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Nanoperm Alloys: Optimization of Digestion Process by Experimental Design and Determination of Some Metal Ions

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ABSTRACT

The demand of the modern times for minimalization has actualized the advance of new materials with extremely fine microstructures. Accordingly, the FINEMETs, NANOPERMs, HITPERMs and some aluminium based heat-treated ribbons symbolize the particular category of the nanocrystalline alloys in which the development of the three-dimensional nanostructure can be controlled by a special thermal treatment of rapidly quenched precursors. In this work, we developed an optimized procedure for rapid digestion of NANOPERM samples by acid attack in an oven under microwave irradiation. Experimental design was used as a multivariate strategy for variable effects evaluation using metal ion concentrations as response variable.

Keywords: Nanoperm Alloy; Digestion Process; Trace Elements; Box-Behnken Design; AAS.

INTRODUCTION

Metallic alloy systems with outstanding properties advantageously exploit the enhancement of properties and special phenomena through the decreasing the size of structural units present in the matter. Nanocrystalline alloys obtained by crystallization from a metastable amorphous rapidly quenched state are an exemplary case of such systems. The size of crystalline grains is typically few nanometres or few tens of nanometres.

One of the most successful industrial applications of nanostructured materials prepared by crystallization of amorphous precursors is with magnetic materials. The development of magnetic materials has a history of over a century. During this period, soft magnetic properties of materials have been progressively improved by means of compositional and/or structural modifications.

Two major alloy systems in this family of nanocrystalline magnetic materials are Fe-Si-B-Cu[1] and Fe-Zr-B-(Cu)[2,3], commercially known as FINEMET and NANOPERM, respectively. Historically, the effect of nanoscale grain sizes on the technical magnetic properties was first studied for Ni-Fe (PERMALLOY) thin films in the 1960's. Hoffmann[4] predicted in his ripple theory that the soft magnetic properties of polycrystalline Ni-Fe films could be improved by refining the grain size. The era of intense research on Fe-rich nanocrystalline soft magnetic materials has opened after the development of nanocrystalline $\text{Fe}_{74.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ by Yoshizawa *et al.*[1].

FINEMET and NANOPERM, with compositions Fe-M-Si-Cu-B and Fe-M-Cu-B, where M is a refractory metal or a mixture of them (M = Nb, Mo, W, Ta, Zr, Hf,...), are extremely good magnetic alloys. This is because of the averaging out of the crystal magnetic anisotropy due to the grain size being lower than the exchange correlation length[5,6].

The distinctive magnetic core properties of Fe-M-B based nanocrystalline soft magnetic alloys (NANOPERM) are the combination of the following characteristics: (1) a high saturation magnetization up to 1.7 T, (2) a high permeability well above 10000 and (3) zero-magnetostriction.

The usual method for obtaining nanocrystalline alloys is heat treatment in a furnace under inert atmosphere. Joule heating by means of a current flowing through the sample is also a useful method, as crystallization is accomplished in very short times and requires no inert atmosphere because oxidation has no time to take place, and, therefore, it can be performed in air. Higher temperatures result in lower grain sizes as compared with conventional, longer, treatments[7-10]. These materials can contain impurities and co-milling of the binary compounds leads to heterogeneous distribution of impurities, which impairs the physical properties of the final nanocrystalline alloy, so that the chemical analysis of these soft magnetic materials can be very important.

In the present work, the optimization was performed using a Box-Behnken design for determination of the critical experimental conditions. AAS have been used after the previous microwave dissolution of the samples for determination of Zn, Mn, Ni and Cu concentrations.

EXPERIMENTAL SECTION

Instrumentation

A Candy microwave oven, model CMG 1773 DW, and a Parr Microwave Acid Digestion Bomb, model 4782, were used for sample digestion. The bombs were cleaned before use with 10% nitric acid for 1 day followed by repeated rinsing with water.

A Varian Model SpectrAA 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis. The zinc, manganese, nickel and copper hollow cathode lamps were run under the conditions suggested by the manufacturer at wavelengths 213.9 nm, 279.5 nm, 232.0 nm and 324.7 nm, respectively.

Reagents

Analytical reagent grade chemicals were used throughout. Standard $1000 \mu\text{g mL}^{-1}$ Zn(II), Mn(II), Ni(II) and Cu(II) solutions (Fluka) were used. Standards of working strength were made by appropriate dilution as required, immediately prior to use. Water was deionised with a Milli-Q system. Concentrated acid HCl and HNO_3 (Merck) were used for digestion of the samples.

