Structural and mechanistic inferences in the mechanochemical synthesis of nanostructured Ni-Sn and Co-Sn alloys

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Abstract. We focus on the synthetic path of nanostructured Ni-Sn and Co-Sn systems by mechanical alloying. A similar reaction path seems to characterize the process for both the systems: the formation of intermediate, metastable, Sn rich phases has been evidenced, not provided for by the corresponding equilibrium phase diagrams. Their crystallographic and thermodynamic properties were evaluated through a structural and calorimetric investigation. Further mechanical processing induced structural evolutions by the progressive alloys enrichment in Ni and Co respectively, according to the stoichiometric constraints. Quantitative assessment of relative abundance of crystallographic phases let us investigate the alloying kinetics. By resorting to a previously developed procedure we evaluated collision frequency and impact energy. Then the analytical solution of the kinetic curves allowed us to relate the conversion degree to the effective collisions undergone by each powder particle.

1. Introduction
Nanostructured tin-based alloys have recently been the focus of rising attention in view of their electrochemical performance as anodes for secondary Lithium ion batteries. Key properties are the tin high electrochemical activity versus Li, i.e. its ability to form Lithium-rich intermetallics [1-5] and the metal partner efficiency in limiting the active phase cell volume variation during battery cycling. The combination of the above characteristics requires the choice of proper intermetallic phases stoichiometries, which can result in the highest theoretical specific capacity coupled with the proper electrode mechanical stability. Research interest for applicative purposes has been then addressed in optimizing alloys composition and synthetic procedures [1,2 6-9]. Concerning this latter topic, mechanical processing techniques allow a simple and proper way to alloy transition metals as Ni, Co and Fe with the low melting Sn, leading also to the desired nanostructured qualities [10-12]. However more basic issues, as reaction path and alloying mechanisms, are also of interest for such systems, since previous studies on NiSn alloys, which discussed the occurrence of intermetallic phases not reported in equilibrium binary phase diagram and whose structures were not definitely clarified [13,14].

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Along this line, in this paper we focus on the synthetic path of nanostructured Ni-Sn and Co-Sn-C systems by mechanical alloying pure elements, and on mechanistic aspects involving the reacting phases.

2. Experimental and data processing

High purity grade (5N at least) powders, purchased from different commercial sources, were employed as starting materials. Mechanical treatments were carried out by employing a Spex Mixer Mill, mod. 8000, and hardened-steel milling media. The experimental methodology to properly qualify the milling dynamics parameters has been previously extensively described [15,16]. Experiments were carried out with a single milling ball of 8.3 g and a powder charge $m_p$ of 8 g in order to allow for a reliable evaluation of both average frequency and energy of collisions. The structural evolution of solid phases was investigated by X Ray Diffraction (XRD), carried out in high resolution mode, employing a Rigaku DMax diffractometer equipped with Cu-Kα radiation and graphite monochromator in the diffracted beam. The off-line data processing of the X-ray patterns and the determination of unknown structures were performed through subsequent steps, according to the so-called “crystallographic “ab-initio” procedures [17]. Peaks localisation and evaluation of their integrated intensities were obtained by “Profit®” software, Philips Analytical X-ray. Once isolated the data relevant to unknown phases, indexing and lattice parameter determination were performed using Monte Carlo based procedures implemented in the McMaille software (kindly made available by A.Le Bail from the web, http://www.cristal.org/). Atomic positions inside the unit cell were determined according to the Endeavour code, from Crystal Impact [17,18] based on simple repulsion potential approximation method. Finally microstructural features and phase abundance were quantitatively evaluated by integral inversion routines according to the Rietveld method through the applicative M.A.U.D. [19]. The thermal stability of the powders was evaluated by Differential Scanning Calorimetry (DSC) in a Perkin Elmer power compensation PE DSC7 apparatus.

3. Results and discussion

We initially focused our attention on the NiSn system, and in particular on the Ni$_{44}$Sn$_{56}$ atomic % composition, selected in light of its good electrochemical performance [6, 20]. For such stoichiometry the relative equilibrium binary phase diagram foresees the existence of the monoclinic Ni$_3$Sn$_4$ structure (JCPDS 4-851) from 273 K up to 1070 K [6]. The XRD patterns sequence, reported in Fig. 1, shows the structural evolution of powders leading to the synthesis of such intermetallic phase as a consequence of the mechanical treatment.

