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ORIGINAL CONTRIBUTION

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Synthesis and characterization of NiSn colloids and active solids prepared in organic solvents by CLD

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Abstract Bimetallic colloidal dispersions were obtained by simultaneous cocondensation of nickel and tin atoms with organic solvents at 77 K using the chemical liquid deposition (CLD) method. The atoms in a 1:1 ratio were produced by resistive heating and were reacted with 2-propanol, 2-methoxyethanol, and acetone to produce colloids.The kinetic stability of the colloid dispersions was related to the solvation effect of organic molecules, e.g., low stability for acetone, higher for 2-propanol, and the highest for 2-methoxyethanol. The colloidal particles were characterized by UV-Vis measurements showing absorption bands at 204 and 270 nm. A 3-day study in which samples were taken every hour showed that the absorption bands decrease probably due to clustering. Electrophoretic measurements revealed that the particles are weakly positively charged. Transmission electron microscopy studies revealed an average particle size distribution ranging from 6 to 10 nm depending on the solvent. Most of the colloids exhibit a spherical shape with some degree of agglomeration.After solvent evaporation several active solids were obtained. The FTIR spectra show the presence of the solvent incorporated in the active solids/films, e.g., for acetone the carbonyl stretching is observed at 1723 cm^{-1}. The thermal stability of these bimetal powders/films was studied by TGA up to 550 °C. Their maximum decomposition temperatures are 350, 415, and 429 °C for NiSn–2-methoxyethanol, –2-propanol, and –acetone, respectively.

Keywords Bimetallic colloids · Nanomaterials · Chemical liquid deposition · Absorption band · Electron microscopy

Introduction

The codeposition of metal atoms with different organic solvents at 77 K produces several interesting reactions [1, 2]. A growing interest in solvated metal atoms in which the atoms are stabilized has been very useful as a precursor of new metal colloids [3, 4]. Some of them have been very stable at room temperature. The stabilization of metal colloids using organic solvents has been attributed to the mechanics involving dielectric constant and viscosity [5].

There are examples, such as the ruthenium–copper system, in which the two components are almost completely immiscible in the bulk, exhibiting selective inhibition of hydrogenation quite similar to that observed with the completely miscible nickel–copper system [6, 7].

The bulk binary phase diagram of Au and Ni has a large miscibility gap, thus no alloy is formed at low temperatures [8]. Nevertheless, it has been found by STM that deposition of Au on Ni(110) or Ni(111) single crystal surfaces can result in a stable surface alloy in the first atomic layer [9, 10]. Low-energy ion scattering in combination with low-energy electron diffraction of Au on Ni(110) has also shown the formation of a surface alloy restricted to the external atomic layer [11]. Based on density functionality theory [12], it was later established that formation of a surface alloy of Au on Ni(110) and Ni(111) is energetically favorable.

The industrial application of bimetallic catalysts is important within the petroleum industry for catalytic reforming of petroleum fractions, but alloys are also used for environmental applications such as car engine catalysts. The alloy formation can change the chemical reactivity and it is supposed that catalysts for novel applications will be prepared on new alloy systems.

The advantage of our method involves the production of colloids that are free of interferents. The preparation of stable bicolloids such as PdSn is very interesting for further applications in heterogeneous catalysis [13]. The present report deals with the synthesis of stable bimetallic NiSn colloids in organic solvents, their properties, and film or active powder formation.

Experimental

Colloid formation

A typical cocondensation was carried out using the specially designed equipment previously reported [14, 15]. Two alumina–tungsten crucibles were charged with around 100 mg of Ni and Sn metal in lumps. Distilled and dried solvents (e.g., acetone, 100 mL) were placed in a ligand inlet tube and freeze–pump–thaw degassed for five cycles. The reactor was pumped to 1×10^{-4} torr while the crucible was warmed to red heat. The temperature in the crucible at red heat should be at the boiling point of palladium and silver since they are heated with separate electrodes (around 992 and 958 °C, respectively). A liquid nitrogen-filled Dewar was placed around the vessel and Ni (2.81 moles), Ag (2.83 moles), and acetone (60 mL) were codeposited over a 1.5-h period at a rate of 2 mL/min approximately. The matrix, which was a black color at the end of the codeposition, was allowed to warm slowly for 1.0 h to room temperature under vacuum by removal of the liquid nitrogen Dewar. Upon meltdown, a black dispersion was allowed to warm for another 0.5 h to room temperature.

