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Reduction of metallic surface oxides via an electrochemically-generated redox species

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A new method is described for removing oxides from metallic surfaces via electroless reduction by the reducing member of a redox couple that is electrochemically regenerated in a closed loop. On tin–lead coatings, which are widely used to enhance the solderability retention of electronic components and circuit boards, naturally-formed oxides are reduced to the metallic state within ten seconds by either vanadous or chromous ions in acidic sulfate solution. Wetting balance data for wire specimens show that this reduction treatment is an effective means of restoring and ensuring solderability.

1. Introduction

Removal of surface oxides is a key requirement for formation of a good bond between metals joined by soldering or welding. Rosin fluxes activated by organic acids effectively dissolve oxides just before or during the bonding operation but leave tenacious residues that can cause corrosion problems if not fully removed. Consequently, for electronic soldering applications, it has been necessary to both limit flux activity and employ chlorofluorocarbon (CFC) solvents to remove flux residues. Because of the CFC ban to go into effect in 1995, aqueous cleaning methods and alternative fluxes have been developed but their effectiveness has not been proven for general use. The lower activity of no-clean and water soluble fluxes is of particular concern.

Earlier work in the authors' laboratory indicated that electrochemical reduction of oxides on tin–lead solder coatings restores solderability and suggested that an electroless analog of this treatment might be developed [1]. However, the hydrazine reducing agent initially employed raises environmental/safety concerns and does not give consistent results, presumably because hydrazine oxidation is kinetically slow on some surfaces. The present paper describes results obtained with metallic ion reducing agents, which are generally efficacious for oxide reduction/solderability restoration and can be regenerated electrochemically in a closed loop. Solderability restoration via this approach is termed 'reduced oxide soldering activation' (ROSA^{TM}) and is the basis for a proprietary process [2, 3].

2. Experimental details

As illustrated in Fig. 1, the metallic ion reducing agents were generated in a cylindrical glass cell (6.7 cm diam.) having a Teflon top sealed via a standard taper joint. Seals for all feed-throughs were provided by standard taper joints or threaded O-ring connectors (not shown). The cathode was usually a mercury pool (36 cm^2) but lead (41 cm^2), which gave similar results, was used in a few cases. The reference saturated calomel electrode (SCE) and platinum anode were immersed in separate compartments (glass tubes) containing background electrolyte (without the redox couple), which were separated from the catholyte by microporous Vycor glass discs (Corning 'Thirsty Glass') sealed via Teflon heat-shrink tubing. These discs were 7 mm in diameter and 3.5 mm thick. The catholyte was saturated with inert gas (argon or nitrogen) and had a volume of 200 mL.

Chromous and vanadous ion solutions (0.8 M) were generated under initially higher current (about 50 mA), which was decreased to a few milliamperes as the final voltage (−0.65 V vs SCE) was approached. Full charge was maintained via a trickle current of 1.0 mA and the cathode voltage was allowed to vary between −0.65 and −1.1 V vs SCE. The starting solutions were prepared by dissolving chromic chloride (J. T. Baker reagent grade), chromic sulfate (Johnson–Matthey reagent grade) or vanadyl sulfate (Johnson–Matthey technical grade) in the appropriate acid (sulfuric or hydrochloric) solution of the desired pH value. As vanadyl (VO^{2+}) was

