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Elaboration of the Cu_3Si compound using a mechanically activated annealing process

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The mechanically activated annealing process was used to produce Cu_3Si compound. This process results from the combinaison of two steps, the first is a mechanical activation of the $3Cu + Si$ powders mixture, the second consists of the annealing of as-milled powders. Based on X-ray diffraction experiment, scanning electron microscopy, the as-milled powders and M2AP end-products were characterized. Various parameters controlling this process such as mechanical activation conditions were studied. In the same time, a study of the reactivity of Cu_3Si towards CuCl was performed to compare the M2AP end-products behavior with that of the Cu_3Si reference powder.

1. Introduction

Chlorosilanes, which are the starting materials in the production of a variety of silicones, are prepared by a gas-solid reaction between CH_3Cl and excess silicon in the presence of the alloy Cu_3Si as catalyst [1–4]. In actual practice a large quantity of silicon is reacted in the solid phase with a small quantity of CuCl (8–10%) to prepare the contact mass for the main reaction. The contact mass consists of silicon and catalytic quantities of Cu_3Si phase and its selectivity is defined by the ratio $CH_3SiCl_3/(CH_3)_2SiCl_2$. Most researchers consider that the formation of Cu_3Si is achieved by the reaction between Si and CuCl to give divided Cu and gaseous $SiCl_4$, Cu then diffusing into the remaining Si matrix to form Cu_3Si [5]. In this reaction, the quality of the silicon metal is considered to be one of the most important factors for both the reactivity and the selectivity of contact mass. The formation of the Cu_3Si compound has been studied by several methods such as those using solid–solid reactions, solid–gas reactions [6, 7] or melting environment [8, 9]. Nevertheless, due to the complexity of the reactional mechanisms and the difficulty to obtain a pure Cu_3Si compound, another elaboration process using a mechanical treatment such as mechanical alloying has been investigated.

Recently, an alternative to synthesize molybdenum disilicide named mechanically activated annealing process (M2AP) was proposed by N. Malhouroux-Gaffet and E. Gaffet [10]. Such a solid state processing combines a short duration high-energy ball milling and a relatively low isothermal annealing. E. Gaffet *et al.* [11] reported on the possibility to obtain pure $MoSi_2$ after an annealing of 2 h at 800°C. By analogy with the solid-state phase transition occurring the annealing of a Fe/Si and Mo/Si systems, the purpose of this study was to determine the effect of isothermal annealing on a nanoscale mixture of copper and silicon crystalline phases which has been obtained by a short milling process. Furthermore, the influence of the residual strains and the ranges of grain size of as-milled copper and silicon crystalline phase on the end-product annealing structure was investigated. This paper reports on first results on the M2A process applied to the synthesis of copper silicides. The nanocrystalline mixtures which have been obtained after a mechanical activation step and for M2AP end-products have been investigated using X-ray powder diffraction, scanning electron microscopy, specific surface measurements and chemical analysis.

2. Experimental procedure

2.1. Ball milling condition

Mechanical activation was performed using a specially designed planetary ball mill (hereafter referred to as

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TABLE I Characteristics of short duration high-energy ball milling

Ω/ω (rpm)	Δt (hours)	Shock energy (JShock-1)
150/50	1-2-3-4-12	0.03
250/50	1-2-3-4-12	0.08
350/50	1-2-3	0.16

TABLE II Phase analysis obtained for all mechanical activated mixture using X-ray diffraction

Milling conditions	1 h	2 h	3 h	4 h	12 h
150/50	Cu, Si	Cu, Si	Cu, Si	Cu, Si	Cu, Si, Cu_3Si
250/50	Cu, Si,	Cu, Si,	Cu, Si,	Cu, Si, Cu_3Si	Cu, Si, Cu_3Si
350/50	Cu, Si	Cu, Si	Cu, Si Cu_3Si		

the G5 machine). This specific machine exhibits the same physical characteristics as the Pulverisette P5 but the rotations of the vials (rotation speed ω) and of the disk (rotation speed Ω) on which are fixed the vials are independently controlled [12]. It has been shown that the injected mechanical power has to be considered as being the pertinent parameter [13]. The duration of the milling process is noted Δt. In summary, each milling condition is characterized by 3 important parameters $G5(\Omega/\omega/\Delta t)$.

