



Parametric optimization of Ti–Ni powder mixtures produced by mechanical alloying

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ABSTRACT

In this study, a set of Ti–50 at.% Ni elemental powder mixtures were processed through mechanical alloying (MA). The objectives were to induce during MA the formation of a lamellar microstructure and to apply a design of experiments, based on the Taguchi method, to optimize the MA parameters. Enthalpy measurements associated to the high temperature reaction between Ni and Ti powders were used to evaluate the effect of the MA parameters. It is known that different ball-impact energies lead to different reaction pathways. The results indicate that milling time affects significantly (74% contribution) the enthalpy of the high temperature reaction while the milling speed has a lower effect (25% contribution). Moreover, whatever the milling conditions, the powder was a mixture of both crystalline phases and an amorphous phase. Their microstructure was composed of a multilayer of alternating Ni and Ti that in some cases was constituted by nanolayers. The oxygen and nitrogen contents of the milled powders ranged between 0.29 and 0.79 wt%, and 0.15 and 0.90 wt%, respectively.

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1. Introduction

The goal of obtaining single-phase NiTi bodies by powder metallurgy (PM) is difficult to achieve because the formation of NiTi from elemental Ni and Ti powders in solid state is thermodynamically unfavorable [1]. Moreover, the possible secondary reactions, involving the products of the primary reactions of the Ni–Ti system for the formation of NiTi, are also thermodynamically weak events. In this respect, NiTi phase formation by solid-state diffusion is possible but kinetically slow. So, it may be speculated that a higher percentage of NiTi is formed via solid-state diffusion in systems where the diffusion distance required for reaction is small, such as in the case of thin multilayer materials [2]. Such microstructural feature may also be obtained with mechanical alloying (MA) [3].

Some of the objectives of this study were to induce during MA the formation of a chemical gradient at nanoscale, to constitute alternated nanolayers of Ni and Ti, and to avoid the formation of unwanted intermetallic phases. Several MA parameters will affect the formation of that specific microstructure, such as the milling time, the milling speed, the ball to powder weight ratio, the size of grinding media, the grinding media material, the mill geometry, the milling temperature, etc. In order to reduce the complexity of the milling parameters, this study focus only in the effects of

milling time and milling speed (energy). Enthalpy measurements associated to the high temperature reaction between Ni and Ti powders were used to evaluate the effect of these two MA parameters. Therefore, the main objective of this study was to apply a design of experiments, based on the Taguchi method, to optimize the process parameters. Generally, the experimental design of the Taguchi method uses orthogonal arrays and uses the signal-to-noise (S/N) ratio to analyze the experimental data and find the optimal parameter combination [4,5]. Moreover, an analysis of variance (ANOVA) is employed to estimate the error variance and determine the significant parameters.

2. Experimental procedure

Elemental Ti (99.9%, <105 μm) and Ni (99.9%, <44 μm) powders were used to prepare powder mixtures with nominal composition of Ti–50Ni (at.%). MA was carried out at room temperature on a PM100 planetary ball mill from Retsch. Twenty grams of Ti–50Ni powder mixture were placed into a stainless steel vial (250 ml in volume) with fifty stainless steel balls (10 mm in diameter) without the addition of a process control agent. Different milling energy intensities were employed by using milling speeds between 150 and 300 rpm while the ball to powder weight ratio of 10:1 was kept in all the experiments. After sealing, the vial was evacuated and filled with argon. The maximum milling time was 32 h and, to avoid temperature increase during MA, 10 min periods of milling were alternated with 5 min periods of rest. The milling was interrupted at regular intervals to collect a small amount of powders for analyses.

The mechanically alloyed powders were analyzed using a Bruker X-ray diffractometer (XRD) with Cu K_α radiation and a Philips XL30 field emission scanning electron microscopy (SEM) fitted with a backscattered electron detector (BSE). Oxygen and nitrogen contents were determined by using the LECO TC-436 inert gas fusion oxygen and nitrogen analyzer (average of three determinations). Thermal sta-

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Table 1
Design of experiments.

