to fuse non-oxidized compounds such as metals. The purpose of this article is to better understand the oxidation strategies available to the analyst. The first part of the paper is dedicated to dry corrosion at high temperature. The second part deals with the use of solid oxidizers. The last part deals with electrochemical principles governing oxidation in an acid environment. It also proposes two oxidation strategies for a tin-lead alloy.

TABLE OF CONTENTS

1. INTRODUCTION

It is well known that only oxides dissolve in molten borates. All other compounds must be oxidized prior to fusion. For example, different oxidation strategies make it possible to melt pure metals and alloys. Figure 1 shows images of beads produced from aluminium filings, copper pipes, paper clips (complex alloys) and ferrous alloys. The oxidation strategies vary considerably and selecting a specific procedure often depends on the analyst's experience. One routinely used procedure is calcination of a sample in a high temperature oven (approximately 1000°C). A second strategy is to mix solid oxidizers with the sample and a fluxing medium, in a crucible. The mixture is then melted. Another strategy is to oxidize the sample using an aqueous solution at low temperature. The oxidized sample is then melted using a traditional fusion procedure. This strategy ensures complete oxidation of the sample and permits the melting of samples that are very difficult to oxidize. However, before describing the oxidation strategies, we will illustrate the difficulties of melting a lead-tin alloy.

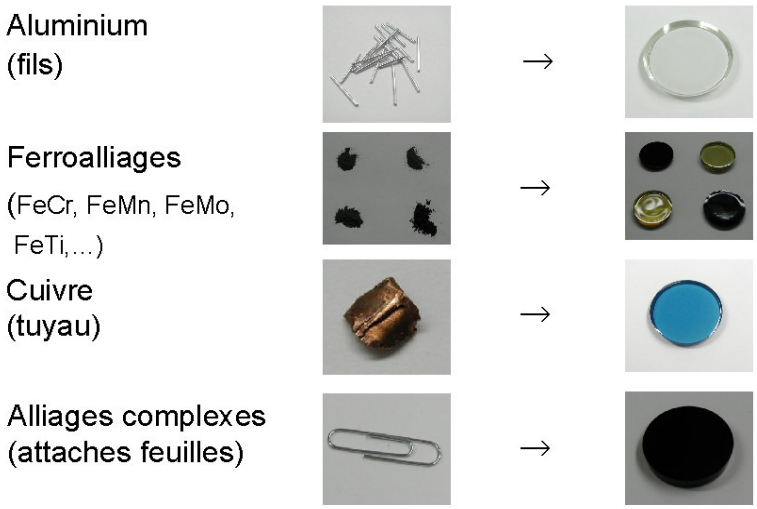
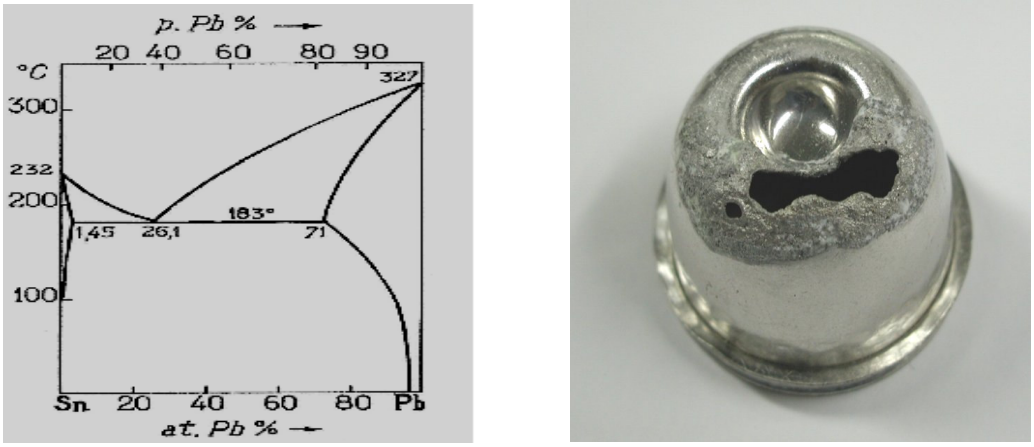


