Vol. 9 Issue 03, March-2020

### Application of Tukey's Test for Statistical Measurement of Percentage Indexes Derived from the Difference Between Predicted Crystallographic Data in Five Nitihf Alloys Obtained by Two Processes

Roniere Leite Soares
Federal University of Campina Grande
UFCG – CCT – UAEP - AEG
Campina Grande – Paraíba - Brazil

Walman Benicio De Castro Federal University of Campina Grande UFCG – CCT – UAEM - LaMMEA Campina Grande – Paraíba - Brazil

Abstract — The present paper uses the Tukey test to measure the minimal significative difference (MSD) between crystallographic data predicted by non-linear mathematical models generated from graphics published by Zarinejad (2008) and Potapov (1997) on 5 nominal compositions of Ni<sub>50</sub>Ti<sub>50-X</sub>Hfx .at% substitutional alloys fused by arc melting and melt spinning processes. Results show that the calculated MSD do not represent a statistically significant difference. Therefore, it is concluded that the independent variable (Hafnium content) does not change the analysed dependent variables (lattice parameters, crystalline structure volume and monoclinic angle β) for any fusing processes.

Keywords— ANOVA; Monoclinic; NiTiHf; Statistical test; Tukey.

#### I. INTRODUCTION

The production of shape memory effect (SME) alloys depends sensibly on particular processes that, based on the variation of parameters involved in the equipment used (maximum melting temperature, vacuum magnitude, purge intensity, purity of the metallic charges, torch exposition time. etc), can or cannot generate different crystallographic features for samples which theoretically have the same chemical compositions. In this sense, it is important to compare the obtained results through predictive modelling functions to observe whether there are any significant statistical difference capable of indicating a great variability in crystallographic characteristics, such as: lattice parameters (a b c [Å]), cell volume (VOL  $[Å^3]$ ) and characteristic angle  $\beta$  (beta [°]) of the monoclinic structure (space group P12<sub>1</sub>/m1). In this work, they are studied as variables dependent on hafnium content, which is considered an independent variable in the nominal composition. The focus of the study is on room temperature B19' martensitic phase B19', which has a monoclinic structure (Pearson symbol mP8) and is considered by the literature as an unstable phase. In addition, the five substitutional compositions Ni<sub>50</sub>Ti<sub>50-X</sub>Hf<sub>X</sub> .at% considered in this instance are X = 8, 11, 14, 17 and 20 .at%, which were obtained by two different processes: Arc Melting (Zarinejad, 2008) [1] and Melt Spinning (Potapov, 1997) [2].

### II. PREDICTION OF THE B19' PHASE OF NI<sub>50</sub>TI<sub>50-x</sub>HF<sub>x</sub> .AT% ALLOYS

Based on the graphs by Zarinejad (2008) [1], which measurements were obtained by XRD [3] refinement method, it was possible to calculate, through numerical proportions, the equivalence of the lattice parameters (a, b, c), volume of the monoclinic structure B19' and axial angle  $\beta$ , as shown in table 1.

Hf	a	b	с	V	β
( at.% )	(Å)	(Å)	(Å)	$(\mathring{A}^3)$	(°)
5	2.8228476	4.1605263	4.6628158	54.195804	98.068493
10	2.9049668	4.1210526	4.7220216	55.758741	98.49315
15	2.9980132	4.1092105	4.7707581	57.972027	99.189041
20	3.0814569	4.0503947	4.8754512	59.807692	100.04657

Table 1 - Values for the four compositions of  $Ni_{50}Ti_{50-X}Hf_X$  .at% alloys (Zarinejad, 2008) obtained by conventional solidification (X = 5, 10, 15 and 20 at.%)

From the obtained results, the same variables were estimated for the five alloys of study (X = 8, 11, 14, 17 e 20 at.%). From the third order nonlinear regression (shown in Figure 1) it was adopted the polynomial function  $\hat{y} = \beta_0 + \beta_1 X + \beta_2 X^2 + \beta_3 X^3 \pm \epsilon$  for each parameter, which resulted in:  $\hat{y}_a = 2,77219 + 0,00562x + 0,00104x^2 - 2,73732E-5x^3$  (R²=1);  $\hat{y}_b = 4,30224 - 0,04354x + 0,00354x^2 - 9,94737E-5x^3$  (R²=1) and  $\hat{y}_c = 4,52671 + 0,03934x - 0,00287x^2 + 8,85679E-5x^3$  (R²=1). The determination coefficient R² are equal to 1. This indicates that the proposed models are suitable to describe the phenomenon in which the parameters a and c increase, while the parameter b decreases. Equally, the models adopted for volume and  $\beta$  angle for b19'phase presented 100% fitting.