The shock energy used to activate 10 g of stoichiometric $3Cu + Si$ elemental powder mixture for each set of ball milling conditions is listed in Table I. These figures are based on the kinematics studies of the G5 machine by Abdelloui and Gaffet [14]. Based on the literature examining the effects of mechanical activation on isothermal annealing process in Fe-Si system [15], different shock powers and milling duration were chosen to investigate the effect of the short ball-milling duration on the reactivity of $3Cu + Si$ powders under low temperature isothermal annealing. The milling duration ranging from 1 to 12 h was chosen to avoid the formation of some Cu_3Si compound fractions, but to allow the formation of a chemical gradient at a nanoscale and very sharp Cu/Si interfaces inside each powder particle. In addition to the milled powders, a reference mixture of stoichoimetric elemental powders was shacked during 3 hours in a Turbula apparatus.[†]

2.2. Reactive annealing conditions

60 mg of milled particles were deposited in a glass cell which was evacuated (10^{-3} Pa) at room temperature and then sealed. The cell was heated at various temperatures from 350 to 500°C during 24 h. The domain of the annealing temperature is close to the eutectoid transformation temperature (75% at. Cu) allowing a solid–solid state reaction.

2.3. Structural and morphological characterizations

X-ray diffraction (XRD) measurements were performed using a diffractometer which is equipped with a curve position sensitive detector having an angular aperture of 120° (INEL CPS 120). Monochromatic Cu-K_α radiation ($\lambda = 0.15406$ nm), was obtained with a primary focusing germanium monochromator. Pattern decomposition was carried out by means of the profile-fitting program so-called PROFILE[‡] to obtain the parameters defining the position, height, area, integral breadth and shape of individual Bragg reflections. In order to evaluate a possible contamination or a depletion of elements which may be occur due to the friction of the particles on the balls and on the wall of the container, scanning electron microscopy (SEM) and local phase composition which was determined by energy dispersive X-ray spectrometry (EDXS) were conducted using an JEOL 6400 F scanning electron microscope fitted with LINK Oxford energy dispersive X-ray analyzer. In addition, the specific surface was measured using the BET method [16] in order to determine the size of the particles after ball milling.

3. Experimental results

3.1. Characterization of as-milled powders

3.1.1. X-ray diffraction phase analysis

As shown in Table II, the short duration millings were performed to avoid the formation of phases by direct mechanical alloying. Typical XRD patterns were given in Fig. 1. In the case of $G5(250/50/\Delta t)$ conditions only the Cu and Si diffraction lines have been revealed except for the G5(250/50/4–12 h) and also in the case of G5(150/50/12 h) and G5(350/50/3 h) milling conditions corresponding to the long milling duration and very intensive milling. The η''-Cu_3Si phase was detected on the X-ray patterns for the latter conditions. According to the published phase diagram [17], η''-Cu_3Si is stable up to 467 °C. Thus, high-energy ball milling is able to stabilize the high temperature phase at room temperature [10]. Nevertheless, the crystalline structure of Cu_3Si (η'') phase is not unique, but consists of an ordered Cu_3Si (η') phase with copper vacancies. These structural differences for Cu_3Si compound, which were obtained for various preparation methods, may be responsible for the differences in the reactivity and the selectivity observed in previous study [3].

3.1.2. Microstructure analysis

The microstructure of the as-milled powders in terms of crystallite size and morphology (size of a region over which the diffraction is coherent) and imperfections (microstrains, stacking faults, etc.) was studied using XRD profile analysis procedure described by Langford [18]. Therefore, the Langford method was used to determine the mean apparent crystallite size and the lattice strains. The analysis of these plots yields to the following details:

[†] Turbula, Schatz system made by W.A. Bachofen firm, Basel.

[‡] Available in the Socabim PC software package DIFFRACT-AT supplied by Siemens.

