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Processing parameters in the ball milling of niobium hydride: An optimization approach

Gilbert Silva[a], Dalton Garcia Borges de Souza[b,c]*, Lucas Catalani Gabriel[b], Geovani Rodrigues[a] & Carlos Eduardo Sanches da Silva[b]

[a]Federal University of Itajubá, Department of Mechanical Engineering, UNIFEI/IEM, Avenida BPS, 1303, Itajubá-MG, 37500 – 903, Brazil

[b]Federal University of Itajubá, Department of Production Engineering and Management, UNIFEI/IEPG, Avenida BPS, 1303, Itajubá-MG, 37500 – 903, Brazil

[c]Polytechnic University of Milan,Department of Civil and Environmental Engineering, POLIMI/DICA, Piazza Leonardo da Vinci, 32, Milano-MA, 20133, Italy

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Due to its particular properties, niobium has been widely used in the industry. In order to produce niobium-base parts, its powder can be obtained through a powder metallurgy's method called ball milling. In this article, the ball milling parameters, in the production of niobium's powder,have been optimized using the Taguchi's method in order to obtain a high yield in the process, considering a particle size smaller than 75 μm. Taguchi's method, among several experimental designs, has been chosen due to its simplicity, efficiency and systematic approach to determine the optimal parameters in a manufacturing process. The experimental results have been indicated that the milling speed and time are the main variables in the process. In addition, the morphology of niobium hydride particles with the lowest and highest yield has been analyzed through the electron microscopy's scanner.

Keywords: Taguchi's method, Niobium hydride, Ball milling

1 Introduction

Due to its positive properties including good corrosion resistance, high melting point, biocompatibility, and relatively low density, the metal niobium has been utilized in different applications areas such as electronics, chemistry, aerospace and nuclear. The majority of niobium is used in the steel's production and its present position in the industry is uncontested in the three main micro alloyed steel domains: pipe, automotive and structural. Niobium is also employed as an alloy element in the nickel-base superalloys, in superconducting Magnets, and as biomaterial[1,2].

In several applications, the production of niobium-base parts uses the powder metallurgy technique (PM). Products obtained by (PM) offers micro structural integrity, compositional homogeneity, and mechanical properties even greater than the molten metal[3]. This technique has been contributing to the crescent use of refractory metal powder[4,5].

*Corresponding author (E-mail: dalgarbor@gmail.com)

The niobium metal powder can be obtained by the hydrogenation-dehydrogenation (HDH) process. To obtain refractories metal powder (Nb, Ta, and V), the submission of these metals is necessary, due to their plasticity, to the hydrogenation process for the formation of fragile hydrates, which allows the particle rupture during the ball milling. The hydrogen extraction of the metal structure is accomplished by the dehydrogenation process, which uses the hydrogen natural reversibility when heated in vacuum, according to Eq. (1)[6,7].

$$RM + \quad - \qquad \dots (1)$$

where, RM is a refractory metal.

The ball milling is usually applied for de agglomeration by reducing the size of particles and to produce powders of fragile materials, such as borates, carbides and in termetallic composites[8]. The parameters of the process influence in the size, morphology, microstructure, chemical composition and the relative cost of the produced powders. Therefore, the selection of the appropriated production process of certain powders depends on the specific properties of the desired alloys[8].

The four main production techniques to obtain metallic powder are based on mechanical reduction, chemical reactions, electrolytic deposition, and atomization. The particle size reduction process depends on specific energy supplies for the formation of new superficial areas.

The particle size reduction process by mechanical action submits the particles to impact, friction, shearing and compression force. The energy impact causes the appearance of crack and results in a reduction of the particle's size. The friction promotes the particle reduction by abrasion/rupture; while the shearing generates cleavage fractures. Finally, the compressive forces can provoke the rupture of the materials depending on the particle[9].

Many authors have discussed the main advantages and disadvantages alongside the decades including Delogu, Gorrasi and Sorrentino[10] who have recently summarized and discussed them. The main advantages are constituted of the reduced temperature requirements, attenuation of undesired thermal or chemical reactions triggered by high temperature, simple manipulation of materials, an absence of solvent phases, simultaneous processing of polymer matrix and heterophase fillers, reduced costs, and possible to scale-up to an industrial level. On the other hand, the principal drawbacks consist of undesired side reactions activated by mechanical deformation, mixing and dispersion ability which are dependent on the mechanical property of materials, and disordered polymers nanocomposites structures.

