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Thermal analysis of indium bimetallic films. Part 6.

Galo Cárdenas T. [a] and L.H. Tagle D. [b]

[a] *Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción (Chile)*
[b] *Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)*

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Abstract

The thermal behaviour of bimetallic films was studied by the thermogravimetric analysis between 25 and 550°C at 10°C min^{-1}. The kinetic parameters derived from non-isothermal thermogravimetric data are presented. The synthesis of several bimetallic films of In–Sn, In–Ga and In–Cd with solvents such as acetone, 2-butanone and 2-propanol is described. The differences in thermal stability are compared with those of indium films prepared with the same solvents. The activation energies of these alloys are less than that of the pure metal. The decomposition reactions were found to be 0.5 and 1.0 order. The decomposition temperatures and pre-exponential factors were determined.

INTRODUCTION

In chemistry, an active and broad area of research has developed over the past two decades that investigates the generation of metal atoms (by metal evaporation) and the interaction of these free atoms with organic chemicals at low temperature [1]. New organometallic compounds and catalysts have been synthesized in this way, and a new understanding of the bonding in such substances has been revealed. The metal vapour is allowed to deposit under vacuum on the cold wall of the reactor (77 K) where organic chemicals are being deposited, the metal atoms being immersed in an excess of reactant compound [2].

Our interest in indium films is related to the application of indium oxide films in solar energy conversion devices. These films are n-type degenerate semiconductors with a band gap of 2.6–3.7 eV [3]. Because of their conductivity and high transparency in the visible part of the spectrum, these films are also used as transparent contacts for solar cells [4].

Correspondence to: G. Cárdenas T., Departamento de Química, Facultad de Ciencias, Universidad de Concepcíon, Casilla 3-C, Concepcíon, Chile.

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We have already reported the synthesis of In films with non-aqueous solvents [5]. Therefore, it is interesting to know the behaviour of new bimetal colloids that include indium, with reference to the behaviour of pure indium films. Again, thermogravimetric studies were carried out to determine the activation energy and pre-exponential factor as well as the reaction order.

The sols and films of In–Ga, In–Sn and In–Cd with acetone, 2-butanone and 2-propanol were investigated.

EXPERIMENTAL

Colloid synthesis

The colloids were prepared by codeposition using a metal atom reactor [6, 7]. As a typical example, a tungsten–alumina crucible was charged with 0.10 g of Ga and 0.14 g of In lamps (Alfa Products) and 2-propanol (100 ml), and dried over molecular sieves. The 2-propanol had been previously distilled in a ligand inlet tube and freeze-thaw degassed in several cycles. The reactor was pumped down to 1×10^{-4} Torr, while the crucible was warmed to red heat. A liquid-nitrogen-filled Dewar of (5 l) was placed around the vessel and the metals, previously melted to obtain the alloy, were codeposited over a 1.5 h period. The matrix was grey at the end of the deposition. The matrix was allowed to warm slowly under vacuum for 1.5 h by removal of the liquid-nitrogen-filled Dewar. Upon meltdown, a black colloid was obtained. After addition of nitrogen, the solution was allowed to warm for another 1.0 h at room temperature. The solution was syphoned off under nitrogen into a flask. The approximate concentration could be calculated, from both the metal evaporated and the 2-propanol uptake.

Bimetal films

The bimetal films were prepared by evaporation under vacuum (10^{-3} Torr) of the corresponding solvents. The films were pumped down for several hours at 25°C. The dried films were analysed for metals; their carbon content ranged between 1.20 and 21.65% depending on the solvent.

Elemental analysis

The microanalyses of the metals were performed by Geolab Laboratories. The carbon and hydrogen were analysed by the Chemistry Department Laboratories (Universidad de Concepción).