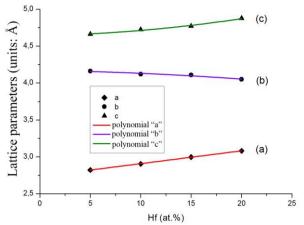


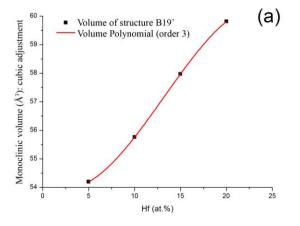
Figure 1 - Scatter diagrams & Cubic regression curves: with the values of lattice parameters (a, b, c) determined for the  $N_{150}Ti_{50\cdot X}Hf_X$ .at% alloys proposed by Zarinejad (2008)

All the values estimated for the five dependent variables are organized in table 2.

Hf (at.%)	a ( Å )	b ( Å )	c ( Å )	VOLreg ( Å <sup>3</sup>	B (°)
8	2.897725 0	4.1295494 6	4.7030967 6	54.99855	98.2847324 6
11	2.996283 7	4.1192405 0	4.7300638 7	56.18361	98.6143636 3
14	3.129822 0	4.1135641 6	4.7579803 1	57.52923	99.0337747 7
17	3.302774 5	4.0964057 1	4.8011940 9	58.81347	99.5192931 4
20	3.519575	4.0516500	4.874053	59.81439	100.047246

Table 2 - Values of the parameters predicted by the 3rd order polynomials: lattice parameters (a, b, c), monoclinic volume and  $\beta$ , for Ni<sub>50</sub>Ti<sub>50-x</sub>Hf<sub>X</sub> .at% alloys (X = 8, 11, 14, 17 and 20 .at %)

A comparison between the values of table 1 and table 2, confirms a coherence in the direct proportion between the percentage of hafnium and the volume of the monoclinic structure (phase B19'). The lattice parameters for the five



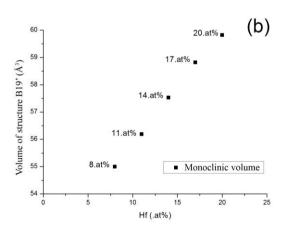


Figure 3 - Nonlinear regression (order 3) from which the volumes of the martensite phase (B19') of the five substitutive  $Ni_{50}Ti_{50-X}Hf_X$ . at% (X = 8, 11, 14, 17 and 20 %.at) alloys were calculated

Ni<sub>50</sub>Ti<sub>50-X</sub>Hf<sub>X</sub> .at% Ni-rich alloys of study are plotted in figure 2:

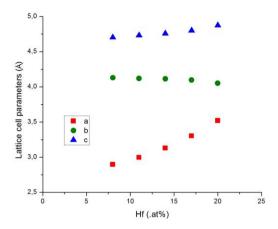
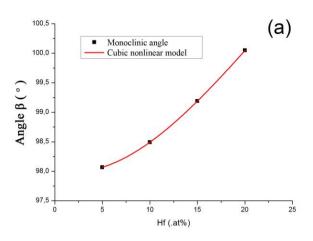


Figure 2 - Scatter Plot with estimated values of the lattice parameters of the crystal structure B19' in  $Ni_{50}Ti_{50.X}Hf_X$  .at% alloys (X = 8, 11, 14, 17, 20 at.%)

According to Figure 3(a), from the regressive function  $\hat{y}_{VOLreg} = 54{,}31119 - 0{,}25944x + 0{,}05413x^2 - 0{,}00137x^3$  ( $R^2 = 1$ ), adopted for all four Zarinejad (2008) alloys, in which X = 5, 10, 15 e 20 at.%, it is possible to predict the volume (ų) of the B19' monoclinic martensitic structure for the five compositions of the alloy  $Ni_{50}Ti_{50-X}Hf_X$  at.% (X=8, 11, 14 17 and 20 at.%), shown in Figure 3(b).

Similarly, using the cubic polynomial function  $y_{\beta}=98,02467-0,03662x+0,00981x^2-1,46128E-4x^3$  ( $R^2=1$ ) adopted for Zarinejad alloys (2008), as seen in Figure 4(a), the  $\beta$  angles of the B19' phase for the five  $Ni_{50}Ti_{50-X}Hf_X$  at.% (Hf = 8, 11, 14, 17 e 20 .at%) alloys of study were predicted and plotted in figure 4(b).



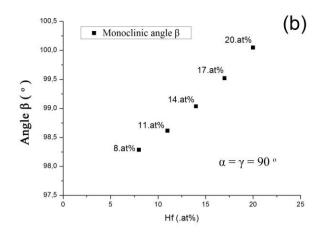


Figure 4 - Nonlinear cubic regression from which the  $\beta$  angles of the B19'martensitic phases were estimated for the five  $Ni_{50}Ti_{50\cdot X}Hf_X$ .at% (X = 8, 11, 14, 17 and 20 at.%) alloys rich in nickel

For the functions used as statistical models it was calculated the analysis of variance in each polynomial, according to table 3.