Figure 1: Example of beads made from metal samples

2. PROBLEMATICS

A lead-tin alloy is very difficult to oxidize. This alloy melts at very low temperatures. Figure 2a illustrates a phase diagram of a tin-lead alloy. The fusion temperature is 183°C at the eutectic point. This alloy melts before the solid oxidizer. It cannot achieve the oxidizing reaction on its own. The molten alloy makes contact with the wall of the platinum crucible. The temperature increases at the point of contact until the platinum fuses and ruins the crucible (Figure 2b). How can this alloy be oxidized without damaging the crucible? To clearly understand, we must first illustrate the inter-atomic forces that occur when dissolving a sample in a borate fluxing medium.



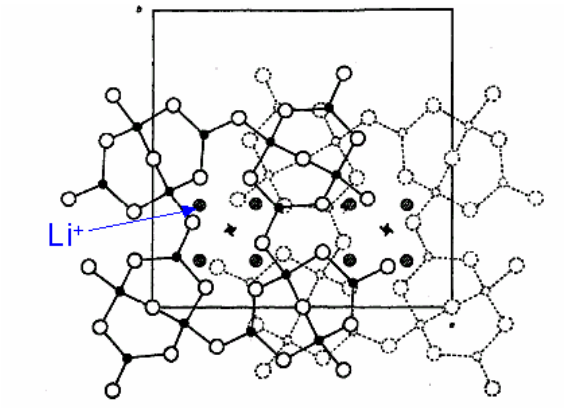
a) b)

Figure 2. Phase diagram of Sn-Pb alloy and image of a ruined crucible.

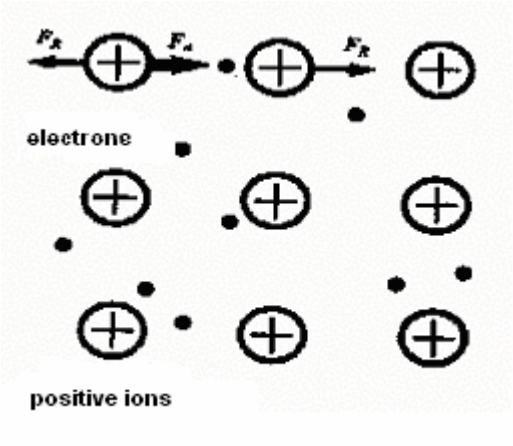
3. ATOMIC STRUCTURES

The three-dimensional structure of lithium tetraborate is presented by Krogh-Moe [1] (Figure 3a). The black spheres represent the boron atoms, the white ones are the oxygen atoms and the cross-hatched ones are lithium atoms. The boron and oxygen atoms are linked by polar covalent bonding and the lithium atoms by ionic bonding. Dissolution of a metal in this structure involves the forming of new ionic bonds with oxygen atoms. The metallic atom must be in the form of a cation; in

other words, one or more electrons must be extracted from the surface of an atom. This reaction is called oxidation. The atoms of a metal are linked by metallic bonds (Figure 3b). To dissolve a metal in a borate fluxing medium, these links must be broken by means of an oxidizing reaction. The metallic cation is then stabilized by extremely negative oxygen atoms within an amorphous boron structure. For example, it is possible to dissolve up to 1.8 g of CaO in 6 g of lithium tetraborate. As mentioned previously, the analyst has a choice of several oxidation strategies. It makes little difference which strategy is selected; it must only take a few minutes and must be complete. The most popular strategy is to calcinate the sample at a high temperature.



a) Structure of $Li_2B_4O_7$ [1].



