

B C R information

The certification of oxygen in non-ferrous metals

Oxygen in titanium-aluminium-vanadium alloy (Ti 6Al 4V)
(BCR – No 59)

J. PAUWELS

Joint Research Centre
Central Bureau for Nuclear Measurements
Geel, Belgium

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1. TECHNICAL CONSIDERATIONS

Oxygen is an element that stabilizes the α -phase of Ti Al6 V4, which means that it increases the $(\alpha + \beta \rightleftharpoons \beta)$ phase transition temperature. An increase in the oxygen content of 100 $\mu\text{g/g}$ displaces this temperature by approximately 2°C. This makes it important to know the exact oxygen content for thermal treatments.

Oxygen also influences the mechanical properties of the alloy. An increase in the oxygen content of 100 $\mu\text{g/g}$ increases the Vickers hardness by approximately 5 points and the ultimate tensile strength by 20 to 30 N/mm^2 , decreasing the ductility at the same time.

Oxygen is consequently a real alloying element of Ti Al6 V4, and has to be present at a well defined concentration in order to obtain the requested mechanical properties of the final product.

2. PROCEDURE

The analysis of the material and the evaluation of the analytical results were carried out under the activities of BCR-Group of Specialists "Non-metals in refractory metals" (Scientific Secretary : J. Pauwels, Joint Research Centre, Central Bureau for Nuclear Measurements, Geel, Belgium; Chairman : J. Hoste, Rijksuniversiteit Gent, Instituut voor Nucleaire Wetenschappen, Gent, Belgium).

The analytical results were discussed by the laboratories taking part, particular attention being paid to the analytical processes in question. The results were evaluated with the statistical assistance of CETIS, Joint Research Centre, Ispra, Italy ⁽³⁾.

3. PARTICIPANTS

- Bundesanstalt für Materialprüfung, Berlin,
Federal Republic of Germany (N)
- C.E.A., Centre d'Etudes Nucléaires de Fontenay-aux-Roses, France (R)
- C.E.A., Centre d'Etudes Nucléaires de Grenoble, France (R)
- C.E.A., Centre d'Etudes de Valduc, Is-sur-Tille, France (R)
- C.N.R.S., G.A.R.N.A.C., Service du Cyclotron, Orléans, France (T)
- Centre de Recherches Pêchiney, Voreppe, France (N)
- Centre de Recherches Vallourec, Aulnoye, France (R)

- Groupe de Physique des Solides de l'Ecole Normale Supérieure,
Paris, France (S)
- Joint Research Centre, Central Bureau for Nuclear Measurements,
Geel, Belgium (SP)
- Joint Research Centre Ispra, Chemistry Division and CETIS,
Ispra, Italy (R)(SE)
- Kernforschungszentrum Karlsruhe GmbH, Laboratorium für
Isotopentechnik, Karlsruhe, Federal Republic of Germany (N)
- Krupp Forschungsinstitut, Essen, Federal Republic of Germany (R)
- Max-Planck-Institut für Metallforschung, Laboratorium für
Reinststoffe, Schwäbisch Gmünd, Federal Republic of Germany (R)
- Metallurgie Hoboken-Overpelt, Hoboken, Belgium (R)
- Rijksuniversiteit Gent, Instituut voor Nucleaire Weten-
schappen, Gent, Belgium (N)
- Staatliches Materialprüfungsamt Nordrhein-Westfalen,
Dortmund, Federal Republic of Germany (N)
- Technische Universität München, Institut für Radiochemie,
Garching bei München, Federal Republic of Germany (N)
- Ugine Aciers, Ugine, France (R)
- Universität Frankfurt, Frankfurt/Main,
Federal Republic of Germany (R)
- Université de Liège, Institut de Physique Nucléaire, Liège,
Belgium (S)

- (SP) : Sample preparation
(S) : Surface analyses
(N) : 14 MeV neutron activation analysis
(R) : Reducing fusion
(T) : Triton activation analysis
(SE) : Statistical evaluation

4. MATERIAL

4.1 STARTING MATERIAL

The starting material was a titanium alloy containing 6% aluminium and 4% vanadium. It was made available in the form of 32 bars of 3 cm diameter, each about 1 m long, from which 21 were selected after gammagraphic control and homogeneity testing by 14 MeV neutron activation analysis (see 4.3)

4.2 SAMPLES

Two types of samples are available within the series :

a) Discs of 26 mm diameter and 9 mm thick

They were prepared by turning off the 30 mm diameter rods to 26.0 mm on a lathe, sawing 9.4 mm thick samples with a diamond saw and reduction to 9.0 mm using a lathe (see Fig. 1). They are particularly intended for 14 MeV neutron activation analysis.

b) 0.2 g samples in bottles of 25

These samples are prepared by cutting into small cubes. They are particularly intended for reducing fusion.

4.3 HOMOGENEITY TESTS

One sample (26 mm diameter and 9 mm thick) of each of the 21 selected one meter rods was analyzed by 14 MeV neutron activation analysis in laboratory N2 to assess the homogeneity of the material. Two series of six analyses were carried out with the following results ^{*}:

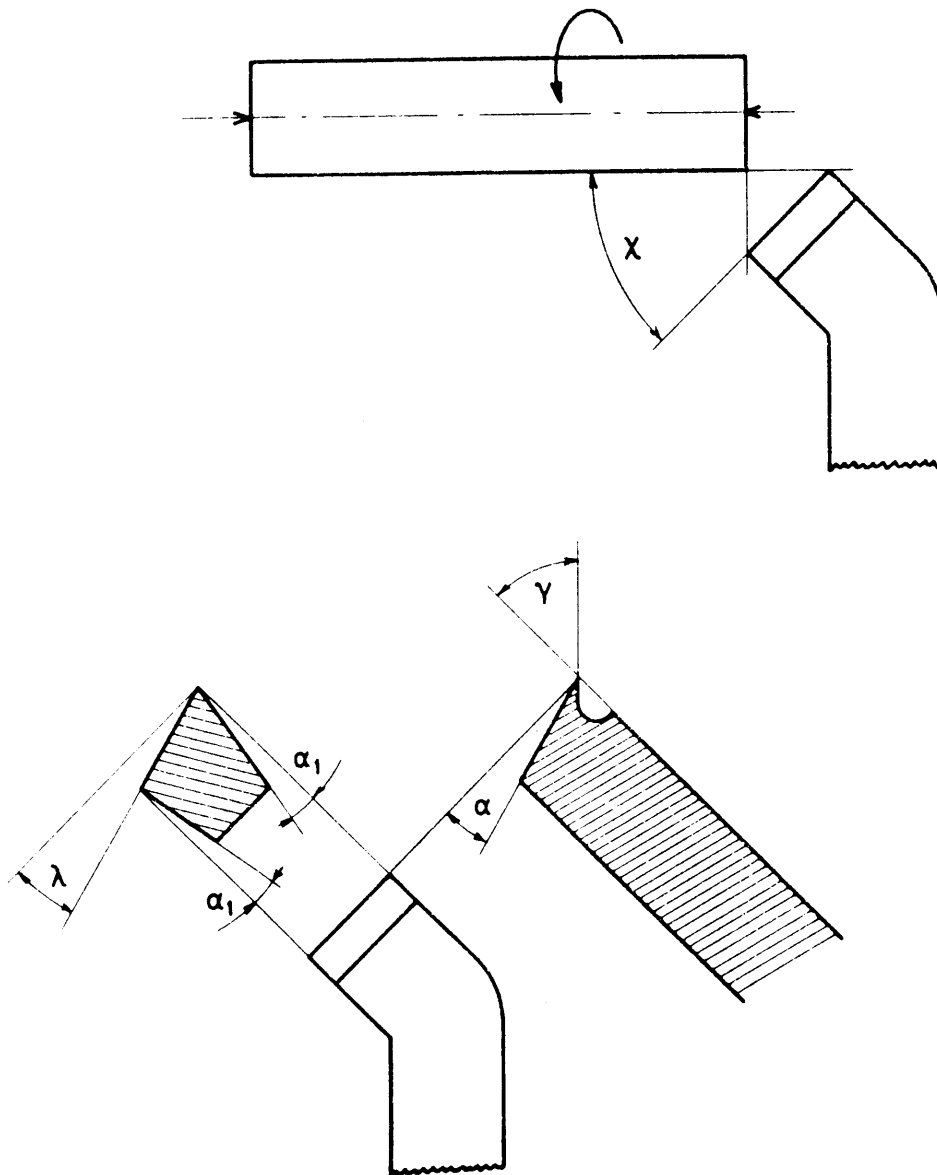
	<u>Series 1</u>	<u>Series 2</u>
- Replicates	126	126
- Outlying means	None	None
- Outlying variances	None	None
- Normality of means	positive	positive
- Bartlett-test	homogeneous	homogeneous
- One-way analysis of variance	homogeneous	homogeneous
- Repeatability (S_r)	3.8 %	4.0 %
- Reproducibility (S_p)	3.9 %	4.0 %

These two tests indicate that at the 20 g level no heterogeneity can be detected over the length of the batch using 14 MeV neutron activation analysis. Nevertheless, further analyses carried out in the framework of the characterization of the material indicate that radial variations of the order of 3 to 4 % are not excluded and that consequently it is not appropriate to certify the oxygen content of the material with a lower uncertainty. This also applies to "reducing fusion size" samples (100 to 200 mg), and at the microlevel as is shown in a study undertaken by laboratory T1 using instrumental activation analysis with 3.5 MeV tritons.

^{*} All test results at 95 % confidence level.

Machining of: Ti A16 V4

Tool material: Hard metal tool P 35



Tool parameters

χ : Angle of attack : $\begin{array}{c} + 45^\circ \\ - \end{array}$
 γ : Clearance angle : $\begin{array}{c} + 28^\circ \\ - \end{array}$
 α : Rake angle : $\begin{array}{c} + 8^\circ \\ - \end{array}$
 α_1 : Rake angle : $\begin{array}{c} + 4^\circ \\ - \end{array}$
 λ : inclination cutting edge : $\begin{array}{c} 0^\circ \\ - \end{array}$

Machining parameters

Cutting speed : 600 rpm
 Feed : 12.5 $\mu\text{m}/\text{revolution}$
 Depth of cut : 100 μm
 Cutting fluid : e.g. Shell Dromusoil

FIG. 1 : Tool and machining parameters for surfacing Ti A16 V4 by turning on a lathe.

As in this type of analysis the layer to be etched away after irradiation has to be known very accurately, this removal was controlled both micrometrically and by measurement of the matrix activity variation after etching. Using those two techniques the 20 irradiations carried out yielded 40 results with a standard deviation of 3 %.

On this basis it can be concluded that the material is homogeneous at ≤ 4 % relative at the 20 g, 100 mg and 0.7 mg sample size.

5. ANALYTICAL TECHNIQUES

5.1 DETERMINATION OF SURFACE OXYGEN

Under atmospheric conditions Ti Al6 V4 acquires an oxidized surface. To allow the specific determination of bulk oxygen, this surface oxygen must be reduced to a low and reproducible level.

The study of the surface treatments and determination of the amount of residual surface oxygen was carried out by the measurement of the protons released from the $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$ reaction. The method is described elsewhere ⁽¹⁾.

5.2 DETERMINATION OF OXYGEN BY 14 MeV NEUTRON ACTIVATION ANALYSIS

The determination of oxygen in non-ferrous metals by 14 MeV neutron activation analysis as well as the principles of its calibration have been described in ⁽²⁾. Six laboratories participated in the analysis of Ti Al6 V4. The shape of samples and types of holder used by the participating laboratories are listed in Table 1. Before analysis samples were etched for 60 s at 20°C in 4 vol. HNO_3 ($d = 1.4$) + 1 vol. HF (40 %). No etching was carried out after irradiation.

The activity induced by the $^{16}\text{O}(\text{n},\text{p})^{16}\text{N}$ reaction was measured by gamma spectrometry using one or two NaI(Tl) detectors. Absorbers were used to reduce interferences due to β -particles. The measurement conditions are outlined in Table 2.

TABLE 1

Samples for 14 MeV neutron activation analysis

Lab. Code N°.	Shape	Diameter (mm)	Thickness (mm)
N 1	Cylinder	26	9
N 2	"	26	9
N 3	" (★)	8	38
N 4	"	26	9
N 5	"	26	8.5
N 6	"	26	9

(★) Sample contained in a polyethylene holder

TABLE 2

Measurement conditions for 14 MeV neutron activation analysis

Lab. Code N°.	NaI(Tl)- Detector size(mm)	γ -Energy range (MeV)	Absorber
N 1	76 x 76	4.5 - 6.5	3 mm Cu
N 2	76 x 76	4.9 - 6.3	1mmAl + 2mmCu
N 3	76 x 76	4.7 - 6.5	5mmPb + 1mmCd + 1 mmCu
N 4	152 x 152	5.3 - 6.5	2 mm Cu
N 5	101 x 101	4.8 - 7.5	3 mm Cu
N 6	126 x 126	> 4.8	2 mm Cu

Particulars of the conditions maintained during irradiations are shown in Table 3.

TABLE 3
Irradiation conditions

Lab.Code N°	Time (in s) for			Beam current (mA)	Reference
	Irr.	Decay	Meas.		
N 1	8	3	15	0.35	Steel box filled with (Fe ₂ O ₃ +graphite) mixture
N 2	10	5	14	2	Al ₂ O ₃ disc
N 3	15	3	30	4	Tetraphenyl-cyclopentadie- none in Polyethylene holder
N 4	10	10	20	1.4	Graphite+Fe ₂ O ₃ mixture
N 5	15	2.5	20	0.6	Al ₂ O ₃ disc
N 6	5	10	20	1.5	Graphite + phenacetin

Depending on the irradiation system used, a number of corrections were applied, e.g. for neutron removal, gamma absorption, ¹⁶N recoil nuclei or surface oxygen. The last two correction factors depend to a great extent on the gas used in the pneumatic system and on whether or not a sample container is used.

5.3 DETERMINATION OF OXYGEN BY REDUCING FUSION

For the analysis of oxygen in Ti Al6 V4 by reducing fusion both carrier gas and vacuum techniques can be used, and both were used in the collaborative investigation.

Furthermore different types of bath metals (platinum, iron and nickel) were used in bath to sample ratios of 8.5 to 20. Table 4 summarizes the experimental conditions used in the various laboratories.

Depending on the apparatus and the operating conditions, the analysis times ranged from 30 seconds to several minutes.

Cubical samples were machined with a diamond saw.

Before analysis they were etched for 60 seconds at 20°C in

4 vol. HNO₃ (d = 1.4) + 1 vol. HF (40 %).

TABLE 4
Reducing fusion conditions

Lab.Code N°	Type of apparatus	Analysis temp. (°C)	Sample mass (g)	Bath metal	Bath/sample ratio	Determination	Extraction yield control
R 1	vacuum	2200	0.12	Fe/Sn	7.5/1/1	CO : I.R.absorption	TiO ₂ : quantitative recovery Al ₂ O ₃ : no quantita- tive recovery
R 2	helium	2200	0.2	Pt	> 10/1	CO ₂ : thermal con- ductivity	Al ₂ O ₃ : (100+3) %
R 3	nitrogen	2600	0.2	Pt	10/1	CO ₂ : coulometric titration	Al ₂ O ₃ in graphite : quant.extr. Supplem. control with BCR-RM N°21
R 4	vacuum	2500	0.08	Ni	20/1	CO : I.R.absorption	CO calibration only
R 5	vacuum	2500	0.1	Pt	10 to 13/1	CO : gas chromato- graphy	Al ₂ O ₃ : (99+1) %
R 6	argon	2100	0.2	Pt	10/1	CO ₂ : coulometric titration	Al ₂ O ₃ ≈ 100 %; control at Pt/TA6V ratio of 20/1
R 7	helium	2600	0.2	Pt	15/1	CO ₂ : gas chromato- graphy	Al ₂ O ₃ extr. is not quantitative
R 8	argon	2000	0.2	94% Ni +6% Sn	10/1	CO : I.R.absorption	Al ₂ O ₃ : (101+1) %
R 9	helium	2500	0.15	Pt	10/1	CO ₂ : thermal con- ductivity	CO ₂ calibration only
R 10	argon	2600	0.2	Pt	10/1	CO : I.R.absorption	Al ₂ O ₃ : (98+4) %

5.4 DETERMINATION OF OXYGEN BY TRITON ACTIVATION ANALYSIS

Oxygen was determined in laboratory T 1 using activation with 3.5 MeV tritons by the reaction $^{16}\text{O}(\text{t},\text{n})^{18}\text{F}$. Samples were polished, irradiated for 10 minutes in a 0.5 μA triton beam, etched twice during 1 minute in a 1 : 1 : 20 mixture of HF (40 %) : H_3PO_4 (d = 1.71) : H_2O (removed layer : 5 to 6 μm) and analyzed by γ spectrometry using a Ge(Li) detector. Calculation of the results was carried out using Ricci's method ⁽⁴⁾ with the values of Janni ⁽⁵⁾ and Ziegler ⁽⁶⁾ and Al_2O_3 as a reference. The amount of material used in a single analysis is 0.7 mg.