Optimization strategy

The experimental variables were optimized by applying a Box-Behnken response surface to design the digestion process. Table 1 shows the experimental design matrix. The experimental data were processed using the STATGRAPHICS 5.1 plus program[11]. The significance of the effects was made by Analysis of the Variance (ANOVA) using p-value significant levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the p-value is less than 5%, the effect of corresponding factor is significant.

RESULTS AND DISCUSSION

In the current work dissolution has been achieved by acid attack (HCl+HNO₃) under microwave-assisted pressure digestion. The advantages of microwave dissolution include faster reaction rates that result from the high temperature and pressures attained inside the sealed containers. The use of closed vessels makes it possible to eliminate uncontrolled trace element losses of volatile species that are present in a sample. Another advantage of microwave dissolution is a decrease in blank values compared with open-beaker work, both because contamination from the laboratory environment is much lower and because closed vessels make it possible to use smaller quantities of reagents.

Different times and power settings were investigated to establish the proper settings required for the digestion of NANOPERM alloy samples without damage to the digestion vessels. Maximum load of the bomb heating at 100% power at the start of the dissolution caused leakage and deformation of the vessels. Lower power settings permit controlled decompositions.

The content of metal species in the samples has been evaluated by AAS. The standard addition procedure has been used in all cases. For the digestion and determination, 50 mg of powdered samples were weighed exactly, added to the digestion vessel with the acid mixture, and digested in the microwave oven using the conditions listed in Table 1. After digestion, the samples were diluted to 25 mL with deionized water in a calibrated flask. For the analysis by standard additions of these digested samples, a blank solution prepared with the same volumes of acids as the samples raised to 25 mL and three sample solutions with standard additions of the elements were used to obtain the calibration graphs.

Over the data given in Table 1 for the zinc, manganese, nickel and copper concentrations obtained a statistical descriptive study has been made and some examples are shown in Figure 1. The p-values from the ANOVA carried out on the data given in Table 1 are shown in Table 2. The principal effect graphs are shown in Figure 2. As can be seen from Table 2 only in the case of Zn, the interaction time- volume of HCl is significant and the interaction power-time is significant in the case of Cu and it can be confirmed with the Pareto graphs shown in Figure 3. The optimum values for the determination of each metal ion are shown in Table 3, also in this table is enclosed the optimum values of the factors for the simultaneous determination of the four metal ions. Figure 4 shows the response surface obtained for each two factors on the Mn, Zn, Ni and Cu concentrations.

Table 1. Box-Behnken design matrix and the results as average Zn, Mn, Ni and Cu concentrations

Ejecution	Power (%) ^a	Time (min)	Vol. HCl (ml)	Vol. HNO ₃ (ml)	[Zn] (ppm)	[Mn] (ppm)	[Ni] (ppm)	[Cu] (ppm)
1	75	2	4	1.5	0.053	0.149	1.693	32.9
2	75	2	2.5	1	0.116	0.207	1.955	32.4
3	75	1	4	1	0.045	0.268	1.743	41.95
4	100	2	1	1	0.136	0.162	1.665	34.3
5	75	2	1	1.5	0.049	0.448	0.993	35.8
6	50	2	1	1	0.148	0.3	1.09	40.1
7	75	2	1	0.5	0.101	0.288	1.633	35.05
8	75	3	1	1	0.069	0.156	1.873	37.05
9	50	2	2.5	0.5	0.079	0.183	1.57	35.1
10	100	2	4	1	0.051	0.195	1.94	42.4
11	75	1	2.5	1.5	0.073	0.304	1.75	44.8
12	75	3	2.5	0.5	0.047	0.214	1.203	34.15
13	75	1	1	1	0.130	0.175	1.66	37.1
14	75	1	2.5	0.5	0.075	0.25	2.095	37.15
15	100	3	2.5	1	0.072	0.213	1.27	47.1
16	50	2	2.5	1.5	0.105	0.186	2.158	38.1
17	75	3	4	1	0.157	0.216	1.985	41.8
18	75	3	2.5	1.5	0.113	0.162	1.485	26.1
19	75	2	4	0.5	0.050	0.244	1.463	37.95
20	50	1	2.5	1	0.069	0.16	1.545	33.55
21	75	2	2.5	1	0.090	0.13	1.775	39.5
22	50	3	2.5	1	0.063	0.199	1.47	26.6
23	100	1	2.5	1	0.068	0.177	1.613	29.7
24	50	2	4	1	0.108	0.18	1.545	37.1
25	75	2	2.5	1	0.084	0.259	1.66	33.45
26	100	2	2.5	1.5	0.046	0.284	1.465	31.6
27	100	2	2.5	0.5	0.087	0.151	1.658	34.55