Variables	ANOVA	DF	SQ	MQ	F	Significance F
	Regression	3	0.03776864	0.012589547	_	_
a	Residue	0	0	_		
	Total	3	0.03776864			
	Regression	3	0.006228132	0.002076044	_	_
b	Residue	0	0			
	Total	3	0.006228132			
	Regression	3	0.024311803	0.008103934	_	_
c	Residue	0	0	l		
	Total	3	0.024311803			
	Regression	3	2.245370993	0.748456998	_	_
Angle β	Residue	0	0			
	Total	3	2.245370993			
	Regression	3	18.21455606	6.071518687	_	_
$Vol_{Reg}$	Residue	0	0			
	Total	3	18.21455606			
	Regression	3	18.46596165	6.155320551	_	_
Vol <sub>Calc</sub>	Residue	0	0			
	Total	3	18.46596165			

Table 3 - ANOVAS calculated for each model  $\hat{y} = \beta_0 + \beta_1 x + \beta_2 x^2 + \beta_3 x^3$  referring to the 5 variables of the B19'martensitic phase of the 5 Ni<sub>50</sub>Ti<sub>50-X</sub>Hf<sub>X</sub> at.% alloys

To make explicit the coherence of the regressive model adopted for the volume, the calculated volume (Vol = a.b.c. $sen\beta$ ) was added in Table 3, on top of which the model  $\hat{Y}_{VOLcalc} = 53,5806847 + 0,018979973x + 0,033586976x^2 + 8,39734E-04x^3$  (R<sup>2</sup> = 1) was created.

All of the  $R^2$  values were equal to 1. This makes unnecessary the calculation of Adjusted- $R^2$ , normally used to measure the real degree of modeling reliability. According to Table 3, since there was no standard error in the coefficients, the general error of the models is 0. For this reason, F value is not presented in table 3. Thus, it can be stated that the mathematical models adopted here are statistically significant as well as predictive for all five dependent variables observed.

Taking the four Zarinejad alloys (2008) as a reference, the residues found for each regression, in each variable of the monoclinic structure B19', are presented in table 4 and figure 5.

Hf (.at%)	a ( Å )	b ( Å )	c ( Å )	β(°)	Vol <sub>regressive</sub>	Volcalculated
5	-1.78E-15	8.88E-16	1.78E-15	-2.84E-14	7.11E-15	-2.84E-14
10	-8.88E-16	1.78E-15	2.66E-15	1.42E-14	1.42E-14	0
15	-8.88E-16	8.88E-16	1.78E-15	1.42E-14	1.42E-14	0
20	-8.88E-16	0	2.66E-15	1.42E-14	1.42E-14	0

Table 4 - Residues of each variable calculated for phase B19 'of the 4 substitutive  $Ni_{50}Ti_{50-X}Hf_X$  at% (X = 5, 10, 15 and 20) alloys from Zarinejad (2008)

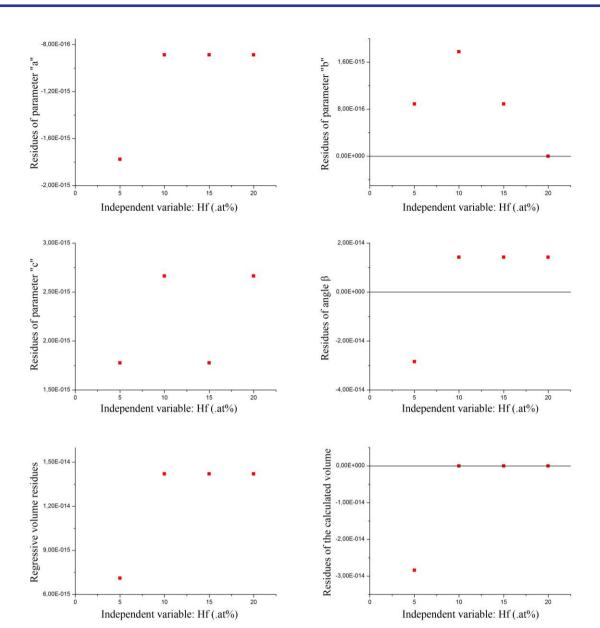


Figure 5 - Dispersive plot of residues in each variable of the B19'monoclinic structure (a, b, c, Volume and Beta [β, °]) for the 4 alloys of Zarinejad (2008)

# III. PREDICTION OF THE PHASE B19'ON $NI_{50}TI_{50-X}HF_X$ .AT% RIBBONS QUICKLY SOLIDIFIED BY MELT SPINNING

Based on the Potapov plots (1997) for the six ribbons of substitutional compositions  $Ni_{49.8}Ti_{50.2-x}Hf_X$  .at% (X= 8, 9.5, 11, 15, 20 e 25 .at%) obtained by *melt spinning*, the calculation of lattice parameters (a, b, c), B19'monoclinic crystal volume and characteristic angle  $\beta$  are shown in table 5:

Hf (.at%)	a ( Å )	b ( Å )	c ( Å )	VOL (Å <sup>3</sup> )	β(°)
8	2.985357	4.100357	4.725	56.961414	99.992857
9.5	2.989285	4.096428	4.755642	57.337329	100.07142
11	3.001071	4.094857	4.779214	57.769323	100.38571
15	3.027785	4.0925	4.827142	58.499286	102.03571
20	3.06000	4.084642	4.89000	59.539886	103.05714
25	3.099285	4.072857	4.937142	60.25763	104.78571