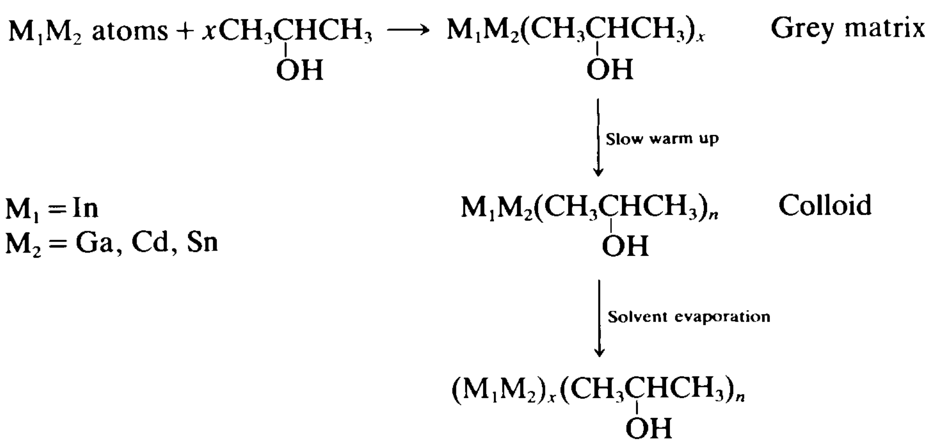
Thermogravimetric analysis

The thermogravimetric data were obtained using a Perkin-Elmer TGA-7 thermobalance. Samples (2–5 mg) were placed in aluminium pans and heated under nitrogen flow (50 ml min^{-1}) at 10°C min^{-1} between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of thin films by evaporation of colloidal sols has recently been reported [6, 8]. The films showed a high metal content and they can easily be prepared as shown in Scheme 1.

Table 1 summarizes the composition data of the bimetal films formed with non-aqueous solvents. It is clear that the solvent has been incorpor-



Scheme 1. Preparation of thin films.

TABLE 1

Composition of bimetallic films

Film [a]	% M_1 [b]	% M_2 [b]	% C [c]	% H [c]
(Ga–In)–2-propanol	23.1	45.1	4.31	1.53
(Ga–In)–2-propanol	30.7	35.9	3.92	1.74
(Ga–In)–2-propanol	14.2	23.1	21.65	4.09
(Ga–In)–acetone	20.9	39.4	1.98	1.64
(Ga–In)–2-butanone	25.0	31.2	21.01	5.10
(In–Cd)–2-propanol	29.3	49.3	1.20	0.87
(In–Cd)–THF	9.2	69.4	2.51	1.46
(In–Sn)–2-butanone	21.2	42.5	17.92	4.52

[a] All the colloids have a negative charge. [b] Microanalysis performed by Geolab & Co. [c] Laboratories Fac. de Ciencias, Universidad de Concepción.

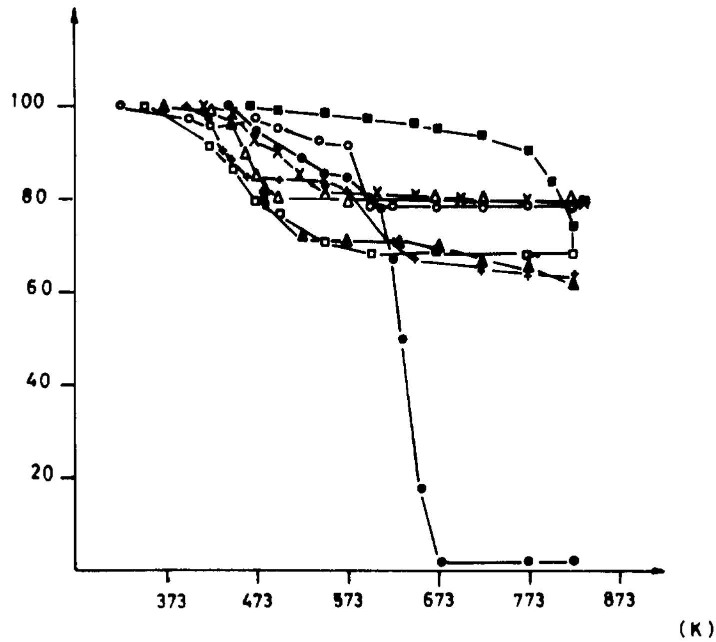


Fig. 1. Thermogram of bimetallic films obtained by heating from 298 to 823 K at 10°C min^{-1}. +, (In–Sn)–2-butanone; ○, (Ga–In)–2-propanol; □, (Ga–In)–2-butanone; ×, (In–Cd)–THF; △, (Ga–In)–2-propanol; ■, (Ga–In)–acetone; ▲, (Ga–In)–2-propanol; ●, (Cd–In)–2-propanol.

ated in the films. The amount of metal incorporated is similar, except when the solvent is tetrahydrofuran (THF). All the films exhibit a significant amount of carbon and hydrogen. The most common feature accounting for the similarities in carbon content is probably the formation of chemical bonds between the metal and the solvents.