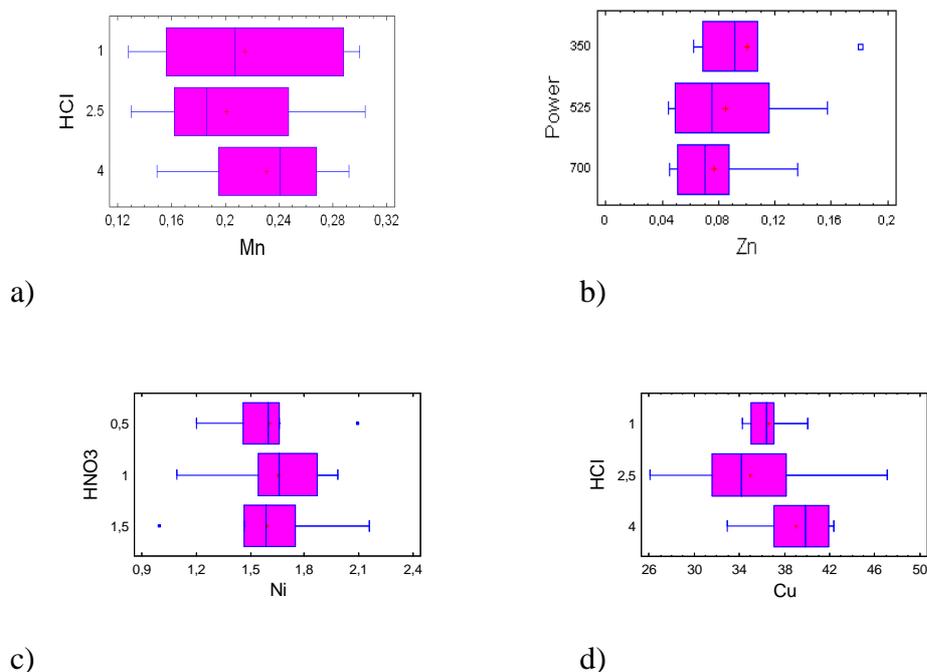
^a Power (%): 100%=700W; 75%=525W; 50%=350W

Table 2. p-Values from ANOVA

Source	p-Value for Zn	p-Value for Mn	p-Value for Ni	p-Value for Cu
A:HCl	0.1034	0.2755	0.2063	0.3969
B:HNO ₃	0.9959	0.4188	0.9444	0.7858
C:Power	0.2681	0.9164	0.8345	0.5965
D:Time	0.5357	0.4867	0.3240	0.5068
AA	0.6396	0.3581	0.4985	0.2061
AB	0.3344	0.0935	0.1916	0.5594
AC	0.4298	0.2958	0.7795	0.2729
AD	0.0089	0.8176	0.9627	0.9919
BB	0.0978	0.2201	0.4360	0.6460
BC	0.2454	0.3713	0.2384	0.5494
BD	0.2422	0.4635	0.3379	0.1301
CC	0.8498	0.5234	0.3528	0.9564
CD	0.8536	0.9833	0.6780	0.0269
DD	0.4870	0.8233	0.7534	0.7297

Table 3. Optimum values of the factors for metal ions determination

Factor	Zn	Mn	Ni	Cu
Power (%) ^a	100	72	100	59
Time (min)	1.0	1.0	1.0	1.2
Volume of HCl (mL)	1.0	1.0	1.4	4.0
Volume of HNO ₃ (mL)	0.5	1.5	0.5	1.5

^a Power (%): 100%=700W**Figure 1. Box-whisker plot for: a) manganese b) zinc c) nickel d) copper**