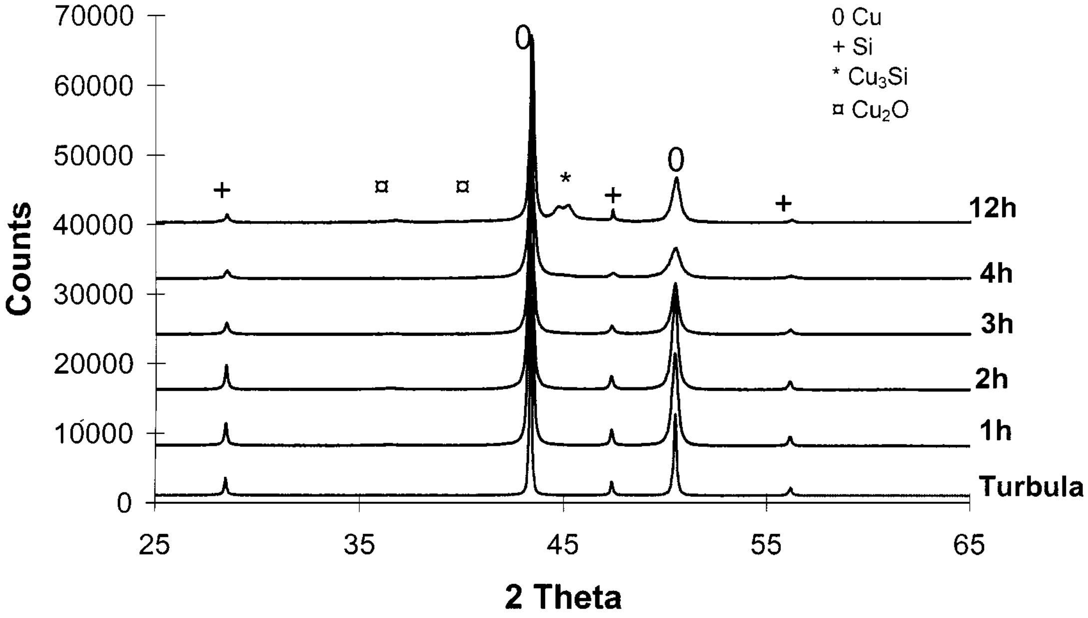

Figure 1 XRD analysis of as-milled powders (3Cu + Si) using k$\alpha 1_{\mathrm{Cu}}$ radiation ($\lambda = 0.154$ nm) in the case of several ball milling conditions in order to show ball milling duration effect: G5(250/50/X h) with $X = 1, 2, 3, 4$ and 12 hour respectively.

(i) the integral breadths of Cu peaks exhibits a [*hkl*] dependence. This suggests the existence of an anisotropic behavior of the Cu powders both in the microdistorsion and/or in the crystallites shape. This anisotropic behaviour can be due to the presence of twin planes in the nanometric copper. Indeed, Ungar *et al.* [19] were proposed to develop a “modified” Warren-Averbach method to take into account the X-ray diffraction profile modification due to the presence of twin walls. Moreover, these twin planes were already observed by Dominguez-Espinos [20] using Transmission Electron Microscopy observation experiment on the nanometric copper which have been elaborated by cryolevitation method. In the Fig. 2a, the apparent size of Cu crystallites which are given perpendicularly to the [*hhh*] direction becomes nanometric (size smaller than 100 nm) after a long or powerful ball milling.

(ii) On the contrary, for Si peaks, it was evident that the Si peak broadening was essentially isotropic. Fig. 2b represents the evolution of crystallites sizes obtained from Langford plots versus the ball milling conditions. This figure shows that the Si crystallites size strongly decreases as the ball-milling duration and the mechanically injected power increases. Indeed, the brittle behaviour of silicon is responsible of amorphous phase apparition and very quick decrease of Si cristallites size. Moelle *et al.* [21] have shown the existence of amorphous phases in these compounds.