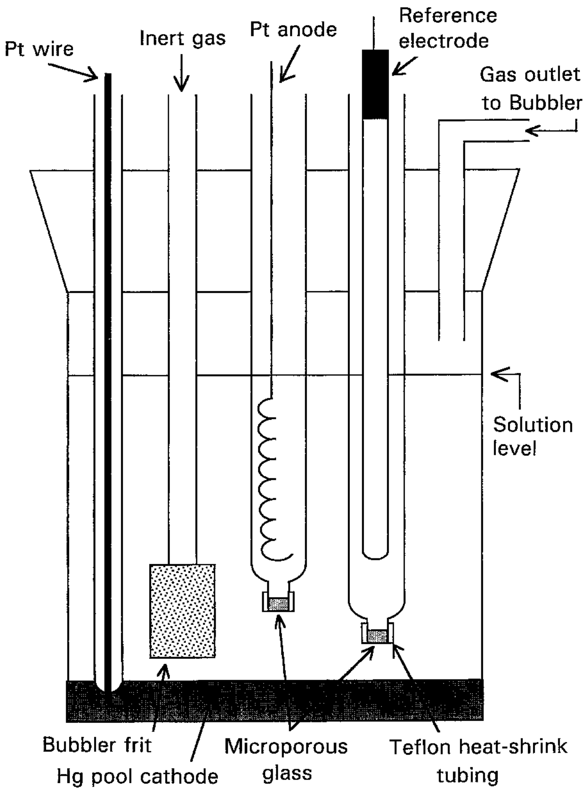

Fig. 1. Schematic representation of cell used to generate metallic ion reducing agents.

converted to vanadic ion (V^{3+}), which consumes protons, the catholyte pH was maintained relatively constant by monitoring (Corning model 125 pH meter) and addition of sulfuric acid. Because of the difficulties associated with measuring pH in highly acidic solutions, the pH values reported are probably precise to only ±0.2 pH units. Note that reducible metallic ion contaminants would be removed by electrodeposition and dissolution in the Hg cathode.

The wetting balance method used for testing solderability in the present work has been described in detail previously [4–7]. The apparent specimen weight is monitored as a solder pot is rapidly raised to immerse the bottom portion of the specimen to a predetermined depth in the molten solder (held at constant temperature). A buoyancy correction is made to account for the density difference between the molten solder and the specimen material so that the forces associated with the wetting process are determined. Initially, the relatively cold specimen does not wet so that the corrected apparent weight is reduced because of the downward solder meniscus around the specimen periphery. As the specimen warms and wetting occurs, the meniscus rises (eventually above the solder pot level) and the apparent specimen weight increases, finally reaching a maximum value determined by the molten solder surface tension. Since the latter is affected by the presence of fluxes and/or solder surface oxides whose compositions may change during the course of the measurement, the maximum wetting force attained may not correspond to the theoretically expected value. Also, the thermal inertia of the specimen plays an important role in determining the wetting rate. Nonetheless, wetting balance measurements provide a relative measure of the speed of wetting, which is an important solderability parameter.

Specimens used for wetting balance tests were 0.85 mm diameter coated copper resistor wires (Allen–Bradley Company) about 5 cm in length. Most of the wires tested had a 'conversion tin' finish formed by chemical conversion of a 90% Pb–10% Sn coating to form a very thin overlayer of pure tin. This finish was selected as a worst case since it rapidly loses solderability after manufacture. For comparison, some measurements were also performed on wires having the typical fused eutectic tin–lead solder coating (63% Sn–37% Pb) that had been dry heat-aged (125 °C for 8 h) to degrade solderability.

Wetting balance tests were performed in the ambient at the solder pot temperature of 235 °C using a multicore universal solderability tester (MUST) controlled by an IBM Model XT personal computer, as described previously [8]. An unactivated rosin (R) flux (Kester Formula 135) was used to prevent reoxidation of electrolessly reduced specimens during testing. For comparison, some untreated specimens were also tested using either a mildly activated rosin (RMA) flux (Kester 185) or a fully activated rosin (RA) flux (Kester 1544). As recommended by Lea [4, 5], specimens were immersed at a speed of $20\,\mathrm{mm\,s^{-1}}$ to a depth of 3 mm (4.0 s total immersion time) and the wetting time was taken as the time required to reach 2/3 the maximum theoretical wetting force ($4\,\mathrm{mN\,cm^{-1}}$). Each data point represents the average for at least five, and usually ten, test specimens.