Table 5 - Crystallographic characteristics of the martensitic phase obtained by XRD refinement for the six ribbons with Potapov (1997) nominal compositions  $Ni_{49.8}Ti_{50.2-x}Hf_x$  .at% obtained by fast melt spinning solidification

Considering the similarity of the composition used by Potapov (1997) regarding the composition  $Ni_{50}Ti_{50-x}Hf_X$  .at%, adopted in this work (difference of 0,2 .at% in the contents of Ni e Ti), the values of table 5 were used to proportionally calculate the same variables having as reference an alloy rich in Ni of nominal composition  $Ni_{50}Ti_{50-x}Hf_X$  .at%, quickly solidified by *melt-spinning*. The results are shown in Table 6:

Hf (.at%)	a (Å)	b (Å)	c (Å)	Vol (Å <sup>3</sup> )	β(°)
8	2.99735	4.08402	4.74398	57.19017	100.39443
9.5	3.00129	4.08011	4.77474	57.5676	100.47331
11	3.01312	4.07854	4.79841	58.00133	100.78887
15	3.03994	4.0762	4.84653	58.73422	102.44549
20	3.07229	4.06837	4.90964	59.779	103.47102
25	3.11173	4.05663	4.95697	60.49963	105.20654

Table 6 - Crystallographic characteristics of the martensitic phase calculated proportionally from Potapov's ribbons  $Ni_{498}Ti_{50.2-x}Hf_x$ . at% (1997) for the theoretical ribbons  $Ni_{50}Ti_{50.x}Hf_x$ . at% (X = 8, 9.5, 11, 15, 20 and 25 .at%) obtained by fast *melt spinning* solidification

Based on the data in table 6, these five variables were calculated with the nonlinear cubic model, which is composed by the third order function  $y_i = \beta_0 + \beta_1 x_i + \beta_2 x_i^2 + \beta_3 x_i^3 + \varepsilon_i$ , (i = 1, 2, ... n). The values of  $R^2$  are, for the dependent variables a, b, c, volume and  $\beta$ , respectively, 0.9986, 0.9938, 0.9987, 0.9986 and 0.9885. This certifies a large percentage of correct answers. The estimated quantities for the five compositions are presented in table 7.

Hf (.at%)	a ( Å )	b ( Å )	c ( Å )	VOL (ų)	β(°)
8	2.995688	4.083342	4.746384	57.208961	100.237795
11	3.012892	4.07906	4.795981	57.93075	100.997707
14	3.031679	4.076048	4.838146	58.594993	101.835911
17	3.051887	4.07311	4.87463	59.199742	102.726977
20	3.073354	4.06905	4.907188	59.743049	103.645474

Table 7 - Estimative of the crystallographic characteristics of the B19' phase in the five ribbons quickly solidified by melt spinning for the composition  $Ni_{50}Ti_{50-X}Hf_{\rm X}$  .at% (8-20 .at%)

Using the matrix adopted for monoclinic crystals [4], according to the Equation 01, the volumes were recalculated to show the coherence of the statistical model. The volumes found were, for the five compositions (Hf = 8, 11, 14, 17 and 20.at%), in this order:  $57.13535181~\text{Å}^3$ ,  $57.85901627~\text{Å}^3$ ,  $58.51514303~\text{Å}^3$ ,  $59.10615326~\text{Å}^3$  e  $59.63533041~\text{Å}^3$ .

$$VOL = \begin{bmatrix} a^2 & 0 & a.c.\cos\beta \\ 0 & b^2 & 0 \\ a.c.\cos\beta & 0 & c^2 \end{bmatrix}^{1/2}$$
 (1)

The model functions were determined based on the coefficients listed in table 8, accompanied by the respective errors.

Coeffici ents	$\beta_0$	$\beta_0$	$\beta_1$	$\beta_1$	$\beta_2$	$\beta_2$	$\beta_3$	$\beta_3$
Sum	Value	Erro ±	Value	Erro ±	Value	Erro ±	Value	Erro ±
a	2.958 78	0.034 34	0.003 71	0.007 16	1.21E- 04	4.61E -04	- 1.00E- 06	9.25E -06
b	4.110 06	0.015 79	0.005 38	0.003 29	3.14E- 04	2.12E -04	7.38E- 06	4.25E -06
c	4.564 45	0.058 9	0.028 21	0.012 29	7.70E- 04	7.90E -04	1.08E- 05	1.59E -05
Volume	55.01 768	0.964 61	0.297 08	0.201	0.0028	0.012 94	- 1.20E- 05	2.60E -04
β	98.78 753	4.197 37	0.115 09	0.875 51	0.0095	0.056	- 1.57E- 04	0.001 13

Table 8 - Coefficient values calculated for third order statistical models for  $Ni_{50}Ti_{50-x}Hf_{\rm X}$ .at%

For each of the cubic functions, the values of Adjusted- $R^2$  computed are, in the decrescent order, in table 8: 0.99643, 0.98445, 0.99682, 0.99658 e 0.97115.