The sol was siphoned into a flask under nitrogen. Based on the amount of metal evaporated and the amount of solvent consumed, the concentration of the alloy could be calculated.

Transmission electron microscopy (TEM)

A drop of each colloid was placed on a copper grid (150 mesh) coated with carbon. The samples were analyzed in a high-resolution electron microscope (JEOL JEM 1200 EXII) at several magnifications.

Electron diffraction was also carried out. In this case the micrographs were obtained using (1) 120 kV; 60 cm; K: 4.209 (cm Å) and (2) 100 kV; 50 cm; K: 3.772 (cm Å). The calibration was carried out with an Au film (Aldrich Chemical, 99.99%) evaporated over a copper grid. The deposition was carried out using an Edwards 5150 Evaporator.

UV-Vis absorption

The absorption spectra of the colloids were measured at 25 °C in a Shimadzu UV 2450 Model spectrophotometer, using quartz cells. The background was set up with the proper solvent and then each colloidal sample was examined. The kinetics of clustering was followed at room temperature, by taking absorption spectra every hour for 72 h.

Electrophoresis

The electrophoresis experiments were carried out using an 11-cm glass U-tube with a stopcock on the base to connect a perpendicular glass tube. Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the pole of a power supply (200 V) [16]. A typical experiment was carried out for a period of 3 h at 25 °C. To corroborate this experiment a Zee Meter Model 501, Pen Kem was used.

FTIR studies

Infrared spectra were measured by using a FTIR Nicolet Magna 5PC spectrophotometer coupled to a PC with OMNIC software analysis. The films were placed in the holder directly in the IR laser beam. Spectra were recorded at a resolution of 4 cm^{-1} and 64 scans were accumulated.

Thermogravimetric studies

A Perkin-Elmer Model TGA-7 thermogravimetric analysis (TGA) system with a microprocessor-driven temperature control unit and a TA data station was used. The mass of the samples was generally in the range 2–3 mg. The sample pan was placed in the balance system equipment and the temperature was raised from 25 to 550 °C at a heating rate of 10 °C/min. The mass of the sample pan was continuously recorded as a function of the temperature.

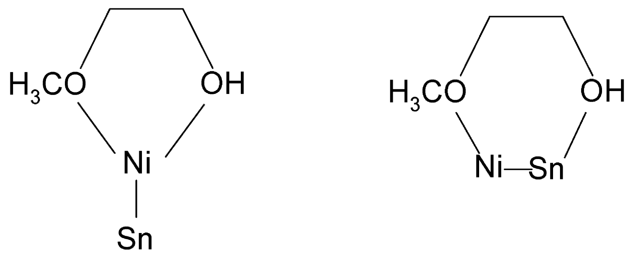
Results and discussion

The NiSn bimetallic colloids were obtained by cocondensation of the metals with organic solvents such as acetone, 2-propanol, and 2-methoxyethanol. Scheme 1 summarizes the synthesis. The stabilities of the colloids depend on the efficiency of the solution and the polarity of the solvents; the greater stability is represented in the NiSn bicolloids prepared with 2-methoxyethanol (>3 months) at room temperature, while in the NiSn–acetone colloids their stability is less than one day (see Table 1). The higher stability of the colloids prepared with 2-methoxyethanol is most probably due to the bond with oxygen of the solvent producing 5- or 6-membered rings which are thermodynamically more stable (Scheme 2).

It is difficult to probe which structure in Scheme 2 is more favorable, either the M–O interactions or, through each metal of the bicolloid, linkage to each oxygen of the 2-methoxyethanol. On the other hand, the particles are positively charged on their surface, which can be probed by electrophoretic measurement which reveals a zeta potential of 45.09 mV for NiSn–2-methoxyethanol colloid. The positive charge comes from the solvent which is surrounding the metal clusters.

During the solvent evaporation process some decomposition of the adduct can occur. Some solvent is recovered and in the solid some alkynes and formaldehyde were detected. This process was observed by analysis of the amorphous solid by FTIR spectrophotometry (see Scheme 3).