The electroless reduction treatments were performed inside an inert atmosphere (nitrogen or argon) glove box. Unless otherwise noted, specimens were rinsed in deaerated deionized water and blown dry with an inert gas stream after the reduction treatment. They were stored in glass vials under inert gas until just prior to wetting balance testing. In some cases, the R flux was applied inside the glove box and testing was performed immediately.

The amount of oxide remaining on specimens after the reducing treatment was determined by chronopotentiometric reduction at a constant current density of $-20\,\mu\mathrm{A\,cm^{-2}}$ in deaerated pH 8.4 borate buffer solution, i.e., sequential electrochemical reduction analysis (SERA$^{\mathrm{TM}}$) analysis [8, 9]. Equipment and procedures were the same as described previously [8]. The oxide remaining analysis was performed inside the glove box; after the reducing treatment, the specimen was rinsed in deionized water and transferred immediately to the borate buffer solution which was contained in a sealed cell. An area of about $0.5\,\mathrm{cm^2}$ was immersed in the solution for analysis. Surface oxide amounts are given in terms of the charge density, i.e., current density multiplied by the time required for complete reduction; $1\,\mathrm{mC\,cm^{-2}}$ is approximately equivalent to

1 nm of SnO or 0.6 nm of SnO_2 (or an intermediate thickness of mixed oxide).

3. Results and discussion

3.1. *Preliminary screening*

Based on a literature survey, common reducing agents that are thermodynamically capable of reducing SnO_2 to the metal include: phosphite, hypophosphite, oxalate, formate, hydrazine, chromous ion and vanadous ion in acidic solution; and hypophosphite, borohydride, hydrazine and dithionite in alkaline solution. For preliminary screening of the relative reduction rates, a small amount (one gram) of $SnO_2 . xH_2O$ powder (prepared by reaction of aqueous $SnCl_4$ with NH_4OH) was added to approximately one molar solutions of each of the reducing agents (at pH 1 or 13). When reduction occurred, formation of finely divided tin metal caused the white powder to darken.

For exposure times as long as one hour at room temperature, only the chromous and vanadous systems were found to visibly reduce the hydrous SnO_2 powder. Kinetic inhibition for the other systems may arise from slow oxidation of the reducing agent on the oxide surface. This explanation is consistent with our finding that hydrazine is sometimes, but not always, effective in reducing tin oxides on Sn–Pb coatings. Porosity or cracks in the oxide film could, in some cases, expose the underlying metal, which is an effective catalyst for hydrazine oxidation. Note that the metal ion reducing agents are highly solvated and probably do not depend on strong adsorptive interactions for their effectiveness. These preliminary studies indicated that both chromous and vanadous ions are capable of reducing tin oxides in less than one minute.

3.2. *Oxide reduction and redox regeneration reactions*

As an example, the half cell and net reactions involved in electroless reduction of tin dioxide (to the metal) by vanadous ion (V^{2+}) may be summarized as

$$4V^{2+} \longrightarrow 4V^{3+} + 4e^- \quad \text{(oxidation reaction)}$$

$$SnO_2 + 4H^+ + 4e^- \longrightarrow Sn + 2H_2O \quad \text{(reduction reaction)}$$

$$SnO_2 + 4V^{2+} + 4H^+ \longrightarrow Sn + 4V^{3+} + 2H_2O \quad \text{(net oxide reduction reaction)}$$

In the absence of electroactive anions or vanadium ions in the anolyte, the anode reaction during electrochemical regeneration of vanadous ion at the cathode is breakdown of water to oxygen. In this case, the half cell and overall reactions for the electrochemical regeneration process are

$$4V^{3+} + 4e^- \longrightarrow 4V^{2+} \quad \text{(cathode reaction)}$$

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^- \quad \text{(anode reaction)}$$

$$4V^{3+} + 2H_2O \longrightarrow 4V^{2+} + 4H^+ + O_2 \quad \text{(net regeneration reaction)}$$

The net reaction for the entire oxide reduction/electrochemical regeneration process is

$$SnO_2 \longrightarrow Sn + O_2$$

The reactions for the chromous ion reducing agent or for reduction of other metallic oxides are exactly analogous. In all cases, the only products of the overall process are the free metal and oxygen gas. Note that protons are consumed during oxide reduction but are catalysts overall since they are generated in equivalent amounts at the anode. When chloride is used as the anion, rather than the unoxidizable sulfate ion, the anode reaction is chlorine evolution but the chemical balance in the system is not disturbed.