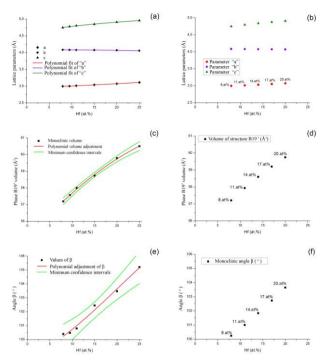


Figure 6 – Left column presents the graphs with estimated values for the six Potapov ribbons (1997), and right column shows the calculated values for the five theoretical ribbons of nominal compositions  $Ni_{50}Ti_{50-x}Hfx$ . at%

For a graphic visualization, figure 6 presents the values calculated for the six Potapov ribbons (1997) plotted in the left column (figure 6(a), figure 6(c) and figure 6(e)) in a way that they are compared with the values predicted for the five ribbons studied here, plotted in the right column (figure 6(b), figure 6(d) and figure 6(f)).

According to the obtained numbers , the values of  $\beta$  angle, volume and "a" and "c" are directly proportional to the atomic percentage of hafnium from the alloy, except in the lattice parameter "b", which is inversely proportional to the content of Hf (.at%).

# IV. COMPARISON OF CRYSTALLOGRAPHIC CHARACTERISTICS OF THE MARTENSITIC PHASE IN ZARINEJAD'S ALLOYS AND POTAPOV'S RIBBONS

Due to the fact that these variables are different, i.e., one-dimensional (lattice parameters) two-dimensional ( $\beta$  angles) and three-dimensional (monoclinic structures volumes) entities. To enable a dimensionless comparison between the predicted data from Zarinejad (2008) and Potapov (1997), it was necessary to consider the percentage indexess of the differences between the estimated values for each parameter (a, b, c, Vol e  $\beta$ ) of the five compositions  $Ni_{50}Ti_{50-X}Hf_X$  .at%. This makes them arbitrary data. Therefore, it was necessary to organize the sample series from table 11 with the dimensionless format of table 9. Percentage indices have arbitrary units.

Using descriptive statistics, the measures of central tendency and dispersion were summarized in table 10.

The normal distribution (differences percentage indexes versus x indexes' density) is represented by equation 2 and plotted in figure 7. It is composed of:  $\sigma$  (standard deviation), e (Constante de Euler-Mascheroni: 2.718),  $\pi$  (proportion) and  $\mu$  (population mean).

Percentage indexes ranked in ascending order								
0.0012	0.0068	0.0137	0.0236	0.0327				
0.0043	0.0091	0.0151	0.0275	0.0347				
0.0055	0.0091	0.0166	0.0302	0.0386				
0.0057	0.0098	0.0182	0.0312	0.076				
0.0065	0.0112	0.0195	0.0314	0.1268				

Table 9 - List of 25 data organized sequentially (indexes of dimensional differences verified between both authors)

Mean (average)	0.0242	Standard deviation	0.0267	Interval	0.1256
Standard error	0.0053	Sample variance	0.0007	Min and Max	0.0012; 0.1268
Median	0.0166	Kurtosis	9.1143	Sum	0.605
Mode (fashion)	0.0091	Asymmetry	2.7719	Confidence level (95 %)	0.011025366

Table 10 - Descriptive summary of the main statistical measurements

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}, \quad X \in (-\infty, \infty)$$
 (2)

It is noticeable, in figure 7, that there is a concentration of minor differences close to bigger densities. This certifies that the values from both authors are close.

Characteristics of phase B19' (monoclinic)		Zarinejad	Potapov	Zarinejad	Potapov	Zarinejad	Potapov	Zarinejad	Potapov	Zarinejad	Potapov
Hf (.a%)	ŷ	ä	ì	1	)	(	2	V	OL	ſ	3
	Estimated values	2.897.725	2.995.688	4.129.549	4.083.342	4.703.097	4.746.384	5.499.855	5.720.896	9.828.473	1.002.378
	Absolute difference (Å)	0.09	0.097963		6207	0.04	3287	2.210.411		1.953	3.065
8	Proximity (%)	96.7	73%	98.8	38%	99.0	)9%	96.1	14%	98.0	)5%
	Mean	29.46	7.065	41.06	4.455	47.24	7.405	561.03	37.555	992.61	12.625
	Percentage difference	3.2	7%	1.1	2%	0.9	1%	3.8	6%	1.9	5%
	Estimated values	2.996.284	3.012.892	4.119.241	407.906	4.730.064	4.795.981	5.618.361	5.793.075	9.861.436	1.009.977
	Absolute difference (Å)	0.010	6608	0.04	0181	0.06	5917	174	.714	2.383	3.347
11	Proximity (%)	99.4	15%	99.0	)2%	98.6	53%	96.9	98%	97.€	54%
	Mean	3.004.588		40.99	40.991.505		0.225	5.705	5.718	998.060.335	
	Percentage difference	0.5	5%	0.98%		1.37%		3.02%		2.3	6%
	Estimated values	3.129.822	3.031.679	4.113.564	4.076.048	475.798	4.838.146	5.752.923	5.859.499	9.903.377	1.018.359
	Absolute difference (Å)	0.098143		0.03	7516	0.08	0166	1.065	5.763	2.802	2.141
14	Proximity (%)	96.86%		99.0	)9%	98.34%		98.18%		97.2	25%
	Mean	30.80	7.505	4.094.806		4.798.063		580.621.115		1.004.348.405	
	Percentage difference	3.1	4%	0.91%		1.66%		1.82%		2.75%	
	Estimated values	3.302.775	3.051.887	4.096.406	407.311	4.801.194	487.463	5.881.347	5.919.974	9.951.929	102.727
	Absolute difference (Å)	3.302	2.775	4.096	5.406	4.80	1.194	5.883	1.347	9.951	1.929
17	Proximity (%)	92.4	10%	99.4	99.43%		19%	99.3	35%	96.8	88%
	Mean	3.177	7.331	4.084	1.758	4.83	7.912	59.00	6.606	1.011.2	31.335
	Percentage difference	7.6	0%	0.5	7%	1.5	1%	0.6	5%	3.1	2%
	Estimated values	3.519.576	3.073.354	405.165	406.905	4.874.053	4.907.188	5.981.439	5.974.305	1.000.472	1.036.455
	Absolute difference (Å)	0.44	6222	0.0	174	0.033135		0.071341		3.598.274	
20	Proximity (%)	87.3	32%	99.5	57%	99.32%		99.88%		96.5	53%
	Mean	3.296	5.465	406	.035	48.906.205		597.787.195		101.846.337	
	Percentage difference	12.6	58%	0.4	3%	0.6	8%	0.1	2%	3.4	7%

