Determination of Gaseous Impurities in Zirconium and Zirconium Alloys

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Summary: Physical and mechanical properties of zirconium metal and its alloys such as resistance to corrosion in hot water, transparency to thermal neutron show its suitability as construction material in nuclear reactors as fuel cladding and pressure tube material in water cooled nuclear reactors. Presence of gaseous impurities like hydrogen, nitrogen and oxygen affect mechanical and corrosion resistance properties of zirconium metal and its alloys. For the production control and metallurgical evaluation of such effects, accurate and precise determination of these impurities is essential. Some selected samples of zirconium metal, its alloys, sponge zirconium, and ingot have been analyzed for the estimation of hydrogen, oxygen and nitrogen impurities in micro amount by melt extraction technique under argon and helium carrier gas stream for hydrogen, oxygen and nitrogen respectively. All the systems were completely optimized in different weight and temperature conditions and the accuracy of the results obtained was statistically evaluated at 5% confidence level. Non-metallic impurities in zirconium metal and alloy samples were found to be in the range of 16-56, 45-118 and 1008-1826 ppm for hydrogen, nitrogen and oxygen respectively.

Introduction

Zirconium belongs to the subgroup of IVB of the periodic table with its sister elements titanium and hafnium. These react with nitrogen to form nitrides. Zirconium forms very stable oxides. Zirconium occurs in at least 37 different mineral forms, but the predominant commercial source is the mineral zircon i.e., zirconium orthosilicate. Other current mineral sources are baddeleyite and eudialyte [1]. Zirconium is hard, shiny, ductile metal similar to stainless steel in appearance. It can be hot-worked to form slab, rods and round from arc-melted ingot. Further cold-working of zirconium with intermediate annealing produces sheet, foil, bar wire, and tubing. Gaseous impurities are commonly present in trace amount in metal and alloys, occurring either as solid solutions in the interstices of the metal lattice, as oxide, hydride, and nitride inclusions, or in some cases, as trapped molecular gases during the metallurgical processes. Hydrogen impurity may induce swelling and rupture of the cladding material whereas nitrogen and oxygen may cause weld embrittlement and decrease in machinability [2-3]. One of the most critical problems in analytical chemistry of the metals has been the quantitative measurement of the gaseous impurities, i.e., hydrogen, oxygen, and nitrogen. Emphasis of the tolerance level of these impurities in many metallurgical materials are gaining tremendous importance and also most essential for production and quality control. Various physico-chemical and radio-analytical techniques are available in the literature for the determination of hydrogen, oxygen and nitrogen impurities in metals, alloys and ceramic materials i.e., chemical and spectroscopic methods [4-6], gamma activation [7], neutron activation [8], charge particle activation [9-11], spark source mass spectrometry [12], impulse heating-thermal conductivity [13], isotopic dilution method [14] and inert-gas fusion extraction techniques [15-16]. The merits and demerits of various analytical methods employed for the determination of gaseous impurities in metals and alloys have been reviewed by Li *et al.* [17]. Due to various promising properties of zirconium as structural material for uranium oxide fuel pellets in nuclear power reactor due to its ready availability and good ductility and certain other applications such as corrosion resistance in many fluids, good mechanical and good fabrication qualities reducing agent for refractory metals, the zirconium metal has great commercial importance in many technical industries but presence of hydrogen, oxygen and nitrogen impurities adversely affects its physical, chemical and mechanical properties. Therefore, exact measurement of hydrogen, oxygen and nitrogen impurities is very essential. Keeping in view the above facts, present work has been made for finding out the optimum analysis conditions of carrier gas melt extraction technique and the evaluation of appropriateness and accuracy of micro amount ($\mu g.g^{-1}$ level) determination of hydrogen, oxygen and nitrogen contents in samples of zirconium and zirconium alloys. The statistical reliability of the melt

Table 1. Hydrogen, nitrogen and oxygen contents of (zircaloy-4) zirconium metal standard sample by varying sample weight for weight optimization.