The TEM studies of the NiSn colloid were obtained at bright and dark fields. The size of the particles is represented in a histogram to calculate the normal deviation (Figs. 1 and 2). We observed that the particle sizes fluctuate between 6.9 and 10 nm for NiSn–acetone and NiSn–2-methoxyethanol. In all cases the histogram exhibits a positive asymmetry which reveals a tendency to particle growth. NiSn–acetone dispersions are those with a greater tendency to agglomerate and their average particle size is bigger than that of other systems (see Fig. 2). Even with the same metal, if the sizes are different, the surface energy is also different [17, 18]. These phenomena are due to quantum size effects, which are extremely important in the nanotechnology field [19, 20]. The colloidal system is not in equilibrium so the particles try to agglomerate to produce a low energy state. Henglein [21] described the term “electronic instability” to explain agglomeration and coagulation of the particles. Even if the particles are stable, there might be electronic instability if the Fermi level in the particles is positioned differently. In the process occurring when clusters of Ni and Sn are stabilized with a ligand [21], the atom transfer velocity or even small clusters are observed. In this case, the colloids are stabilized by solvation in organic solvents and the process is faster than flocculation.



Scheme 2 Possible intermediates of NiSn with 2-methoxyethanol

The effect of concentration in the alloy did not change the dispersion stability; this behavior has been observed in Ni/Cu alloys. In a dispersion prepared using a commercial Ni/Cu alloy, it was found that the colloids are more stable than those prepared by simultaneous evaporation of Ni and Cu [22, 23].

According to TEM analysis, the clustering is due to the association of several particles. Similar stability and behavior were observed in other previously reported colloidal dispersions of Pd, Au, and Ag [24, 25, 26].

The electron micrographs of bimetallic particles showed areas with high contrast, where the majority of the particles were bigger, most probably due to clustering of small particles on the grid. The areas with higher contrast were easier to measure and were always surrounded by smaller clusters. This is probably due to the expansion process of the microdrop on the grid [27]. The concen-

Scheme 1

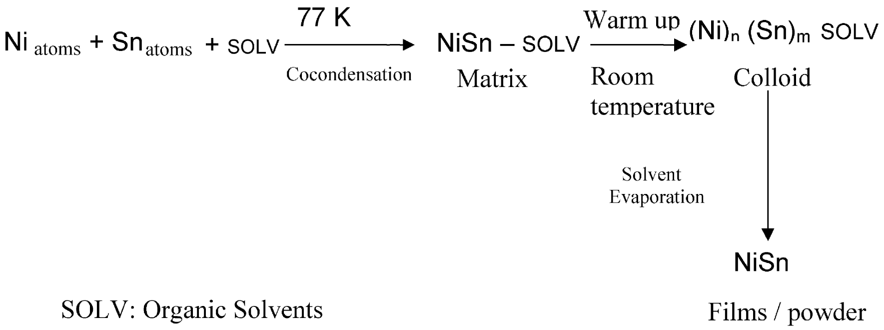
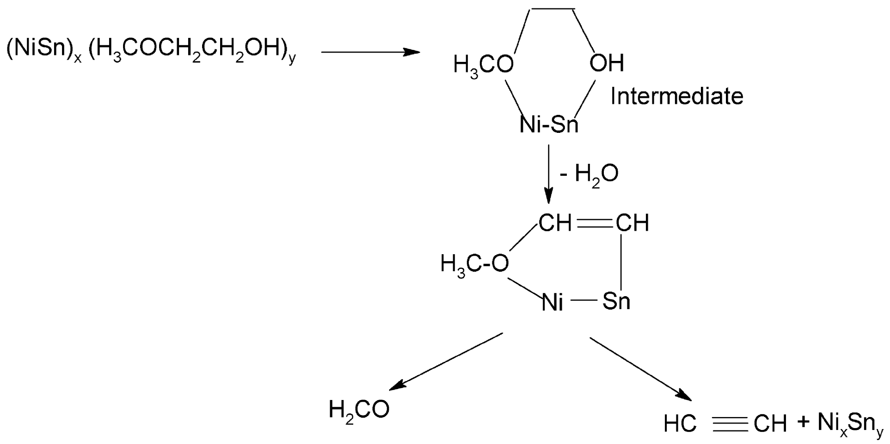