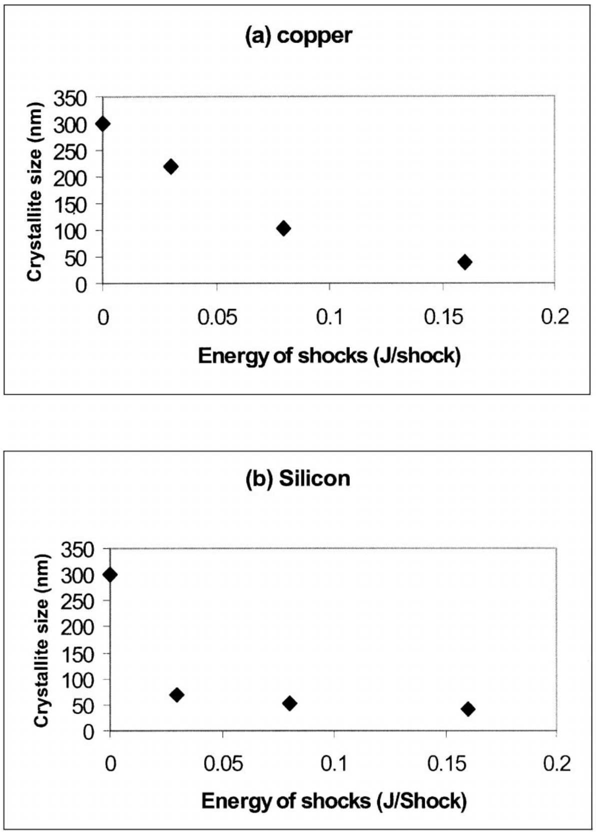

Figure 2 Evolution of the crystallites size versus the energy of shocks respectively (a) for the copper and (b) for the silicon.

3.1.3. Chemical analyses and specific surface measurements

The contamination by the milling vials or by the stainless steel balls used during the mechanical activation process, was evaluated by EDX microanalyses. There was no contamination since no chromium or iron was detected before 4 h of milling. In the case of such powders which are quite abrasive materials, the short duration milling avoids the contamination of the end-product by the milling vials and balls. The specific surfaces have been measured using BET method and have been found to increase as a function of the injected power (Fig. 3). However, from a shock energy equal to 0.16 Jshock^{-1}, a stabilization of the aggregate sizes has been observed. Indeed, whatever the ball milling conditions, the BET grains size is larger than the one determined by XRD investigation. As confirmed by scanning electron microscopy (SEM), ball milling induces the formation of aggregates by fracture-cold welding processes during the severe mechanical treatment.

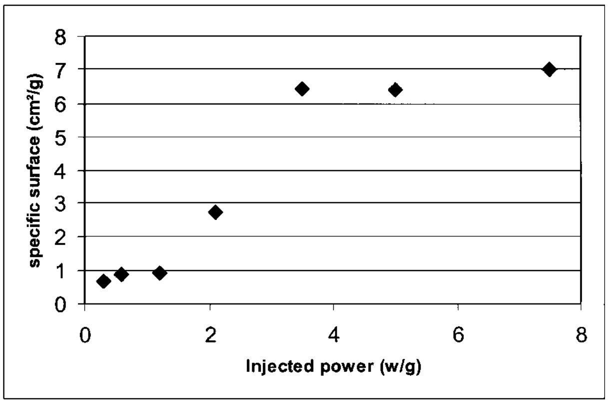

Figure 3 Evolution of the specific surface versus the injected power when a ball milling duration is equal to two hours.

Finally, as-milled powders may be considered as aggregates (1 to 10 μm) composed of nanometric crystallites of copper and silicon without any Cu_3Si compound formation.

Taking into account the phase and the microstructure analyses, the following ball milling condition G5(350/50/2 h) was selected in order to put in evidence the mechanical activation effect on subsequent annealing. Indeed, this latter condition was chosen because of the following characteristics: no sticking between the powder and the milling tools was observed, no contamination was detected, no Cu_3Si fraction induced by mechanical alloying has been formed, each elemental component exhibits a nanosize.

