Preparation and Certification of Low Alloy Steel Reference Materials for Spectrometric Analysis

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Abstract

Matrix certified reference materials (CRMs) are versatile tools to support quality, correctness and credibility of measurement results. CRMs are used to provide the traceability of the measurement results to the SI unit. Seven low alloy steel certified reference materials were developed by the national institute of standards (NIS), Egypt. Homogeneity is studied using x-ray fluorescence spectrometer (XRF) and optical emission spectrometer (OES). The characterization of RMs was performed using independent chemical methods as gravimetric methods, x-ray fluorescence spectrometry, optical emission spectrometry and atomic absorption spectrometry. Both the assigned values and their associated uncertainty were calculated by weighted mean approach after the statistical analysis of the results of measurements for the homogeneity of variances, equality of means, normality of data and outliers.

Keywords: Low alloy steel, Homogeneity, Reference materials, Traceability

1. Introduction

The quantities of steel products used for different industrial activities are enormous. The determination of chemical composition of steel products is important not only for the users but also for the manufacturing as well. The assessment of compliance of iron and steel products with their technical specifications is the main tool to judge their quality and to decide their industrial application. This assessment is done by measurements using different techniques such as X-ray fluorescence spectrometry (XRF), optical emission spectrometry (OES), atomic absorption spectrometry (AAS), and inductivity coupled plasma (ICP) [**Al-Eshaikh M. A.-2011**].

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Laboratories are required to use standard methods or validated methods if possible. Certified reference materials are versatile tools for internal validation studies.They play important role in the verification of the accuracy of analytical measured results. Certified reference materials are used to: 1) assure the quality of the resulting

measurements; 2) establish the traceability of internationally agreed standards to SI units, 3) calibration of the measuring instrument to establish the reliability of its readings and 4) estimate the uncertainty of the measurement process enabling the measurement results to be compared with other results, references, specifications or standards [**Amigo J.M.-2011, Emons H.-2004**]. P. Hoffmann et al examined seven steel samples as reference materials, which were produced by the research institute of CKD, Praha, CSFR (Czech Republic). They have been analyzed using atomic emission spectrometry with inductively coupled plasma (ICP-AES), atomic absorption spectrometry with flame and graphite furnace atomization (FAAS, GFAAS), differential pulse anodic stripping voltammetry (DPASV), X-ray fluorescence analysis with total reflection sample carrier (TXRF) and instrumental neutron activation analysis (INAA). The authors reported that over 90 % of all results were in good agreement with the values determined by wet analytical methods. They, moreover, owed the deviations to systematical errors for special elements analyzed by distinct methods and to statistical errors for other elements which have low concentrations and were not homogeneously distributed in the given material [**Hoffmann P.-1992**].

In the present work, seven compositions of low alloy steel are prepared. The process of certification and characterization is described in the ISO Guide 35 [1992]. These reference materials are certified for mass fraction of carbon, silicon, phosphorus, sulphur, manganese, chromium, nickel, tin, molybdenum, copper, cobalt, aluminum, titanium and vanadium using independent analytical methods. Both the assigned values and their associated uncertainty are calculated by weighted mean approach according to Paule and Mandel approach [**Schilier S.B. -1991**] after the statistical evaluation of measured results for the homogeneity of variances, equality of means, normality of data and outliers.

2. Materials and Methods

2.1. Raw materials and steel production

Low carbon steel (carbon ≤ 0.1 %), ferrosilicon alloy (silicon content: 75%), low carbon ferromanganese alloy (carbon ≤ 0.1 % and manganese content: 80%), pure metallic copper (99.50%), pure nickel, (99.5%), low carbon ferrochromium (carbon ≤ 0.1 % and chromium

content: 70%) and Ferrovanadium alloy (vanadium content: 70 %) are used for the manufacture of low alloy steel. The production technology is developed to guarantee the maximum homogeneity of readability of the chemical composition of these alloys. Melting was conducted in a medium frequency electric induction furnace with 100 kg capacity at Central Metallurgical Research and Development Institute (CMRDI) experimental foundry, (El Tabeen-Egypt). Low carbon steel containing ≥ 0.1**%** carbon was charged at the top of the furnace crucible and remelted at certain temperatures. During the melting process, some elements such as nickel, chromium, manganese, vanadium, tungsten and other elements were added to improve properties of the produced steel. After the addition of the desired elements, the furnace temperature was raised to 1550 °C for 10 minutes. The hot liquid steel was transported into certain thermal crucibles with the addition of 0.02% of aluminum to remove the oxygen. Special designed water cooled copper molds were used for steel casting to ensure the maximum cooling rates, to minimize the segregation of the alloying elements and to maximize the homogeneity of the produced steel.