3.3. *Separator characteristics*

Although not evident from the literature, a porous separator under unipolar voltage bias selectively transports anions in one direction and cations in the other since the dominant transport mode is usually electromigration rather than diffusion [3]. Thus, the microporous glass separator used to separate the anolyte and catholyte in the present work, for which all electrolyte channels are subject to a comparable electric field strength, functions as a semipermeable ionic barrier. Consequently, transport of cationic redox species from the catholyte to the anolyte is negligible except at very low current levels (at which the migration and diffusion rates are comparable) since the polarity of the separator voltage drop favours transport of protons from the anolyte to the catholyte but opposes transport of the cations in the reverse direction. Of course, anions experience the opposite influence but the primary current carriers are protons, which are consumed in the catholyte and generated at the anode. In practice, some transport of metallic cations to the anolyte occurs when the cell is being maintained at full charge by a trickle current, but this presents no difficulties since the various oxidized redox species are also soluble in the acidic solution and should migrate back to the catholyte when the current density is increased.

3.4. *Oxide-remaining analysis*

Figure 2 shows typical SERA curves for conversion tin wire specimens treated for various times in the pH 0.5 vanadous sulfate solution. The curve for the untreated specimen exhibits a single plateau (with considerable tailing) corresponding to reduction of a mixed stannous-stannic oxide [4, 6]. The amount of oxide indicated is a factor of two greater than that normally found on production printed wiring boards [10]. The more negative final plateau voltage for the untreated specimen (Fig. 2) apparently reflects a small amount of residual oxide that raises the hydrogen overvoltage (increases the local current density). This explanation is consistent with the somewhat higher average wetting time of 0.95 s observed for such SERA reduced specimens compared to 0.6 s

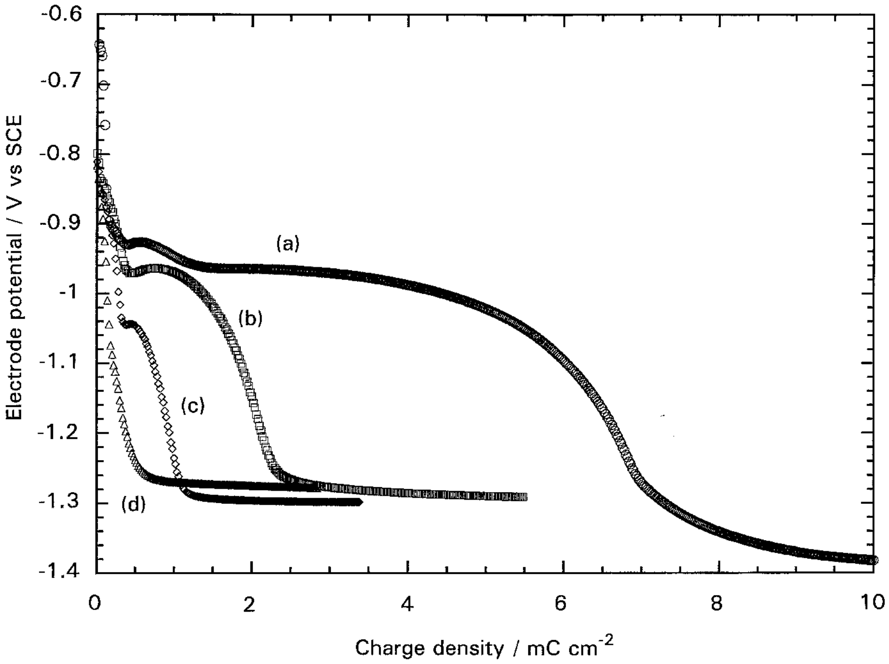

Fig. 2. Typical SERA curves for conversion tin wire specimens treated for various times in pH 0.5 vanadous sulfate solution (0.8 M). Treatment time: (a) 0, (b) 5, (c) 10 and (d) 30 s.