3.2. Characterization of M2AP end-products

The approach of this study was to determine the temperature for which only the Cu_3Si compound is formed. In reference to the phase diagram, four temperatures were studied (200°C, 350°C, 450°C and 500°C). The end-products relative to the isothermal annealing from mechanically activated powders in the G5(350/50/2 h) ball milling condition were investigated using XRD experiments. The following results are:

(i) up to $T = 450°C$ during 24 h, it appears Fig. 4 that the formation of Cu_3Si is incomplete.

(ii) at $T = 500°C$ during 24 h, as be shown on Fig. 4, only Cu_3Si phase is observed and its amount increases as a function of the mechanical injected power.

This study shows that the mechanical activation step modifies the powders reactivity. Indeed, the Fig. 4 shows clearly the difference between an end product obtained from a mechanically activated mixture and those obtained from an inactivated mixture using a Turbula machine.

Some scanning electron microscopy was carried out on reacted samples. In Fig. 5, this micrograph shows that the microstructure of the M2AP end-products obtained after an annealing at 500°C during 24 hours from mechanically activated powders (G5(350/50/2 h)). Cu_3Si grains present two aspects: (i) a large distribution of small particles and (ii) a prismatic shape in which the preferential faces were developed. This shape is an agreement with other observations [22].

4. Discussion

The results obtained in this paper show that: (i) the formation of Cu_3Si compound by an isothermal annealing at 500°C during 24 h starting from mechanically activated powders in the G5(350/50/2 h) ball milling condition is possible. Whereas in the case of a non activated mixture (Turbula), in the similar conditions the reaction to form Cu_3Si is not complete. From an investigation of the microstructure of as-milled several hypotheses could be formulated to explain this phenomenon. As reported in recent literature, short duration ball-milling

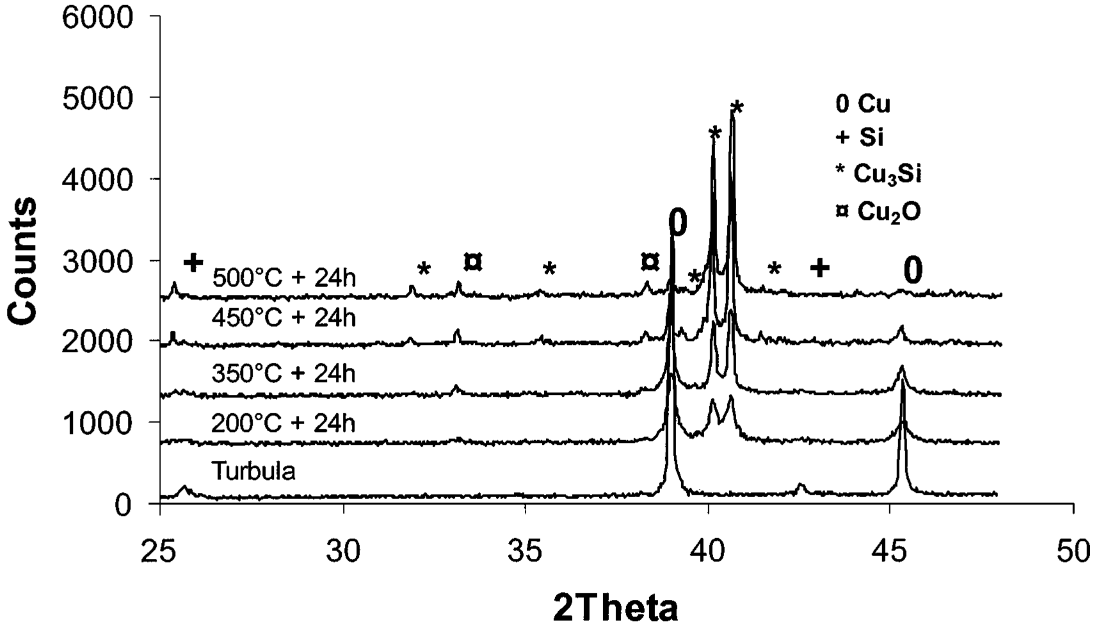

Figure 4 XRD analysis of ERAM end-products using $k\alpha l_{Cu}$ radiation ($\lambda = 0.154$ nm) in the case of several annealing conditions ($T = 200°C$, 350°C, and 500°C) corresponding to G5(350/50/2 h) ball milling condition and in comparison with Turbula mixture in the similar domain of temperature.