2.2. Chemicals and reagents for sample digestion

Nitric acid, 69% was purchased from Analar, England. Hydrochloric acid, 37% and hydrofluoric acid, 40% were obtained from Merck, Germany. Lanthanum chloride, 99.99% and cesium chloride, 99.9% were obtained from Alfa Aesar, Germany. Hydrogen peroxide 30% and ammonium persulphate were purchased from Elnasr Co., Egypt.

2.3. Analytical instruments

 X-ray fluorescence spectrometer (XRF), Axios, Panalytical, Elmelo, the Netherlands, with Rhodium target, V=60 kV and A=160 mA is used for the quantitative analysis and homogeneity study. The atomic absorption spectrometer (AAS) (ZEEnit 700, Analytik Jena, Germany) used for quantitative analysis was equipped with a hollow cathode of the element operated at a current recommended by the lamp and instrument manufacturer. An automatic deuterium background-correction was used for flame atomizer measurement. Microwave digestion instrument, TOPwave Analytic Jena, Germany, was used for sample preparation. Optical emission spectrometer (OES), Analytical Instrument, Thermo Electron, USA, is used for the quantitative analysis as well. Combustion cell, Leco, U.S.A. was used for direct analysis of carbon in oxygen atmosphere.

2.4. Sample preparation for atomic absorption spectrometer (AAS)

2.4.1. Wet preparation

Half gram of sample is weighed and transferred into 100 mL volumetric flask. 25 mL of 3N sulphuric acid are added and then heated until sample was completely dissolved then10 mL of 12 % ammonium persulfate solution are added. The sample is boiled vigorously until a clear solution is obtained. It is left to cool then diluted to the specified volume with deionized water [**Perkin Elmer publication-1996**].

2.4.2. Microwave digestion preparation

Two hundred mg of the sample are weighed into the digestion vessel. 3 mL of HNO_3, 3 mL of HCl and 3 mL of HF are added. The mixture is stirred carefully and the sample is left for 10 minutes before closing the microwave vessel [**Perkin Elmer publication-1996**]. Parallel with the sample preparation, the same procedure is used to prepare a blank sample using the same quantities of all the reagents. Also two NIST SRMs are used to check the accuracy of the measurements.

2.5. Homogeneity study

The produced steel samples are divided into several groups. Each group is labeled prior to analyses. The samples are selected from all groups to ensure good sample representation. The selected samples are polished and quantitatively measured using XRF and OES to check the homogeneity of the prepared samples. Every sample is measured three times in order to check the within and between sample variability [**ASTM international E572-02a**]. The calibration of XRF is performed using NIST SRMs1765, 1766, 1767, 1761a, 1762a, 1261a and 1263a which were certified for carbon, aluminum, silicon, phosphorus, sulfur, titanium, vanadium, chromium, manganese, cobalt, nickel, cupper, arsenic and molybdenum. Two control samples are used to check the drift of XRF during measurements. One way-analysis of variance (ANOVA) is used to judge the homogeneity of the samples.

3. Results and discussion

Seven sets of low alloy steel were produced and quantitatively analyzed. They were labeled in the alphabetical order (A, B, C, D, F, K & S). The chemical compositions (%) of the produced alloys are shown in **Table 1.**

3.1. Traceability of measurements

The traceability is achieved by using NIST SRMs for XRF, OES and AAS calibrations which are1765, 1766, 1767, 1761a, 1762a, 1261a, 361, 363,1261a, 1262a and 1263a.