Table 11 - Comparison between Ni<sub>50</sub>Ti<sub>50-X</sub>Hf<sub>X</sub> .at% alloys and ribbons based on the models by Zarinejad (2008) and Potapov (1997)

However, there is a clear comprehension that the crystallographic characteristics depend not only on the hafnium content, but they are also sensitive to the peculiarities of the two production processes as well as the typical variables of each one of them: electric arc melting (*Arc Melting*) and quick solidification *Melt Spinning*.

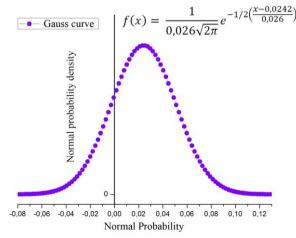


Figure 7 - Plot of the probability curve (100 points) of the difference indexes estimated by the statistical models adopted for Zarinejad alloys (2008) and Potapov ribbons (1997)

Depending on how the peculiarities involving each one of the processes are treated, one can directly influence the main properties of the samples such as: homogeneity, amount of residual stress and minimization of oxidation, among others. These physical and mechanic properties, among others are derived from atomic arrangementknown as crystallographic structures (or crystalline structures).

It can be mentioned as variables of these processes: the number of times that the *bulk* was melted, exposure time to the torch, type of material of the mold, efficiency of the applied vacuum, rotating speed of the copper flywheel in quickly solidified ribbons *etc*. Hence, all the possibilities of variation and instrumental errors generate conditions of solidification which interfere in the micro structure of the alloys and obtained ribbons.

#### V. CONCLUSIONS

The analysis of variance (ANOVA) is an unilateral test based on the F-Snedecor table, which after calculating the F-value, it measures whether it is inside or outside of the acceptance area, according to the following hypothesis test:

$$\begin{cases} H_0 \colon \mu_{Potapov} = \mu_{Zarinejad} \\ H_1 \colon there \text{ is at least one difference between the means} \end{cases}$$

As it is an *OneWay* ANOVA, the only factor (independent variable) is the atomic percentage of Hf (.at%). As a rule, in terms of null hypothesis (H<sub>0</sub>), the calculated F-value is inside the area of acceptance, i.e., minor than critical F. Otherwise, if H<sub>0</sub> is rejected, the alternative hypothesis (H<sub>1</sub>) will be accepted having necessarily, the F-value calculated outside the area of acceptance, i.e., bigger than the critical F.

In this case, we considered that F(5%); DF1 (DFW); DF2 (DFR) = 3,12 (tabulated), according to the standard table for *Tukey's Test* ( $\alpha$ =0.05) [5]. According to Table 12, as the calculated F = 3.13 is bigger than the critical tabulated value, we concluded that there is a difference between the averages of both treatment groups: Potapov and Zarinejad. This conclusion is also confirmed by the P-value, which is smaller than 0.05. The lower the P-value, lower is the possibility for  $H_0$  be true. It is important to note that  $DF_1$  [horizontal = numerator] is the degree of freedom between groups (DFW) and that  $DF_2$  [vertical = denominator] is the degree of freedom of the residues (DFR).