Measurements/	Zirconium Metal Specimens ZM-1	ZM-2	ZM-3	ZM-4	Statistical Analysis Mean	Standard deviation	C.V (%)	Skewness	Kurtosis	t-value calculated	Certified Values [23]
Weight (gm)											
H_2	0.1225	0.2010	0.2501	0.4040							
N_2	0.1309	0.2256	0.2902	0.4563							
O_2	0.1257	0.2335	0.3206	0.4238							
Hydrogen ontent (ppm)	106.6 ± 1.5	109.4 ± 2.23	111.8 ±1.2	109.3 ± 1.1	109.3	2.125	1.9	-0.122	-0.998	4.31^*	>104
Nitrogen Content (ppm)	27.65 ± 0.86	28.77 ± 1.29	30.88 ± 0.53	31.16± 0.92	29.61	1.689	5.7	-0.198	-1.708	4.112^*	>25.6
Oxygen content (ppm)	1275 ± 13.6	1208 ± 9.7	1187 ± 6.39	1162 ± 9.42	1208	48.463	4.00	0.657	-1.000	3.859^*	> 1100

Triplicate analysis

Extraction temperature for hydrogen =2000 °C

For nitrogen = 2400 °C

For oxygen = 2200 °C

Co-efficient of Variation (CV) = Standard deviation/Mean x 100

*Significant at Probability (P) (5% level)

Probability at 5% level = 3.18

Table 2. Hydrogen, nitrogen and oxygen contents of (zircaloy-4) zirconium metal standard sample by varying temperature of analysis for temperature optimization.

Measurements/	Temperature optimization (°C) ZRS-1	ZRS-2	ZRS-3	ZRS-4	Statistical Analysis Mean	Standard deviation	C.V (%)	Skewness	Kurtosis	t-value calculated	Certified Values [25]
Temperature (°C)											
H_2	1850	1950	2100	2450							
N_2	1750	1800	2000	2200							
O_2	1850	1900	2050	2400							
Hydrogen content (ppm)	112 ± 2.1	110 ±3.9	109 ± 3.3	108 ±1.8	109.75	1.708	1.6	0.435	-1.154	5.83^*	>104
Nitrogen content (ppm)	29.16 ± 2.92	29.63 ± 1.53	28.67 ± 1.09	29.01 ±1.25	29.12	0.398	1.4	0.267	-1.074	15.318^*	>25.60
Oxygen content (ppm)	1301 ± 9.42	1287 ± 6.39	1277 ± 7.3	1245 ±3.5	1277	23.80	1.9	-0.585	-1.020	5.60^*	<1200

Triplicate analysis

Co-efficient of Variation (CV) = Standard deviation/Mean x 100

*Significant at Probability (P) (5% level) extraction technique has also been ascertained for the measurement of these gaseous impurities.

Results and Discussion

Zirconium is one of the essential metal in the nuclear technology and the utilization of zirconium metal is almost entirely for the cladding uranium fuel elements for nuclear power plants. Some chemical-processing industries have been using zirconium metal and alloys for corrosion-resistance vessels and piping for withstanding hydrochloric and sulphuric acids. The effects of gaseous impurities on mechanical and physico-chemical properties of zirconium metal and alloys are gaining immense interest over the past several years. To determine the best conditions for estimation of hydrogen, nitrogen and oxygen impurities using the melt extraction technique, the procedure of analysis was first optimized with the variation of weights and temperature and other conditions. For this purpose, different temperatures and weights of standard zirconium metal specimens were employed. To assess the accuracy of the result obtained, all the data was statistically analyzed. All the results are given with the relevant confidence intervals. The precision (ε) was expressed as a 95% confidence limits and calculated using the following equation.

$$\varepsilon = t\left(\frac{\sigma}{\sqrt{n}}\right)$$

where t (student's t-factor), when a 95% confidence is required and three replicates are available and n = number of replicates (three here). The standard deviations (σ), percent deviation (Co-efficient of Variation), skewness and kurtosis quoted refer to three measurements [18]. The "Micro-origin scientific" and "TC-plot statistical" packages for personal computer were used for all statistical calculations. The student's t-test is used to compare the mean from sample with some standard values. The t-test and skewness values of the standard samples emphasized the use of correct standard concentration. The t-test values affirm the probability that whether the obtained result was significant or not. The probability of significance of the results compared with the true figures for 5% tabulated values (95% confidence) are presented in Tables 1 and 2. Analytical reproducibility is characterized by Co-efficient of variation (relative standard deviation) for a single measurement of 0.1225-.4040 for hydrogen content of 1.9%. Since calculated t-values were found to be greater than tabulated values at 5% level of confidence in case of hydrogen and nitrogen estimation and nearly non-significant effect was observed in mean values of oxygen at 95% level of confidence. Using the optimum conditions, zirconium metal and alloy samples were analyzed for the gaseous impurities. Except for a few isolated samples, all of the data reported in Tables 1 and 2 represent the average of three determinations.