*Table 1. Wetting time and oxide remaining for conversion tin wire specimens after various electroless reduction treatments**

Treatment /pH	*Time* /s	*Flux type*	*Wetting time* /s	*Oxide remaining* /mC cm^{-2}
None		R	2.46 (0.79)	6.64 (0.74)
None		RMA	0.65 (0.04)	
None		RA	0.45 (0.06)	
SERA reduced		R	0.95 (0.11)	
Chromous chloride				
0.0	2	R	0.37 (0.01)	0.65 (0.20)
	5	R	0.45 (0.08)	0.35 (0.12)
	10	R	0.38 (0.03)	0.12 (0.02)
	20	R	0.37 (0.02)	0.21 (0.03)
0.2	2	R	0.46 (0.07)	1.14 (0.15)
	5	R	0.44 (0.05)	0.60 (0.37)
	10	R	0.40 (0.02)	0.25 (0.10)
	20	R	0.57 (0.04)	0.25 (0.10)
Chromous sulfate				
0.2	2	R	1.01 (0.18)	5.04 (0.69)
	5	R	0.79 (0.17)	1.06 (0.57)
	10	R	0.54 (0.09)	1.11 (0.32)
	20	R	0.58 (0.15)	0.26 (0.20)
	30	R	0.57 (0.02)	0.53 (0.30)
0.5	5	R	1.53 (0.67)	1.97 (0.45)
	10	R	0.73 (0.19)	1.04 (0.56)
	20	R	0.66 (0.09)	0.14 (0.02)
	30	R	0.54 (0.08)	0.12 (0.00)
1.1	5	R	2.32 (0.33)	2.90 (0.45)
	10	R	1.36 (0.24)	2.57 (0.33)
	20	R	1.17 (0.14)	1.03 (0.37)
	30	R	1.19 (0.15)	0.65 (0.07)
	60	R	1.11 (0.04)	0.48 (0.21)
Vanadous sulfate				
0.5	5	R	1.48 (0.41)	2.21 (0.41)
	10	R	0.88 (0.11)	1.43 (0.50)
	20	R	0.77 (0.10)	0.64 (0.16)
	30	R	0.64 (0.02)	0.56 (0.10)
	60	R	0.64 (0.05)	0.46 (0.02)

* Values in parentheses are standard deviations for the total population.

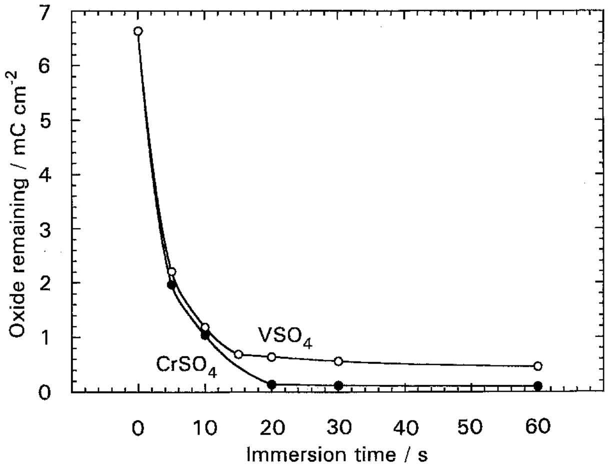

Fig. 3. Average amount of oxide remaining for conversion tin resistor wires against immersion time in pH 0.5 chromous or vanadous sulfate solutions (0.8 M).