Figure 1 shows the change in sample weight as a function of time and temperature when the alloy films are heated from 298 to 823 K. (Cd–In)–2-propanol showed the smallest residual weight, due to its very low C/H content; moreover, this film derives from the least stable colloid. The residual weight of this bimetallic film is similar to those of indium films reported previously [9]. The most stable film is (Ga–In)–acetone, with only 10% weight loss at 773 K, which is similar behaviour to that of In–acetone films and also of (Ga–In)– and (In–Cd)–2-propanol. However (In–Cd)–THF displays 20% of the total weight loss at 823 K.

Table 2 lists the thermal decomposition kinetic parameters for each film obtained from the first marked change in the slope of the TG curves.

Most of these In alloys degrade in two stages with different thermal

TABLE 2

Kinetic parameters for In bimetallic films

Film	n	E_a (kJ mol^{-1})	Weight loss (%)	A (s^{-1})	Temp. (K)
(In–Ga)–acetone	−1	22.14	0–3.5	4.56×10^1	150–300
	0	59.68	10–26.2	6.66×10^3	510–550
(In–Sn)–2-butanone	−1	124.98	2.3–14.7	3.33×10^{26}	150–180
	−1	60.76	18.2–32.9	3.94×10^7	300–375
(In–Ga)–2-butanone	−0.5	17.06	9.3–32.5	1.92	145–305
(In–Cd)–THF	−2	43.47	1.0–18.1	1.13×10^6	150–275
(In–Cd)–2-propanol	−2	43.45	4.1–14.5	1.14×10^6	150–275
	0	40.21	16.6–89.0	5.02×10^2	320–390
(In–Ga)–2-propanol	−0.5	48.63	1.8–4.7	1.74×10^7	150–225
	−0.5	41.45	-4.7–11.7	2.64×10^4	250–325

decomposition temperatures, T_D. This is most probably due to the presence of two metals bonded to the solvent. Previously, we reported the behaviour of In films with organic solvents [9], and in all the films they exhibited one decomposition stage.

Considering that the decomposition reaction is irreversible, the rate-dependent parameters such as activation energy and reaction order may be calculated from a single experimental curve [10]. The thermal decomposition kinetics of the thermogravimetric weight loss can be described in terms of the kinetic equation

$$-d\alpha/dt = k_n(1-\alpha)^n \tag{1}$$

where α is the fraction of the sample weight reacted at time t, n is the reaction order and k_n is the specific rate constant. The reaction rate ($d\alpha/dt$) was calculated using a differential technique with a heating rate v of 10°C min^{-1}. We can establish that

$$\frac{d\alpha}{dt} = v\frac{d\alpha}{dT} \tag{2}$$

The specific rate constant k can be expressed by the Arrhenius equation

$$k_n = A\exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor, E the activation energy, T the absolute temperature and R the gas constant. After combining eqns.