Table 1 Stability and particle size of NiSn colloids

Colloid	Conc (mol/L)×10^3		Stability (days)	Particle size (nm)	Color
	Ni	Sn			
NiSn–2-methoxyethanol	2.7	2.7	> 30[a]	7.8	Light brown
	4.2	4.2	> 30		Light brown
NiSn–2-propanol	2.7	2.7	15	6.9	Dark brown
	4.5	4.5	15		Dark brown
NiSn–acetone	2.8	2.8	< 1	10	Dark brown
	4.2	4.2	< 1		Dark brown

[a] The colloid remains in solution for several months at room temperature



Scheme 3 Decomposition of NiSn adduct with 2-methoxyethanol

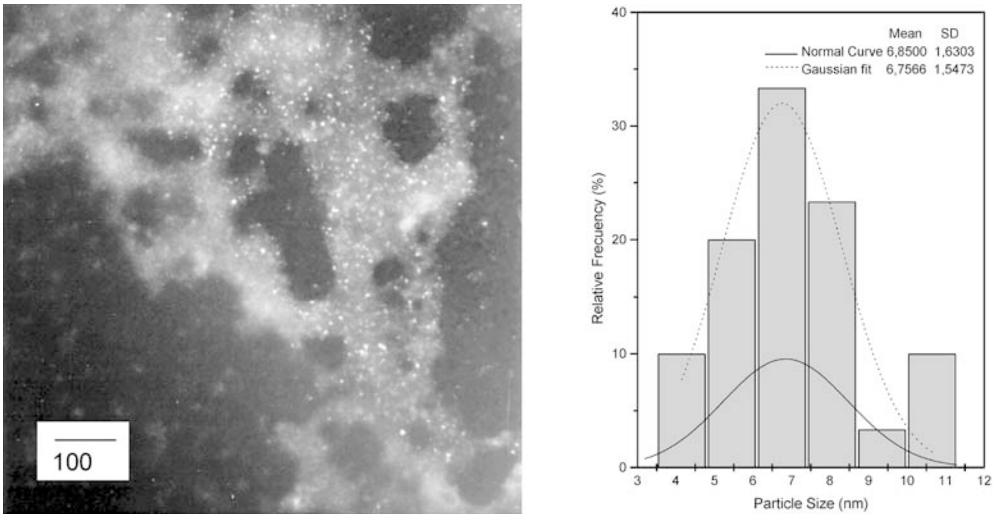


Fig. 1 Electron micrograph (100 K) and histogram of NiSn–2-propanol, using dark field. Average particle size of NiSn cluster $\mu = 6.9$ nm, $\sigma = 1.63$ nm

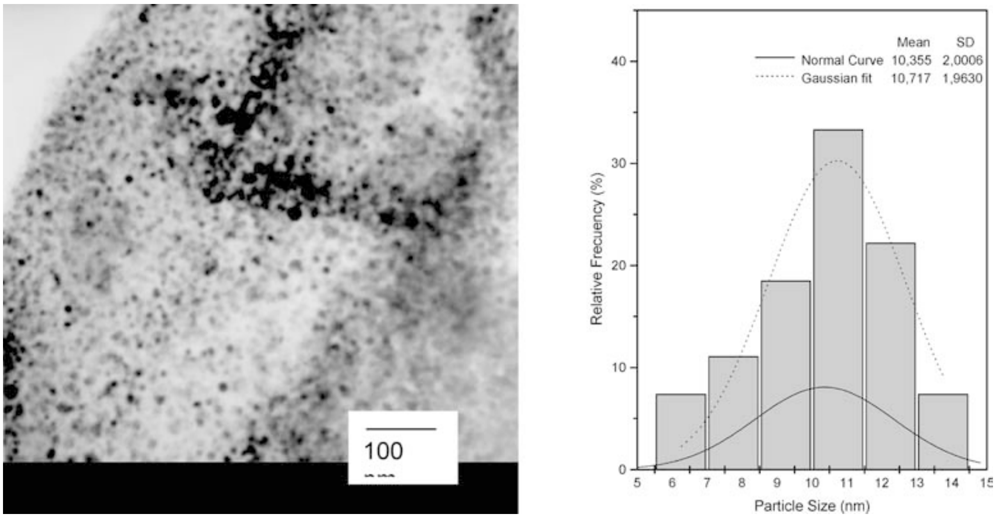


Fig. 2 Electron micrograph (120 K) and histogram of NiSn–acetone, using bright field. Average particle size of NiSn cluster $\mu = 10.4$ nm, $\sigma = 2.00$ nm