Exp. No.	Parameter [level]	
	A – milling speed (rpm)	B – time (h)
1	150 [1]	8 [1]
2	150 [1]	16 [2]
3	150 [1]	32 [3]
4	170 [2]	8 [1]
5	170 [2]	16 [2]
6	170 [2]	32 [3]
7	190 [3]	8 [1]
8	190 [3]	16 [2]
9	190 [3]	32 [3]

bility studies of the powder mixtures were performed in a SETARAM Labsys TG/DTA differential thermal analyser. In those studies, the powder mixtures were heated up to a maximum temperature of 1100 °C, with heating and cooling rates of 20 °C/min, under an argon flow at a rate of 15 cm³/min. The enthalpies and the temperatures associated to peaks of the DTA curves were determined using the Data Processing Module version 1.38 of SETSOFT, the thermal analysis software from SETARAM.

An orthogonal array (OA), the S/N ratio and the ANOVA were used to find the optimal levels and the effect of the MA parameters. The layout of the OA is shown in Table 1. This is not a standard Taguchi OA and their selection was based on the degrees of freedom of the parameters. The choice of the levels was based on milling efficiency criterions that were related with the powder yield (see Section 3).

3. Results and discussion

As was state previously, the powder yield was taken into account for choosing the levels of each parameter. Due to their ductile behavior, Ni and Ti powder mixtures show a great tendency to stick to the milling media, resulting in a low powder yield [6,7]. In this study, a value of 75% was established as an acceptable yield. For the experiments carried out at 200, 250 and 300 rpm it was observed that after 16 h, 3 h and 2 h, respectively, the powder yield obtained was lower than that value. Moreover, in those experiments an ineffective mixing between Ni and Ti was also observed for lower milling times [8]. For these reasons the milling speed and the milling time were limited to an upper value of 190 rpm and 32 h, respectively.

Typical DTA heating curves obtained for the unmilled (enclosed) and milled Ti50Ni powders are shown in Fig. 1. Since no events were detected during cooling, the corresponding curves are not shown. The only distinct thermal event in the unmilled powder is an exothermic peak, with an onset close to 950 °C, which is related with the high temperature reaction between Ni and Ti for the for-

Table 2
Enthalpies (absolute values) and S/N ratio.

Exp. No.	Enthalpy (μV s/mg)		S/N
	#1	#2	
1	10.26	10.63	-20.38
2	2.56	2.29	-7.71
3	0.91	0.90	0.87
4	5.01	5.14	-14.11
5	1.51	1.35	-3.11
6	0.30	0.30	10.48
7	2.22	2.10	-6.69
8	0.67	0.68	3.44
9	0.18	0.18	15.06

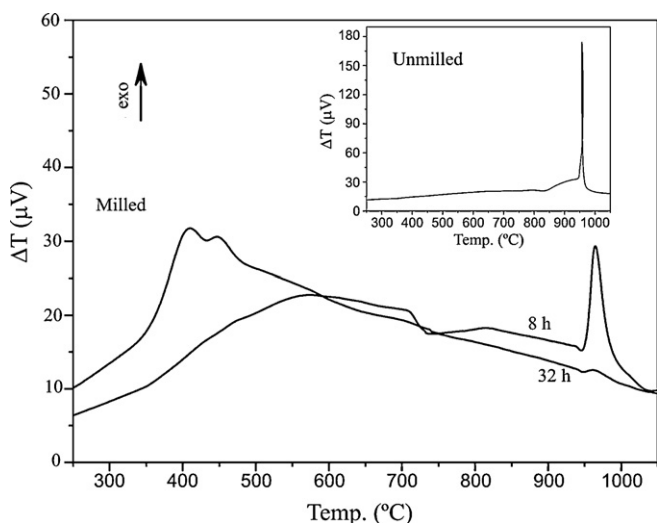
mation of the Ni–Ti intermetallics. As Fig. 1 clearly exemplifies for the 170 rpm milled powder, this reaction is partially or totally suppressed as the milling time increases. At the same time, other exothermic peaks appear in those powders at lower temperatures, initially as a broad peak (DTA curve corresponding to 8 h of MA in Fig. 1) and then as two small peaks (DTA curve corresponding to 32 h of MA in Fig. 1). In previous studies it was already demonstrated that these peaks are related to the structural relaxation of an amorphous phase and with the initial step of the synthesis of Ni–Ti intermetallics [9,10]. The shifting of the Ni–Ti synthesis to lower temperatures is a very important occurrence because it will allow the densification of such materials at much lower temperatures when compared with the conventional PM routes. On the other hand, an accurate definition of the beginning and ending of the peaks present on the DTA curves was only possible for the peak associated with the high temperature reaction. For these reasons, the effect of the selected MA parameters was evaluated only with the variability of the high temperature reaction enthalpy.