3.2. Homogeneity study

The homogeneity study is designed so that the between sample variability and within sample variability can be studied [**Adriaan M.H. -2000 and 2001**]. The results obtained from the homogeneity study are analyzed by ANOVA (one-way layout). From these data, $F_{cal}\backslash F_{tab}$ for

Table1: Chemical compositions of the produced low alloy steel alloys

Batch (%)	A	B	C	D	F	K	S
C	0.366	0.566	0.382	0.563	0.46	0.185	0.455
Si	0.361	0.851	1.00	0.295	0.191	0.292	0.270
P	0.015	0.020	0.010	0.010	0.0162	0.011	0.020
S	0.0035	0.002	0.020	0.009	0.003	0.0028	0.030
Mn	1.61	0.273	0.459	0.900	0.650	1.190	0.800
Cr	1.85	1.020	4.900	1.070	0.170	1.050	1.100
Ni	0.904	0.113	0.170	1.51	0.0501	0.067	0.200
Cu	0.135	0.130	0.090	0.140	0.020	0.060	0.016
Mo	0.150	0.090	1.200	0.454	0.005	0.0190	0.198
Sn	0.010	0.012	0.007	0.010	0.008	0.0055	-
V	0.005	0.150	0.900	0.066	-	0.0050	-
Ti	0.001	0.002	0.0015	-	0.035	0.0030	-
Al	0.0313	0.0255	0.0202	0.013	0.035	0.0341	0.0287
W	-	1.800	-	-	-	-	-
Co	0.001	0.015	0.006	-	0.010	-	-
Fe	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

α (=5%) is small which means that the result of the homogeneity is insignificant. Thus, it can be concluded that the samples were homogenous. The uncertainty of the material homogeneity, σ_h^2, is also calculated from the ANOVA using equation (1).

$$\sigma_h^2 = \frac{MS_{Between} - MS_{Within}}{n} \qquad (1)$$

Where, MS $_{between}$ is the mean square for the between sample variability, MS $_{within}$ is mean square for the within sample variability and n is the three measurements taken for each of the

6 samples. Values of P-values, F_{cal}, F_{Crit} and σ_h^2 for batch D as an example are shown in **Table 2.**

3.3. Statistical treatment of the measurement results

The results obtained are tested for normality, outliers, equality of means, and homogeneity of variances at 95% confidence level [**Fangmeyer H.- 1977, Costat statistical Software, Minitab Inc., XLSTAT 7.5.2**]. The tests indicate that the measurement results are normal after removing the outliers and the method variances are homogeneous expect those of the elements in batches shown in **Table 3.**