In the case of ball milling, many factors affect the particle size reduction, such as rotation speed, powder composition, milling time, balls' size and weight ratio[11]. To find the best parameters in the milling process of niobium hydride, a large number of experiments are required. Among several experimental designs, Taguchi's method has been chosen due to its simplicity, efficiency, and systematics to determine the optimal parameters in a manufacturing process and because it also reduces the number of experiments[12,13].

The experimental design method developed by Taguchi has, as objective, to generate a methodology for the productivity improvement, and reducing the variability with quality improvement[14,15]. In general, to obtain a quality product with low cost, a great effort is necessary to determine which are the best-optimized conditions of the manufacturing process. For this reason, the Taguchi's method is widely used in industrial research and in quality engineering[16-18]. Thus, by using this method, it is possible to obtain the necessary information for the studied process of variables control. The experimental design method controls the entrance variables and observes their effects on the parameters of the final product[16].

Taguchi's method of experimental design uses three basic tools: orthogonal arrays, variance analysis, and the signal-to-noise ratio. The orthogonal arrays are experimental matrices generically called Ln, where "n" represents the number of experiments to be performed. The orthogonal array is based on the degrees of freedom determination, as shown in Eq.(2).

$$FDA_i = (n_i - 1) \quad ... (2)$$

where, FDA is the degrees of freedom and n_i is the number of factor levels.

The variance analysis, ANOVA, is a decision tool statistically formatted to determine the significant factors of the process. The signal-to-noise ratio (S/N) combines several repetitions of a value that reflects the influence of the variations with the intention of minimizing the variability. The higher-to-better signal-to-noise ratio can be calculated with Eq.(3).

$$S/N_{HtB} = -10 Log \sum_{i=1}^{r} \frac{1}{y_i^2} \quad ... (3)$$

where, *HtB* is higher-to-better, *r* represents the number of repetitions and *y* is a specific value.

The signal-to-noise ratio is treated as the result of the experiment that constitutes an average variation inside the statistical test when the noise factors are present[19]. With the signal-to-noise and ANOVA analysis, the optimal combination for the process parameters was obtained. Three objectives can be reached by the Taguchi's method: (a) determination of the optimal parameters of the design for a process or product; (b) estimation of each design parameter contribution and the quality characteristics, and (c) forecast of the quality characteristics based on optimal design parameters[20,21].

In this work, Taguchi's method was used to optimize the ball milling parameters to improve the yield, in order to obtain niobium hydride with a particle size below 75 μm, though the HDH process. The influence of the following variables in the niobium hydride milling was studied: (A) volumetric fraction of the milling balls; (B) milling speed; (C) milling time; (D) speed in the rheostat, and (E) screening time. An L_{18} orthogonal array with process variables operating in 3 levels, a signal-to-noise ratio for higher-to-better function and a statistical variance analysis ANOVA to test the significance of the effects, were employed. The morphology of niobium hydride particles in the experiments with low and high yield was also investigated via the electron microscopy scanner.

2 Experimental Procedures

High purity Nb (min. 99,7%) obtained by electron beam melting, was utilized in the experimental procedures. Table 1 presents the chemical composition of the niobium ingot produced with this method. The chemical composition of the material could be obtained through an optical emission spectroscopy. The method was chosen due to the versatility of the equipment, which can be portable and traces an analysis covering all relevant elements in the metal alloy.

Obtained through the machining of a Nb ingot, pieces with 1 to 2 mm in thickness were utilized in the hydrogenation process. The material was chemically cleaned and dried, followed by uniaxial pressing in the form of briquettes with 90 x 55 mm^2. After this initial preparation, the scraps were inserted in a hydrogenation reactor, in order to obtain β-NbH_{1-x}.

The milling operation of the niobium hydrate was accomplished in a fritch epicycloidal ball mill, with vial and balls made of niobium, avoiding contamination thusly. A group of vibratory sieves allowed to classify the niobium powder's granulometry. After the screening, the masses of niobium hydrate were determined, the yield milling was calculated on the particles of niobium hydrate that passed in the sieve with an opening of 75 μm, and the data were analyzed using the Statistical software Minitab 17®, version 6.0. In addition, the morphology of niobium hydride particles in the experiments with the lowest and highest yield was observed through the electron microscopy.

For the optimization, the ball milling parameters, the chosen controlled variables, and their levels appear in Table 2.