Zirconium and Zirconium Alloys

Various samples of zirconium and zirconium alloys were analyzed for hydrogen and nitrogen contents and their results were presented in Table 3. The amount of hydrogen and nitrogen contents in these samples were in the range of 16.9-56.7 and 45-118 ppm respectively. The result data was found to be statistically adjacent to the certified and literature values. [19] Because of their position in the periodic table of the elements, zirconium and titanium are in general, similar in behavior towards dissolved gases, and therefore offer similar problems in the analysis. The principal gaseous impurities found in these metals are oxygen, nitrogen and hydrogen. Like most impurities in metals, these may have favorable or unfavorable effects on the physical and mechanical properties of the metals. Hydrogen is of great concern mainly because in sufficient concentration, it causes embrittlement. [20] This is true for two metals (Zr,&Ti), but the susceptibility to embrittlement varies considerably from alloy to alloy. Recently, Chang *et.al.* [21] has studied the slow displacement-rate tensile on D6ac steel tempered specimens to investigate the influence of gaseous hydrogen on the notched tensile strength (NTS) and associated fracture characteristics. He observed that smaller the integranular and/or flat fracture regions, the greater the resistance to hydrogen embrittlement of the specimen would be expected. Zirconium reacts with nitrogen to form nitride at elevated temperatures. In general, nitrogen causes an increase in hardness and strength. In the case of zirconium and titanium, nitrogen has been found to be very detrimental to the corrosion resistance of the metal. [22] Ashley [14] measured hydrogen impurities in titanium and zirconium alloys by isotope-dilution technique. The precision and accuracy over a wide range of sample size and hydrogen concentration were approximately the same as obtainable by melt extraction method.

Table: 3 Gaseous contents in zirconium and zirconium alloys.

Sr. #	Sample Identification	Hydrogen (ppm)	Nitrogen (ppm)	Oxygen (ppm)
1	Standard	25 ± 1.8	65 ± 2.8	1600 ±25
2	French Zircaloy-4	18 ± 0.5	51 ± 2	1040 ±12
3	ZRM-11	20 ±1.8	74 ±2.8	1540 ±42
4	ZRM-112	56 ±1.4	109 ± 22	1826 ±15
5	ZRM-13	19 ± 2	102 ± 3.2	1472 ±21
6	ZRM-132	28 ± 2	55 ±1.5	1695 ±20
7	ZRM-14	24 ±1	75 ±2.2	1767 ±9.3
8	ZRM-142	19 ± 1.5	65 ±2.0	1185 ±13.6
9	ZRM-15	17 ±1.7	118 ± 0.15	1408 ± 16.4
10	ZRM-152	25.78 ± 3.6	45 ±2.4	1367 ±8.1
11	ZRA-18	18.21 ± 4.1	80±3.1	1235 ±13.6
12	ZRA-19	26.5 ± 2.2	118 ± 1.5	1452 ± 11.4
13	ZRA-20	40 ±1.3	74 ±2.8	1400 ±12
14	ZRA-21	56 ±1.9	109 ± 2.2	1526 ±13
15	ZRA-22	22 ± 2.3	72 ± 0.4	1442 ±12
16	ZRC-23	16.9 ± 1.5	49 ±0.3	1095 ±8.5
17	ZRC-24	23 ±0.5	55 ±1.1	1107 ±5.3
18	ZRC-25	39 ± 2.5	95 ±1.9	1077 ±8.3
19	ZRC-26	27 ±1.6	105 ± 1.3	1008 ± 15.4
20	ZRA-27	47.7 ± 1.5	69 ±0.2	1307 ±3.3
21	ZRA-28	18.85 ± 2.18	61 ±0.33	1014 ±6.6
22	ZRA-29	26.47 ± 2.4	54 ± 1.5	1220 ± 2.4
23	ZRA-30	20.07 ± 1.2	67 ± 2.1	1115 ± 5.4
24	ZRC-317	19.54 ± 2.32	53 ±0.9	1067 ±2.3
25	ZRC-318	38.21 ± 2.18	61 ±2.1	1211 ±4.6
26	ZRA-319	56.7 ± 2.5	85 ± 1.4	1308 ± 2.4
27	ZRA-319	33.91 ± 3.24	73 ± 1.1	1279 ± 1.4
27	ZRA-320	26.7 ± 1.18	68 ± 15	1308 ± 3.8
29	ZRC-331	20 ±1.8	74 ±2.6	1260 ±4.2
30	ZRC-332	42 ±1.23	71 ±1.8	1119 ±2.9

Triplicate analysis
Certified values of French Zircaloy-4:
H_2 : 9.0 ppm , N_2 :56.00 ppm and O_2: 1260.0 ppm
ZRM = Zirconium metal
ZRA = Zirconium Alloy
ZRC = Zircaloy

Table 3 also portray the result of oxygen impurity content in different samples of zirconium metal, zirconium alloys. The oxygen impurity were found to be in the range of 1008-1826 ppm. Oxygen has a very pronounced strengthening effect on these metals (Zr and Ti) and also increases the hardness. Low oxygen concentrations may be helpful in strengthening the metal, while high concentrations may be harmful with regard to ductility. Oxygen reacts very rapidly with zirconium and titanium metals at elevated temperatures and therefore creates a problem in welding and rolling operations involving exposure of the metal to the air. In general, oxygen and nitrogen have a substantial strengthening effect. However, they cause weld embrittlement and decrease in machinability. Their detrimental effects are magnified by the presence of hydrogen.