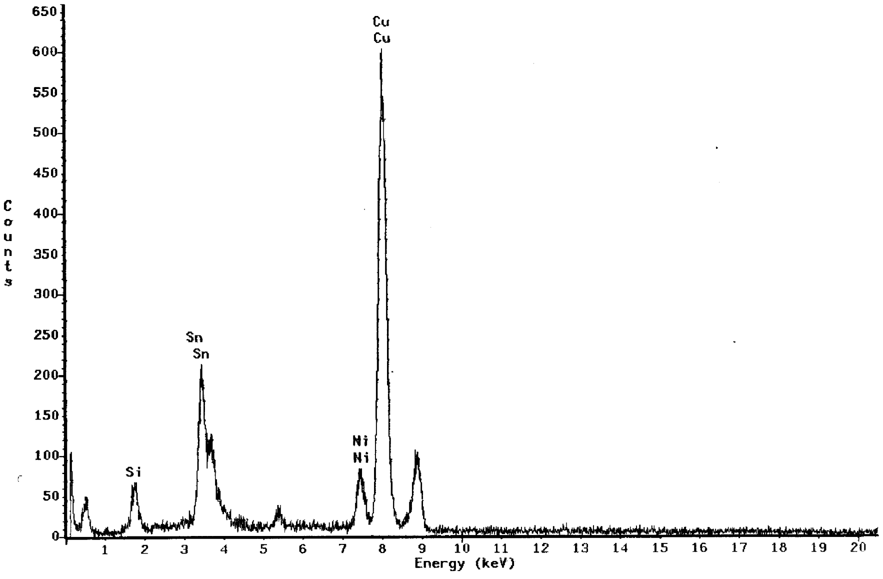


Fig. 3 EDAX of NiSn–2-methoxyethanol colloids

tration of particles was higher in the center. Very diluted sols were difficult to observe due to the poor contrast.

In the colloidal dispersions there is a mixture of Ni and Sn colloidal particles and also a smaller amount of NiSn bicolloid particles. Several particle size studies were carried out on NiSn (1:1 ratio) colloid prepared with organic solvents. From this experiment we can conclude that growth of particles is due to the association of several particles at the same time to form a bigger cluster. EDAX analysis shows the presence of Ni and Sn metals in the particles (see Fig. 3).

It has been observed that Pd produces a size control effect in the bimetallic particles, the sizes being smaller than those found in Ag colloids and similar to those of Pd colloids [28]. Electron diffraction analysis of NiSn–2-methoxyethanol shows the presence of a mixture of alloys and metal oxides (see Fig. 4). The nickel and tin alloys identified were NiSn, $NiSnO_3$, Ni_3Sn_4, and Ni_3Sn. Only oxides from tin were detected, such as SnO_2 and SnO. No nickel oxides were found (see Table 2). In other measurements the NiSn–2-propanol shows almost the same pattern and composition.

In Fig. 5 we can see the two absorption bands at 210 and 267 nm for NiSn–2-methoxyethanol colloids. The absorption band at 210 nm decreases in intensity with time and appears at 205 nm, while the peak at 267 nm exhibits a maximum around 270 nm but the absorption decreases. Similar results were observed for the system NiSn–2-propanol, in which the bands at 204 and 270 nm at $t = 0$ decrease up to 202 and 269 nm, respectively. Clustering is observed, with the presence of bigger particles decreasing the absorption intensity of the colloids. Initially, 2-propanol colloids have a particle size of 6.9 nm and absorbances of 0.4 and 0.35, which decrease to 0.32 and 0.28; 8.9-nm 2-methoxyethanol particles absorb at 0.15 and 0.10 initially and decrease to 0.13 and 0.085. These values are consistent with those reported by Creighton [29] for 10-nm nanoparticles. The initial spectra decrease their absorption due to clustering phenomena, which has been observed for NiCu [30].