Table 2: Homogeneity data of batch D

Element		D1-1	D1-2	D1-3	D1-4	D1-5	D1-6	F_{cal}	P-value	F_{crit}	σ_h^2
C	R1	0.5350	0.5400	0.5500	0.5430	0.5480	0.5455	0.1697	0.9689	3.1059	0.0000117
	R2	0.5560	0.5410	0.5380	0.5500	0.5410	0.5380				
	R3	0.5390	0.5460	0.5470	0.5470	0.5440	0.5529				
Si	R1	0.2880	0.2990	0.2920	0.2816	0.2830	0.2909	0.4247	0.8229	3.1059	0.000005
	R2	0.2970	0.2890	0.2900	0.2952	0.2890	0.2909				
	R3	0.2810	0.2900	0.2950	0.2899	0.2920	0.2909				
P	R1	0.0094	0.0098	0.0095	0.0086	0.0103	0.0092	1.8435	0.1787	3.1059	0.0000001
	R2	0.0106	0.0096	0.0105	0.0099	0.0115	0.0095				
	R3	0.0103	0.0100	0.0107	0.0095	0.0109	0.0110				
S	R1	0.0030	0.0041	0.0038	0.0033	0.0049	0.0020	0.272727	0.770255	5.143253	0.00000006
	R2	0.0042	0.0035	0.0031	0.0030	0.0048	0.0020				
	R3	0.0043	0.0036	0.0037	0.0030	0.0049	0.0020				
Mn	R1	0.9100	0.8880	0.8980	0.9000	0.8940	0.8806	2.2756	0.1129	3.1059	0.00001
	R2	0.8806	0.8770	0.8572	0.8970	0.9180	0.9010				
	R3	0.8696	0.8880	0.8572	0.9030	0.9140	0.9090				
Cr	R1	1.0700	1.1000	1.1100	1.0600	1.0797	1.0950	1.8121	0.1849	3.1059	0.000005
	R2	1.1000	1.0900	1.0700	1.0700	1.1070	1.0940				
	R3	1.1000	1.1100	1.0800	1.0600	1.0934	1.0540				
Ti	R1	0.0011	0.0015	0.0011	0.0012	0.0012	-	3.1427	0.0646	3.4780	0.000000009
	R2	0.0012	0.0012	0.0014	0.0012	0.0012	-				
	R3	0.0010	0.0015	0.0012	0.0012	0.0012	-				
Ni	R1	1.4600	1.4500	1.4900	1.5100	1.5015	1.5012	2.3130	0.1087	3.1059	0.000021
	R2	1.4700	1.4800	1.4900	1.5200	1.5036	1.5012				
	R3	1.4900	1.4300	1.5100	1.4400	1.5026	1.5012				
Mo	R1	0.4630	0.4780	0.4610	0.4848	0.4730	0.4770	2.5843	0.0826	3.1059	0.000056
	R2	0.4610	0.4750	0.4540	0.4528	0.4520	0.4830				
	R3	0.4560	0.4560	0.4540	0.4554	0.4620	0.4900				
Sn	R1	0.0100	0.0090	0.0094	0.0081	0.0090	-	3.0332	0.0704	3.4780	0.00000015
	R2	0.0096	0.0100	0.0089	0.0095	0.0090	-				
	R3	0.0105	0.0098	0.0095	0.0090	0.0090	-				
Cu	R1	0.1410	0.1490	0.1390	0.1430	0.1420	0.1410	1.7054	0.2078	3.1059	0.0000017
	R2	0.1420	0.1400	0.1400	0.1440	0.1420	0.1400				
	R3	0.1390	0.1460	0.1390	0.1430	0.1420	0.1480				
Co	R1	0.0152	0.0186	0.0168	0.0150	0.0148	0.0162	3.0830	0.0511	3.1059	0.00000059
	R2	0.0172	0.0161	0.0178	0.0151	0.0150	0.0161				
	R3	0.0164	0.0157	0.0168	0.0150	0.0149	0.0142				
V	R1	0.0665	0.0691	0.0688	0.0603	0.0660	0.0672	2.9123	0.0600	3.1059	0.0000006
	R2	0.0679	0.0682	0.0649	0.0660	0.0640	0.0717				
	R3	0.0676	0.0688	0.0651	0.0670	0.0650	0.0694				

Where P-value, F_{cal} and F_{Crit} are statistical parameters. R1, R2 & R3 are the measurement replicates respectively.

Table 3: Results which were not normal

Element	Batch symbol
S	B, F
P	B
Cu	S
Mo	F
Sn	S
V	A, C, F, K, S
Al	A, K, S
Co	C, F, S

The mass fractions of these elements are reported as information values in the certification process.

3.4. Assignment of reference value and its uncertainty

Several methods in different laboratories are used for characterization of the elements in low alloy steel RMs. The average mass fraction of each element obtained by the methods is calculated. The steps involved in combining the available data to form a certified value and an uncertainty are: estimate the uncertainty of the method mean for each method used; estimate the between-method variance component and compute weights; compute the weighted mean and its variance; estimate and incorporate material variability; estimate the effective degrees of freedom for the combined variance; estimation of the bias allowance. [**Schilier S.B- 1991 and 1996, Epstein M.S, 1991**].

Uncertainty of measurements of the mean of each method

Since more than one analytical method are compared to determine the certified value, it is important that the variability of the mean for each method is estimated correctly [**Adel B. S.- 2010, Eurachem/Citac guide CG 4-1993**]. In order to estimate the standard uncertainty of the mean, two- way fully nested ANOVA was used to determine which design factors have a significant effect on the measurements. To calculate the type A uncertainty of each of the method means, equation (2) is used.

$$Var(\overline{y}) = \frac{MS_{Sample} + MS_{run} - MS_{error}}{Total\ Number\ of\ measurements} \qquad (2)$$

Where Var(y) is type A uncertainty, MS $_{sample}$ is the sample mean square, MS $_{run}$ is the run mean square and MS $_{error}$ is error mean square.