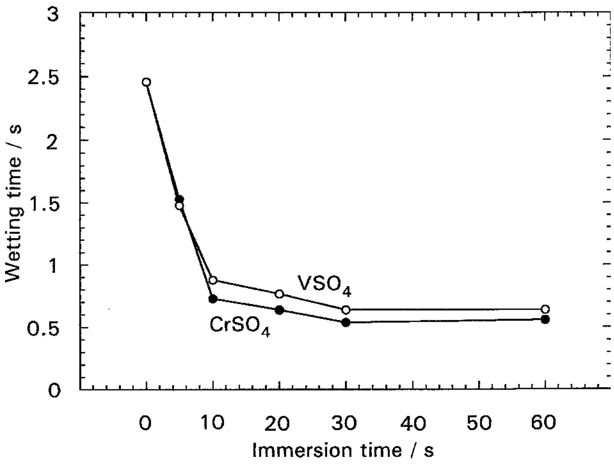

Fig. 4. Average wetting time for conversion tin resistor wires against immersion time in pH 0.5 chromous or vanadous sulfate solutions (0.8 M).

(see Table 1) for those reduced for 30–60 s in the pH 0.5 vanadous sulfate solution. The surface oxide is greatly diminished after even 5 s in the vanadous solution, and is completely removed by the 30 s treatment.

3.5. *Oxide reduction effectiveness*

An R flux was used in the present work to prevent reoxidation of the specimen during wetting balance testing. Such fluxes have little or no activity for removing oxides on Sn–Pb surfaces so that the reduced wetting times observed can be attributed almost entirely to the prior oxide removal. In fact, excellent wetting of tin–lead surfaces after reduction in the vanadous electrolyte employed here has been demonstrated for printed wiring board coupons wave soldered under a nitrogen atmosphere without a flux [11].

Table 1 gives the average wetting time (R flux) and amount of oxide remaining (standard deviations in parentheses) for conversion tin wire specimens after various electroless reduction treatments and times. For comparison, the wetting times obtained for untreated specimens with mildly activated rosin flux (RMA) and fully activated rosin flux (RA) are also given. Values obtained without a flux were always greater than the maximum measurable time of 4.0 s. For untreated specimens, the unacceptably-long wetting time of 2.5 s (R flux) decreased to about 0.5 s with increasing flux activity. Comparable values (0.4–0.6 s) were attained with an R flux within 2 s in the very acidic (pH 0.0 and 0.2) chromous chloride solutions, within 10 s in the most acidic (pH 0.2) chromous sulfate solution, and within 30 s in either chromous or vanadous sulfate solution of intermediate acidity (pH 0.5). In all of these cases, the decrease in the amount of oxide remaining paralleled the decrease in wetting time. The electroless reduction treatment also tended to decrease the standard deviation of the wetting time. The variation in the small amount of oxide remaining after the longer times was probably associated with minor reoxidation that occurred between the times of treatment and analysis.

At the highest pH investigated (pH 1.1 chromous sulfate solution), the wetting time was not reduced below 1.1 s even for the longer treatment times (20–60 s). This is consistent with our more recent findings [12], based on analysis of a wide variety of specimen types, that the metallic ion electroless reduction process is ineffective at pH values above 0.9. Since the amount of oxide remaining continued to decrease after 20 s at the highest pH (Table 1), the higher wetting times may be associated with residues from the reducing solution (other than oxides) left on the surface.

It should be emphasized that while protons are required in the metallic oxide reduction process, they do not by themselves remove the surface oxides investigated here. Comparable treatments with background acidic solutions (no reducing redox couple) produce no appreciable effect on the wetting time.

Table 2. Average wetting time for dry heat-aged eutectic Sn–Pb specimens with and without rinsing after 10 s reduction treatments

Treatment	*Wetting time*	
	Rinsed and blow dried /s	*Blow-dried only* /s
None	1.78 (0.57)	
Chromous sulfate	0.56 (0.04)	1.79 (0.73)
Vanadous sulfate	0.56 (0.09)	0.70 (0.10)

* Values in parentheses are standard deviations for the total population.