6. RESULTS AND STATISTICAL EVALUATION

6.1 SURFACE ANALYSES

Surfaces prepared by different mechanical techniques were analyzed without and with etching. From the results mentioned in Table 5 one may conclude that the residual surface oxygen content is 0.3 to 0.6 $\mu\text{g}/\text{cm}^2$ after etching according to the recommended technique. Surface contents of that level may be fully neglected in mass oxygen assays at the concentration level present in Ti Al6 V4.

TABLE 5

Surface analysis results obtained by laboratories S 1 and S 2

Surface	Without etching	With etching (*)
A) Cut with diamond saw	5 to 8 $\mu\text{g}/\text{cm}^2$	0.5 to 0.9 $\mu\text{g}/\text{cm}^2$
B) A + polished with diamond paste 10-20 μm	1.3 to 1.6 $\mu\text{g}/\text{cm}^2$	0.4 to 0.6 $\mu\text{g}/\text{cm}^2$
C) A + grinding	2.6 to 2.9 $\mu\text{g}/\text{cm}^2$	0.3 to 0.5 $\mu\text{g}/\text{cm}^2$
D) Turned on a lathe	0.6 to 0.8 $\mu\text{g}/\text{cm}^2$	0.3 to 0.4 $\mu\text{g}/\text{cm}^2$

(*) Samples must be etched for 60 s at 20°C in a solution containing 4 volumes HNO_3 (d=1.4) and 1 volume HF (40 %) under ultrasonic vibration; the remains of the etching solution are removed by successive immersion of the sample in 3 vessels containing distilled water (the first one under ultrasonic vibration) and 3 vessels containing methanol (same remark). The samples are dried in a warm air stream.

6.2 14 MeV NEUTRON ACTIVATION ANALYSIS

Each laboratory carried out six analyses on three different samples. Except laboratory N 3, which used a rotating irradiation device, all laboratories carried out three analyses on each sample side turned towards the tritium target. The mean values ($\bar{x}$) of the 18 determinations, together with the standard deviations (s)[★] are given in Table 6 :

TABLE 6
Results of 14 MeV neutron activation analysis

Lab. Code N°.	$\bar{x}$ (mg/g)	s (mg/g)
N 1	1.756	0.036
N 2	1.761	0.031
N 3	1.726	0.047
N 4	1.751	0.031
N 5	1.746	0.061
N 6	1.705	0.039

The statistical evaluation of these results leads to the following conclusions :

- Neither the means, nor their variances show outlying values, and the distribution of the means is normal.
- The distribution of the 108 results is normal, and shows acceptable skewness and kurtosis.
- A one-way analysis of variance leads to an estimation of the repeatability and of the reproducibility (see annex).

Considering the calibration uncertainty of the method, estimated at $\pm 3 \%$, the results may be considered in good agreement with each other, the 108

$$\star \quad s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

values obtained by the six laboratories resulting in a

mean value of 1.741 mg/g
 a repeatability [★] of 0.042 mg/g
 and a reproducibility ^{★★} of 0.046 mg/g

6.3 REDUCING FUSION

Each laboratory carried out 12 individual analyses, the values obtained being corrected for the residual oxygen on the surface of the samples and for the blank values of the bath metal and equipments used. The mean values ($\bar{x}$) and their standard deviations (s) are listed in Table 7.

TABLE 7
 Reducing fusion results

Lab. Code N°.	$\bar{x}$ (mg/g)	s (mg/g)
R 1	1.787	0.058
R 2	1.740	0.036
R 3	1.749	0.032
R 4	1.708	0.032
R 5	1.829	0.026
R 6	1.742	0.052
R 7	1.691	0.063
R 8	1.823	0.054
R 9	1.691	0.045
R 10	1.780	0.067

The statistical evaluation of these results leads to the same general conclusions as for 14 MeV neutron activation analysis, although the one-way analysis of variance produces a rather greater difference between the repeatability and reproducibility. The reproducibility standard deviation s_R is nevertheless technically acceptable.

★ Standard deviation of repeatability (s_r) : within-laboratory error : gives an idea about the precision of the laboratories

★★ Standard deviation of reproducibility (s_R) : combined error on each single result due to the within-laboratory error and between-laboratory error.

The 120 values obtained by the ten participating laboratories result

in a <u>mean value</u> of	1.754 mg/g
a <u>repeatability</u> of	0.048 mg/g
and a <u>reproducibility</u> of	0.068 mg/g

6.4 TRITON ACTIVATION ANALYSIS

Twelve analyses were carried out by one laboratory (T 1). Despite the very small amount of material analyzed, the dispersion is comparable with that obtained by the other methods used.

They lead to the calculation of a

<u>mean value</u> of	1.775 mg/g
and a <u>standard deviation</u> of	0.031 mg/g

6.5 INTERCOMPARISON OF METHODS

Finally the results of three methods and 17 laboratories were accepted to determine the certified value.

- 14 MeV NAA (6 laboratories - 108 results)
- reducing fusion (10 laboratories - 120 results)
- triton A.A. (1 laboratory - 12 results)

These results are summarized in Table 8.

Considering the overall values no outlying means nor variances are found. The means of the 17 labs. and of the individual results are normally distributed. However the one-way analysis of variance leads to a clear between-laboratory and/or method effect.

From the total set of 240 results a

- mean value 1.749 mg/g
 - s_r (repeatability) 0.045 mg/g
 - s_R (reproducibility) 0.058 mg/g
- were calculated.

This result is in good agreement with values calculated for the individual methods used, which can be considered as equally accurate. Nevertheless, 14 MeV neutron activation analysis has a better reproducibility than reducing fusion for the analysis of oxygen in the alloy under investigation.

TABLE 8
Results used for certification

Method	Lab.	$\bar{x}$ (mg/g)	s (mg/g)	Method $\bar{x}$ (mg/g)	Method s_r (mg/g)	s_R
N	N 1	1.756	0.036	1.741	0.042	0.046
	N 2	1.761	0.031			
	N 3	1.726	0.047			
	N 4	1.751	0.031			
	N 5	1.746	0.061			
	N 6	1.705	0.039			
R	R 1	1.787	0.058	1.754	0.048	0.068
	R 2	1.740	0.036			
	R 3	1.749	0.032			
	R 4	1.708	0.032			
	R 5	1.829	0.026			
	R 6	1.742	0.052			
	R 7	1.691	0.063			
	R 8	1.823	0.054			
	R 9	1.691	0.045			
	R 10	1.780	0.067			
T	T 1	1.775	0.031	1.775	0.031	0.031

7. CONCLUSION

From the results discussed in section 6 as well as from the homogeneity tests described in section 4.3, oxygen was certified in Ti Al6 V4.

A certified value of 1.75 mg/g

and an uncertainty of 0.07 mg/g

were calculated, representing respectively

a) the unweighted mean of 240 individual measurements obtained with three independent methods by 17 laboratories :

and

- b) the total uncertainty based on the precision of the methods used, and on differences between the results which may be due to systematic errors or heterogeneity of the metal.

This inhomogeneity was within the certified uncertainty on both the total batch scale and the micro scale (0.7 mg samples).

The reference material (BCR - No. 59 "Oxygen in titanium-aluminium-vanadium alloy") is available as discs 26 mm in diameter and 9 mm high (intended for 14 MeV neutron activation analysis), and in the form of 0.2 g cubes (intended for reducing fusion). Before use the samples have to be etched in a 4 : 1 HNO_3 (d = 1.4) : HF (40 %) solution as described under 6.1.

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(*) Air Force Weapons Laboratory, Res. & Techn. Division,
Air Force Systems Command, Kirtland Air Force Base,
New-Mexico

C E R T I F I C A T E

BCR N°. 59
OXYGEN IN TITANIUM-ALUMINIUM-VANADIUM ALLOY
Ti Al6 V4

Mass fraction	Certified value (1)	Uncertainty (2)
of oxygen	1.75 mg/g	0.07 mg/g

- (1) This value is the unweighted mean of 240 individual measurement results obtained with three independent methods by 17 laboratories.
- (2) This value takes into account the precisions of the methods used and the differences between the results which may be due to systematic errors or heterogeneity of the metal (may be used as one standard deviation).

DESCRIPTION OF SAMPLE

The samples are available as :

- a) discs : 26 mm in diameter and 9 mm thick;
- b) 0.2 g samples (in bottles of 25).

INSTRUCTIONS FOR USE

1. Before use, samples must be etched for 60 s at 20°C in a solution containing 4 volumes HNO_3 ($d = 1.4$) and 1 volume HF (40 %) under ultrasonic vibration; the remains of the etching solution are removed by successive immersion of the sample in 3 vessels containing distilled water (the first one under ultrasonic vibration) and 3 vessels containing methanol (same remark). The samples are dried in a warm air stream. Surface oxygen on freshly prepared samples is negligible (0.3 to $0.6 \mu\text{g}/\text{cm}^2$).
2. The analysis should be performed as soon as possible after chemical etching of the sample.
3. The minimum quantity that can be considered as representative is 1 mg.

PARTICIPATING LABORATORIES

- Bundesanstalt für Materialprüfung, Berlin,
Federal Republic of Germany
- C.E.A., Centre d'Etudes Nucléaires de Fontenay-aux-Roses,
France
- C.E.A., Centre d'Etudes Nucléaires de Grenoble, France
- C.E.A., Centre d'Etudes de Valduc, Is-sur-Tille, France
- C.N.R.S., G.A.R.N.A.C., Service du Cyclotron, Orléans,
France
- Centre de Recherches Péchiney, Voreppe, France
- Centre de Recherches Vallourec, Aulnoye, France
- Groupe de Physique des Solides de l'Ecole Normale Supérieure,
Paris, France
- Joint Research Centre, Central Bureau for Nuclear Measurements,
Geel, Belgium
- Joint Research Centre Ispra, Chemistry Division and CETIS,
Ispra, Italy
- Kernforschungszentrum Karlsruhe GmbH, Laboratorium für Isotopen-
technik, Karlsruhe, Federal Republic of Germany
- Krupp Forschungsinstitut, Essen, Federal Republic of Germany
- Max-Planck-Institut für Metallforschung, Laboratorium für
Reinstoffe, Schwäbisch Gmünd, Federal Republic of Germany
- Metallurgie Hoboken-Overpelt, Hoboken, Belgium
- Rijksuniversiteit Gent, Instituut voor Nucleaire Wetenschappen,
Gent, Belgium
- Staatliches Materialprüfungsamt Nordrhein-Westfalen, Dortmund,
Federal Republic of Germany
- Technische Universität München, Institut für Radiochemie,
Garching bei München, Federal Republic of Germany
- Ugine Aciers, Ugine, France
- Universität Frankfurt, Frankfurt/Main,
Federal Republic of Germany
- Université de Liège, Institut de Physique Nucléaire,,
Liège, Belgium

METHODS USED

- 14 MeV neutron activation analyses
- Reducing fusion
- Triton activation analyses
- Surface analysis by prompt (d,p) reaction.

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NOTE

A detailed technical report on the analysis procedure and the treatment of the analytical data has been published (BCR-report ...) and is available from BCR.

European Communities — Commission

EUR 6242 — The certification of oxygen in non-ferrous metals
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As the oxygen content of Ti 6Al V4 strongly influences its physical and mechanical properties, the certification of oxygen in this alloy was carried out in the framework of the BCR-group of specialists 'non-metals in refractory metals'. The homogeneity of the batch was examined by 14 MeV neutron activation analysis and its analysis based on reducing fusion, 14 MeV neutron activation and triton activation analysis. The reference material (BCR — No 59) is available in the form of discs 26 mm in diameter and 9 mm thick intended for 14 MeV neutron activation analysis and in bottles containing twenty-five 0.2 g specimen intended for reducing fusion.

BCR information

Surface treatment of non-ferrous metals for the purpose of gas analysis

L. QUAGLIA and G. WEBER

Institut de Physique Nucléaire de l'Université de Liège (Belgium)

D. DAVID

Université de Technologie de Compiègne (France)

J. TRIFFAUX, J. GEERTS, J. VAN AUDENHOVE, J. PAUWELS

Central Bureau for Nuclear Measurements, Geel (Belgium)

Joint Research Centre
Geel Establishment - Belgium

I. INTRODUCTION

The interest that non-ferrous metal producers, users and analytical laboratories have shown in the Commission of the European Communities activities aiming to optimize assaying techniques and the production of reference materials for gases in non-ferrous metals, indicates quite clearly that the analysis of gases, especially at low concentration levels, remains an important problem. Interference by surface contamination is one of the main sources of error that analysts are endeavouring to detect and to eliminate in this context.

For this reason initially the Eurisotop Office and the Community Bureau of Reference (BCR) later on, undertook important efforts to develop appropriate treatments to reduce surface contamination and to quantify their effect. The importance of reducing surface oxygen is illustrated in Table 1 for reducing fusion.

The present report is an updating of earlier reports published in 1972 ⁽¹⁾ and 1976 ⁽²⁾. Its major improvement compared to the earlier reports is that greater importance has been devoted to quantify the parameters of mechanical shaping techniques to be used with or without subsequent chemical etching.

II. MEASUREMENT OF SURFACE CONTAMINATION

A. DESCRIPTION OF THE METHOD

Surface contamination is measured by the method of microanalysis by nuclear reactions ^(3,4,5,6). It consists in bombarding the surface of a sample with accelerated charged particles and simultaneous counting of the particles produced by a nuclear reaction using a silicon surface-barrier detector. The charged particle source is generally a Van de Graaff accelerator of 2-3 MeV.

Fig. 1 shows the diagram of the experimental apparatus used at the Institut de Physique Nucléaire de l'Université de Liège and at the Université Technologique de Compiègne.