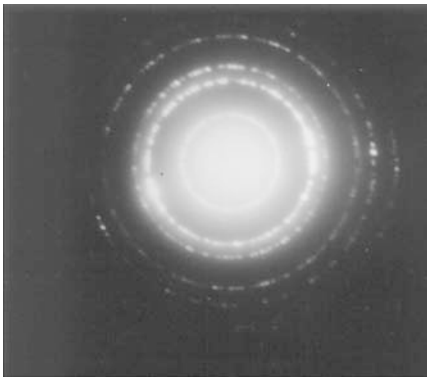


Fig. 4 Electron diffraction of NiSn–2-methoxyethanol colloids

Table 2 Electron diffraction pattern of NiSn–2-methoxyethanol particle

Diameter (cm)	D_{hkl} (Å)	Phase
1.903	2.215	NiSn $(2.217)^a$ (811) SnO_2 $(2.211)^a$ (201)
3.205	1.315	$NiSnO_3$ $(1.310)^a$ (000) NiSn $(1.314)^a$ (211) Ni_3Sn_4 $(1.314)^a$ (422) SnO $(1.311)^a$ (220)
3.625	1.169	Ni_3Sn_4 $(1.160)^a$ (911) $NiSnO_3$ $(1.160)^a$ (000)
5.000	0.842	Ni_3Sn $(0.849)^a$ (421)

[a] Data obtained from literature

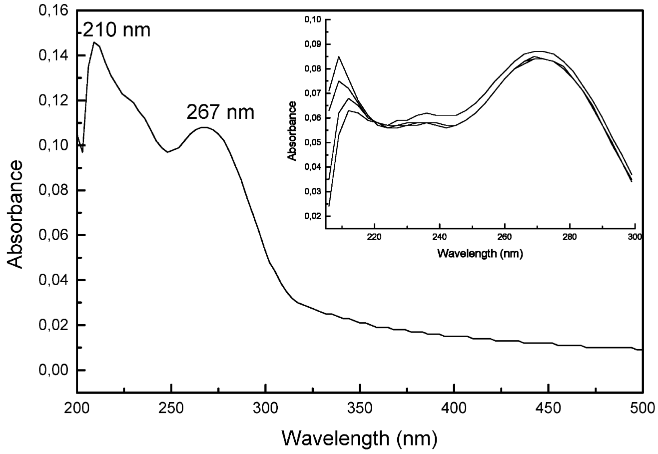


Fig. 5a, b UV-Vis absorption spectrum of NiSn–2-methoxyethanol studied over three days: **a** initial t = 0, **b** sequence each hour for t = 72 h

The FTIR spectra of the NiSn active solids exhibit characteristic bands corresponding to the incorporation of the solvents in the solids. Figure 6 shows the infrared spectrum of 2-methoxyethanol solvent and then the spectrum of the active powders. The bands in the active solid are the same as in the pure solvent but with lower intensity due to the low amount incorporated. Table 3 summarizes the bands of the solvents in the active solids. At 2053 cm^{-1} a signal appears corresponding to $\nu(\text{C} \equiv \text{C})$. It is interesting to observe the $\nu(\text{C}=\text{O})$ displacement from 1715 cm^{-1} in the solvent to 1723 cm^{-1} in the solid interacting with metal clusters. This is also corroborated by the ν(C–O) shift indicative of a single double bond of the acetone on the cluster's surface.

The TGA–FTIR studies of NiSn–2-methoxyethanol show the presence of some alkyne products and corroborate the IR spectra of the solid (Table 4).