3.6. *Comparison of chromous and vanadous systems*

Figures 3 and 4 show plots of amount of oxide remaining and wetting time, respectively, as functions of immersion time in pH 0.5 chromous and vanadous sulfate solutions. From the close correspondence of the oxide remaining and wetting time curves for the same solution, it is evident that the electroless reduction treatment functions by removing the surface oxide layer. The oxide reduction rates are comparable for the chromous and vanadous sulfate system but in the latter case the small amount of residual oxide remaining (Fig. 3) increases the wetting time by 0.2 s (Fig. 4). These differences may be due to the greater reducing power of the chromous ion (chromic/chromous equilibrium potential is 0.15 V negative of that for vanadic/vanadous) but only vanadous ion completely removes a variety of oxides from eutectic tin-lead coatings [12]. It is more likely that the interaction between vanadous ion and conversion-tin-coated surface is anomalous, possibly involving adsorption.

Although the vanadous solution leaves a very small oxide residue on conversion-tin-coated resistor wires (which has a very minimal effect on the wetting time), practically complete oxide removal is attained for eutectic Sn–Pb surfaces [12]. Since eutectic Sn–Pb coatings are used on the vast majority of PWB's and component leads, the vanadous system generally provides performance comparable to that attained with the chromous system.

The effects of residues from both the chromous and vanadous sulfate solutions (pH 0.5) on eutectic Sn–Pb solderability were investigated by performing wetting balance tests (R flux) on dry heat-aged specimens that had simply been blown dry with inert gas (without water rinsing) after 10 s electroless reduction treatments. Table 2 summarizes the results. For rinsed specimens, both treatments were equally effective, reducing the average wetting time from 1.8 to 0.6 s. Without specimen rinsing, however, the wetting time was very short for the vanadous treatment (0.7 s) but long for the chromous treatment (1.8 s). These data indicate that any vanadous residues left by the reduction procedure have a negligible effect on the wetting time, whereas chromous residues increase the wetting time substantially. Presumably, chromium ions interact strongly with the Sn–Pb surface and, unless removed, form a stable oxide film that is detrimental to solderability. The apparent absence of such interactions for vanadium ions is an advantage for the vanadous system.

A considerable database showing that a 10 s treatment in the pH 0.5 vanadous sulfate solution effectively reduces a wide variety of surface oxides on eutectic tin–lead coatings is now available [12]. Even after long-term natural aging and treatments that induce formation of lead oxides, electrolessly-reduced specimens yield wetting times (0.4–0.7 s) equivalent to those provided by a fully active (RA) flux. Even for the worst-case specimens studied here, a 10 s treatment in any of the solutions having a pH of 0.5 or less (Table 1) provides wetting times of less than 0.9 s, which is quite fast from a practical standpoint. An exposure time of 30 s would be adequate for in-line use with current production mass soldering equipment.

4. Conclusions

Surface oxides on tin–lead surfaces are effectively reduced by vanadous or chromous ions that can be regenerated electrochemically in a cell employing a microporous glass separator. The net reaction of this reduced oxide soldering activation (ROSA^{TM}) process in the absence of electroactive anions in the solution is reduction of the oxide to the free metal and liberation of oxygen gas. Vanadous ion in sulfate solution (about pH 0.5) is the preferred reducing agent since the environmental considerations associated with chromium are avoided and oxygen is the anode product (rather than chlorine which would be evolved from a chloride electrolyte). In addition, small amounts of residue from the vanadous treatment do not significantly affect solderability of eutectic tin-lead coatings, which is not the case for the chromous system. At treatment times appropriate for in-line use with mass soldering equipment, the ROSA^{TM} process provides wetting times comparable to those attainable with a fully activated (RA) flux.

Acknowledgements

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