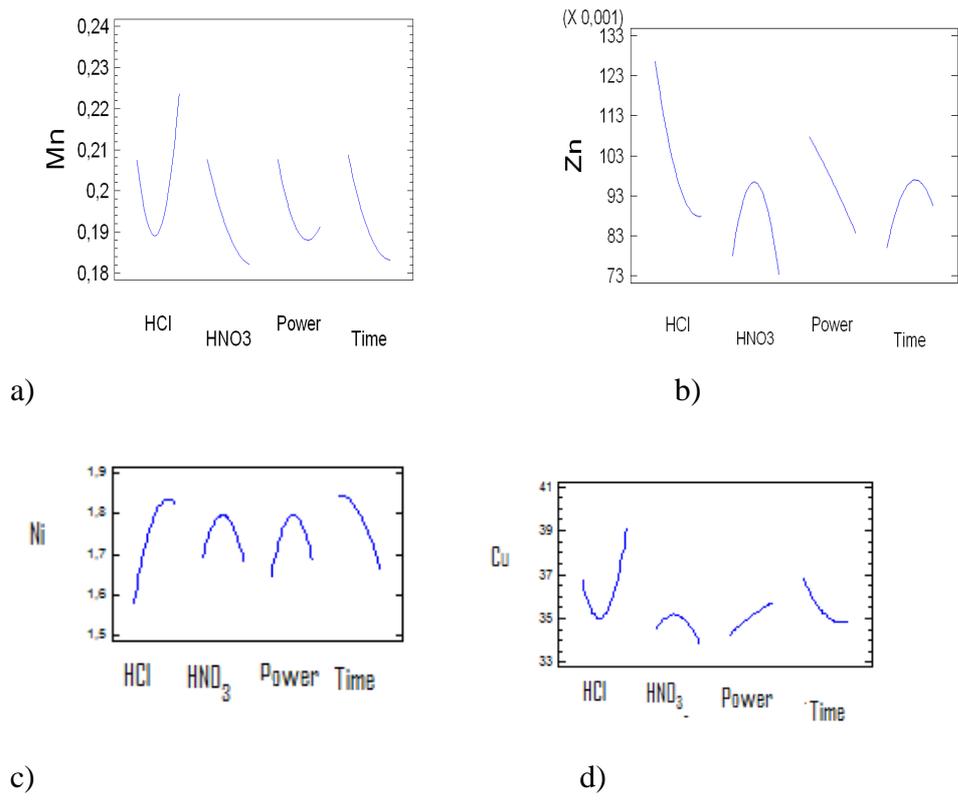


Figure 2. Principal effects graph for: a) manganese b) zinc c) nickel d) copper

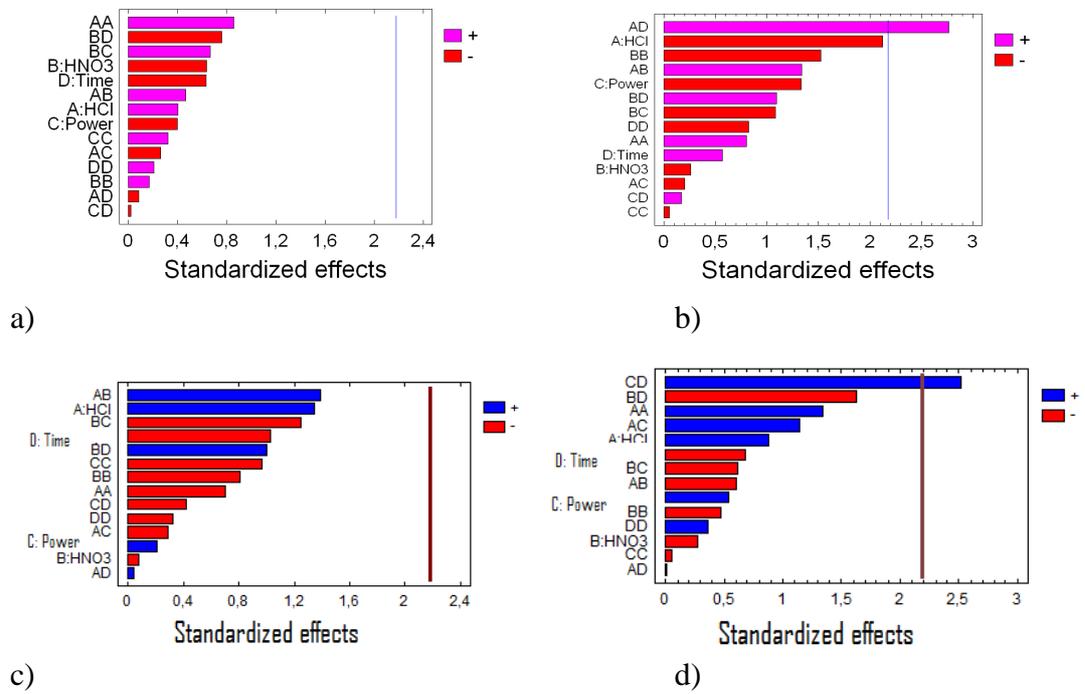


Figure 3. Pareto graphs for: a) manganese b) zinc c) nickel d) copper

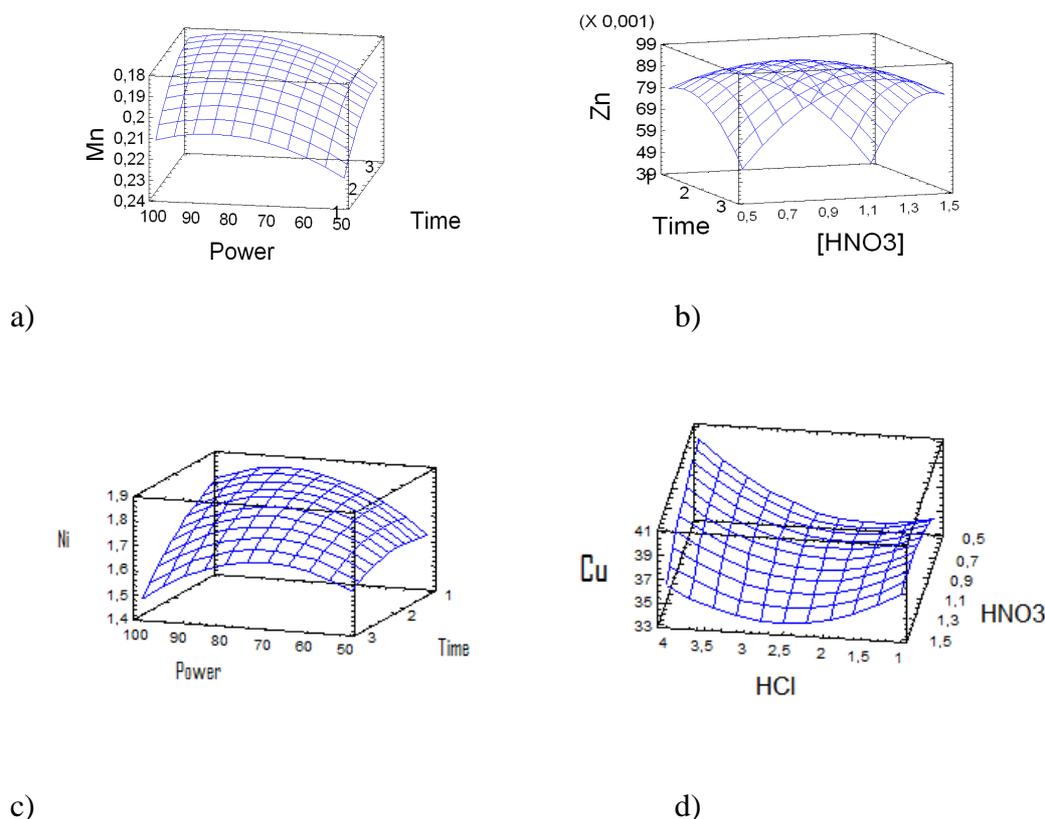


Figure 4. Response surfaces graph for: a) manganese b) zinc c) nickel d) copper

CONCLUSIONS

The determination of metal ions in NANOPERM alloys can be achieved by the dissolution in acids under microwave irradiation, followed by the analysis of AAS, although the dissolution step is time-consuming and the use of high purity acids is absolutely necessary. Dissolution under microwave irradiation shortens appreciably the time of the acid attack.

Optimization of digestion procedures, based on a traditional univariate approach, involves a great many experiments; the more variables the more experiments. In this study it has been shown that the application of a Box-Behnken design considerably reduces the amount of experimental work required. By using such a design we have been able to establish the optimum condition for the determination of Mn(II), Zn(II), Ni(II) and Cu(II). Furthermore, as atomic spectroscopy moves more towards multivariate analysis, the need for multivariate experimental design and optimization techniques becomes important in establishing valid methodology.

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