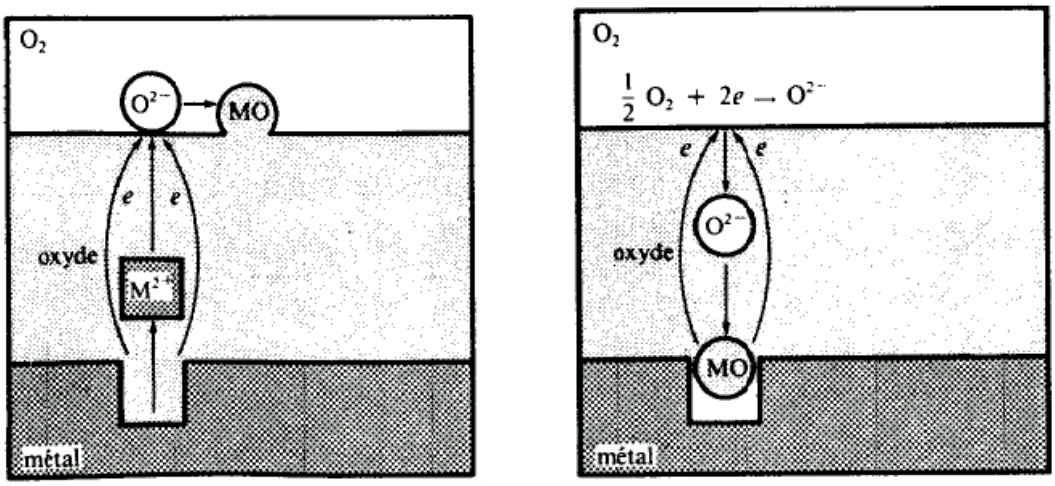
b) Representation of metallic bonds [2].

Figure 3. Atomic structures.

4. HIGH TEMPERATURE DRY CORROSION

This article does not claim to give a detailed explanation of the mechanisms of high temperature dry corrosion. Instead, its purpose is to broadly outline the basic mechanisms as well as the limitations of this strategy. In a high temperature oven, oxygen contained in the atmosphere serves as the oxidizer. The oxygen reacts with the sample to form an oxide layer. Initially, the metallic ion may diffuse through the oxide layer and react with the surface oxygen (Figure 4a). Growth of the oxide layer takes place on the surface. Alternatively, the

oxygen is diffused through the oxide layer (Figure 4b). The growth of the oxide layer takes place at the interface of the metal and the metallic oxide. It makes little difference what mechanisms are involved; ion transport is based on the laws of diffusion. The kinetics associated with this type of oxidation are often slow. Furthermore, there is a greater risk of volatilization of the compounds used.



a) Metallic ion diffusion b) Oxygen diffusion

Figure 4. Growth mechanism of the oxide layer [2].

To illustrate the slowness of these kinetics, we will look at the corrosion of a Cu-Ti alloy at 850°C [3]. Figure 5 illustrates the effect of titanium concentration. The equation for the growth of the oxide layer as a function of time is as follows:

$$X = \left[\frac{2N_O^{(s)} D_o}{\nu N_B^{(0)}} \; t \right]^{1/2}$$

where: X is the thickness of the oxide layer
$N_O^{(s)}$ is the solubility of the oxygen
$N_B^{(o)}$ is the initial concentration of the metal
D_o is the oxygen diffusion constant
ν is a stoichiometric factor
t is the time

This equation is parabolic. The growth is a function of the square root of time. The greater the concentration of titanium, the longer the time required to achieve a specific oxide thickness. Furthermore, the sample must be finely crushed. As

metals are often ductile, it is difficult to produce fine powders. Use of oxidizer compounds other than oxygen often provides a much quicker alternative solution.

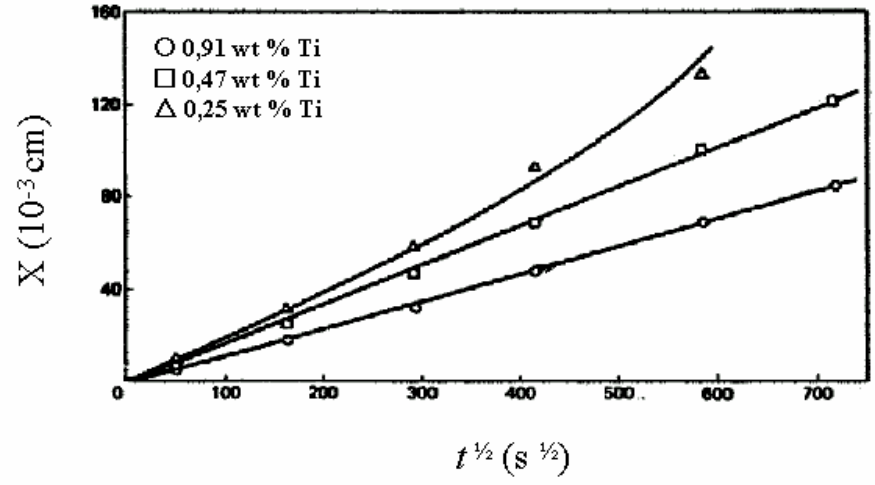


Figure 5. Oxidation of the Cu-Ti alloy at 850°C [3].