Fig. 2 shows a SEM/BSE image and the XRD patterns of some of the Ti50Ni powder mixtures milled up to 32 h. Fig. 2a reveals the formation of a lamellar microstructure constituted by alternated nanolayers of Ni and Ti. It should be pointed out that the thickness of those layers has been very dependent on the levels of the MA parameters. The XRD patterns of Fig. 2b indicate the presence of the Ni and Ti crystalline peaks superimposed with an amorphous halo. The existence of this halo was more pronounced for the higher milling speed level. Additionally, the XRD patterns confirm that no new chemical compound was produced through the MA process, fulfilling one of the objectives of this study. The absence of the intermetallic phases NiTi, Ni₃Ti and NiTi₂ is confirmed by comparing the 2θ position of the three major XRD diffraction peaks of those phases, selected from the Powder diffraction files (PDF) of the International Centre for Diffraction Data (ICDD) (NiTi – ICDD PDF #00-018-0899: 42.80°, 61.98° and 78.15°; Ni₃Ti – ICDD PDF #01-075-0878: 46.57°, 42.35° and 43.56°; NiTi₂ – ICDD PDF #01-072-0442: 41.42°, 38.95° and 45.28°), with the experimental XRD diffraction peaks observed in Fig. 2b.

Table 2 shows the enthalpies determined by integrating the area of the exothermic high temperature reaction DTA peak. Since a minimum (absolute) enthalpy value is the desirable condition, the S/N ratio for the “lower the better” type of response was computed (Eq. (1)) [4,5], and the results are also presented in Table 2. In Eq. (1), *n* is the number of experiments in a trial and *y_i* is the characteristic property for the *i*th experiment in that trial.

$$S/N \text{ ratio} = -10 \log_{10} \left(\left(\frac{1}{n} \right) \sum_{i=1}^n y_i^2 \right) \quad (1)$$

The average S/N ratio for each level of the parameters and the ANOVA results are summarized in Table 3. According to the principles of the Taguchi method [4,5], the average S/N ratio values,

**Fig. 1.** DTA curves for the unmilled and milled (170 rpm) Ti50Ni powder mixtures.

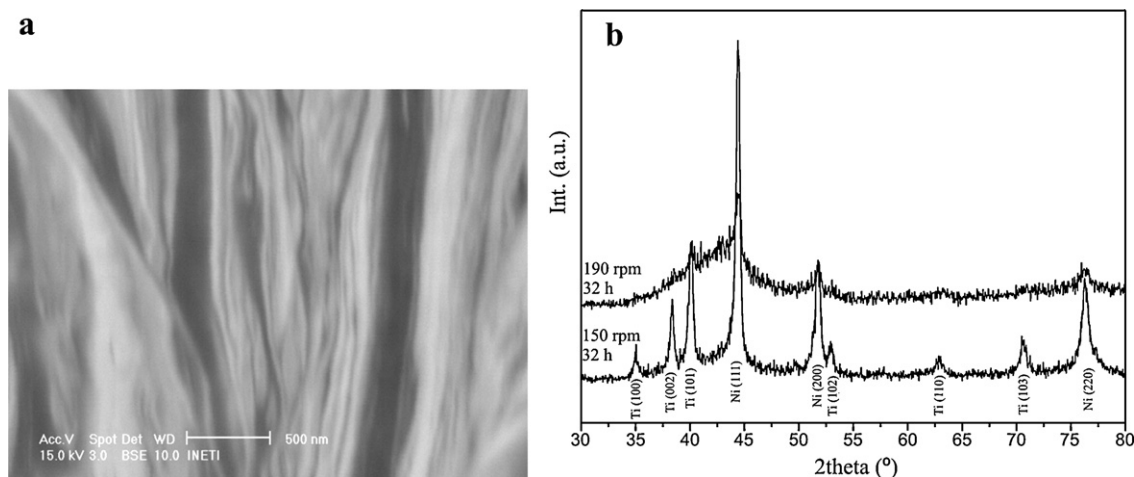


Fig. 2. (a) Typical SEM/BSE image showing the presence of Ni/Ti nanolayers after MA at 170 rpm/32 h; (b) typical XRD patterns after MA at 150 rpm/32 h and at 190 rpm/32 h.