T A B L E 1

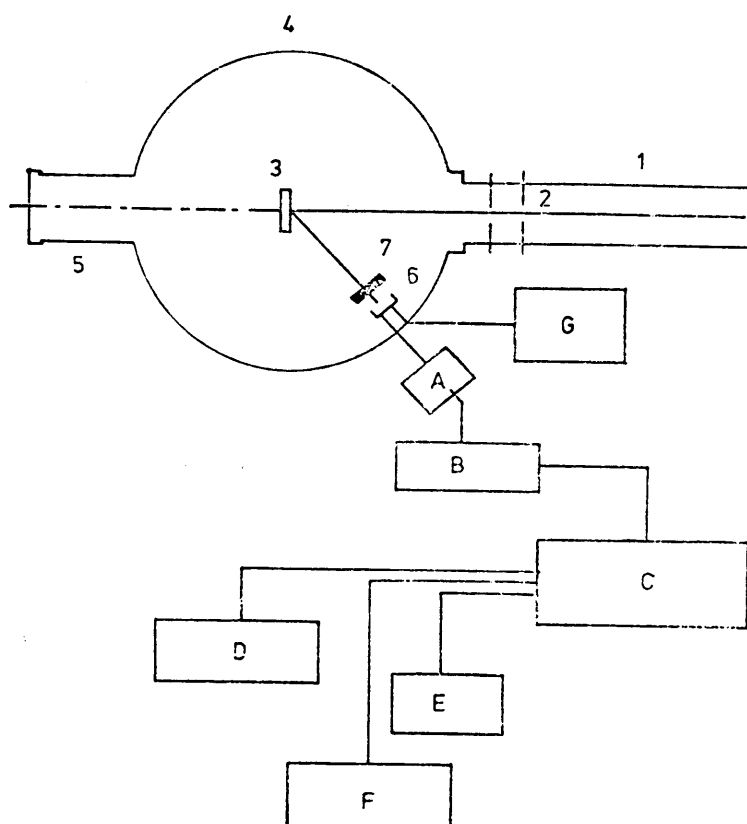
Influence of surface contamination on bulk content.
(Oxygen in non-ferrous metals)

Metal	Actual content ($\mu\text{g/g}$)	Specimen		Plus error if 1 $\mu\text{g/cm}^2$ (%)	Permissible error (%)	Permissible contamination ($\mu\text{g/cm}^2$)
		weight (g)	Surface area (cm^2)			
Al	< 1	2.00	4.9	> 250	20	< 0.1
Al-Si	< 1	2.00	4.9	> 250	20	< 0.1
W	< 1	0.50	0.5	> 100	20	< 0.2
Cu	2	2.00	2.2	55	10	0.2
Cu-Zn	2	2.00	2.3	58	10	0.2
Pb	< 1	3.00	2.5	> 83	20	< 0.2
Pb-Sb	< 1	3.00	2.5	> 83	20	< 0.2
Ti	800	0.25	0.9	0.5	0.5	1.0
Zr	600	0.25	0.7	0.5	0.5	1.0
Nb	25	0.50	0.9	7	5	0.7
Ta	25	0.50	0.6	5	5	1.0
Mo	15	0.50	0.8	11	5	0.5

The figure shows :

- 1. end of incident beam
- 2. double collimator for definition of a beam of 1-4.5 mm diameter
- 3. target and its support in the geometrical centre of the reaction chamber
- 4. reaction chamber (400 mm diameter)
- 5. Faraday cage
- 6. silicon surface-barrier detector (ORTEC, 300 μm)
- A. preamplifier (ORTEC 109 A)
- B. amplifier (ORTEC 410 A)
- C. multichannel amplitude selector (Intertechnique SA 40 B)
- D. plotting table (MOSELEY)
- E. carriage printer (IBM)
- F. paper tape punch (Tally 420)
- G. polarization voltage supply for detector

Fig. 1. Experimental apparatus



From the number dn of particles detected, the surface content y in g/cm^2 can be calculated from the following equation :

$$dn = n_0 y \frac{N_0}{M} \sigma(E, \theta) d\Omega \quad (1)$$

n_0 = number of accelerated particles that actually reach the target

N_0 = Avogadro number

M = atomic mass of the element to be determined

$\sigma(E, \theta)$ = differential cross-section of the nuclear reaction at the given energy and angle

$d\Omega$ = solid detection angle.

The principle of the method is very simple, however, experimental determination of the various parameters included in (1) calls for certain precautions.

(n_0). The number of particles that actually reach the target can be measured from the integrated charge C received by the target expressed in coulombs

$$n_0 = \frac{C}{Z \cdot 1.6 \cdot 10^{-19}} \quad Z = \text{charge of the particle}$$

This can be simply measured, provided that measures are taken to discount the influence of the secondary electrons torn from the target by the incident beam. If these electrons are not collected when the beam intensity is measured, they cause an overestimation of the value of this parameter.

To minimize this effect, the currents collected on the target and on the walls of the reaction chamber have been placed in parallel. A study by L. Quaglia⁽⁷⁾ using electrostatic and magnetic suppressors has shown that the contribution made by secondary electrons amounts to only a few tenths of a percent in normal collimation conditions. This incident charge C is therefore measured to within the precision of the current integrator, checked against a reference source, i.e. 1.5 percent.

($d\Omega$). The solid detection angle is measured by two methods : by geometric evaluation of the distance from target to detector and the diameter of the collimator, and by using a source of alpha particles calibrated in absolute activity and substituted for the target to be irradiated. Comparison of the results obtained by the two methods gives $d\Omega$ to within 2 percent.

$\sigma(E, \theta)$. The difficulty in determining accurately the absolute value of the differential cross-section of a nuclear reaction is no new problem. In the literature numerous examples can be found where, for the same reaction, at identical energies and angles, the numeric values given by different authors are scattered over such a wide range that the absolute nature of the measurements ceases to have any significance.

It is extremely difficult to compare and diagnose the causes of error in published results because of the failure, often unintentional, to give certain essential data.

It is extremely rare to find :

- precise details of the experimental conditions in which the work was carried out (type of beam current measurement, type of detector, vacuum measurement in the reaction chamber, type of target, measurement of target thickness, etc ...)
- tables of numeric values, generally the authors publish curves which are difficult to interpret because of the great reduction in the size of the figures and the appreciable probability of errors that could affect the definition of scale factors.

The situation as far as the purpose of this study is concerned can be summarized as follows :

- oxygen : $^{16}\text{O} (d, p_1) ^{17}\text{O}$

In this case, measurements at the Institut de Physique Nucléaire of the Liège University ⁽⁸⁾, standardized by measurement on a gaseous target ⁽⁹⁾, agree well ($\pm 10\%$) with the curve given by G. Amse1 ⁽¹⁰⁾. It should be noted that the latter, obtained on a target of Ta_2O_5 made by anodic oxidation, is particularly reliable.

Exceptional care was taken in preparing the target and as quantitative analysis was the purpose of the measurement, the author's main concern was to ensure accurate results in absolute terms.

- nitrogen : $^{14}\text{N}(d, p_5) ^{15}\text{N}$, $^{14}\text{N}(d, p_4) ^{15}\text{N}$, $^{14}\text{N}(d, \alpha_0) ^{12}\text{C}$, $^{14}\text{N}(d, \alpha_1) ^{12}\text{C}$

The differential cross-sections used are given by G. Amse1 ⁽¹¹⁾.

- carbon : $^{12}\text{C} (d,p_0)^{13}\text{C}$

In view of the extremely scattered values obtained in the literature^(12,15) the differential cross-section was determined at the Institut de Physique Nucléaire of the Liège University⁽¹⁶⁾. This gives an absolute value to within ± 20 percent.

It should be stressed that to avoid systematic errors introduced by a possible modification of experimental parameters from one series of determinations to another, a Ta_2O_5 target obtained by anodic oxidation is always used as a reference.

When using this method, another phenomenon must be taken into account. It has frequently been observed that the surface content varies during irradiation^(17,19).

To allow significant extrapolation, it is essential to make a prior study, for each type of target used, of its behaviour under the beam. This allows the optimum experimental conditions to be determined, in particular as regards the density of the charge received by the target.

B. ALTERNATIVE METHODS

The method of microanalysis by nuclear reaction is obviously not the only method capable of supplying data on surface content.

There are also :

- the electronic microprobe;
- the SIMS ionic microanalyser;
- the AES Auger electron spectrometer;
- the ESCA electronic spectrometer;
- ellipsometry.

As it is not within the scope of this study to make a detailed comparison of these methods, it is enough to say that microanalysis by nuclear reactions is particularly suitable for the study of mass/surface interference.

This is because :

- it is based on the principle of an essentially nuclear phenomenon supplying absolute values; this makes it independent of the mode of fixation (chemical or physical) of the element to be determined on the matrix. This independence also applies to the crystalline structure of the material studied,

- if the effect of charged-particle "channeling" in the crystals (a phenomenon that occurs only at extremely precise angles of incidence) is ignored;
- the unit in which the surface content is obtained (g/cm^2) is ideally suited to the study, if the results were given in units of length, for example, determination of the apparent content would require an additional hypothesis concerning the specific mass and the stoichiometry of the layer analysed.

A detailed literature survey and critical evaluation of surface analysis methods has been published by L. Quaglia and G. Weber as BCR-information (20).

C. RESULTS

Surface treatments have been studied and standardized for a number of non-ferrous metals. Recommendations were generally made on the basis of the following :

- the proposed treatment must give a minimum surface content;
- it must exhibit good reproducibility;
- it must be easy to perform with equipment normally available in analytical laboratories.

The practical solution of course often represents a compromise between these requirements. There is no point in proposing a treatment calling for the use of complicated, unusual and often very expensive equipment. Likewise, when the purpose is to obtain a result for use in calculating corrections for the bulk content, it is sometimes necessary to discard a treatment giving the minimum content in favour of another that is less effective but more reproducible.

The recommended treatments are presented in the form of sheets. They give full information on mechanical shaping parameters if these are important, and - if needed - the subsequent chemical etching conditions. Typical residual surface contents are given for all contaminants studied. They refer to samples freshly prepared.

A summary of recommended surface treatments is given in Table 2.

T A B L E 2

Recommended surface treatments and residual surface contaminations

METAL	Surface treatment		Residual Surface contents ($\mu\text{g}/\text{cm}^2$)			
	Mech. Shaping (*)	Subsequent Etching (**)	Oxygen	Carbon	Nitrogen	Fluor
Al - 99.5	T, R	1 HF + 1 HNO ₃ (20°C, 2 min)	0.3 - 0.4	0.1 - 0.2		Without etch < 0.01
Al - Si	T, R	Idem	0.2 - 0.4			
Cu	T	a) HCl (20°C, 2 - 3 min) b) 1HNO ₃ + 1CH ₃ COOH (20°C, 1 min)	0.2 - 0.4			
Pb PbSnCd PbCuTe	T, R, P	3 CH ₃ COOH + 1 H ₂ O ₂ (20°C, 45 s)	0.2 - 0.4	0.15 - 0.2		
Ni	T, SiC	75 CH ₃ OOH + 25 HNO ₃ + 1.5 HF (60°C, 60 s, ultrasonics)	0.1 - 0.2	0.15 - 0.2	< 0.03	
Ti	T, S, HSS	4 HNO ₃ + 1 HF (20°C, 1 min)	0.4 - 0.6	0.1 - 0.3	< 0.1	
TiAl6V4	T, HSS	Idem	0.3 - 0.6	0.1 - 0.3	< 0.05	
Zr	T, S	5 HNO ₃ + 0.5 HF + 5 H ₂ O (20°C, 50 s)	0.4 - 0.6	0.1 - 0.2	< 0.05	
W	S	1 HF + 4 HNO ₃ (20°C, 2 min)	0.1 - 0.2		< 0.05	
Mo	S, HSS	a) 4 HF + 1 HNO ₃ (20°C, 10 s) b) HCl (20°C)	0.2 - 0.4	0.1	< 0.05	

(*) Mech. Shaping : T : turning on a lathe; S : sawing with a diamond saw; SiC : sawing with a SiC saw;
R : rolling; P : punching; HSS : high speed sawing

(**) Chem. Etching : Bath is given in volumes of each component (concentrated acids)
Arrest is carried out in water (when not stated otherwise) and rinsing by dipping in
two more water vessels and three methanol vessels.
Drying carried out in warm air stream ($\approx 60^\circ\text{C}$).

RECOMMENDED SURFACE TREATMENT FOR PRIMARY INGOT ALUMINIUM (99.5 %)

PRESHAPING OF ANALYSIS SAMPLES

2 shaping techniques were examined and found to be acceptable for samples etched subsequently in case of O- and C- determinations and without subsequent etching for F- determination.

1. Turning on a lathe

<u>Tool material</u> : High speed steel		<u>Design</u> : Annex 1
<u>Tool parameters</u>		<u>Turning parameters</u> (Workpiece $\varnothing$: 30 mm)
χ :	45°	Cutting speed (rpm) : 1000 - 1500
γ :	20 - 30°	Pre-turning
α :	6 - 10°	Feed(mm/revol) : 0.5 - 1
α_1 :	3 - 6°	Depth of cut(mm) : 0.5 - 1
λ :	0°	Final-turning
Top radius : 0.2 to 0.3 mm		Last 0.1 to 0.2 mm
		Feed(mm/revol) : 0.01 - 0.02
		Depth of cut(mm) : 0.05 - 0.1
Cutting fluid : Kerosene		

2. Rolling

In order to prepare thin plates, freshly turned pieces were cold rolled with a maximum reduction in area of 5 % per rolling pass.

SUBSEQUENT CHEMICAL ETCHING

Bath	:	1 Vol HF (min. 40 %) + 1 Vol HNO ₃ (min. 65 %; d $\approx$ 1.4)
Temperature	:	20°C
Duration	:	60 s
Arrest	:	3 x H ₂ O
Drying	:	3 x CH ₃ OH + hairdrier ($\pm$ 60°C)

TYPICAL RESIDUAL SURFACE CONTENTS

O	:	0.3 - 0.4 $\mu\text{g}/\text{cm}^2$
C	:	0.1 - 0.2 $\mu\text{g}/\text{cm}^2$
F	:	without chemical etching : < 0.01 $\mu\text{g}/\text{cm}^2$

RECOMMENDED SURFACE TREATMENT FOR
ALUMINIUM - 3 %; 7 % and 13 % SILICIUM

- PRESHAPING OF ANALYSIS SAMPLES

2 shaping techniques were examined and found to be acceptable for samples etched subsequently.

1. Turning on a lathe

<u>Tool material</u>	: High speed steel	<u>Design</u>	: Annex 1
<u>Tool parameters</u>		<u>Turning parameters</u>	(Workpiece $\varnothing$: 30 mm)
χ	: 45°	Cutting speed (rpm)	: 1000 - 1500
γ	: $20 - 30^\circ$	Pre-turning	
α	: $6 - 10^\circ$	Feed(mm/revol)	: 0.5 - 1
α_1	: $3 - 6^\circ$	Depth of cut(mm)	: 0.5 - 1
λ	: 0°	Final-turning	
		Last 0.1 to 0.2 mm	
		Feed(mm/revol)	: 0.01 - 0.02
		Depth of cut(mm)	: 0.05 - 0.1
		Cutting fluid	: Kerosene

2. Rolling

In order to prepare thin plates (1 mm thick), freshly turned pieces were cold rolled.

For AS 3	:	Starting thickness	: 10 mm
		Max. reduction	: 5 % per pass
For AS 7 and 13	:	Starting thickness	: 3 mm
		Max. reduction	: 2 % per pass.

- SUBSEQUENT CHEMICAL ETCHING

Bath	:	1 Vol HF (min. 40 %) + 1 Vol HNO_3 (min. 65 %; $d \approx 1.4$)
Temperature	:	20°C
Duration	:	2 min
Arrest	:	3 x H_2O
Drying	:	3 x CH_3OH + hair drier ($\pm 60^\circ\text{C}$)

- TYPICAL RESIDUAL SURFACE CONTENT

O	:	0.2 to $0.4 \mu\text{g}/\text{cm}^2$
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RECOMMENDED SURFACE TREATMENT FOR COPPER

- TURNING ON A LATHE

<u>Tool material</u> : High speed steel		<u>Design</u> : Annex 1
<u>Tool parameters</u>		<u>Turning parameters</u> (Workpiece $\varnothing$: 30 mm)
χ :	45°	Cutting speed (rpm) : 1000 - 1500
γ :	20 - 30°	Pre-turning
α :	6 - 10°	Feed(mm/revol) : 0.5 - 1
α_1 :	3 - 6°	Depth of cut(mm) : 0.5 - 1
λ :	0°	Final-turning
Top radius : 0.2 to 0.3 mm		Last 0.1 to 0.2 mm
		Feed(mm/revol) : 0.01 - 0.02
		Depth of cut(mm) : 0.05 - 0.1
Cutting fluid : Kerosene		

- SUBSEQUENT CHEMICAL ETCHINGS

Bath 1	:	1 Vol HCl (min. 30 %; $d \approx 1.15$)
Temperature	:	20°C
Duration	:	2 - 3 min
Arrest	:	3 x H ₂ O
Bath 2	:	1 Vol HNO ₃ (min. 65 %; $d \approx 1.4$) + 1 Vol CH ₃ COOH (min. 96 %; $d \approx 1.06$) + 1 Vol H ₃ PO ₄ (min. 85 %; $d \approx 1.71$)
Temperature	:	20°C
Duration	:	1 min
Arrest	:	3 x H ₂ O
Drying	:	3 x CH ₃ OH + hair drier ($\pm$ 60°C)

- COMMENTS

Turning on a lathe is essential but chemical etching is not.