Table 4 revealed the results of gaseous impurities i.e., hydrogen, nitrogen and oxygen contents in different samples of zirconium metal, sponge and ingot. Zirconium metal in the form of sponge or electrolyte powder is not suitable for direct fabrication into massive shape without consolidation by melting or powder–metallurgy techniques. Sponge is a form of metal characterized by a porous condition that is the result of decomposition or reduction of compound without fusion. Essentially all zirconium is reduced from the chloride or iodide by magnesium at 900 °C. Zirconium sponge is a highly pyrophoric material at standard temperature and pressure (STP). Physically it has irregular geometric shape but pure metallic form of non-melted product of $ZrCl_4$. Zirconium ingot is a solid material comprising of regular geometric shape after the melting of sponge at 1852 °C. Ingot is more dense and non-pyrophoric material. Table 4 indicates considerable higher oxygen content and the slight higher nitrogen content of sponge as compared to zirconium metal and ingot. The oxygen and nitrogen

Table: 4 Gaseous impurities in zirconium sponge ingot and melt.

Sr. #	Sample Identification	Hydrogen (ppm)	Nitrogen (ppm)	Oxygen (ppm)
1	ZRSP-10	69 ± 1.8	65 ± 2.3	1380 ±11
2	ZRSP-11	64 ± 2.5	79 ± 2	1317 ±3
3	ZRSP-12	56 ±3.8	89 ±2.8	1431 ±12
4	ZRSP-13	59 ±3.0	73 ± 2.2	1397 ±15
5	ZRSP-14	50 ± 2	82 ± 1.2	1308 ±13
6	ZRSP-15	54 ± 2.7	94 ±3.5	1283 ±15
7	ZRSP-16	67 ±1.3	75 ±2.2	1313 ±3
8	ZRSM-A	47 ± 4.5	61 ±2.0	1305 ±5
9	ZRSM-B	53 ±1.1	78 ± 4.1	1237 ± 16
10	ZRSM-C	48 ± 3.6	69 ±2.4	1159 ±8
11	ZRSM-D	45 ± 1.5	80±3.1	1205 ±13
12	ZRSM-E	66 ± 2.2	74 ± 1.5	1288 ± 11
13	ZRSM-F	48 ±1.3	91 ±2.8	1142 ±12
14	ZRI-111	24 ±1.9	53 ± 3.2	1132 ±9
15	ZRI-222	26 ± 2.3	51 ± 1.4	848 ±7
16	ZRI-333	17 ± 1.5	49 ±1.3	756 ±8
17	ZRI-444	19 ±0.5	55 ±1.1	860 ±5
18	ZRI-555	29 ± 2.5	53 ±1.9	980 ±4
19	ZRI-666	27 ±1.4	59 ± 1.3	898 ± 13
20	ZRM-777	25 ± 1.9	49 ±3.2	969 ±15

Triplicate analysis
ZRSP = Zirconium Sponge
ZRSM = Zirconium Sponge melt
ZRI = Zirconium Ingot
ZRM = Zirconium metal

impurities were found to be in the range of 1283-1431, 61-94 ppm. In sponge materials respectively. It has been shown in literature [22] that the major difference between iodide- and sponge based alloys is the lower oxygen and nitrogen content of the former; also the range in impurity content in the former is less than in the later.

Experimental

Zirconium metal, alloys, sponge and ingot samples were obtained from the Alloy Development Group, PINSTECH. Strohlein H-mat 251, Dinimat-450 and O-mat 350 were used for determination of hydrogen, nitrogen and oxygen respectively as shown in Figures 1 and 2. Different sampling techniques were used in accordance with the ASTM specifications for different categories of samples of zirconium metal and alloys. [24] Uniform chips sample in ~ 1.18 mm dimensions were made free of grease, dirt and dust. Standard samples of zirconium metal and zircaloy-4 were analyzed for the calibration of these instruments, to ascertain the precision and accuracy of specific method and also for statistical analysis.

Some experiments were performed to modify the existing melt extraction method for determination of gaseous impurities in zirconium and zirconium alloys. Protective coating elements like nickel was used as facilitator for evolving of nitrogen and oxygen in carrier gas melt extraction .