Fig. 6 FTIR spectrum of NiSn–2-methoxyethanol active solid

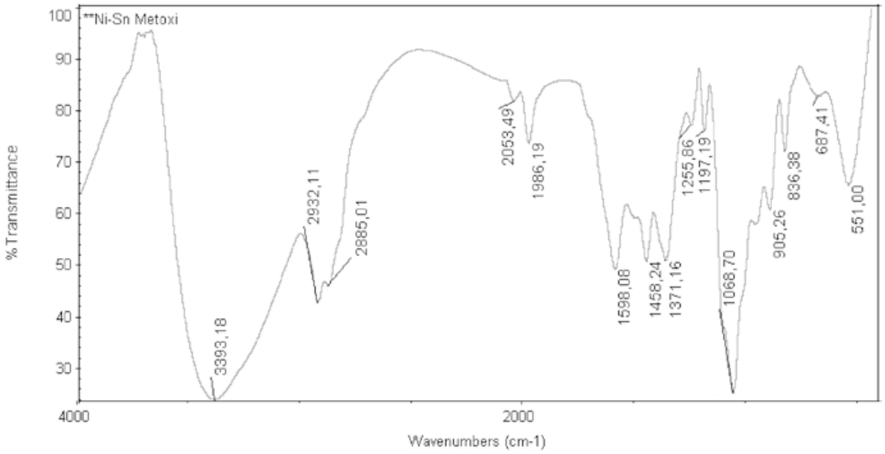


Table 3 FTIR band (cm^{-1}) of the NiSn bimetallic films[a]

Solvent	ν(O–H)	ν(C–H)	ν(C=O)	δ(C–H)	δ(O–H)	ν(C–O)	ν(C–C)
2-Methoxyethanol[b]	3393	2932	–	1458	1255	1068	–
2-Propanol	3411	2966	–	1413	1263	1091	1024
Acetone	3375	2961	1723	1384	–	1014	1067

[a] Films prepared in KBr

[b] Present two bands, 2053.5 and 1986.2 cm^{-1}, that correspond at stretching $\nu(\text{C} \equiv \text{C})$

Table 4 TGA–FTIR spectrum of gas-phase products from NiSn–solvent powders

Films	ν(O–H) (cm^{-1})	ν(C–H) (cm^{-1})	$\nu(\text{C} \equiv \text{C})$ (cm^{-1})	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})	ν(CH) (cm^{-1})	ν(C–O) (cm^{-1})	ν(C=C) (cm^{-1})
NiSn–2-methoxyethanol								
(5–20 min)	3741		2362	1752	1696	1527		1464
(31–48 min)	3742		2360	1740	1696	1527		1464
NiSn–2-propanol								
(2–16 min)	3741		2358	1742	1697	1518		
(35–47 min)	3740		2357	1742	1697	1519		
NiSn–acetone								
(1–15 min)		3740		1752	1699	1531		1460
(19–49 min)		3741		1752	1692	1533		1460

Table 5 Thermal stability and percentage weight loss of the NiSn bimetallic films

Metal films/powder	Total % weight loss	Decomposition temp. T_0 (°C)
NiSn–2-methoxyethanol	15	80.2
	32	301.1
	38	350.7
NiSn–2-propanol	14	91.7
	17	177.9
	21	294.7
	38	415.8
NiSn–acetone	22	126.7
	31	215.5
	35	352.7
	41	429.8

TGA reveals that NiSn bimetallic films are stable with a maximum weight loss of 40% at 550 °C (see Table 5). The NiSn–2-methoxyethanol shows the first weight loss due to humidity. The second peak is probably due to the loss of the alkoxy group and the third peak is due to some organometallic residual part of the molecule, such as the metal clusters and metal alloys (see Fig. 7a).

The NiSn–2-propanol exhibits a loss near 92 °C due to humidity. The next weight losses at 178 and 295 °C represent 17 and 21%, respectively. The highest weight loss of 38% at 416 °C is due to the alcohol and the remaining mass of 10% is due to the metal alloy (see Fig. 7b). The NiSn–acetone shows a loss at 126 °C due to water. Then peaks at 215 and 352 °C with 30% weight loss are observed. The highest weight loss is at 429 °C with 40% of the mass, mainly due to the acetyl group from acetone (see Fig. 7c).

Conclusions

1. It is possible to obtain stable dispersions of NiSn alloy in 2-propanol and 2-methoxyethanol, along with Ni and Sn colloids prepared by codeposition at 77 K.
2. The stability of the alloys is not directly dependent on the molar ratio between both metals in different solvents.
3. The particle size studies reveal that the clustering process occurs at room temperature, and flocculation of bigger particles is observed.
4. The TEM dark field technique was a useful technique to measure this transformation.
5. The decreasing UV absorption bands for NiSn–2-methoxyethanol as a function of time are indicative of the clustering process of the colloidal particles.
6. Electron diffraction shows the presence of NiSn, $NiSnO_3$, Ni_3Sn_4, and Ni_3Sn. Also, SnO and SnO_2 were detected. No presence of nickel oxide was found.