![Figure 1. Ni$_{44}$Sn$_{56}$Cu Ka XRD patterns sequence.](image1)

![Figure 2. Cu Ka XRD pattern and fitting refinement profile relevant to the Ni$_{44}$Sn$_{56}$ mixture after 8 hrs of mechanical treatment](image2)
The pattern at the bottom of the figure is relevant to the starting as-mixed powders and may be accounted for by the structure factor of tetragonal tin (JCPDS 4-673) and cubic nickel (JCPDS 4-850) phases. The ball milling process induced progressive line broadening, disappearance of the tin peaks and appearance of signals pertaining to a new phase, not provided for by the equilibrium phase diagram, see patterns b and c. The relative amount of Ni and Sn, the already assessed Ni role as a fast diffuser in Sn [10, 12, 13], as well as stoichiometric constraints, suggest a tin-rich composition for the newly formed phase. Moreover its relative abundance reaches the highest value after 8 hrs of mechanical alloying, trace d, in which sample remaining traces of pure Ni and Sn are also present together with a fraction of freshly formed monoclinic Ni₃Sn₄. This last one is conversely the only phase in the sample milled for 16 hrs, and microstructural refinement leads to nanocrystalline conditions observable in the powders treated up to 50 hrs, traces e and f respectively.

The previously cited procedure was employed to reach a structure solution of this Ni-Sn phase, as we are going to describe in the following. As a first step we selected, in the d pattern, seven peaks that can not be misunderstood with reflections arising from Ni, Sn and Ni₃Sn₄ structures. The indexing of such peaks, through Mc Maille, resulted in the following lattice parameter estimation, according to an orthorhombic system: a = 5.7486; b = 4.124; c = 4.787 Å. The $2\theta$ angular positions and estimated relative intensities are reported in Table I.

| $2\theta$ | Estimated Intensities |
|-----------|-----------------------|
| 28.575    | 17                    |
| 31.117    | 100                   |
| 40.840    | 20                    |
| 42.745    | 76                    |
| 46.621    | 49                    |
| 68.194    | 30                    |
| 75.265    | 10                    |

The subsequent step in the structure solution, i.e. the assessment of space group was performed by Endeavour software. Our best fit for the Ni and Sn atoms position within the unit cell was obtained using the primitive space group n° 16 in International Tables, IT, P222 according to Hermann Mauguin classification. However some doubts still remain concerning the exact atoms location.

Finally the microstructural details and the relative weight % composition were evaluated by diffraction profiles refinement, according to Rietveld method, and in Fig.2 we report experimental data together with fitting curves. About 55 weight % was the relative abundance of the orthorhombic phase, with average crystallite size $\equiv 330$ Å and average r.m.s. microstrain $\equiv 0.001$. About 20 % of Ni₃Sn₄, 22 % of fcc Ni and the remaining 3% of Sn were measured for the other phases.

Nevertheless the analyses do not allow a definite solution of the matter. The exact composition of the new phase may be different from the assumed NiSn₃ stoichiometry. However other trials to solve the structure on the basis of a NiSn₂ composition were less successful. Broad lines emerging from the background, which are not assignable to the NiSn₃ phase, might be a sign of a still going reactivity of the mixture. Moreover it is possible that considerable texture is present in our specimen, in the newly formed structure, as well as in some unreacted tin, while the three lines observed for the nickel appear to show a conventional, isotropic intensity ratio. Finally, weak reflections expected in the context of
the selected space group for the new orthorhombic phase, do not occur experimentally. This leaves the
door open to a more definite resolution of the investigated structure.

The DSC study and subsequent XRD analyses, here not reported, assessed the structure evolution
occurring at relatively low temperature and underlined the metastability character of the intermetallic.
Such behaviour does not allow a further deepening in its characterization through the crystal growth
process. Isothermal annealing for 500 ks at 300 K induced the orthorhombic NiSn3 demixing towards
the pure elements, whereas the thermogram under scanning conditions was dominated by the partial
overlapping of the endothermal signal relevant to tin melting, at 496 K, and the exothermal peak
corresponding to the crystallization to the equilibrium Ni3Sn4 phase at 500 K. More details on this
subject will be reported at a later stage.