After calculating the degrees of freedom, the minimum number of experiments of 18 was obtained. The choice of the orthogonal array was adapted to the present study, based on the L_{18}, as shown in Table 3.

The matrix L_{18} (Table 3) shows the combination and levels used in the experiments carried out in this work. Concerning the analysis, the columns 1, 7 and 8, in the matrix L_{18} were not considered. Column 1 was not considered because it only considers 2 of the 3 levels set for the experiments. The columns 7 and 8 were not considered because the 5 variables used in the experiments were allocated between the columns 2 and 6, therefore, no more columns were necessary.

3 Results and Discussion

All experiments were performed twice by objectifying the reduction of possible biased results. Figure 1 shows the yield averages obtained for each milling experiment, with the percentage of niobium hydrate particles smaller than 75 μm. The initial mass inserted in the milling vial was always settled at 461 grams.

As observed in Fig. 1, the experiments 3 and 6 obtained the highest milling efficiency average. Considering experiments with the highest efficiency and Table 3, the variables (B), (C), (D) and (E) of

Table 1 — Chemical composition of the Nb ingots produced by electron beam melting.

Maximum content of impurities (ppm-weight)							
Al	Fe	Ta	Si	C	S	O	N
10	10	600-2000	30	30	20	50	30

Table 2 — Variables and levels used in the process analysis.

	Variables Studied in the Process		Levels Used in the Process		
			1 (low)	2 (medium)	3 (high)
A	Volumetric fraction of the milling balls (%)	*Small*	25	50	25
		Medium	25	25	50
		Large	50	25	25
B	Milling speed (%)		30	60	80
C	Milling Time (min)		15	30	45
D	Rheostat speed in the screening (%)		30	60	90
E	Screening Time (min)		15	30	45

Small ball = ϕ16mm, Medium ball= ϕ24mm e Large ball= ϕ32mm

Table 3 — Levels and position of the factors in the L_{18} matrix.

Experiment number	Number of Columns, Levels and Position of the Factors							
	1	2	3	4	5	6	7	8
	e	A	B	C	D	E	e	e
1	1	1	1	1	1	1	1	1
2	1	1	2	2	2	2	2	2
3	1	1	3	3	3	3	3	3
4	1	2	1	1	2	2	3	3
5	1	2	2	2	3	3	1	1
6	1	2	3	3	1	1	2	2
7	1	3	1	2	1	3	2	3
8	1	3	2	3	2	1	3	1
9	1	3	3	1	3	2	1	2
10	2	1	1	3	3	2	2	1
11	2	1	2	1	1	3	3	2
12	2	1	3	2	2	1	1	3
13	2	2	1	2	3	1	3	2
14	2	2	2	3	1	2	1	3
15	2	2	3	1	2	3	2	1
16	2	3	1	3	2	3	1	2
17	2	3	2	1	3	1	2	3
18	2	3	3	2	1	2	3	1

*e = empty column (1, 7 and 8); A= Volumetric fraction of the milling balls (%); B= Milling speed (%); C= Milling Time (min); D= Rheostat speed in the screening (%). E=Screening Time (min)

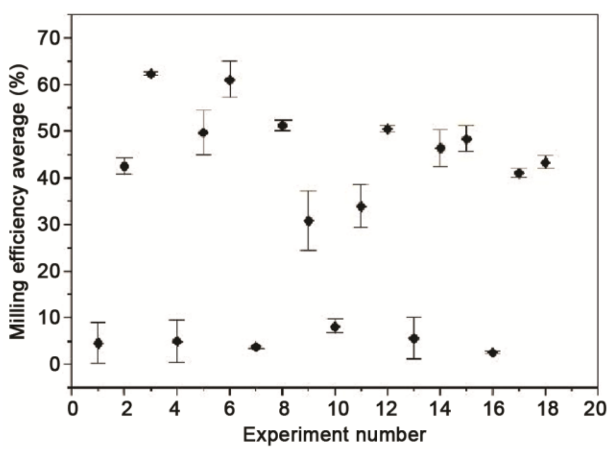

Fig. 1 — Milling efficiency averages in relation with to the niobium hydrate particles smaller than 75 μm.