Table 3

Average S/N ratio for each level of the parameters and analysis of variance (ANOVA) for S/N ratio.

Parameters	Average S/N ratio			Source of variation	Degree of freedom (<i>f</i>)	Sum of squares (<i>S</i>)	Variance (<i>V</i>)	Expected (<i>S'</i>)	<i>F</i> ratio (<i>F</i>)	Percent (<i>P</i>) (%)
	Levels									
	1	2	3							
A	-9.07	-2.25	3.93	A	2	253.98	126.99	250.21	67.33	24.46
B	-13.73	-2.46	8.80	B	2	761.49	380.74	757.71	201.86	74.07
				Error	4	7.54	1.89			1.48
				Total	8	1023.01				100

Table 4

Oxygen and nitrogen contents (wt%) measured for the 150 rpm, 170 rpm and 190 rpm milled powders.

Milling speed (rpm)	150			170			190			
	32	8	16	32	8	16	32	8	16	32
Oxygen	0.48 ± 0.03	0.32 ± 0.04	0.53 ± 0.03	0.79 ± 0.07	0.29 ± 0.02	0.41 ± 0.04	0.59 ± 0.02	0.19 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Nitrogen	0.56 ± 0.06	0.15 ± 0.03	0.38 ± 0.04	0.90 ± 0.05	0.15 ± 0.03	0.35 ± 0.01	0.69 ± 0.07	0.15 ± 0.03	0.35 ± 0.01	0.69 ± 0.07

calculated for each factor at a given level, allow the establishment of the best levels. Regardless of the type of response, the S/N ratio analysis is always interpreted the same way: the larger the S/N ratio the better [4,5]. Consequently, the best levels for parameter A and parameter B were selected on the basis of the S/N analysis and the level corresponding to the highest average S/N ratio was selected. From Table 3 it can be seen that the maximum impact on the final results will be achieved for parameter A (milling speed) in level 3 (190 rpm) and for parameter B (time) in level 3 (32 h). Those levels should be the best choice among the three levels of each parameter.

A statistical analysis of variance (ANOVA) and Fisher (*F*) tests were performed on each individual set of S/N values to see which parameter were statistically significant. As state by the Taguchi method [4,5], a design parameter is considered to be significant if its influence is large compared to the experimental error as estimated by the ANOVA statistical method. Table 3 shows that parameter B (time) has the most contribution (74%) and, according to the *F* factor, the degree of confidence on the data recorded is higher than 99.5%. The expected amount of sum of squares (*S'*) for each factor is computed by using variance [4,5]. The percent contribution (*P*) for each factor is calculated by using expected amount of sum of squares (*S'*) [4,5]. These results may be understood taking into account that these levels will induce the formation of a more homogeneous lamellar microstructure with a reduced diffusion distance. When the 190 rpm milled powders are heated, the formation of the intermetallic phases takes place at low temperatures. As a result, nearly all the Ni and Ti are consumed by a solid state reaction

and this contributes to the almost absence of the high temperature reaction.

A final remark needs to be done in relation to the oxygen and nitrogen contents that were measured for the milled Ti50Ni powder mixtures. The results of those measurements are shown in Table 4. Even with the preventive procedures that were adopted taking into account the contents of the starting powder mixture (oxygen: 0.19 wt% and nitrogen: 0.01 wt%), Table 4 shows a constant and systematic increase of these impurities with the milling time, being most significant for the nitrogen. The effects of oxygen and nitrogen contents on the mechanical alloying process of Ni–Ti powders mixtures will be the subject of further research.

4. Conclusions

Two important mechanical alloying parameters, milling speed and milling time, were analyzed by applying a design of experiments based on the Taguchi method. The approach used indicates that the enthalpy of the high temperature reaction can be reduced significantly and that an acceptable powder yield can be achieved after mechanical alloying at 190 rpm during 32 h. Taguchi method showed that, within the milling energy range used, the milling time had bigger contribution than the milling speed (74% vs. 25%) for the suppression of the high temperature reaction. The results obtained are of the most significance for future work of densification of the milled powders.

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