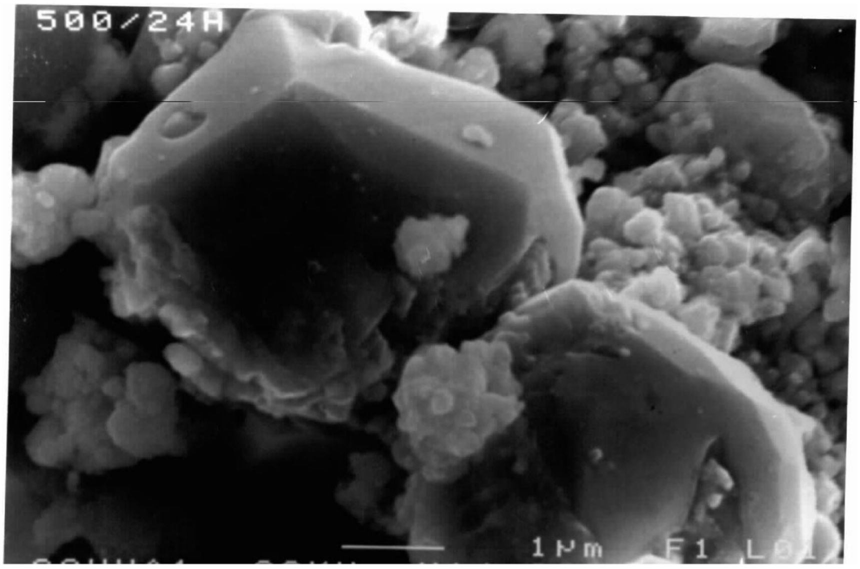

Figure 5 Scanning electron microscope images of Cu_3Si compound obtained after ERAM process.

before annealing [15] is able to change the powder's behavior during the subsequent heat treatment. The copper silicide formation reaction is due to the formation of three-dimensional polyinterfaces between small crystallites of Cu and Si inside each powder grain. This mechanical treatment before sample heating is able to destroy surface oxide layers on grains from commercial powders which results in good contact between the surfaces of Cu and Si small crystallites in as-milled powders. This result leads us to believe that the distribution of atoms in as-milled powders is very close to that of Cu_3Si and that diffusional mixing is easier than in the case of Turbula mix. According to [22], energy storage during mechanical activation could modify the thermodynamic situation by changing the energy (i.e. the mechanical activation depends on the mode of transfer of mechanical energy to the ground powders) in the system before combustion reaction. It constitutes thus a very flexible way to influence phase transformations.

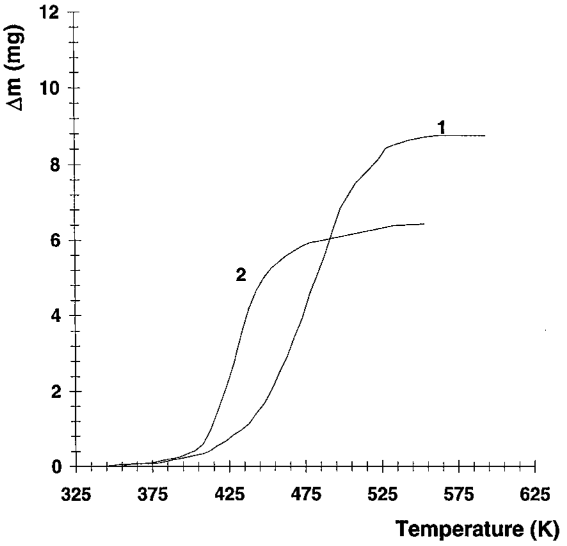

Figure 7 Evolution of Dm versus the temperature during the reaction between Cu_3Si and CuCl respectively in the case of (1) Cu_3Si (reference)/CuCl and (2) Cu_3Si(ERAM)/CuCl.