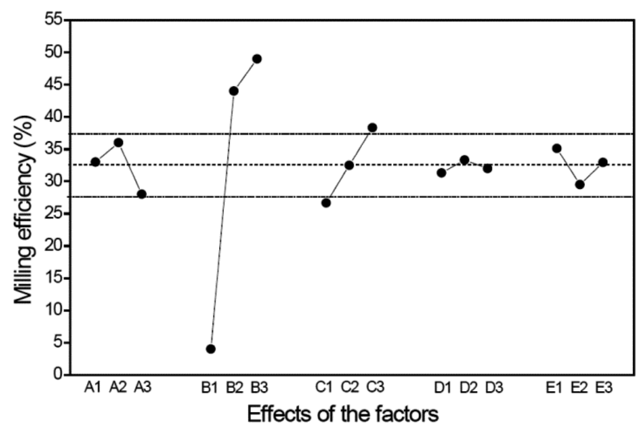

Fig. 2 — Effects of the factors versus milling efficiency (A, B, C, D, and E – processes variables; 1, 2, and 3 – levels used in the process).

experiment 3 and (B) and (C) in experiment 6, used the 'high' level input value for the variables in the process. Thus, it can be inferred that the variables B (Milling Speed) and C (Milling Time), having the same value in both experiments, demonstrate that the higher the value is, more efficient is the process.

Figure 2 confirms the statement above by demonstrating quantitatively the influence of each variable in the experiments. It is noticed that the milling speed (B) and the Milling Time (C) had the highest influence on the process and when the level set is higher, according to Table 2, higher is the efficiency.

Table 4 shows the results of the ANOVA analysis, considering the yield average of the niobium hydrate milling. According to the (F) test values, the milling speed (B) was the most significant variable followed by milling time (C), with a value of 155 and 8 respectively.

The objective of the signal-to-noise (S/N) ratio's maximization consists of minimizing the variability of the output variables. From effects analysis of the

Table 4 — Analysis of variance for yield average milling of niobium hydrate.

	Variables studied in the process	Q.S.F	D.F	Q.S.A	F
(A)	*Volumetric fraction of the balls mill*	179	2	89	4
(B)	Milling speed	7250	2	36251	155
(C)	Milling time	385	2	192	8
(D)	Rheostat speed in the screening (%)	9	2	4	0,2
(E)	Screening time	95	2	47	2
	Total Error	46	2	23	

DF: Degrees of Freedom; Q.S.F: Quadratic Sum of the Factors; Q.S.A.: Quadratic Sum Average; F: Factor of Significance = $Q.S.A._{efect}/Q.S.A._{error}$

Table 5 — Variance analysis of the S/N ratio.

	Efeitos	Q.S.F	D.F	Q.S.A.F	F
(A)	Volumetric fraction of the balls mill	23	2	11,5	6,5
(B)	Milling speed	2088	2	1044	592,6
(C)	Milling Time	31,7	2	15,8	9
(D)	Rheostat speed in the screening (%)	13	2	6,4	3,6
(E)	Screening Time	4,4	2	2,2	1,3
	Residue	3,5	2	1,7	

Q.S.A.F.:Quadratic Sum Average of the factors

Table 6 — Proposed optimal adjustment for input variables.

	Variables studied in the process	Proposed levels
(A)	Volumetric fraction of the balls mill (%)	50, 25, 25 (medium level)
(B)	Milling speed (%)	80 (high level)
(C)	Milling time (min)	45 (high level)
(D)	Rheostat speed in the screening (%)	60 (mediumlevel)
(E)	Screening time (min)	15 (lower level)

variables, Table 2, on the S/N ratio, Fig. 3, the strong influence of the milling speed (B) can be observed followed by milling time (C).

Table 5 demonstrates the ANOVA analysis of the variables' impact on the S/N ratio. The most significant variables, considering the *F test*, were milling speed (B), 592.6, followed by the milling time (C), 9. As inferred by the difference in the scale of the values, B had the highest level of significance among the other variables.

A final experiment was executed considering the adjustments proposed in Table 6. The results showed an average yield in the milling of 64%, based on the initial mass. In comparison with experiment 3, the efficiency of the adjusted experiment in Table 6 increased by approximately 2%. Therefore, experiment 3 was already close to the optimal values for input variables. The morphology and particles' distribution of the niobium hydride powder (<75 µm), obtained by the experiments with the lowest and highest yield, 1 and 3 respectively, were analyzed by the scanning electron microscopy (SEM). The powder obtained by Experiment 1 presented angular particles and low superficial roughness. The distribution of cleavage degree and particle size was pretty homogenous (Fig. 4).