Between method variance and method weights

The measured values produced by each method are modeled as the sum of the true value (m), method bias (b_i) and random error (e_{ij}) using equation (3).

$$\text{The measured value} = m + b_i + e_{ij} \tag{3}$$

Method weights are derived by assuming that the random errors (e_{ij}) are independent, have mean 0, and have different variance of each method (σ_i^2). The variance σ_b^2 may be estimated from the between method difference. According to this model, the variance of the average of n_i measurements from the i_{th} method is:

$$\frac{\sigma_i^2}{n_i} + \sigma_b^2 \tag{4}$$

To combine the averages of the analytical methods for each element, a weighted average of the method means was calculated according to the weighing algorithm of Paule and Mandel which is implemented for multi- method CRMs certification. The weight for each method, W_i is inversely proportional to the sum of the combined standard uncertainty of the mean, S_i^2 and the between- method variance, σ_b^2. The method weights (W_i) are defined implicitly as follows:

$$W_i = \frac{1}{S_i^2 + \sigma_b^2} \tag{5}$$

The weighing factor (w_i) is given by:

$$w_i = \frac{W_i}{\sum_1^M W_j} \tag{6}$$

And $\tilde{X}$ the weighted average of the $\overline{X}$s is calculated from:

$$\tilde{X} = \sum_1^M w_i \overline{X_i} \tag{7}$$

The combined uncertainty

The combined standard uncertainty of the weighted mean ($\tilde{X}$) is the weighted root sum of squares of the combined standard uncertainties for the methods according to:

$$S^2 = \sum_1^M \omega_i^2 \ S_i^2 \tag{8}$$

This variance estimate (S^2) does not include the between method variance. The variance of the mean summarizes random errors in the mean [**Schilier S.B- 1991and 1996, Adel B. S.-2015**]. It seems more realistic to include an allowance for bias or systematic error due to the difference in the methods. It is taken as the maximum absolute deviation of any method mean from the weighted mean:

$$Bias\ allowance = max\left|\tilde{X}_i - \overline{X}\right| \tag{9}$$

In order to estimate an appropriate interval for the certified value, the effective degree of freedom of the total variance is estimated according to SATTERTHWATTE formula which is:

$$df(effective) = \frac{\left(\sum_1^M \omega_i^2 S_i^2 + \sigma_h^2\right)}{\left(\sum_1^M \frac{\left(\omega_i^2 S_i^2\right)^2}{n_i - 1} + \frac{\sigma_h^4}{df_h}\right)} \tag{10}$$

Where, df_h is the number of samples measured induplicate for material variability estimation minus one.

The total expanded uncertainty (U) associated with the certified values is according to:

$$U = t_{1-\alpha/2}\sqrt{\left(S^2(\tilde{X}) + \sigma_h^2\right)} + Bias\ allowance \tag{11}$$

Where, $S^2(\tilde{X})$ is the weighted combined standard uncertainty and σ_h^2 is the uncertainty of the material heterogeneity.

The certified values and their associated expanded uncertainties are shown in **Table 4.**

Table 4: The certified values and their associated expanded uncertainties for seven
low alloy steel batches