- TYPICAL RESIDUAL SURFACE CONTENTS

O : 0.2 to 0.4 $\mu\text{g}/\text{cm}^2$

RECOMMENDED SURFACE TREATMENT FOR
PURE Pb and Pb-0.2 % Sn- 0.07 % Cd,
Pb-0.4 % Cu-0.04 % Te ALLOYS

PRESHAPING OF ANALYSIS SAMPLES

3 shaping techniques were examined and found to be acceptable for samples etched subsequently in case of O and C- determinations.

1. Turning on a lathe

<u>Tool material</u>	: Hardmetal ISO-P35	<u>Design</u>	: Annex 1
<u>Tool parameters</u>		<u>Turning parameters</u>	(Workpiece Ø : 30 mm)
χ	: 45°	Cutting speed (rpm)	: 1000 - 1500
γ	: 20 - 30°	Pre-turning	
α	: 6 - 10°	Feed(mm/revol)	: 0.5 - 1
α_1	: 3 - 6°	Depth of cut (mm)	: 0.5 - 1
λ	: 0°	Final-turning	
Top radius	: 0.2 to 0.3 mm	Last 0.1 to 0.2 mm	
		Feed(mm/revol)	: 0.01 - 0.02
		Depth of cut (mm)	: 0.05 - 0.1
		Cutting fluid	: Kerosene

2. Rolling

In order to prepare thin plates, freshly turned pieces were cold rolled with a maximum reduction in area of 10 % per rolling pass.

3. Punching

Cutting with a punching die using kerosene as cutting fluid of round or rectangular pieces up to 10 mm thick.

SUBSEQUENT CHEMICAL ETCHING (Annex 2)

Bath	: 3 Vol CH ₃ COOH (99.7 %) + 1 Vol H ₂ O ₂ (30 %)
Temperature	: 20°C
Duration	: 45 s
Arrest	: 1 x H ₂ O 60 to 80°C 1 x H ₂ O 20°C + ultrasonic
Drying	: 1 x CH ₃ OH + ultrasonic Stream of Argon (N 50) at 80°C
Bath Volume for 1 to 2 g samples	: 100 ml
Special equipment	- see Annex 2.

TYPICAL RESIDUAL SURFACE CONTENTS

O	: 0.2 - 0.4 µg/cm ²
C	: 0.15 - 0.2 µg/cm ²

RECOMMENDED SURFACE TREATMENT FOR NICKEL

- PRESHAPING OF ANALYSIS SAMPLES

2 shaping techniques were examined and found to be acceptable for samples etched subsequently in case of O-, C- and N- determinations.

1. Turning on a lathe

<u>Tool material</u>	: Hardmetal ISO-K05	<u>Design</u>	: Annex 1
<u>Tool parameters</u>		<u>Turning parameters</u>	(Workpiece $\varnothing$: 30 mm)
χ	: 45°	Cutting speed (rpm)	: 500 -700
γ	: $20 - 30^\circ$	Pre-turning	
α	: $6 - 10^\circ$	Feed(mm/revol)	: 0.5
α_1	: $3 - 6^\circ$	Depth of cut (mm)	: 0.5 - 1
λ	: 0°	Final-turning	
		Last 0.1 to 0.2 mm	
		Feed(mm/revol)	: 0.01 - 0.02
		Depth of cut (mm)	: 0.05 - 0.1
		Cutting fluid	: 1 Vol Dromusoil (Shell) + 1 Vol H_2O

2. Sawing

<u>Tool</u>	: Bakelite bonded SiC wheel (Feldmuhle 80N/99001)
<u>Speed</u>	: 4000 rpm
<u>Cutting fluid</u>	: Water

- SUBSEQUENT CHEMICAL ETCHING

Bath	: 75 Vol CH_3COOH (glacial) + 25 Vol HNO_3 (min. 65 %; $d \approx 1.4$) + 1.5 Vol HF (40 %) Magnetic stirring
Temperature	: $60^\circ C$
Duration	: 60 s
Arrest	: 30 x H_2O ultrasonic
Rinsing	: 3 x H_2O
Drying	: 3 x CH_3OH + hairdrier ($\pm 60^\circ C$)

- TYPICAL RESIDUAL SURFACE CONTENTS

O	: 0.1 to $0.2 \mu g/cm^2$
C	: 0.15 to $0.2 \mu g/cm^2$
N	: $< 0.03 \mu g/cm^2$

RECOMMENDED SURFACE TREATMENT FOR UNALLOYED TITANIUM

PRESHAPING OF ANALYSIS SAMPLES

3 shaping techniques were examined and found to be acceptable for samples etched subsequently.

1. Cutting with diamond saw

Cutting blade : diamond bronze bonded wheel
 Diameter : 150 mm
 Thickness : 0.65 mm
 Speed : 2300 rpm
 Cutting fluid : water
 Material diameter : 30 mm

2. Slicing and dicing on high-speed sawing machine (Annex 3)

<u>Slicing machine</u> ROTO(Semitron Ltd.)	<u>Dicing machine</u> AUTO 2000(Semitron Ltd.)
Spindle Speed (rpm) : 8750	Spindle Speed (rpm) : 8000
Lathe feed speed : 0.025 mm/revol	Feed : 20 mm/min
at 80 rpm	Number of wheels : 2, 3 and 5
Material diameter : 30 mm	Material thickness : 3 mm

Cutting wheel for Slicing : Phenolic resin bonded green SiC
 Diameter : 150 mm; Thickness : 0.5 mm
 Cutting wheel for Dicing : Phenolic resin bonded mixture of diamond and SiC
 Diameter : 101,6 mm; Thickness : 0.5 mm
 Coolant : Slicing : current water
 Dicing : 80 Vol water + 1 Vol Miracol 80 (Castrol)

3. Turning on a lathe

<u>Tool material</u> : Hardmetal ISO-P35	<u>Design</u> : Annex 1
<u>Tool parameters</u>	<u>Turning parameters</u> (Working piece $\varnothing$: 30 mm)
x : 45°	Turning speed (rpm) : 500 - 800
γ : 20 - 30°	Pre-turning
α : 6 - 10°	Feed(mm/revol) : 0.5
α_1 : 3 - 6°	Depth of cut(mm) : 0.5
λ : 0°	Final-turning
	Feed(mm/revol) : 0.01 - 0.02
	Depth of cut (mm) : 0.05 - 0.1
	Cutting fluid : 1 Vol Dromusoil (Shell) + 1 Vol Water.

SUBSEQUENT CHEMICAL ETCHING

Bath : 4 Vol HNO_3 (min 65 %; $d \approx 1.4$) + 1 Vol HF (min. 40 %)
 Temperature : 20°C
 Duration : 60 s
 Arrest : H_2O
 Rinsing : 2 x H_2O + 3 x CH_3OH

TYPICAL RESIDUAL SURFACE CONTENTS

O : 0.4 - 0.6 $\mu\text{g}/\text{cm}^2$
 C : 0.1 - 0.3 $\mu\text{g}/\text{cm}^2$
 N : < 0.1 $\mu\text{g}/\text{cm}^2$

RECOMMENDED SURFACE TREATMENT FOR

Ti-alloy : Ti - 6 % Al - 4 % V

- PRESHAPING OF ANALYSIS SAMPLES

2 shaping techniques were examined and found to be acceptable for samples etched subsequently in case of 0- determinations.

1. Turning on a lathe

Tool material : Hardmetal ISO-P35

Design : Annex 1

Tool parameters

Turning parameters (Workpiece $\varnothing$: 30 mm)

χ : 45°

Turning speed (rpm) : 500 - 800

γ : $20 - 30^\circ$

Pre-turning

α : $6 - 10^\circ$

Feed(mm/revol) : 0.5

α_1 : $3 - 6^\circ$

Depth of cut (mm) : 0.5

λ : 0°

Final-turning

Feed(mm/revol) : 0.01 - 0.02

Depth of cut (mm) : 0.05 - 0.1

Cutting fluid : 1 Vol Dromusoil (Shell)
+ 1 Vol Water.

2. Slicing and dicing on high speed sawing machine

Slicing machine ROTO (Semitron Ltd.)

Dicing machine AUTO 2000(Semitron Ltd.)

Spindle speed (rpm) : 8750

Spindle speed (rpm) : 6000

Lathe feed speed : 0.025 mm/revol
at 80 rpm

Feed : 2 cm/min

Material diameter : 30 mm

Number of wheels : 2, 3 and 5

Material thickness : 3 mm

Cutting wheel for slicing : Phenolic resin bonded green SiC

Diameter : 150 mm; Thickness : 0.5 mm

Cutting wheel for dicing : Phenolic resin bonded mixture of diamond and SiC

Diameter : 101,6 mm; Thickness : 0.5 mm

Coolant : Slicing : current water

Dicing : 80 Vol water + 1 Vol Miracol 80 (Castrol)

- SUBSEQUENT CHEMICAL ETCHING

Bath : 4 Vol HNO_3 (min. 65 %; $d \approx 1.4$) + 1 Vol HF (min. 40 %)

Temperature : 20°C

Duration : 60 s

Arrest : H_2O

Rinsing : $2 \times \text{H}_2\text{O} + 3 \times \text{CH}_3\text{OH}$

- TYPICAL RESIDUAL SURFACE CONTENTS

O : 0.3 to $0.6 \mu\text{g}/\text{cm}^2$

N : 0.1 to $0.3 \mu\text{g}/\text{cm}^2$

C : $< 0.05 \mu\text{g}/\text{cm}^2$

RECOMMENDED SURFACE TREATMENT FOR
ZIRCONIUM

- PRESHAPING OF ANALYSIS SAMPLES

2 shaping techniques were examined and found to be acceptable for samples etched subsequently in case of O- and N- determinations.

1. Turning on a lathe

<u>Tool material</u>	: Hardmetal ISO-P35	<u>Design</u>	: Annex 1
<u>Tool parameters</u>		<u>Turning parameters</u>	(Workpiece $\varnothing$: 30 mm)
χ	: 45°	Cutting speed (rpm)	: 500 - 700
γ	: $20 - 30^\circ$	Pre-turning	
α	: $6 - 10^\circ$	Feed(mm/revol)	: 0.5 - 1
α_1	: $3 - 6^\circ$	Depth of cut (mm)	: 0.5 - 1
λ	: 0°	Final-turning	
		Last 0.1 to 0.2 mm	
		Feed(mm/revol)	: 0.01 - 0.02
		Depth of cut (mm)	: 0.05 - 0.1
		Cutting fluid	: 1 Vol Dromusoil (Shell) + 1 Vol Water.

2. Sawing

Cutting wheel : Bakelite bonded SiC wheel (Feldmuhle 80N/99001)
Diameter : 150 mm; thickness : 1 mm

Speed : 2300 rpm

Cutting fluid : water

Material diameter : 30 mm

- SUBSEQUENT CHEMICAL ETCHING

Bath : 5 Vol HNO_3 (min. 65 %; $d \approx 1.4$) + 0.5 Vol HF (40 %) + 5 H_2O

Temperature : 20°C

Duration : 50 s

Arrest : 3 x H_2O

Drying : 3 x CH_3OH + hairdrier ($\pm 60^\circ\text{C}$)

- TYPICAL RESIDUAL SURFACE CONTENTS

O : 0.4 to 0.6 $\mu\text{g}/\text{cm}^2$

N : $< 0.05 \mu\text{g}/\text{cm}^2$

C : 0.1 to 0.2 $\mu\text{g}/\text{cm}^2$

RECOMMENDED SURFACE TREATMENT FOR
TUNGSTEN

- PRESHAPING OF ANALYSIS SAMPLES

1 shaping technique was examined and found to be acceptable for samples etched subsequently.

Sawing

Cutting wheel : diamond bronze bonded wheel (NORTON PD180-N100G-1 11044Z)
 diameter : 150 mm
 thickness : 0.65 m

Speed : 4000 rpm

Coolant : Water.

Material diameter : 10 mm

- SUBSEQUENT CHEMICAL ETCHING

Bath : 1 HF (40 %) + 4 HNO₃ (min. 65 %; d ≈ 1.4) to be used with ultrasonic if possible

Duration : 2 min

Temperature : 20°C

Arrest : H₂O (with ultrasonic) + 2 x H₂O

Drying : CH₃OH (with ultrasonic) + 2 x CH₃OH + hairdrier (± 60°C)

- TYPICAL RESIDUAL SURFACE CONTENTS

O : 0.1 to 0.2 μg/cm²

N : < 0.05 μg/cm²

C : 0.1 to 0.3 μg/cm²

RECOMMENDED SURFACE TREATMENT FOR
MOLYBDENUM

PRESHAPING OF ANALYSIS SAMPLES

2 shaping techniques were examined and found to be acceptable for samples etched subsequently.

1. Cutting with diamond saw

Cutting wheel : diamond bronze bonded (NORTON PD180-N100G-1 11044Z)
Diameter : 150 mm
Thickness : 0.65 mm
Speed : 4000 rpm
Coolant : water

2. Slicing and dicing on high-speed sawing machine

<u>Slicing machine</u>	ROTO 2000 (Semitron Ltd.)	<u>Dicing machine</u>	AUTO 2000 (Semitron Ltd.)
Spindle speed (rpm) :		Spindle speed (rpm) :	8000
Lathe feed speed :	mm/revol at rpm	Feed :	20 mm/min
		Number of wheels :	2, 3 and 5
Material diameter :	30 mm	Material thickness :	6 mm
Cutting wheel :	Rubber bonded Al_2O_3 Diameter : 150 mm; Thickness: 0.4 mm		
Coolant :	Slicing : current water Dicing : 80 Vol Water + 1 Vol Miracol (Castrol)		

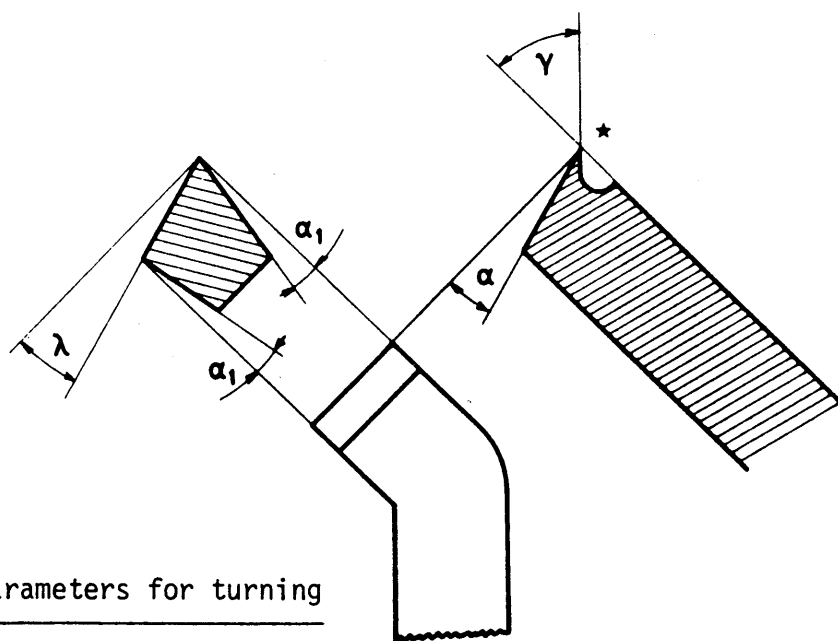
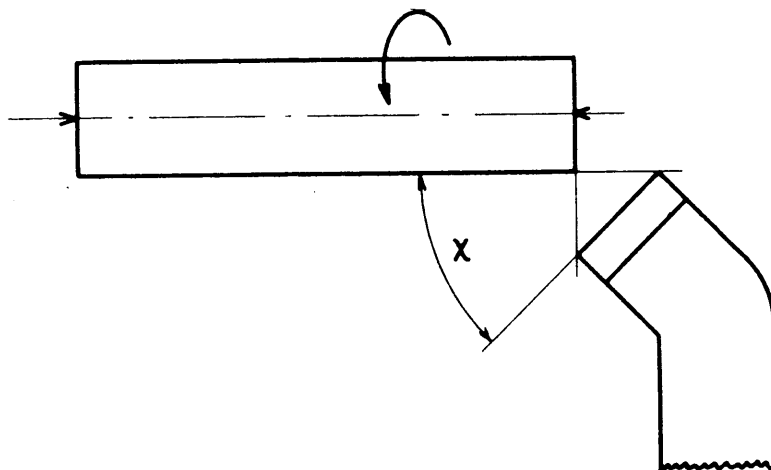
SUBSEQUENT CHEMICAL ETCHING