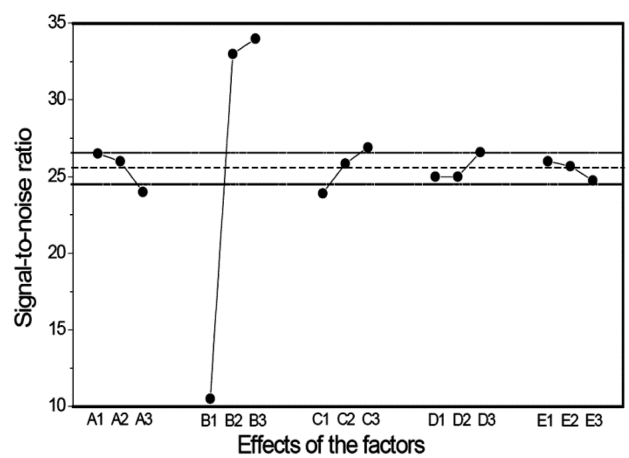

Fig. 3 — Effects of the factors on the S/N ratio (A, B, C, D, and E – processes variables; 1, 2 and3 – levels used in the process).

In the Experiment 3, when compared to Experiment 1, as shown in Fig. 5, there was a smaller number of angular particles, a larger superficial roughness, a larger incidence of cleavage degree, and

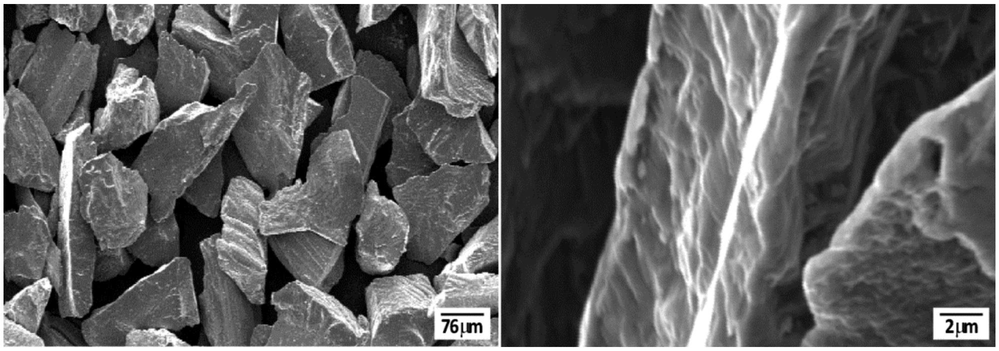

Fig. 4 — SEM/BSE micrography of the powder obtained in the experiment 1.

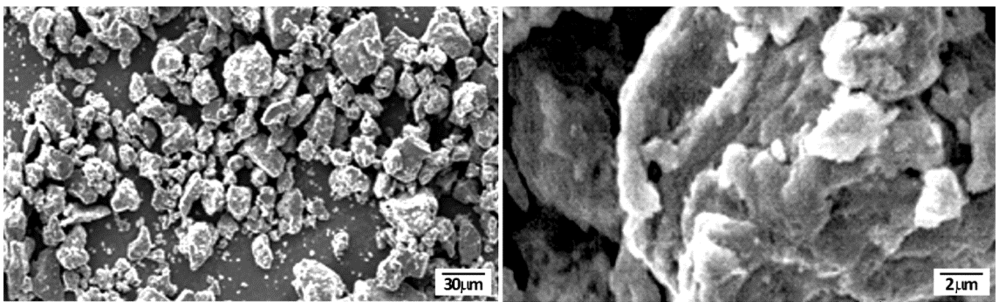

Fig. 5 — SEM/BSE micrography of the powder obtained by the experiment 3.

slighter particles. However, the particles presented a heterogeneous distribution. Finally, more formations of agglomerates coexisting with particles of angular shape were observed when compared with Experiment 1. The authors believe that these effects result from a more aggressive process with high milling speed and high milling time.

4 Conclusions

The obtained results with Taguchi's method were important in the study of the niobium hydride production. The results determined the best adjustment of input variables, optimizing the milling and screening process.

The most important variable was milling speed (B), which could be evidenced through high-efficiency average and high F value for S/N ratio. The second variable that mostly affected the process was milling time (C). The variables screening time (E), rheostat speed in the screening (D) and volumetric fraction of the balls mill (A) had insignificant influences in the process. The optimal values for milling speed and time were respectively 80% and 45 minutes. However, when was used the adjustment experiment suggested by the statistical software Minitab 17® was used, the process yield increased by only 2%.

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