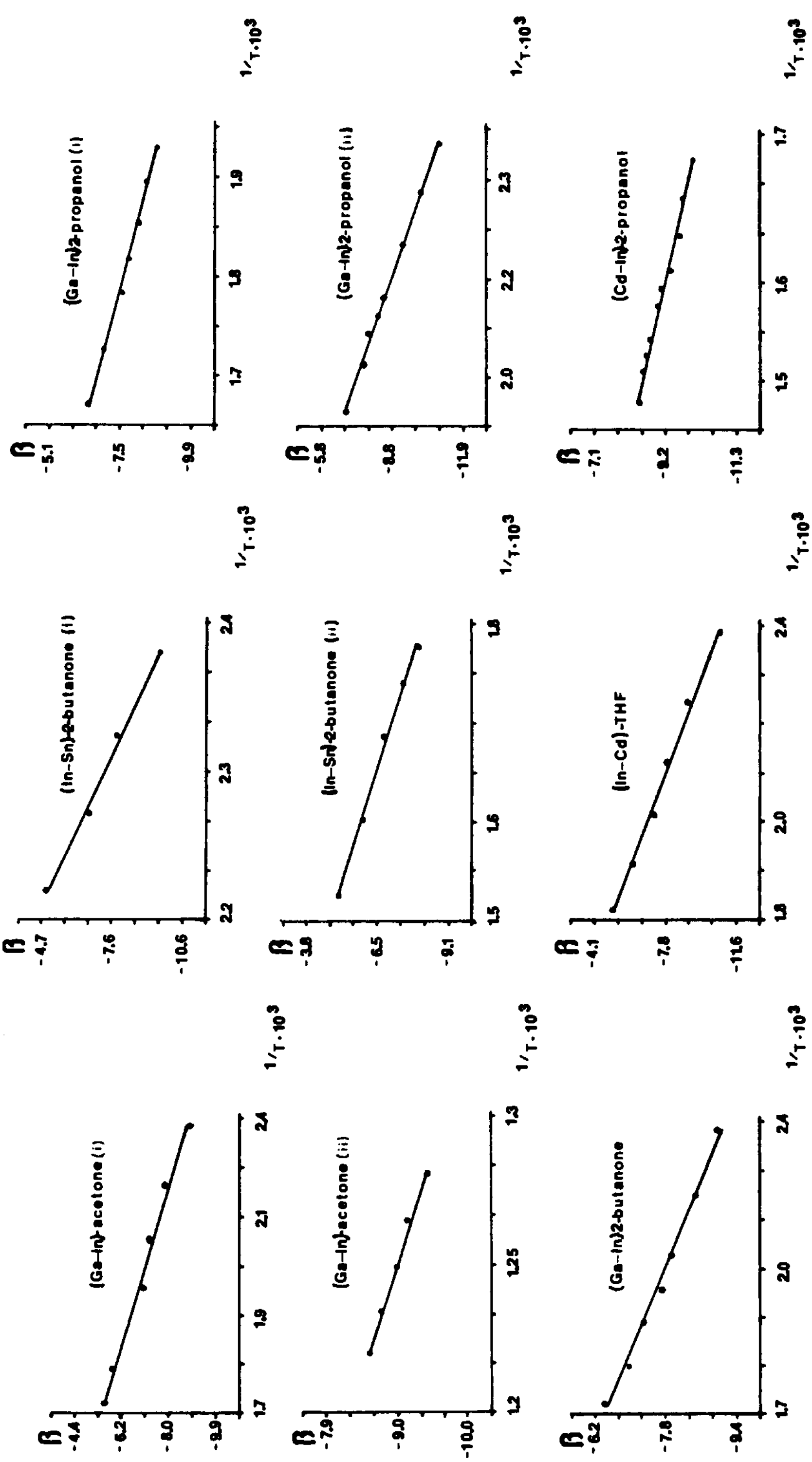


Fig. 2. Arrhenius plots for the thermal degradation of bimetallic films. (Ga–In)–acetone: (i) 423–573 K; (ii) 783–823 K. (Ga–In)–2-butanone: 416–576 K. (In–Sn)–2-butanone: (i) 423–453 K; (ii) 573–646 K. (In–Cd)–THF: 423–546 K. (Ga–In)–2-propanol: (i) 523–598 K; (ii) 423–498 K. (Cd–In)–2-propanol: 593–663 K.

(1)–(3) and incorporating v, we obtain

$$\beta = \ln\left[-\frac{\mathrm{d}\alpha/\mathrm{d}t}{v(1-\alpha)^n} \right] = \ln A - E/RT \tag{4}$$

Assuming a first-order reaction model, a multiple regression program was used to plot β against $1/T$ (see Fig. 2). A straight line should be obtained, and E and A can be calculated from the slope and intercept, respectively. This program is very similar to that reported by Ma et al. [11].

There are several values of extraction energy due to the very complicated decomposition patterns. The coefficients of linear correlation vary from 0.917 to 0.997. The kinetic parameters E and A calculated from these plots are summarized in Table 2. In some cases, two values of activation energy are reported because the bimetal decomposes in two stages, over different ranges of temperatures. For example, (In–Ga)–acetone shows a first-order decomposition between 423 and 673 K, but zero-order between 783 and 823 K. This is probably due to the lower melting point of Ga and its affinity for oxygen. (In–Ga)–2-butanone has the lowest E_a, with a fractional order rate; this is typical of complicated decomposition processes. This behaviour, with similar E_a values but different activation energies, occurs in the same temperature range. The more relevant difference is the percentage weight loss, acetone being the most volatile, as expected. However, (In–Ga)–2-propanol also has a fractional order rate, but an E_a value twice as high, in both temperature ranges. Probably, the loss of water from an alcohol requires more energy than the loss of CO from ketones.

It is also interesting to observe the In–Cd alloys. 2-Propanol and THF films show similar E_a values in the same temperatue range and also similar percentage weight losses. This is mostly due to the similarities in the linkage of the metals to the solvents.

Finally, (In–Sn)–2-butanone is the film with the highest activation energy in both temperature ranges. It is evident in this case that the presence of tin leads to an increase in activation energy. We have recently determined [12] that Sn films are very stable at room temperature.

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