Bath : 4 Vol HF (40 %) + 1 Vol HNO_3 (min. 65 %; $d \approx 1.4$)
Temperature : 20°C
Duration : 10 s
Arrest : HCl (36 %)
Rinsing : 3 x H_2O
Drying : 3 x CH_3OH + hairdrier ($\pm 60^\circ C$)

TYPICAL RESIDUAL SURFACE CONTENTS

O : 0.2 to 0.4 $\mu g/cm^2$
C : 0.1 - 0.2 $\mu g/cm^2$
N : < 0.05 $\mu g/cm^2$

Annex 1



Tool parameters for turning

- χ : Angle of attack
- γ : Clearance angle
- α : Rake angle
- α_1 : Rake angle
- λ : Inclination cutting edge
- $\star$: Top radius

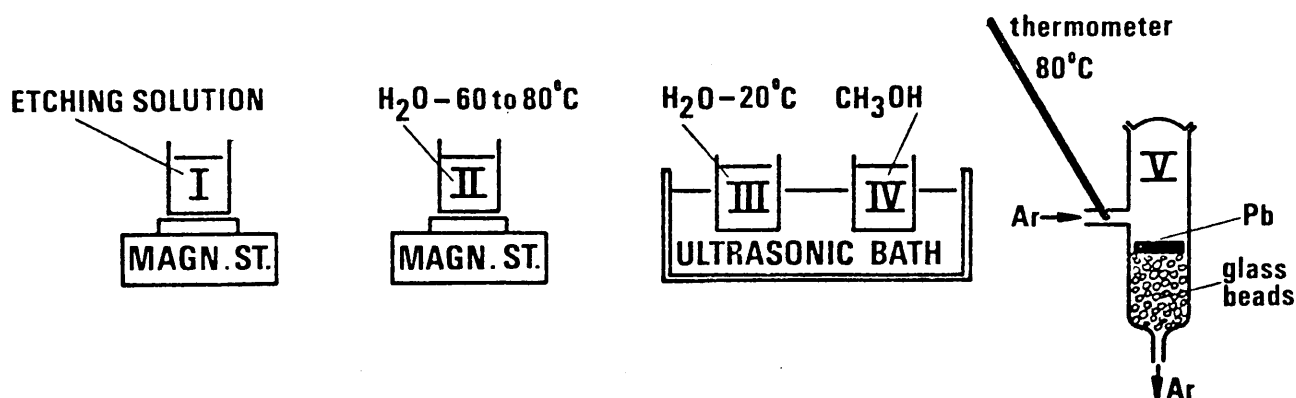
Annex 2

ETCHING PROCEDURE FOR Pb and Pb-Sn-Cd; Pb-Cu-Te ALLOYS

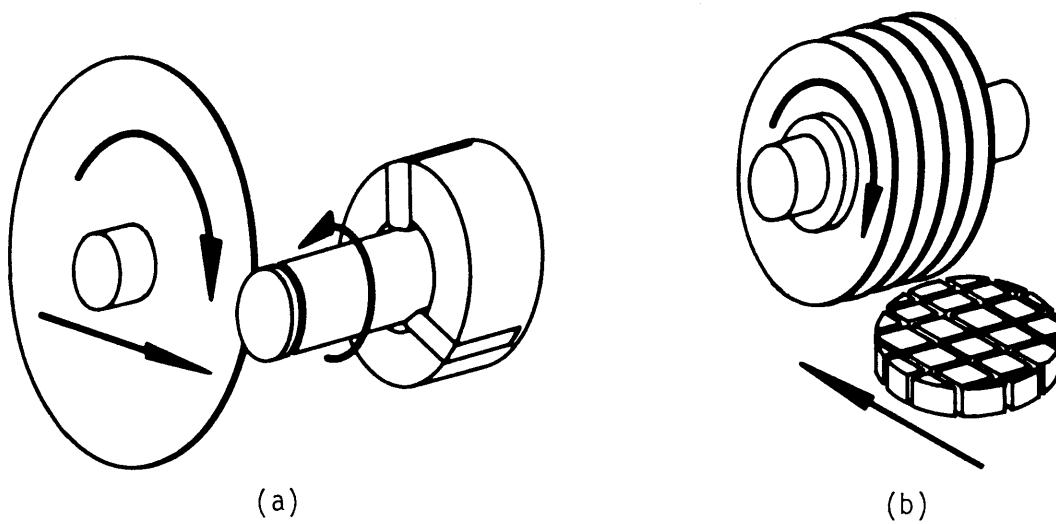
The etching procedure used needs an equipment as shown in Fig. 1, and goes as follows :

1. Etching in 3 volumes CH_3COOH (99.7 %) + 1 volume H_2O_2 (30 %) at 20°C during 45 s. For a 1 to 2 g sample the bath volume is 100 ml. The etching bath has to be replaced by a fresh one after each sample. Particular attention must be paid to good evacuation of acid vapours. The sample is hold into the etching bath (as well as in further baths) with chromium coated tweezers.
2. Rinsing for 5 s in 200 ml H_2O at 60 to 80°C . Also this bath is renewed after each sample.
- 3 & 4. Rinsing for 5 s in 200 ml H_2O at 20°C and for 5 s in 200 ml CH_3OH under ultrasonic vibration. These baths are replaced after six samples.
5. Drying is carried out in a vessel through which a dry and warm (80°) stream of pure argon (N 50) is passed.

Fig. 2: Special apparatus for etching of lead.



A n n e x 3



Schematic presentation of Slicing (a) and Dicing (b)
A detailed description of this technique as used for Mo, Ti
and Ti-6 % Al-4 % V is given in ref. ⁽²¹⁾

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BCR information

Conditioning of non-ferrous reference materials

Oxygen in Molybdenum (BCR No. 23)

Oxygen in Titanium (BCR No. 24)

Oxygen in TiA 16V4 (BCR No. 59)

J. GEERTS, J. TRIFFAUX, J. VAN AUDENHOVE

Joint Research Centre
Geel Establishment (Belgium)
Central Bureau for nuclear measurements

A b s t r a c t

The present paper is concerned with the mechanical shaping and surface treatment of important amounts of Mo-, Ti- and TA6V reference samples certified for their bulk oxygen content.

High speed air bearing sawing conditions have been determined to prepare cubic samples of suitable size.

Deburring of these cubes by an appropriate barrel finishing or chemical etching technique gives samples with an acceptable residual surface oxygen content of $(0.5 \pm 0.05) \mu\text{g}/\text{cm}^2$.

1. MECHANICAL SHAPING

In order to produce the above mentioned samples in form of cubes of suitable sizes cutted from the available round bars, two machining operations are necessary : slicing of the bar into discs and subsequent dicing into cubes.

For the slicing operation a high speed air bearing sawing SEMITRON attachment, called ROTO, is fitted on the saddle of a lathe as shown in Fig. 1. An appropriate thin abrasive wheel is fitted to the arbor of the ROTO and the bar is held in the chuck of the lathe. The rotating abrasive wheel is advancing into the bar at 90° to the centre of the chuck which is also rotating, as schematically indicated in Fig. 2a.

The dicing operation involved the use of multiple wheel arbors fitted to an automatic SEMITRON machine as shown in Fig. 2b and Fig. 3. In this instance the slice or disc is clamped in a fixture and is sawn three times, so that cubes of correct size are obtained.

A number of parameters have been investigated to obtain optimum slicing and dicing conditions. The most important are :

- choice of the cutting blade material and thickness,
- spindle speed, relative rotational direction, lathe chuck speed and feed for dicing,
- coolant composition and effectiveness of coolant distribution.

The most practical results are reported in Tables I, II and III.

As a results of this investigation we came to the conclusion that, compared to other more conventional sample preparation techniques, this sawing technique permits high production rates (10 x quicker) with close dimensional tolerances (max. mass variation for 1 g samples : 2 %).

2. SURFACE TREATMENTS

The resulting cubes present burrs at one face as a result of the dicing procedure as can be seen on Fig. 4a.

Removal of these burrs by chemical etching of important amount of Mo-cubes in batch operation is possible but introduces erratic surface contamination due to redeposition of soils.

For this reason barrel finishing has been chosen for deburring Mo-cubes. Barrel finishing involved the agitation of the cubes in contact with an abrasive medium. In this case 50 % random shaped Al_2O_3 pieces (size 2 to 4 mm) mixed with 50 % fine Al_2O_3 powder of 240 grit in 2 times its volume of water are used as an abrasive medium. A TURBULA (WAB Maschinen Fabrik, Basel 5, Schweiz) shaking mixer with a P.V.C. container is used as barrel finishing machine as shown in Fig.5. Batches of 150 Mo cubes are perfectly deburred after 4 hours in this equipment as can be seen in Fig. 4b.

For Ti and TiAl6V4-cubes the removal of burrs could not be achieved by barrel finishing. The burrs were rounded over instead of be removed. We therefore preferred to use a basket immersion chemical etching technique (4 Vol HNO_3 + 1 Vol HF at 20°C during 20 s. Rinsing with H_2O). For Ti and TiAl6V4 there is no soil redeposition onto the cubes during chemical etching. Batches of 50 cubes can be processed in this way.

The above described mass production technique following the scheme Fig. 6, gives similar residual oxygen contents after appropriate chemical etching as the piece by piece preparation by turning on a lathe.

3. CONCLUSION

The production of great numbers of reference samples for oxygen in Mo, Ti and TiAl6V4 by slicing and dicing, and subsequent surface cleaning has been described.

Three BCR reference materials have been prepared :

- a) BCR-N° 23 "Oxygen in Molybdenum" ($14.7 \pm 2.1 \mu\text{g/g}$), which is available in bottles containing twenty five 1 g cubes ⁽¹⁾
- b) BCR-N° 24 "Oxygen in unalloyed Titanium" ($608 \pm 23 \mu\text{g/g}$), which is available in bottles containing twenty five 0.2 or 0.4 g samples ⁽²⁾ as shown in Fig. 7.
- c) BCR-N° 59 "Oxygen in Titanium-aluminium-vanadium alloy TiAl6V4" ($1750 \pm 70 \mu\text{g/g}$) which is available in bottles containing twenty five 0.2 g samples ⁽³⁾

A limited number of samples of all these reference materials are also available as 26 mm diameter discs of 9 mm thickness, intended for 14 MeV neutron activation analysis, prepared by turning on a lathe.

The described method allowed a fast, reproducible and economic production of high quality samples with mass variations limited to 1 - 2 % and residual surface oxygen contents which are, after appropriate etching, comparable to those of samples prepared by classical techniques.

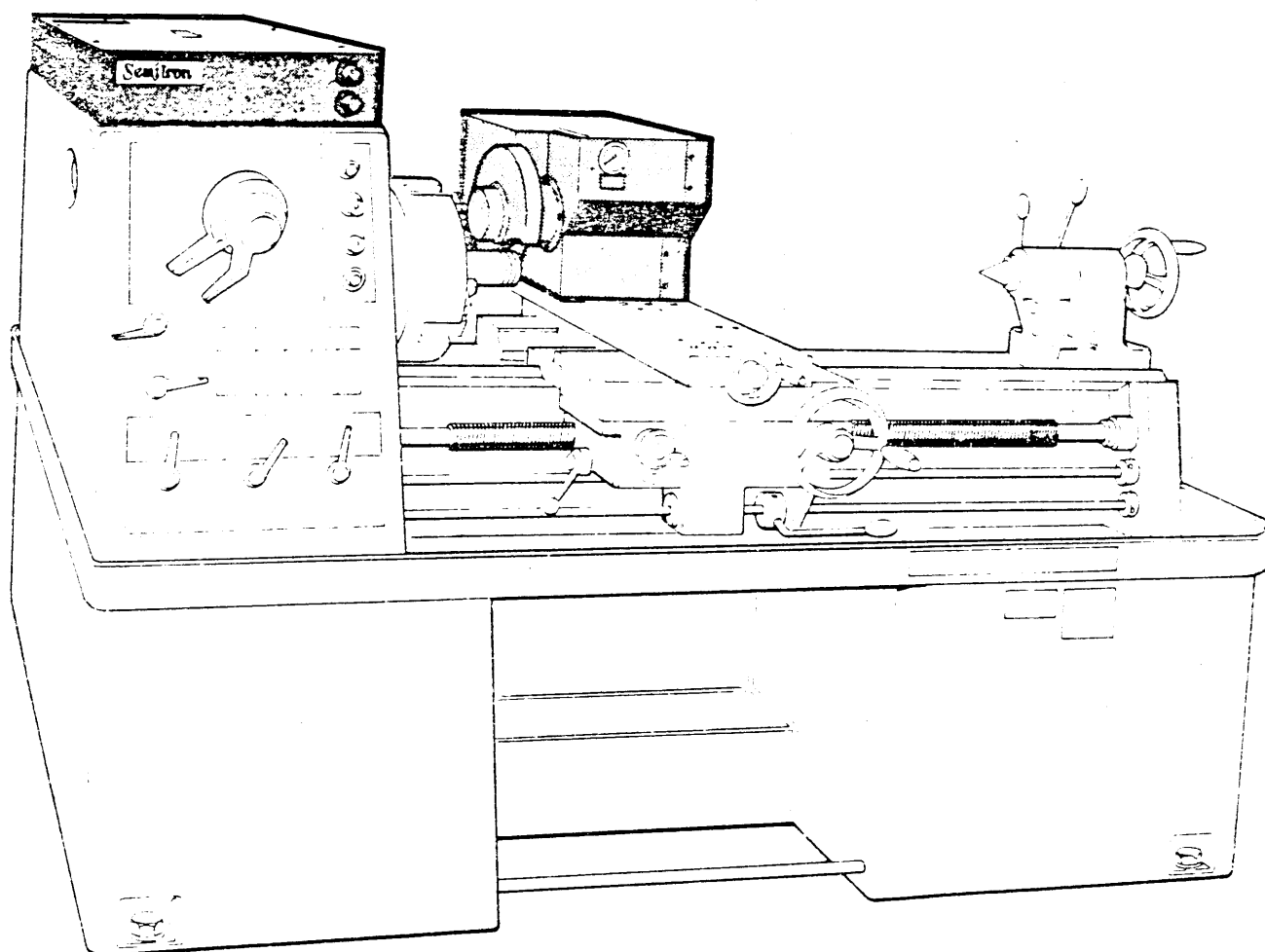


Fig. 1 : Slicing attachment (ROTO-SEMITRON) mounted on a lathe.

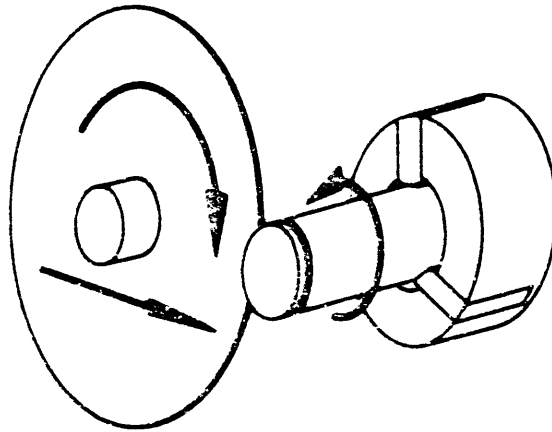


Fig. 2a Principle of slicing.

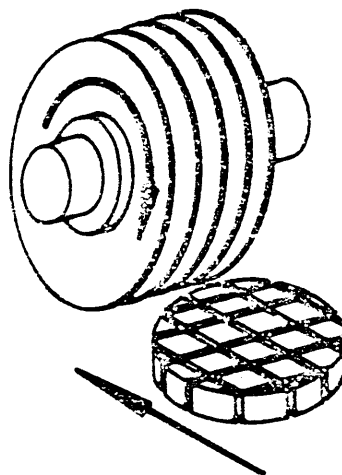


Fig. 2b Principle of dicing.