Batch / Element		A	B	C	D	F	K	S
C	Certified Value, (%)	0.3714	0.5708	0.3919	0.5508	0.4430	0.1858	0.4309
	Uexp (%)	0.0225	0.0443	0.0200	0.0352	0.0329	0.0136	0.0270
Si	Certified Value, (%)	0.3546	0.8315	1.0072	0.2940	0.1893	**0.2900**	0.2734
	Uexp, (%)	0.0291	0.0353	0.0324	0.0115	0.0119	-	0.0187
P	Certified Value, (%)	0.0158	0.02	0.0106	0.0101	0.0126	0.0114	0.0184
	Uexp (%)	0.0027	-	0.0022	0.0020	0.0028	0.0025	0.0022
S	Certified Value, (%)	0.0035	**0.003**	**0.005**	0.0027	**0.003**	0.0034	0.0324
	Uexp (%)	0.0004	-		0.0010	-	0.0010	0.0075
Mn	Certified Value, (%)	1.6156	0.2768	0.4735	0.8572	0.6148	1.2115	0.8282
	Uexp (%)	0.0282	0.0203	0.0205	0.0334	0.0396	0.0604	0.0239
Cr	Certified Value, (%)	1.8975	1.0381	4.8832	1.0681	0.1744	1.0744	1.0931
	Uexp (%)	0.0313	0.0211	0.0580	0.0326	0.0181	0.0374	0.0682
Ni	Certified Value, (%)	0.9512	0.1148	0.1640	1.5107	0.0514	0.0672	0.2150
	Uexp (%)	0.0181	0.0114	0.0033	0.0515	0.0044	0.0038	0.0114
Cu	Certified Value, (%)	0.1348	0.1287	0.0843	0.1430	0.0218	0.0603	**0.016**
	Uexp (%)	0.0136	0.0074	0.0062	0.0074	0.0048	0.0040	-
Mo	Certified Value, (%)	0.1449	0.0903	1.2085	0.4786	**0.005**	0.0197	0.2131
	Uexp (%)	0.0091	0.0055	0.0329	0.0428	-	0.0015	0.0099
Sn	Certified Value, (%)	0.0106	0.0123	0.0070	0.0094	0.0070	0.0106	-
	Uexp (%)	0.0029	0.0033	0.0019	0.0026	0.0019	0.0029	-
V	Certified Value, (%)	**0.005**	0.1534	**0.900**	0.0671	**0.003**	**0.005**	**0.002**
	Uexp (%)	-	0.0039	-	0.0064	-	-	-
Ti	Certified Value, (%)	**0.001**	0.0017	**0.002**	**0.0013**	**0.001**	**0.003**	**0.001**
	Uexp (%)	-	0.0009	-	-	-	-	-
Al	Certified Value, (%)	**0.031**	0.0136	0.0198	0.0142	0.0349	**0.033**	**0.025**
	Uexp (%)	-	0.0007	0.0028	0.0022	0.0021	-	-
Co	Certified Value, (%)	0.01225	0.01608	**0.01**	0.0155	**0.010**	0.0122	**0.004**
	Uexp (%)	0.0025	0.0004	-	0.0037	-	0.0025	-
W	Reference Vaue, (%)	**0.015**	1.8428	**0.015**	**0.015**	**0.012**	**0.001**	**0.0012**
	Uexp (%)	-	0.097	-	-	-	-	-

Values edited in bold are information values since they did not pass the test for normality of data and the between method variance was very large as well. In addition there was a large difference between the means of the analytical methods used for analysis. Therefore, it was not possible to estimate the associated uncertainties in clear traceability to the SI units.

4. Conclusion

Low alloy steel reference materials were manufactured and certified for the mass fraction content of carbon, silicon, manganese, phosphorus, sulfur, chromium, nickel, copper, molybdenum, vanadium, tungsten, aluminum, cobalt and niobium using six independent analytical methods in four different laboratories. Certification was carried out in full compliance with ISO Guide 35 and measurement results were statistically treated for normality, outliers, equality of means and variances. The certification process revealed that certified values have been obtained for most of the elements except for V, Ti and W, where information values were obtained except in one batch for each element. The produced certified reference materials provide a basis for further improvement in quality of low alloy steel analysis and production.

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<u>**الملخص العربي**</u>

تحضير و توصيف بعض انواع المواد المرجعية من سبائك الصلب

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تلعب المواد المرجعية المعتمدة دورا هاما في التحقق من دقة نتائج القياسات التحليلية. وهي تستخدم فى الاغراض الاتيه:

- ضمان جودة نتائج القياس،
- معايرة الأجهزه المستخدمة فى التحاليل الكيميائيه و انشاء الإسناد المترولوجي لوحدات SI
- تقدير اللايقين فى نتائج القياس

وبذلك يمكن عمل مقارنات مع نتائج أخرى أوالمراجع أوالمواصفات أو المعايير.