Variation source	Sum of sQrs	DF	Mean square	F <sub>calc</sub>	valor-P (same)	critical F <sub>tabulated</sub>	
Between groups:	6739.09	2	3369.55	3.131	0.04968	3.123907449	
Within groups:	77488	72	1076.22	Permutation p (n=99999)			
Total:	84227.1	74	0.04909	Table F-Snedecor - F(5%): 2.74			

Table 12 - OneWay ANOVA calculated for two series of samples of the crystalline dimensions of the B19 'monoclinic phase in Ni<sub>50</sub>Ti<sub>50-X</sub>Hf<sub>X</sub>. at% alloys and ribbons obtained by conventional and rapid solidifications (Zarinejad and Potapov, respectively)

(1) Between groups (W) = Treatment = Between treatments = Between

(2) Within groups (R) = Residue = Error = Within

(3) DF = degree of freedom

Therefore, the null hypothesis is rejected (H<sub>0</sub>). However, to ascertain whether this difference is statistically significant, it is necessary to perform a parametric test to certify this significance. This decision was taken based on the normality test of Anderson-Darling [6], which predicts as "normal" the set of 25 data organized in table 9, as shown in figure 8:

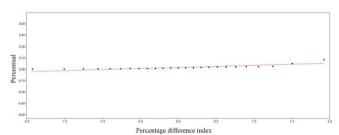


Figure 8 - Anderson-Darling Normality Test for the percentage indexes

A comparative analysis was made between two different solidification methods (arc melting e melt spin), when applying the TUKEY's Test (through table 13) [7] to, in a complementary form to ANOVA, calculate the minimum significant difference (m. s. d.) there is between the averages in the martensitic crystallographic characteristics, according to the original dimensional data predicted by the adjustment models, shown in table 2 and table 7. It is concluded that the method to obtain the alloys doesn't interfere in the dimensions here evaluated, that is, there is no significant statistical difference. This is due to the fact that the calculated difference ( $|\mu_{Potapov} - \mu_{Zarinejad}|$ ) was of 0.75. According to equation 3, the m.s.d [ $\Delta$ ] necessary for both groups (data series) to have a significant difference is 19.027.

$$\Delta = q * \sqrt{\frac{Mean Square (residues)}{Number of treatment repetitions}}$$
 (03)

In this calculation, q [q(5%); k; DF of residues = 2.899943] is a tabulated value (F-Snedecor table,  $\alpha$ =0.05), the QMR is 1076.22 (highlighted in table 12) and the number of repetitions is equal to 25. This count of 25 is contained in table 13, before the summary (resume).

Hf (at.%)	Dimensions	Zarinejad (2008)	Potapov (1997)		
	a (Å)	2.897725078	2.995688		
	b (Å)	4.129549466	4.083342		
8	c (Å)	4.703096765	4.746384		
	Volume (Å <sup>3</sup> )	54.99855	57.208961		
	β(°)	98.28473246	100.237795		
	a (Å)	2.996283729	3.012892		
	b (Å)	4.119240505	4.07906		
11	c (Å)	4.730063875	4.795981		
11	Volume (Å <sup>3</sup> )	56.18361	57.93075		
	β(°)	98.61436363	100.997707		
	a (Å)	3.129822061	3.031679		
	b (Å)	4.113564167	4.076048		
14	c (Å)	4.757980318	4.838146		
	Volume (Å <sup>3</sup> )	57.52923	58.594993		
	β(°)	99.03377477	101.835911		
	a (Å)	3.302774532	3.051887		
	b (Å)	4.096405712	4.07311		
17	c (Å)	4.801194093	4.87463		
	Volume (ų)	58.81347	59.199742		
	β(°)	99.51929314	102.726977		
	a (Å)	3.5195756	3.073354		
	b (Å)	4.0516504	4.06905		
20	c (Å)	4.8740532	4.907188		
	Volume (Å <sup>3</sup> )	59.81439	59.743049		
	β(°)	100.047246	103.645474		
	Sum	843.0616395	861.829798		
	Mean (average)	33.72246558	34.47319192		
Resume	Standard deviation	39.50325635	40.6129109		
	Variance	1560.507263 1649.4085			
	Difference between means	39.05 – 40.61  =	0.75072634		

Table 13 - Paired values of the crystallographic characteristics of the B19 'martensitic phase in Ni<sub>50</sub>Ti<sub>50-X</sub>Hf<sub>X</sub> at% alloys predicted by the fitting

### REFERENCES

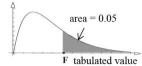
- Zarinejad, M., Y. Liu, and T.J. White, The crystal chemistry of martensite in NiTiHf shape memory alloys. Intermetallics, 2008. 16(7): p. 876-883.
- [2] Potapov, P., et al., Effect of Hf on the structure of Ni-Ti martensitic alloys. Materials Letters, 1997. 32(4): p. 247-250.
- [3] 3. Rietveld, H., A profile refinement method for nuclear and magnetic structures. Journal of applied Crystallography, 1969. **2**(2): p. 65-71.
- [4] Koch, E., Twinning, in International Tables for Crystallography Volume C: Mathematical, physical and chemical tables. 2006, Springer. p. 10-14.
- Tukey, J.W., The future of data analysis. The annals of mathematical statistics, 1962. 33(1): p. 1-67.
- [6] Pettitt, A., Testing the normality of several independent samples using the Anderson-Darling statistic. Journal of the Royal Statistical Society: Series C (Applied Statistics), 1977. 26(2): p. 156-161.
- [7] Rojas, I., et al., Analysis of the functional block involved in the design of radial basis function networks. Neural Processing Letters, 2000. 12(1): p. 1-17.