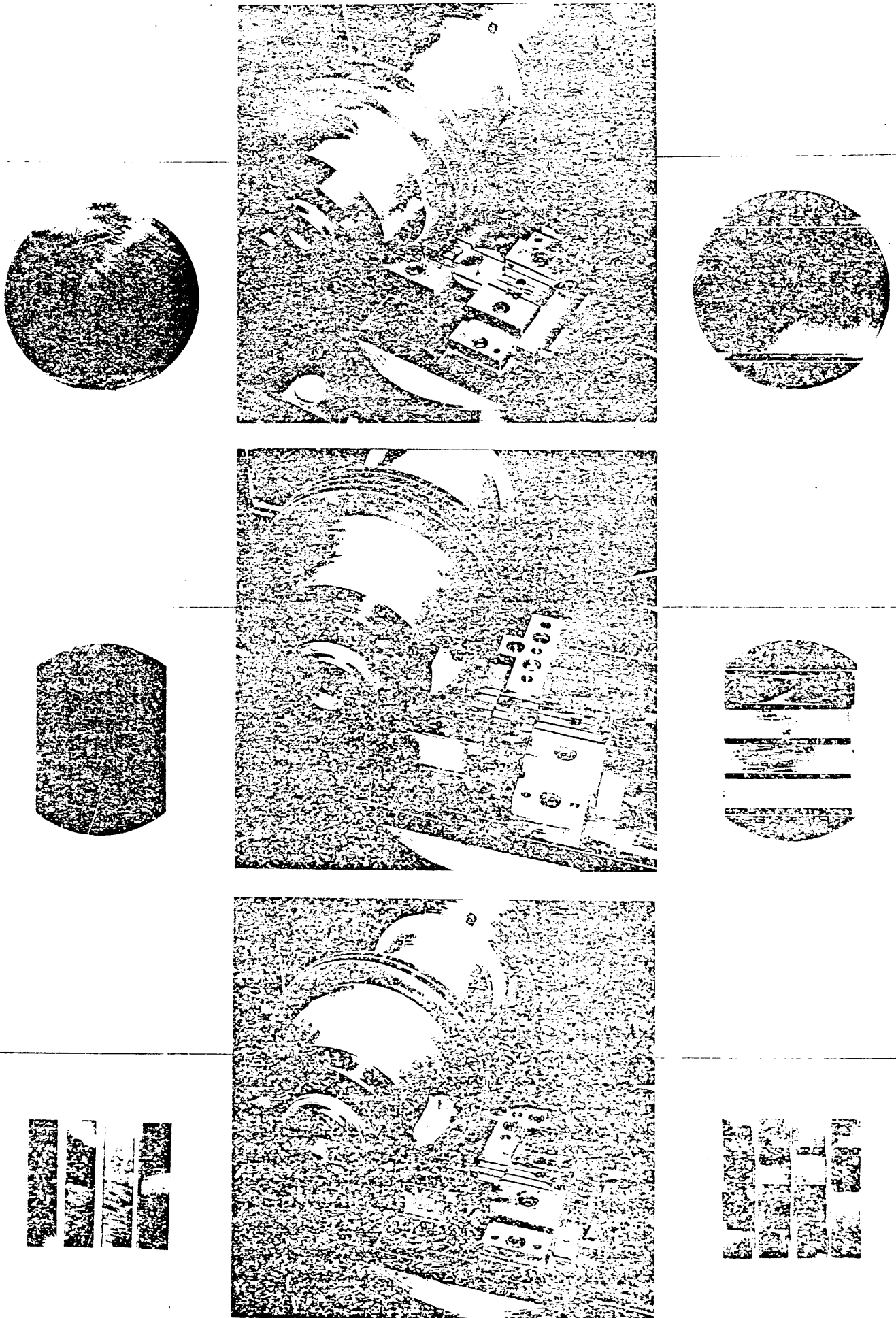


Fig. 3 : Dicing machine with multiple cutting wheels (Semitron Ltd.)



Fig. 4.a : Burrs as a result of the dicing.

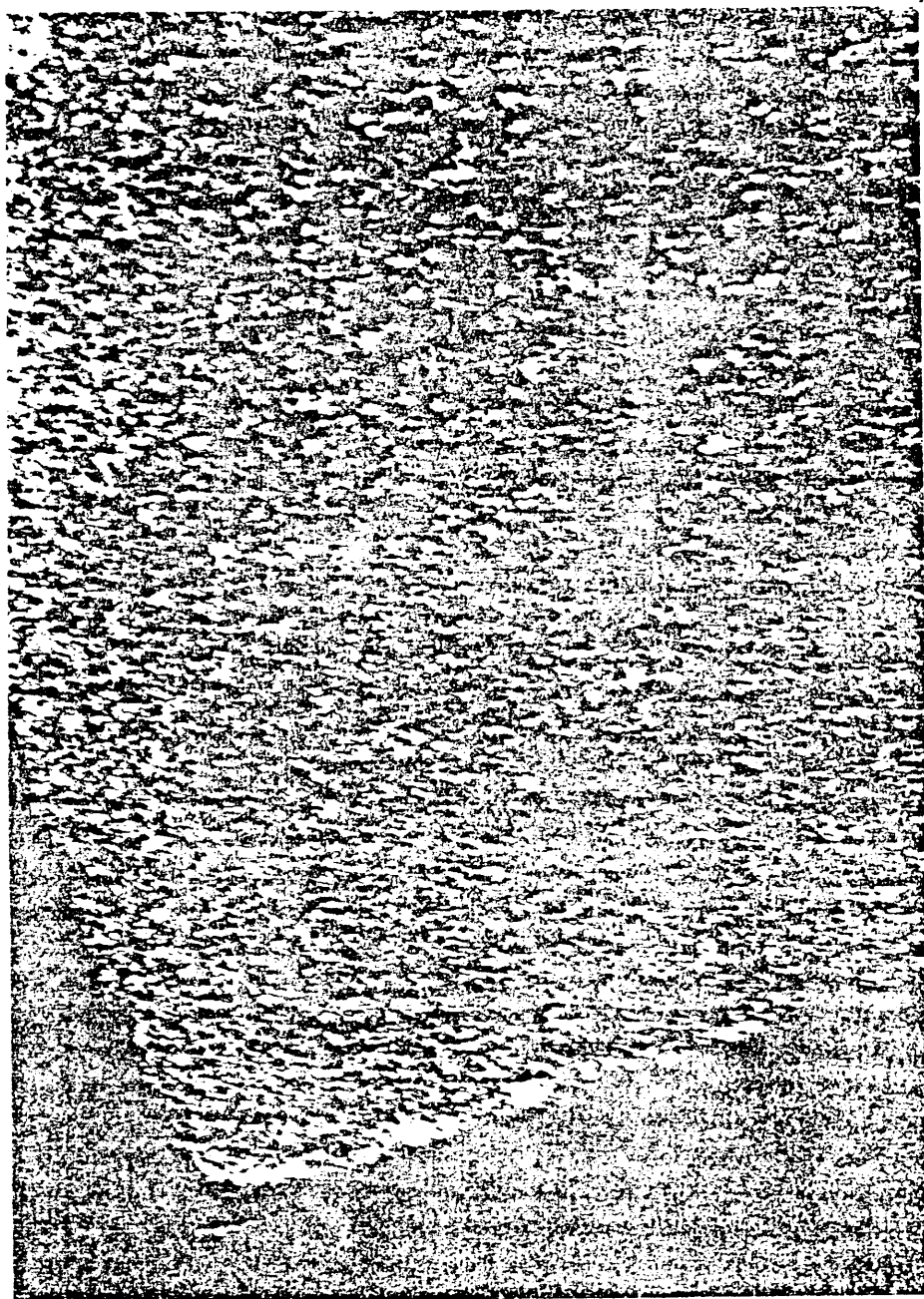


Fig. 4.b : Deburred cubes after barrel finishing.

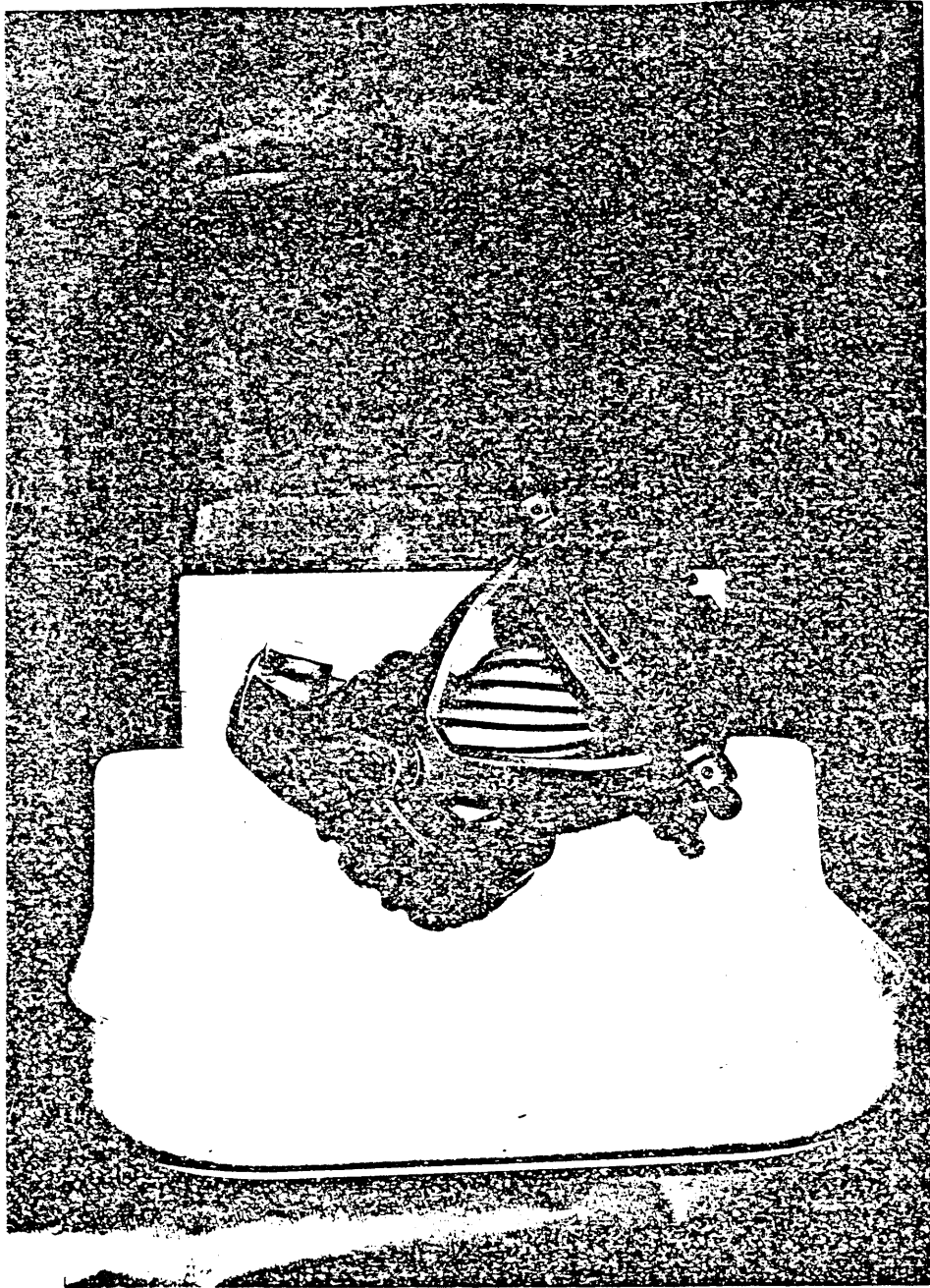


Fig. 5 : Barrel finishing in a shaking mixer
TURBULA

TABLE I : Slicing and dicing conditions for Mo

SLICING

Type	Cutting blade		Roto	Lathe		Radial wear/cut (mm)
	Size (mm)			Chuck Speed (rpm)	Feed (mm/revol)	
	Ø	th				
★ A 240 NB 60	150	0.4	8750	80	0.025	+ 3

Coolant

Current water

★ Phenolic Resin bonded Al_2O_3 wheel

DICING

Cutting blade			Multicut on Semitron Auto 2000			
Type	Size (mm)		Number of blades	Spindle Speed (rev/min)	Feed Speed (mm/min)	Radial wear/cut (mm)
	Ø	th				
★★ A 150 QR 12 DT	101.6	0.5	2	8000	20	0.1

Coolant

Composition :

80 Vol Water
+ 1 Vol Miracol 80
(Castrol)

Feed : 3 l/min

★★ A 150 QR 12 DT : Rubber bonded Al_2O_3

TABLE II : Slicing and dicing conditions for unalloyed Ti

SLICING

Type	Cutting blade		Roto	Lathe		Radial wear/cut (mm)
	Size (mm)	th		Spindle Speed (rpm)	Chuck Speed (rpm)	
★ GC 150 NB 34	150	0.5	8750	80	0.025	+ 3

Coolant

Current water

★ GC 150 NB 34 : Phenolic Resin bonded green SiC wheel

DICING

Type	Cutting blade		Multicut on Semitron Auto 2000				Radial wear/100 cuts (mm)
	Size (mm)	th	Number of blades		Spindle Speed (rev/min)	Feed Speed (mm/min)	
★★ GSD Type GIA801 SD 100R 13B01	101.6	0.5	2	5	8000	20	0.1

Coolant

Composition :

80 Vol Water
+ 1 Vol Miracol 80
(Castrol)

Feed : 3 l/min

★★ GSD Type GIA801SD100R 13B01 : Phenolic Resin bonded mixture of diamond and SiC wheel

TABLE III : Slicing and dicing conditions for TiAl6V4

SLICING

Cutting blade				Roto	Lathe		Radial wear/cut (mm)
Type	Size (mm)		Chuck Speed (rpm)		Feed (mm/revol)		
	Ø	th					
★ GC 80 NB 34	150	0.5	8750	80	0.025	+ 2	

Coolant

Current water

★ GC 80 NB 34 : Phenolic Resin bonded green SiC

DICING

Cutting blade			Multicut on Semitron Auto 2000				
Type	Size (mm)		Number of blades		Spindle Speed (rev/min)	Feed Speed (mm/min)	Radial wear/100 cuts (mm)
	Ø	th					
★★ GSD Type G1A801 SD 100R 13B01	101.6	0.5	2	5	8000	20	0.1
				3			

Coolant

Composition :

80 Vol Water
+ 1 Vol Miracol 80
(Castrol)

Feed : 3 l/min

★★ GSD Type GIA801SD100R 13B01 : Phenolic Resin bonded mixture of diamond and SiC wheel

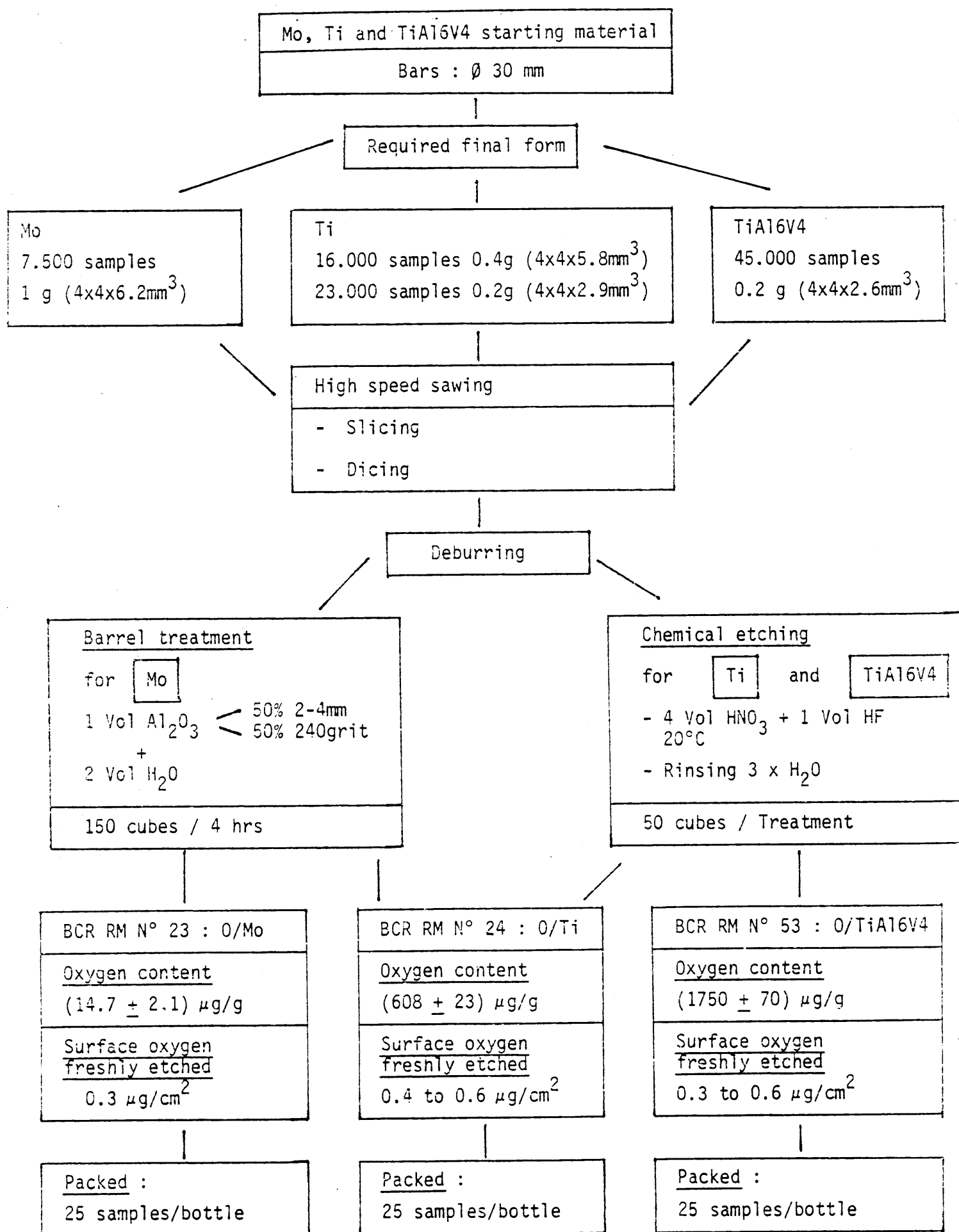




Fig. 7 : Reference Material BCR N° 24 "Oxygen in Titanium".