The Co-Sn system was then the object of our further scrutiny. For this material recent works
evidenced very good electrochemical activity as anodes for Li ion batteries within a selected
compositional range [7,8,20]. It was also highlighted the active role played by the C when added to the
metals mixture directly in the synthesis step. Electrochemical characterization suggested that it offered
a conductive support to the Co-Sn phases, hosting their nanostructured domains, and probably directly
interacting with Li, while electronic microscopy investigations and XRD analyses showed that the
allloying process did not induce the formation of carbide materials. It appeared then of relevance to
investigate the synthetic path during mechanical treatment of such materials and we selected the
Sn31Co28C41 at.% composition. The first step of the alloying process involved the crystallinity loss of
C, followed by the formation of an intermetallic phase, again not provided for by the relative binary
phase diagram. Further mechanical processing then induced its structural evolution to CoSn3 (JCPDS
25-256) and CoSn (JCPDS 2-559) nanosized type phases [20]. Following the procedure above
described for the Ni-Sn system we attempted the crystallographic determination of the intermediate
phase whose relative abundance was maximum after 16 hours of mechanical treatment. The analyses
indicated the occurrence of a tetragonal phase, which coexists with residual pure elements, as reported
in Fig. 3. Such phase belongs to the space group n° 99 in IT, P4mm, which is non-centrosymmetric,
being a = b= 3.089 Å, c =5.846 Å, with atoms location: Co 1(b) (0, 0, 0.714), Sn 1(a) (0, 0, 0.091), Sn
1 (b) (0.50, 0.50, 0.595). The assumed stoichiometry is then CoSn2, its relative amount is ≅ 38 weight
% (average crystallite size ≅ 510 Å, average r.m.s. microstrain ≅ 0.0014), with unreacted Sn ≅ 47%
and hcp Co ≅ 15%. The unit cell above described is very similar to the one for CuGa2 (space group
P4/mmm, centrosymmetric structure), differing only in the value of a axis. However, a simulation of
the pattern for a hypothetic structure of CoSn2 in the CuGa2-structure type, yields a sequence of peak
intensities not well respondent to the experimental findings. For these reasons, the non-
centrosymmetric space group supplied by the symmetry analyses by Endeavour code, seems more
appropriate.

In spite of the difficulties come out in the structural determination of the intermediate phases, relative
abundance evaluation allowed us to investigate the kinetics of the whole transformation process. Such
study was carried out by resorting to a statistical model aimed at describing the effect of mechanical
treatment of powders [21], and based on three main assumptions. First, the mechanical energy is
delivered to the reagents just at collision events entrapping powders between milling bodies. Second,
powder amount involved and worked at each collision is negligible with respect to the total charge
within the vial. Third, the milling dynamics provides, between two subsequent impacts, an effective
remixing of the worked material with the rest of the powder in the reactor, so ensuring to each powder
particle the same probability to be involved in the subsequent collision.
Moreover, experimental evidences suggest that the powder volume entrapped between colliding
bodies remains approximately constant, depending on the milling sphere diameter, on the total powder
within the reactor and the relative impact velocity. A further simplification is assumed, the average
density of powders \( \rho \) is considered roughly constant for all the phases formed during the mechanical
processing.
As a consequence of each collision, loaded material undergoes structural modifications whose extent
depends on the transferred mechanical energy. It occurs when a powder fraction \( k \) experiences a
mechanical stress $\sigma$ higher than a threshold $\sigma_0$, $\sigma > \sigma_0$. Then the model describes the evolution of the weight fraction of crystallographic phases, evaluated by XRD, as a function of treatment time or collision number. Before the start of treatment the powder fraction which did not undergo collisions, $\chi_0$, is $= 1$. It follows that, after the first loading, the value decreases to $\chi_0(1) = 1 - k$. As the process continues, the general expression describing the evolution of such fraction as a function of impact number is:

$$\chi_0(n + 1) = \chi_0(n) - k \chi_0(n). \quad (1)$$

Conversely the powder fraction which experienced $i$ collisional events, while the total number of occurred impacts was $n$, can be expressed by:

$$\chi(n + 1) = \chi(n) - k \chi(n) + k \chi_{i-1}(n). \quad (2)$$

Two contributions are here recognizable: the first expresses the decrease of $\chi(n + 1)$ fraction due to the transformation of a powder fraction which was impacted $(i + 1)$ times, and its value is $= - k \chi(n)$. The second one is related to an increase due to the transformation of the fraction $k \chi_{i-1}(n)$ relevant to powders impacted $i - 1$ times, into $\chi(n + 1)$, a fraction impacted $i$ times. Since $k$ is a negligible fraction with respect to the total amount of powder within the vial, and being the number $n$ of impacts very high, the discrete Eqs. 1 and 2 can be expressed in continuous form as:

$$d\chi_0(n) = - k \chi_0(n) \, dn \quad (3) \quad d\chi(n) = - [k \chi(n) - k \chi_{i-1}(n)] \, dn \quad (4)$$

whose respective solutions are:

$$\chi_0(n) = e^{-kn} \quad (5)$$

and

$$\chi(n) = \frac{(k n)^i}{i!} e^{-kn} \quad (6)$$

Equations 5 and 6 allow the fitting of experimental results relative to the weight fraction for reagents, intermediate phases and products. In Fig. 4 we show the data relevant to the Ni$_{44}$Sn$_{56}$ mixture, as a function of effective collision number. This last can be obtained by scaling the time of mechanical treatment to the collision frequency, which, in the above experimental conditions, was 62 Hz.

Figure 3. Sn$_{31}$Co$_{28}$Cu$_{41}$ Cu Ka XRD pattern and fitting curve of the sample subjected to 16 hrs of BM. The contribution of the new CoSn$_2$ phase has been displaced also as a separate curve.

Figure 4. Weight fraction relevant to reagent, intermediate and product phases reported as a function of effective collision number. Red curves represent interpolation of experimental data plotted as (●).
Curves in Fig. 4 can be reproduced by summing cumulants in \( i, \chi(n) \), whose expression is given by Eq. 6. Number of cumulants is determined by the best fitting of the experimental data, shown in Fig.4 as weight fraction \( \alpha \). It yields the number of collision events necessary to allow the transformation of reactants into the intermediate phase, and from this one into the final products. It results that the terms from \( i = 0 \) to \( i = 2 \) are needed to fit the experimental data of the reagents, while the interpolation of intermediate phase curve requires those from \( i = 3 \) to \( i = 5 \), and from \( i = 6 \) to \( i = +\infty \) for the final products. This suggests that reacting powders should experience at least 2 effective collisions to transform into the intermediate metastable phase, which, in turns, requires 3 further mechanical loading to complete the transformation into the Ni\(_{3}\)Sn\(_{4}\) structure. Finally, through the same interpolation of experimental data, the constant \( k \) can be evaluated. This represents an estimation of the powder subjected to a mechanical stress \( \sigma > \sigma_0 \) at each impact and can be considered as an apparent rate constant of the observed phase transformation. In the process under scrutiny, its value approached \( 2.7\times10^{-6} \).

4. Conclusions
The study of synthetic process of Sn based nanostructured materials is of current interest in view of their superior electrochemical activity in new lithium ion batteries. With this regard, the occurrence of Sn rich new phases during the mechanical alloying process with Ni and Co, not reported in crystallographic or thermodynamic databases, could be of concern in the field. The results of structural analyses of these phases and the evidence of the thermodynamic metastability behaviour here reported, could open new opportunities, and a further effort will permit to reach a definite clarification of the crystallographic pattern. Moreover the mechanochemical approach, based on experimental and theoretical evaluation and employed in the definition of the process kinetics, highlighted some mechanistic inferences in the whole transformation path of the Ni\(_{44}\)Sn\(_{56}\) alloy. On one hand such approach could permit the optimization of the mechanical alloying conditions for the above studied systems, and on the other hand, being the method of ore general relevance, it allows to relate experimental observation to microscopic models in the scrutiny of chemical transformation under mechanical processing.

5. Acknowledgements
This work was funded by MIUR, University of Sassari and University of Cagliari.

6. References

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