5. SOLID OXIDIZERS

The principle of the solid oxidizer reaction is simple. The oxidizer melts before the fluxing medium and it oxidizes the sample. The oxidizer extracts electrons from the metal: metallic oxides are formed. The advantages of forming a liquid coating are numerous. First of all, the transport of ions is increased in the liquid phase. Furthermore, adhesion of the oxide layer to the surface of the metal is greatly reduced. Finally, the metal can be directly attached without the problem of diffusion through an oxide layer. Several oxidizers are available on the market. Table 1 shows some of the physical properties of the oxidizers most commonly encountered.

Table 1. Physical properties of some solid oxidizers [4]

	Point de fusion (°C)	Point d'ébullition (°C)
$LiNO_3$	264	d 600
Li_2CO_3	723	d 1310
$NaNO_3$	307	d 380
Na_2CO_3	851	d
NH_4NO_3	170	210

* d represents decomposition temperature

Experimentation and study of high temperature chemistry make it possible to deduce oxidation equations. For example, lithium nitrates and carbonates oxidize metal as follows:

$$Li_2CO_3 + M \rightarrow Li_2O + MO + CO \nearrow$$
$$2LiNO_3 + M \rightarrow Li_2O + MO + N_2O \nearrow + 1½O_2 \nearrow$$

However, when the fluxing medium reaches the fusion point, the oxidizer reacts concurrently with the latter. This is a competition reaction that consumes the oxidizer.

$$Li_2CO_3 + flux \rightarrow flux \bullet Li_2O + CO_2 \nearrow$$
$$2LiNO_3 + flux \rightarrow flux \bullet Li_2O + NO_2 \nearrow + 1½O_2 \nearrow$$

Other oxidation reactions may also be initiated from the products of decomposition. An example is the oxidizing reaction of CO_2 with metals.

$$CO_2 + M \rightarrow CO + MO$$

The advantage of this technique is that fusion takes place in a single step. The risk with this type of oxidation is the uncertain outcome of the oxidation reaction:

an unstable bead may result and the crucible may be destroyed. One way to ensure that oxidation occurs is to oxidize the sample by means of wet chemistry.

6. OXIDATION BY WET CHEMISTRY

6.1 Theory

Wet chemistry oxidation is widely used in the field of atomic emission and absorption analysis. Many digestion procedures facilitate the solubilization of rocks, sediments and metals, for example. The solution is then analyzed using various analytical techniques. It is now possible to modify these procedures for the preparation of beads. The objective is to oxidize a sample, using a solution, in the platinum crucible. However, before going into detail about the oxidizer solutions available, it is important to review the basic principles of electrochemistry. An electrochemical reaction always comprises an anodic and a cathodic reaction. The metal's oxidizing reaction is the anodic reaction. There may be several cathodic reactions with the oxygen. However, only the cathodic reaction in an acid environment will be considered here. It is represented by the second equation.

$$M \rightarrow M^{n+} + ne$$
$$O_2 + 4\,H^+ + 4e \rightarrow 2H_2O \quad \varepsilon^o = 1{,}23\ V$$

For an electrochemical equation to be spontaneous, it is essential that the first equation's half-reaction potential be less than 1.23 V. Fortunately, when we refer to a table of potential reduction standards, the potential of most metals is lower and they can be oxidized in an acid environment. A reaction may be spontaneous but that provides no information on the kinetics of oxidation. Faraday's law makes it possible to calculate the oxide mass formed as a function of time.