يهدف هذا العمل إلى إنتاج مواد مرجعية معتمدة (CRMs) من أنواع مختلفة من سبائك الحديد والتي لا يتم إنتاجها في مصر أو في الشرق الأوسط بهدف تعزيز الابتكار التكنولوجي وتحسين القدرة التنافسية للقطاعات الصناعية للسبائك المعدنية في مصر. . كما أن هده المواد تهدف إلى تحسين الوعي الفني فى صناعة الحديد والصلب حول أهمية CRMs في تعزيز جودة المنتجات. وقد تم إنتاج ثلاث أنواع من المواد المرجعية المعتمدة من الصلب عالي التسابك وسبعة أنواع مختلفة التركيب الكيميائي من الصلب منخفض التسابك. تتكون المواد المرجعية من الصلب منخفض التسابك من العناصر التالية: الكربون، السيليكون والمنجنيز والفوسفور، الكبريت، والكروم، والنيكل والنحاس والموليبدينوم والفاناديوم، التنجستن، والألمنيوم والكوبالت والنيوبيوم

تكنولوجيا التصنيع

تم إنتاج السبائك المختلفة فى معهد بحوث وتطوير الفلزات (CMRDI) باستخدام فرن الحث الكهربي ذي البوتقة الثابتة سعة 100 كجم. تبدأ عملية تصنيع سبائك الصلب المنخفض التسابك بصهر الصلب الكربوني ثم إضافة باقى العناصر تباعا. بعد إضافة جميع المكونات يتم رفع درجة حرارة الفرن مابين 1550الى 1630 درجه مئويه لمدة 10 دقائق. بعد الإنتهاء من عملية الصهر يتم صبها فى بواتق حرارية معده لذلك مع اضافة حوالى 0.02 % من الالومنيوم للتأكد من إزالة الأكسيجين. يتم تصنيع سبائك الصلب عالي التسابك بإستخدام نفس طريقة تصنيع سبائك الصلب منخفض التسابك بإستخدام خردة الصلب الكربوني عند درجات حرارة 1630-1620 درجة مئوية.

تم إختبار العينات المنتجة للتأكد من درجة التجانس بإستخدام جهاز التحليل بالأشعة السينية الفلورنسية , وكذلك بإستخدام مطياف الأنبعاث الضوئي و تحليل البيانات إحصائيا باستخدام تحليل التباين الأحادي (ANOVA). وقد وجد أن المواد المرجعية المنتجة متجانسة بما فيه الكفاية. كما تم إجراء التحليل الكمي للسبائك المنتجه فى اربعة معامل مختلفة لقياس نسب العناصر المختلفة في كل سبيكة باستخدام جهاز التحليل بالأشعة السينية الفلورنسية وجهاز مطياف الإنبعاث الضوئي و جهاز الإمتصاص الذري وطرق الجرافيمتري. و قد تم إختيار خمسة عينات عشوائيا لإجراء الاختبارات المختلفة.

تم إختبار النتائج التي تم الحصول عليها باستخدام الطرق الاحصائيه للتاكد من ان النتائج تنتمي للتوزيع الطبيعي ،التحقق من عدم وجود قيم شاذه ومدي تجانس المتوسطات الحسابيه للقياسات المختلفه، عند مستوى ثقة 95٪. وقد تبين أن نتائج القياس تنتمي الى التوزيع الطبيعي بعد إزالة القيم الشاذه، وأن المتوسطات الحسابيه متجانسه.

وقد تم الجمع بين جميع نتائج القياس و التي تم الحصول عليها عن طريق أجهزة مختلفة من معامل مختلفة عن طريق استخدام النموذج الإحصائي بول وماندل. وفي هذا النموذج. يتم وزن المتوسط الحسابى لكل طريقة وحساب متوسط

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المتوسطات الموزونه (القيمة المرجعيه). كما يتم تقديراللايقين الموزون المصاحب لمتوسط المتوسطات الموزونه وتم تقديرها من ثلاثة مصادروهي:

- اللايقين المصاحب لكل طريقة
- درجة عدم تجانس المواد المصنعه
- سماحية الخطأ

تعتبرعملية تصنيع وتوصيف المواد المرجعيه من سبائك الصلب هي الاولى فى مصر . وهي تستخدم فى عمليات المعايرة ولتوكيد جودة المنتجات من الصلب منخفض التسابك والصلب عالى التسابك وضمان إنتاجها طبقا للمواصفات الفنية المطلوبة.