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BCR information

THE CERTIFICATION OF NITROGEN IN TITANIUM AND TITANIUM-ALUMINIUM VANADIUM ALLOY (Ti6Al4V) (BCR Nrs 24 and 59)

C. VANDECASTEELE

Institute of Nuclear Sciences
Rijksuniversiteit Gent
Gent, Belgium

E. COLINET

Community Bureau of Reference
Brussels, Belgium

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Abstract

The experimental procedures used for the centrifugation of nitrogen in titanium and titanium-aluminium-vanadium alloy are described. The mass fraction of oxygen has already been certified in each of these materials. Samples were analysed by nine laboratories using five different analytical methods : heat extraction, the Kjeldahl method and proton, fast neutron and photon activation analysis.

Sample preparation, the analytical methods used and the statistical approach employed to analyse the data are presented.

The certified values are 117 $\mu\text{g/g}$ with an uncertainty of 13 $\mu\text{g/g}$ and 172 $\mu\text{g/g}$ with an uncertainty of 27 $\mu\text{g/g}$ for nitrogen in titanium and titanium-aluminium-vanadium alloy, respectively.

Résumé

Les techniques expérimentales utilisées pour la certification de l'azote dans le titane et l'alliage titane-aluminium-vanadium sont décrites dans ce rapport. La fraction massique d'oxygène a déjà été certifiée dans chacun de ces matériaux.

Des échantillons ont été analysés par neuf laboratoires utilisant cinq méthodes d'analyse différentes : fusion réductrice, méthode de Kjeldahl, analyse par activation par protons, par neutrons rapides et par photons.

La préparation des échantillons, les méthodes d'analyse employées et l'approche statistique utilisée pour l'évaluation des résultats sont présentées.

Les valeurs certifiées obtenues à l'issue de la campagne d'analyses sont 117 $\mu\text{g/g}$ avec une incertitude de 13 $\mu\text{g/g}$ et 172 $\mu\text{g/g}$ avec une incertitude de 27 $\mu\text{g/g}$ respectivement pour l'azote dans le titane et dans l'alliage.

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5. Analytical techniques	6
6. Results and statistical evaluation	10
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1. INTRODUCTION

Nitrogen has a strong influence on the mechanical properties of titanium and titanium alloys. The mass fraction of nitrogen is therefore usually specified in sale contracts.

Industrial laboratories often determine nitrogen and oxygen in one single operation by heat extraction. Therefore, it was decided to certify CRM n° 24 (Oxygen in titanium) and CRM n° 59 (Oxygen in titanium-aluminium-vanadium alloy - Ti6Al4V) also for nitrogen. The certification of oxygen in these materials was described by Pauwels (1) (2).

2. CERTIFICATION PROCEDURE

The work was carried out by a group of laboratories using various analytical methods. The possible sources of inaccuracies were studied and discussed extensively by the participants and measures were taken to reduce them. After the last analysis campaign, the details of the methods and the individual results were thoroughly discussed with all the participants.

3. PARTICIPANTS

- Bundesanstalt für Materialprüfung, Berlin, Federal Republic of Germany (H) (P)
- CEZUS, Usine de Venthon, Albertville, France (H)
- CNRS, GARNAC, Service du Cyclotron, Orléans, France (F)
- JRC, Central Bureau for Nuclear Measurements, Geel, Belgium (SP)
- Groupe de Physique des Solides de l'Ecole Normale Supérieure, Paris, France (S)
- Krupp Forschungsinstitut, Essen, Federal Republic of Germany (K)
- Max - Planck Institut für Metallforschung, Schwäbisch Gmünd, Federal Republic of Germany (K)

- Universität Frankfurt, Frankfurt, Federal Republic of Germany (H)
- Metallwerk Plansee GmbH, Reutte, Tirol, Austria (H)
- Rijksuniversiteit Gent, Instituut voor Nucleaire Wetenschappen, Gent, Belgium (C)
- Ugine Aciers, Ugine, France (SP)
- Université de Liège, Institut de Physique Nucléaire, Liège, Belgium (S)

(K) : Kjeldahl method;
(H) : Heat extraction;
(C) : Charged particle activation analysis;
(F) : Fast neutron activation analysis;
(P) : Photon activation analysis;
(S) : Surface analysis by nuclear methods;
(SP) : Sample preparation.

4. MATERIAL, HOMOGENEITY STUDY

4.1. Starting material

The preparation of the starting material was described by Pauwels (1) (2).

4.2. Reference material

Three types of reference samples are available :

- discs of 26 mm diameter and 9 mm thick (Ti, Ti6Al4V);
- bottles containing 25 cubes of 0,2 g (Ti, Ti6Al4V);
- bottles containing 25 cubes of 0,4 g (Ti only).

The preparation of the samples was described elsewhere (1) (2).

4.3. Homogeneity study

In order to assess the homogeneity of the reference materials, the heat extraction method was applied, since it is fast and one of the most precise methods available.

Laboratory H 1 analysed 18 titanium samples (0.2 g) and 15 Ti6Al4V samples (0.2 g). One sample was taken from every one of the original rods from which the samples were prepared. This corresponds to the numbering 13 - 32 in Table 1. The coefficients of variation (4.1 and 5.2 % for Ti and Ti6Al4V resp.) are of the same order of magnitude as the expected repeatability of the heat extraction method at the concentration level considered.

Table 1 : Homogeneity control for nitrogen in titanium and titanium-aluminium-vanadium alloy by heat extraction (Lab H 1)

<u>Rod n°</u>	<u>Ti</u>	<u>Rod n°</u>	<u>Ti6Al4V</u>
	<u>Result (µg/g)</u>		<u>Result (µg/g)</u>
13	123	13	173
14	116	14	182
15	112	15	158
16	114	16	174
18	122	17	181
19	115	18	182
20	114	19	171
22	124	21	157
23	116	23	165
24	111	24	171
25	118	25	184
26	125	28	174
27	121	29	175
28	115	30	181
29	116	32	160
30	127		
31	119		
32	113		
Mean value (µg/g)			172.5
Standard deviation (µg/g)			9.0

It was thus concluded that, as no important material inhomogeneity has been detected within the precision limits of the heat extraction method, the batch was suitable for certification

5. ANALYTICAL TECHNIQUES

5.1. Determination of surface nitrogen

To perform the determination of bulk nitrogen, the surface nitrogen must be reduced to a low and reproducible level.

A number of different surface treatments were studied and the amount of residual surface nitrogen was determined by measurement of protons and α -particles from the $^{14}\text{N}(\text{d}, \text{p}_5)^{15}\text{N}$, $^{14}\text{N}(\text{d}, \text{p}_4)^{15}\text{N}$, $^{14}\text{N}(\text{d}, \alpha_1)^{12}\text{C}$ and $^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$ reactions. The method is described in some detail elsewhere (3).

It appeared that satisfactory results were obtained by chemical etching in the following way :

- dip the sample for 60 s in a mixture of 4 volumes of nitric acid (min 65 %; $d = 1.4$) and 1 volume of hydrofluoric acid (min 40 %) at 20° C;
- immerse successively in 3 vessels with distilled water and 3 vessels with methanol;
- dry in a stream of warm air (60°).

From a freshly etched sample the residual surface nitrogen is $< 0.1 \text{ } \mu\text{g}/\text{cm}^2$ (Ti) and $0.1 - 0.3 \text{ } \mu\text{g}/\text{cm}^2$ (Ti6Al4V) (3).

5.2. Determination of bulk nitrogen

Nitrogen was determined using heat extraction and the Kjeldahl method, two methods commonly applied in industry, and using proton, fast neutron and photon activation, nuclear methods employed by some research laboratories.

5.2.1. Heat extraction (Labs H1 to H4)

Both the helium carrier gas and the vacuum technique were used. Experimental details are given in Table 2. All laboratories applied a "sandwich-technique", whereby the sample and the platinum bath metal are packed together in platinum foil. Before the analysis the samples were etched as described in 5.1. No corrections were applied, since under these conditions the influence of surfaces nitrogen is negligible.

Table 2 : Experimental conditions for heat extraction

<u>Laboratory</u>	<u>Technique</u>	<u>Extraction temperature (°C)</u>
H 1	Helium carrier	2000
H 2	Helium carrier	2060
H 3	Helium carrier	2350
H 4	Vacuum	2300

<u>Sample mass (g)</u>	<u>Bath metal</u>	<u>Bath metal to sample ratio</u>	<u>Blank (µgN)</u>
0.20-0.25	Pt	20/1	1
0.20	Pt	50/1	
0.20	Pt	25/1	0.5
0.20	Pt	25/1	6

5.2.2. Kjeldahl method (Labs K1 and K2)

Before the analysis, the samples were chemically etched as described in 5.1.

Laboratory K 1 dissolved 0.4 g of sample in a mixture of 10 ml of water and 5 ml of hydrofluoric acid (40 %). After distillation of ammonia according to Kjeldahl, ammonia was determined photometrically with Nessler reagent. The blank value correspond to 2 µg of nitrogen and was subtracted.

Laboratory K 2 dissolved 0.4 g of sample in 2.5 ml of a mixture of 10 volumes of hydrofluoric acid and 1 volume of perchloric acid by heating for 8 hours to 140° C in a PTFE -lined steel bomb. The micro-Kjeldahl distillation technique described by Werner and Tölg (4) was applied (Distillation time = 45 min). The ammonia was determined by coulometric titration. The blank value corresponded to 3.3 µg of nitrogen and was subtracted.

5.2.3. Proton activation analysis (Lab C1)

The method is based on the $^{14}\text{N} (p, n) ^{14}\text{O}$ reaction, threshold energy = 6.3 MeV. ^{14}O has a 70.5 s half-life and emits γ -rays of 2313 keV. For proton energies below 22 MeV the method is free from nuclear interferences.

The samples and the references, covered with a thin copper foil serving as a beam intensity monitor via the $^{63}\text{Cu} (p, n) ^{63}\text{Zn}$ reaction, were irradiated with 15 MeV protons. After the irradiation the samples were etched in a mixture of equal volumes of hydrofluoric (50 %) and nitric (14 M) acids to remove a 8-14 mg of metal per cm^2 . The ^{14}O activity was measured with a Ge (Li) γ -spectrometer. Nylon-6 was used as a reference.

Its nitrogen concentration had been checked versus that of NaNO_3 and was in good agreement with that expected from the formula $\text{C}_6\text{H}_{11}\text{NO}$.

Ricci's method (5) using the stopping power data of Andersen and Ziegler (6) was used for the calculation of the results.

5.2.4. Fast neutron activation analysis (Lab F1)

The method is based on the $^{14}\text{N} (n, 2n) ^{13}\text{N}$ reaction. ^{13}N is a pure β^+ -emitter with a 10.0 min half-life.

25 MeV deuterons were sent on a beryllium target to produce fast neutrons according to the $^9\text{Be} (d, n) ^{10}\text{B}$ reaction. The samples were irradiated with fast neutrons for 10 min at a 30 µA beam intensity.

After the irradiation, the sample was etched in a mixture of 2 volumes of hydrofluoric acid, 3 volumes of nitric acid and 3 volumes of acetic acid to remove a surface layer of at least 20 μm , dried and weighed. The sample was dissolved in a mixture of 8 volumes of hydrofluoric acid, 1 volume of sulphuric acid and 30 volumes of water, transferred to a steam distillation apparatus and neutralized with excess of 10 M sodium hydroxide. Ammonia was then steam distilled and measured with a Ge (Li) detector).

Diammoniumhydrogenphosphate was used as a reference. The samples and the references were irradiated separately, sandwiched between aluminium foils serving as flux monitors via the $^{27}\text{Al} (n, \alpha) ^{24}\text{Na}$ reaction. The concentrations were calculated using the ^{13}N activities in the distillate and in the reference, normalized to the same weights and to the same ^{24}Na activities of the flux monitors. The different detection efficiencies for the measurements of the sample (distillate) and the reference (pellet) were taken into account.

5.2.5. Photon activation analysis (Lab P1)

Photon activation analysis for nitrogen is based on the $^{14}\text{N} (\gamma, n) ^{13}\text{N}$ reaction. ^{13}N is a pure β^+ -emitter with a 20.4 min half-life.

Photons were produced by irradiation of a suitable target with 30 MeV electrons (beam intensity = 150 μA). After irradiation for 10 min, the samples (420 mg) were etched in a mixture of equal volumes of hydrofluoric and nitric acids at 95° C for 5 s. The weight loss was ca. 70 mg.

^{13}N was isolated as nitrogen gas by heat extraction. A "sandwich technique" with addition of 8 - 10 g of platinum was applied. The extraction temperature was 2180° C and the helium flow 0.4 l/min. Carbon monoxide was oxidised to carbon dioxide by Schütze reagent and the carbon dioxide trapped by ascarite. Nitrogen reacted with titanium at 1020° C to give titanium nitride.

The ^{13}N activity was measured with 2 Na I (TL) detectors in coincidence.

Boron nitride was used as a reference.

6. RESULTS AND STATISTICAL EVALUATION

The results obtained by all the participating laboratories are given in Tables 3 and 4. In figs. 1 and 2 the series of results (each series corresponds to the analysis carried out in one laboratory using one particular analytical technique) are represented in the form of bar graphs. The length l of the bars corresponds to the 95 % confidence interval of the mean values of the series, i.e.

$$l = 2 \cdot t_{\alpha/2}^{v_i} \cdot s_i / \sqrt{n_i}$$

where $t_{\alpha/2}^{v_i}$ is the value of the Student's distribution for $v_i = n_i - 1$ degrees of freedom and significance level $\alpha = 0.05$; $s_i / \sqrt{n_i}$ is the standard error of the mean of the i th set, n_i being the number of replicate measurements of the set.

In order to detect any possible effect due to a particular analytical method, the results have been grouped according to the techniques. No obvious method-dependent systematic effect appeared from the available results.

Oneway analysis of variance (F-test) was applied to the results of the certification campaign to determine and assess what was the major source of variation between the results.