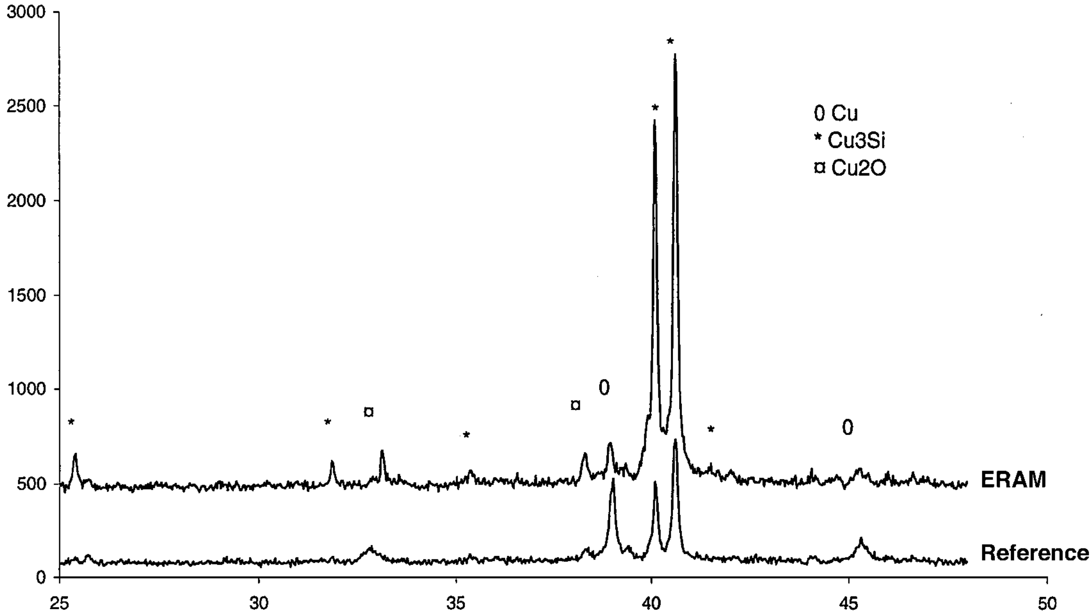

Figure 6 XRD analysis ($K_{\alpha Cu} = 0.154$ nm) of the Cu_3Si compound elaborated using ERAM process in comparison with the Cu_3Si reference powder.

5. Conclusion

Indeed, starting from a mixture of elemental powders, the first M2AP milling step is basically a solid state mixing process due to the fracture/cold-welding process, with limited chemical combinaison of elements, which leads to the formation of micrometer-sized powders containing nanoscale three-dimensional poly-interfaces between the elemental components. In mechanical activation studies, the solid state reaction which forms the target phases occurs only during the subsequent annealing step. The effect of milling conditions on grain sizes were reported to modify the phase transformation kinetics induced by the final isothermal annealing.

This M2A process seems to be an interesting route to elaborate a pure Cu_3Si as be shown on Fig. 6 which compares X-ray diffraction patterns obtained respectively from M2AP end-products and commercial powders. This figure shows that the amount of Cu_3Si is greater than that the reference powder. Consequently a comparative study of the reactivity of Cu_3Si (solid) towards CuCl (solid) (i.e. (1) $Cu_3Si\ (s) + 4\ CuCl\ (s) \rightarrow 7\ Cu\ (s) + SiCl_4\ (g)$) was performed. The preliminary results indicate that the reactivity of M2AP end-products is more important. Indeed, this study shows that the difference between the experimental weight loss and the theorical weight loss is respectively equal to 3.8 mg in the case of Cu_3Si(ref)/CuCl and 1.3 mg in the case of Cu_3Si(M2AP)/CuCl. This difference can be observed clearly in the Fig. 7. Consequently, The M2AP appears as an alternative way to prepare a pure Cu_3Si compound from a solid-solid reaction between nanocrystallites of Cu and Si.

The high energy mechanical treatment of short duration before the annealing reaction may be a possible alternative to enlarge the scope of synthesis. This possibility was illustrated by the investigations on Cu-Si and could be a promising solution for the synthesis of inorganic compounds based on the Cu_3Si phases as catalysts.

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