$$m = \frac{\mathrm{M}\ i_{corr}\ t}{n\ \mathrm{F}}$$

where: m is the oxide mass
i_{corr} is the corrosion current
M is the mole weight
t is the time
F is the Faraday constant
n is the number of electrons exchanged

The reaction speed depends on the corrosion current. The current is limited by a number of parameters. The first factor is the activation polarization. This factor represents the reduction effect of the intermediate reactions and the temperature on the oxidation kinetics. The second factor is diffusion polarization. As with high temperature dry corrosion, the diffusion of ions through the oxide layer limits the oxidation kinetics. The last factor is passivation. If a very stable oxygen layer is formed and it blocks the solubilization of ions, the oxidation reaction ceases. A well-known example is that of an iron bar immersed in a nitric acid solution. Even though nitric acid is a powerful acid, the iron is not soluble in the concentrated solution. A protective layer forms that halts the oxidation reaction. However, this layer does not form in dilute nitric acid and the iron bar is easily dissolved. Therefore, what procedure is recommended to oxidize a lead-tin alloy? A number of strategies are possible but only two will be presented.

6.2 Oxidation procedure for a lead-tin alloy in a wet environment

The first procedure consists of oxidizing a lead-tin alloy directly in a platinum crucible, by using a hydrobromic acid. Metallic bromide forms. Then the bromium is flushed with a hydrogen peroxide solution. The reactions may be activated by simply heating the plate slightly. This procedure makes it possible to control the X-ray fluorescence with a reactive error of 0.1%. The overall and intermediate reactions are as follows:

1) $Pb^{o} + 2\ HBr \rightarrow Pb(Br)_2 + H_2\uparrow$

2) $Sn^{o} + 2\ HBr \rightarrow Sn(Br)_2 + H_2\uparrow$

3) $Pb(Br)_2 + x\ H_2O_2 + \Delta \rightarrow PbO + Br_2\uparrow + O_2\uparrow + H_2O\uparrow$

4) $Sn(Br)_2 + x\ H_2O_2 + \Delta \rightarrow SnO_2 + Br_2\uparrow + O_2\uparrow + H_2O\uparrow$

$$Sn\text{-}Pb + 4HBr + xH_2O_2 \rightarrow PbO\downarrow + SnO_2\downarrow + 2Br_2\uparrow + xO_2\uparrow + 2H_2\uparrow + xH_2O\uparrow$$

The second procedure consists of oxidizing the lead-tin alloy using nitric acid. The oxidizing reaction is as follows:

$$Sn\text{-}Pb + x\ HNO_3 \rightarrow SnO_2 + PbO + x\ NO\uparrow + x\ H_2O\uparrow + x\ O_2\uparrow$$

However, even if this solution is heated on a plate, oxidation takes place slowly. This reaction may be catalyzed using hydrofluoric acid. The fluoride ion is very small and Table 2 shows that it forms very stable bonds with the metals. The

hydrofluoric acid depassivates the oxide layer. In summary, if hydrofluoric acid is added first and nitric acid is added subsequently, oxidation occurs spontaneously.

Table 2. Some important metal ion/fluoride complexes [5].

Metal	Strength of the M-F bond (kJ/mol)	Major ionic species in an aqueous solution (log K)
B(III)	644	BF_4^-
Al(III)	581	AlF_6^{3-} (19,8)
Si(IV)	564	SiF_6^{2-}
Ti(IV)	585	TiF_6^{2-}
Zr(IV)	648	ZrF_6^{2-} (38,4)
Nb(V)	568	$Nb(OH)_2F_5^{2-}$ (2,5)
U(VI)	-	$UO_2F_4^{2-}$ (12,6)

7. CONCLUSION

High temperature dry corrosion is a slow reaction. Solid oxidizers such as lithium carbonate and nitrate may also be used but the outcome of the fusion is uncertain. Finally, oxidation in an acid environment makes it possible to visually ascertain that oxidation is complete. Thus, one is assured of not damaging the crucibles. Furthermore, this strategy makes it possible to dissolve the sample within the solubility limits of the beads. The subject of oxidation is broad and it can be seen that analysts will soon have a choice of several standardized oxidation procedures.