A value for the Snedecor F-variable (7) was obtained from the ratio of the between- to the within-laboratory variances. When the value of this variable was larger than the theoretical value (at the 0.01 level of significance), a dominant variability effect could be ascribed to the difference between laboratories. The certified value was then calculated as the mean of the laboratory means, i.e. as

$$\bar{x} = \frac{1}{p} \sum_{i=1}^p \bar{x}_i$$

where p is the number of accepted laboratory series;
 $\bar{x}_i$ is the mean result obtained by the i th laboratory. The 95 % confidence interval of the certified value is given by

$$\bar{x} \pm t_{1-\alpha/2}^{\nu} \cdot s / \sqrt{p}$$

where $t_{1-\alpha/2}^{\nu}$ is the value of the Student's distribution for $\nu = p - 1$ degrees of freedom and a significance level of $\alpha = 0.05$, $s/\sqrt{p}$ is the standard error of the mean $\bar{x}$.

When the F-value was smaller than the theoretical value showing that no dominant "laboratory" effect was detectable, the certified value was calculated as the overall mean of the individual results, i.e. as

$$\bar{x} = \frac{1}{N} \sum_{j=1}^N x_j$$

where N is the total number of accepted results; x_j is the j th result (whichever the laboratory).

Table 3 : Nitrogen in titanium

<u>Lab</u>	<u>Replicates</u>					<u>Mean</u>	<u>St. Dev.</u>
H 1	123	116	112	114	122	117.8	4.8
	115	114	124	116	111		
	118	125	121	115	116		
	127	119	113				
H 2	115	112	112	115	122	115.6	4.5
	117	110	122				
H 3	123	118	132	125	124	123.7	6.3
	125	109	116	128	115		
	114	134	122	129	130		
	129	126	116	123	128		
	123	125	119	122			
H 4	118	124	123	97	116	119.5	7.8
	123	123	122	128	132		
	118	120	117	118	122		
	111						
K 1	116	119	122	123	117	121.4	3.6
	125	125	124				
K 2	111	114	113	112	109	112.6	2.3
	115	111	116				
C 1	103	118	103	113	109	111.8	12.3
	93	130	125				
F 1	101	96	103	106	108	106.9	6.6
	113	114	114				
P 1	101	127	122	121	124	126.7	15.9
	132	137	144	144	149		
	105	112	129	145	103		

Table 4 : Nitrogen in Ti6Al4V

<u>Lab</u>	<u>Replicates</u>					<u>Mean</u>	<u>St. Dev.</u>
H 1	173	182	158	174	181		
	182	171	157	165	171		
	184	174	175	181	160	172.5	9.0
H 2	166	179	187	169	193		
	183	185	171			179.1	9.6
H 3	166	172	170	156	170		
	158	186	175	168	175		
	157	173	183	182	162		
	168	167	174	164	165		
	176	170	174	171		170.5	7.8
H 4	176	177	155	185	193		
	153	168	160	183	183		
	175	181	172	208	163		
	189					176.3	14.5
K 1	168	167	180	167	179		
	174	173	175			172.9	5.2
K 2	180	180	146	160	138		
	174	184	177	142	164		
	172					165.2	16.5
C 1	172	171	175	166	176		
	175	168	187			173.8	6.4
F 1	163	163	163	167	170		
	173	173	175			168.4	5.0
P 1	159	152	188	182	197		
	150	172	186			173.7	17.9

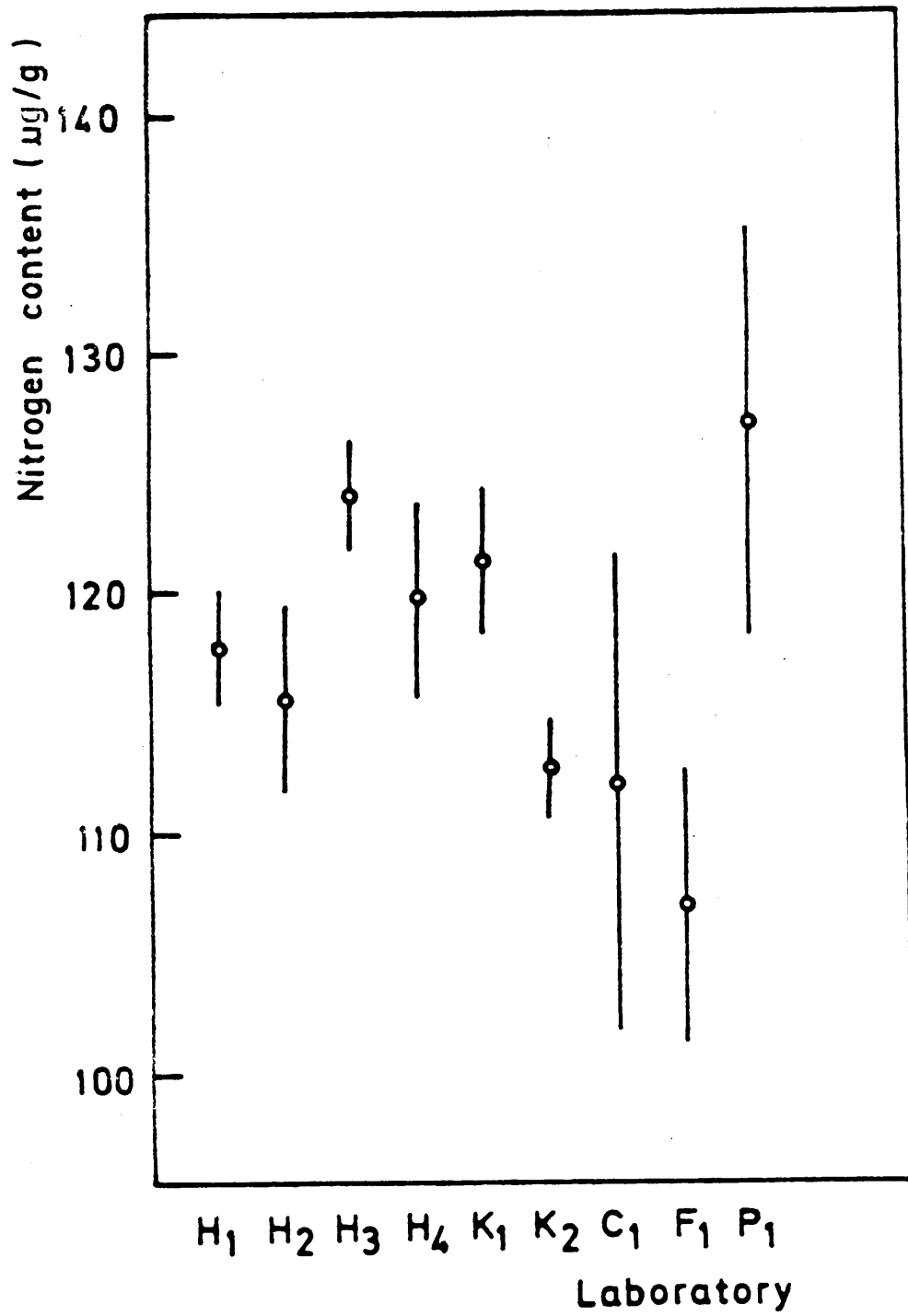


Fig. 1 : Nitrogen in titanium

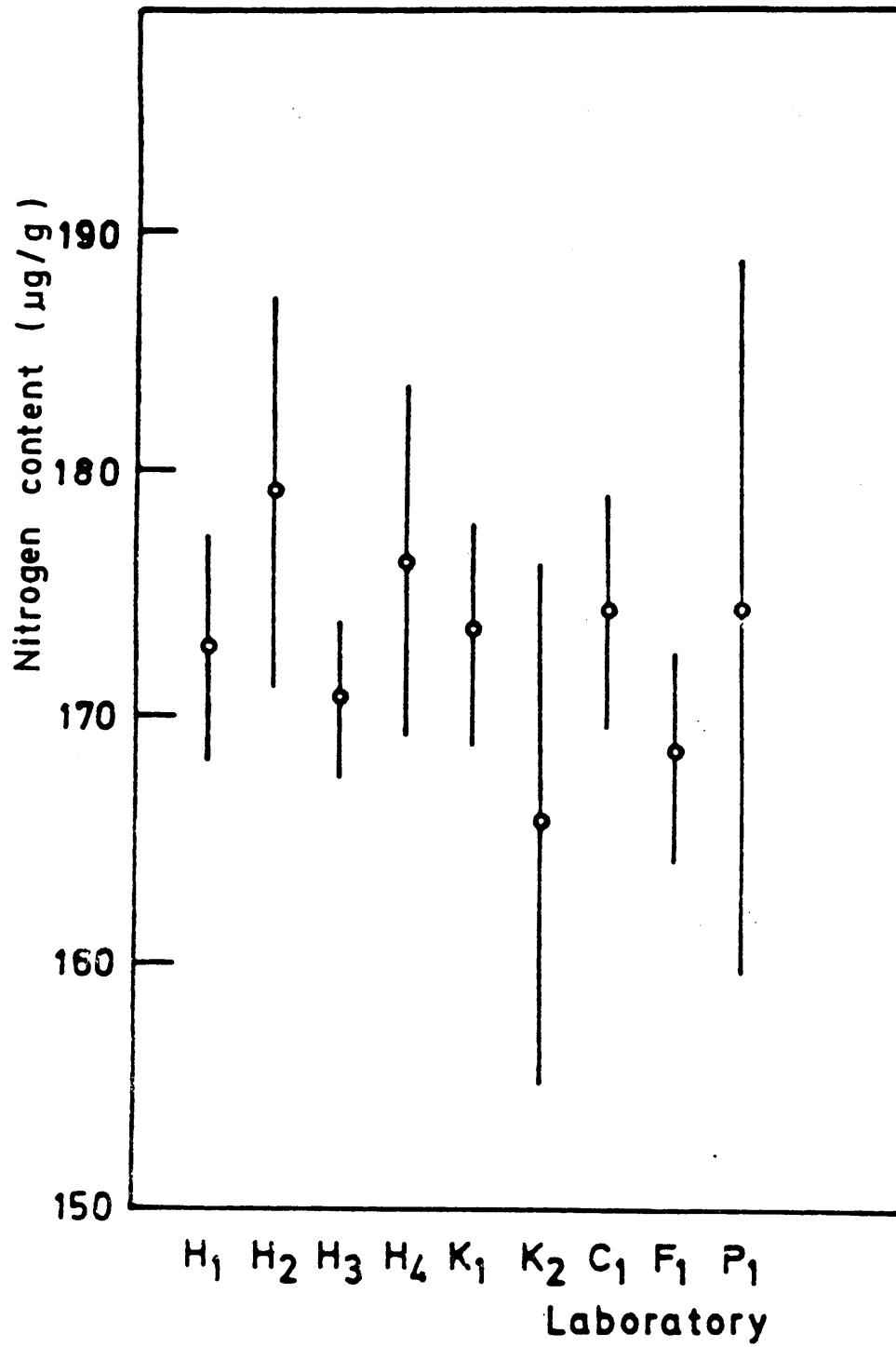


Fig. 2 : Nitrogen in Ti6Al4V

The corresponding 95 % confidence interval is given by

$$\bar{x} \pm t_{1 - \alpha/2}^Y \hat{s}/\sqrt{N}$$

where $\hat{s}/\sqrt{N}$ is the standard deviation of the mean $\bar{x}$.

These two approaches were used; the former for the results of the determination of nitrogen in titanium and the latter for the results of the determination of nitrogen in the titanium alloy.

Nitrogen in titanium

Only the mean values provided by the laboratories were used for the calculation of the certified value.

The series of results C1 and P1 were detected as outliers of variance by the Cochran Test. However, as the corresponding $s_i/\sqrt{n_i}$ are smaller than the standard deviation of the certified value they were kept for the subsequent calculation. On the whole, the laboratories having achieved different repeatability performance, the values given for s_w should be taken as an indicative figure. No outlier for mean was detected by the Dixon Test.

The mean value of the series were found normally distributed as assessed by the Kolmogorov-Smirnov-Lilliefors Test.

A summary of the results obtained from the statistical analysis is given in Table 5.

Nitrogen in Ti6Al4V

The whole set of individual results has been used for the calculation of the certified value.

Among the individual results, no single value appeared to be outlying as appeared from a t-test adapted to this kind of check.

Table 5 : Certification campaign for the determination of nitrogen in titanium

Number of accepted laboratory series	P = 9
certified value	M = 117 µg/g
95 % confidence interval	± 5 µg/g
Within-laboratory std. dev.	S _w = 8.4 µg/g
between-laboratory std. dev.	S _B = 5.4 µg/g
value of the variable of Snedecor	F = 6.19

$$F_{0.95}^{\text{theor}} = 2.0$$

$$F_{0.99}^{\text{theor}} = 2.7$$

The distribution of the individual results can be accepted as normal. A summary of the results of the statistical evaluation is given in Table 6.

Table 6 : Certification campaign for the determination of nitrogen in Ti6Al4V

Number of accepted individual results	N = 106
certified value	M = 172 µg/g
95 % confidence interval	± 2 µg/g
Within-laboratory std. dev.	S _w = 11.1 µg/g
between-laboratory std. dev.	S _B = 2.2 µg/g
value of the variable of Snedecor	F = 1.44

$$F_{0.95}^{\text{theor}} = 2.0$$

$$F_{0.99}^{\text{theor}} = 2.7$$

Statement of the uncertainty

For the statement of the uncertainty, it seemed unrealistic to use the 95 % confidence interval of the certified mean as this would make no allowance for a possible material inhomogeneity.

The certification campaign gave the following estimates of the certified values :

for N in titanium	117 µg/g
for N in Ti6L4V	172 µg/g

The uncertainties were established to take into account sample-to-sample variation. They were derived from the results of the homogeneity study (sect. 4.3.) and expressed in terms of statistical tolerance intervals (8). The spreads of values given by such intervals provide indeed for more reliable estimates of the overall uncertainties of the measurement results when the absence of inhomogeneity is not definitely proven.

When a few samples have been analysed, statistical tolerance intervals can be constructed to include, at the 95 % level of confidence, 95 % of the values of the whole population of samples. The computation is based on the following equation :

$$\bar{x}_N \pm k[N, p-1; 1-\alpha] s_N$$

where $\bar{x}_N$ is the arithmetic mean of the N measured samples and s_N is the corresponding estimate of the standard deviation. k is a statistical factor which takes account of the level of significance ($\alpha = 0.05$) at which the interval is stated, of the number of samples N and of the proportion p of the population values (i.e. 95 %) that one wishes to include within the limits of the intervals

It must be emphasized that in this case the values obtained for the standard deviations (s_N) by measuring a few samples by the heat extraction technique include both analytical variability, due

to that particular method, and possible material inhomogeneity. They are thus overestimating sample-to-sample variations.

The above equation was applied to the data reported in Table 1 after having checked that the results were normally distributed. The computed intervals located the mean values within the following symmetrical limits :

for N in titanium	$\pm 13 \mu\text{g/g}$
for N in Ti6Al4V	$\pm 27 \mu\text{g/g}$

The results of the homogeneity study thus provided for a statement of the uncertainty as a 95 %, 95 % statistical tolerance interval while the data of the certification campaign were used for the assessment of the accurate mean value.

When combined, those results lead to the following conclusions :

	Certified value	Uncertainty
	(expressed in $\mu\text{g.g}^{-1}$)	
N in titanium	117	± 13
N in Ti6Al4V	172	± 27

This statement of the uncertainty gives the user confidence (at the 95 % level) that at least 95 % of the samples have a value which lies within the limits of the interval.

Another result provided by the certification campaign which might prove useful is the overall estimate of the dispersion of the results on one single sample. It is given by s_R which derives from the combination of the between- and the within- laboratory variances as :

$$s_R^2 = s_B^2 + s_W^2$$

From Tables 5 and 6, the values of s_R were the following :

for N in titanium $s_R = 10 \mu\text{g/g}$

for N in Ti6Al4V $s_R = 11 \mu\text{g/g}$

Should the user employ n samples, the corresponding estimate of the dispersion of his results should be calculated from the following expression :

$$\sqrt{s_B^2 + s_W^2/n}$$

These kinds of expressions provide the user with a means to estimate the various components (random and systematic) which affect the reproducibility of his method.

7. REFERENCES

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