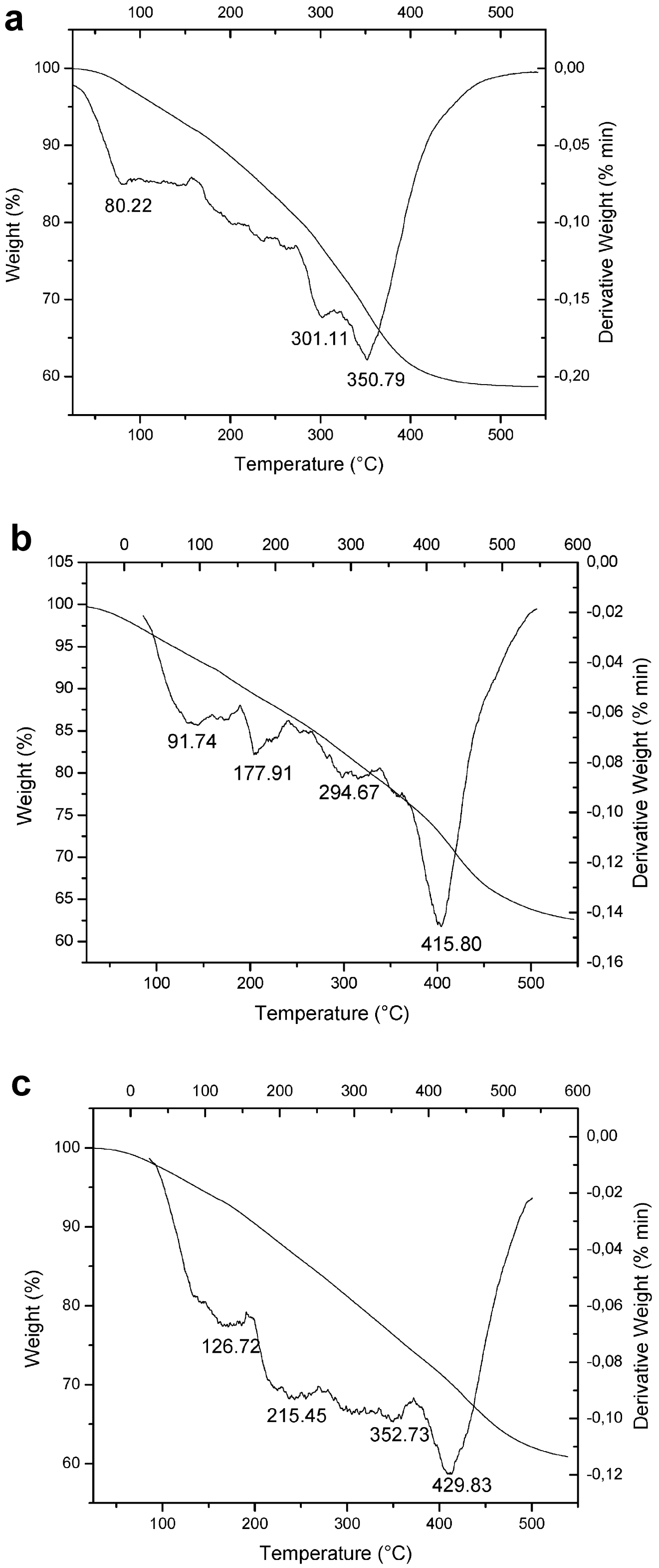


Fig. 7a–c Thermograms of **a** NiSn–2-methoxyethanol, **b** NiSn–2-propanol, and **c** NiSn–acetone films obtained from 25 to 550 °C at a heating rate of 10 °C/min

7. TGA of the NiSn active solids exhibits several decomposition peaks, with the highest weight losses being at 350, 415, and 429 °C.
8. FTIR spectrophotometry can probe the presence of the solvents incorporated in the solid. Some oxides are produced on the active surface of the fine powders.
9. This NiSn–2-methoxyethanol can be dispersed in Al_2O_3 and MgO to be tested as a supported catalyst. The advantage is that zero valence and some clusters of higher valence species can be obtained in the inorganic support.

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