### ATTACHMENTS

DF	k levels								
(n - k)	2	3	4	5	6	7	8	9	10
5	3.64	4.6	5.22	5.67	6.03	6.33	6.58	6.8	6.99
6	3.46	4.34	4.9	5.3	5.63	5.9	6.12	6.32	6.49
7	3.34	4.16	4.68	5.06	5.36	5.61	5.82	6	6.16
8	3.26	4.04	4.53	4.89	5.17	5.4	5.6	5.77	5.92
9	3.2	3.95	4.41	4.76	5.02	5.24	5.43	5.59	5.74
10	3.15	3.88	4.33	4.65	4.91	5.12	5.3	5.46	5.6
11	3.11	3.82	4.26	4.57	4.82	5.03	5.2	5.35	5.49
12	3.08	3.77	4.2	4.51	4.75	4.95	5.12	5.27	5.39
13	3.06	3.73	4.15	4.45	4.69	4.88	5.05	5.19	5.32
14	3.03	3.7	4.11	4.41	4.64	4.83	4.99	5.13	5.25

	1	1	i	i	1	1	1	1	
15	3.01	3.67	4.08	4.37	4.59	4.78	4.94	5.08	5.2
16	3	3.65	4.05	4.33	4.56	4.74	4.9	5.03	5.15
17	2.98	3.63	4.02	4.3	4.52	4.7	4.86	4.99	5.11
18	2.97	3.61	4	4.28	4.49	4.67	4.82	4.96	5.07
19	2.96	3.59	3.98	4.25	4.47	4.65	4.79	4.92	5.04
20	2.95	3.58	3.96	4.23	4.45	4.62	4.77	4.9	5.01
24	2.92	3.53	3.9	4.17	4.37	4.54	4.68	4.81	4.92
30	2.89	3.49	3.85	4.1	4.3	4.46	4.6	4.72	4.82
40	2.86	3.44	3.79	4.04	4.23	4.39	4.52	4.63	4.73
60	2.83	3.4	3.74	3.98	4.16	4.31	4.44	4.55	4.65
120	2.8	3.36	3.68	3.92	4.1	4.24	4.36	4.47	4.56
∞	2.77	3.31	3.63	3.86	4.03	4.17	4.29	4.39	4.47

Table 14 - Tukey test table ( $\alpha = 0.05$ ): degrees of freedom and levels [studentized]



				ı ta	ourated varue					
Table VI	Degrees of Freedom (DF) in the numerator									
DF in denominator	1	2	3	4	5	6	7	8	9	10
1	161.45	199.5	215.71	224.58	230.16	233.99	236.77	238.88	240.54	241.88
2	18.51	19	19.16	19.25	19.3	19.33	19.35	19.37	19.38	19.4
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6	5.96
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.1	4.06
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64
8	5.32	4.46	4.07	3.84	3.69	3.58	3.5	3.44	3.39	3.35
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14
10	4.96	4.1	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98
11	4.84	3.98	3.59	3.36	3.2	3.09	3.01	2.95	2.9	2.85
12	4.75	3.89	3.49	3.26	3.11	3	2.91	2.85	2.8	2.75
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67
14	4.6	3.74	3.34	3.11	2.96	2.85	2.76	2.7	2.65	2.6
15	4.54	3.68	3.29	3.06	2.9	2.79	2.71	2.64	2.59	2.54
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49
17	4.45	3.59	3.2	2.96	2.81	2.7	2.61	2.55	2.49	2.45
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41
19	4.38	3.52	3.13	2.9	2.74	2.63	2.54	2.48	2.42	2.38
20	4.35	3.49	3.1	2.87	2.71	2.6	2.51	2.45	2.39	2.35
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32
22	4.3	3.44	3.05	2.82	2.66	2.55	2.46	2.4	2.34	2.3
23	4.28	3.42	3.03	2.8	2.64	2.53	2.44	2.37	2.32	2.27
24	4.26	3.4	3.01	2.78	2.62	2.51	2.42	2.36	2.3	2.25
25	4.24	3.39	2.99	2.76	2.6	2.49	2.4	2.34	2.28	2.24
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.2
28	4.2	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19
29	4.18	3.33	2.93	2.7	2.55	2.43	2.35	2.28	2.22	2.18
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16
35	4.12	3.27	2.87	2.64	2.49	2.37	2.29	2.22	2.16	2.11
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08
45	4.06	3.2	2.81	2.58	2.42	2.31	2.22	2.15	2.1	2.05
50	4.03	3.18	2.79	2.56	2.4	2.29	2.2	2.13	2.07	2.03
100	3.94	3.09	2.7	2.46	2.31	2.19	2.1	2.03	1.97	1.93

Table 15 - F distribution of Snedecor ( $\alpha = 0.05$ )