Procedure for Hydrogen and Nitrogen

The experimental approach used in this study was based on the standard ASTM specification, single sample per crucible technique for the quantitative determination of gaseous impurities in metal and alloy solid samples [25]. Before analyses, all samples were degreased with trichloroethylene, pickled for few minutes in 1:1 hydrochloric acid, washed with water, then with acetone and finally dried. All the graphite crucibles were also degassed. Approximately o.5 gm sample chips were placed in graphite crucible and melted in impulse furnace at specified temperature higher than melting point. Hydrogen, nitrogen and carbon monoxide, which were liberated from the sample, were pumped into a gas reservoir for subsequent separation and measurement. Hydrogen or nitrogen was determined by the difference of thermal conductivity of hydrogen or nitrogen and carrier gas (argon for hydrogen and high purity helium for nitrogen) through the microprocessor.

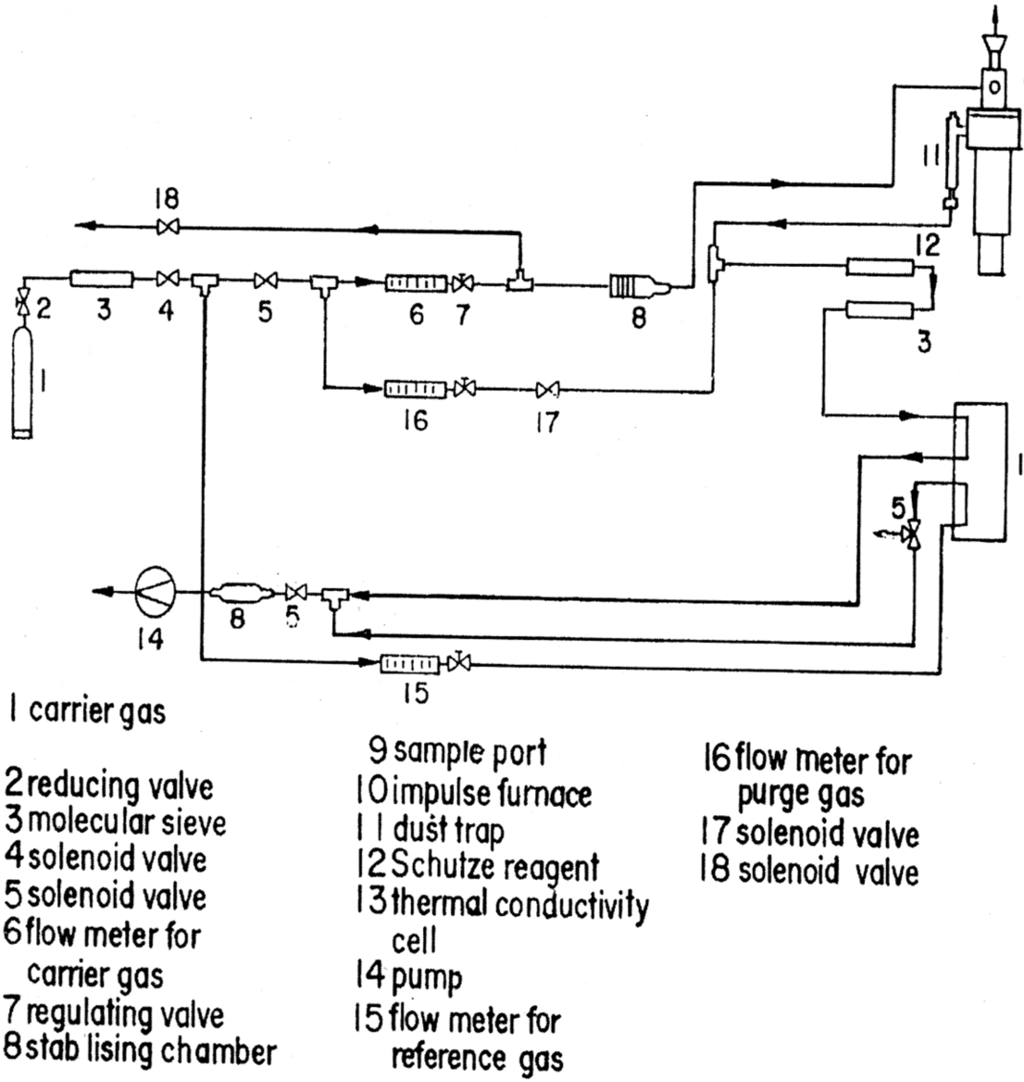

Fig. 1: Block diagram of instrument for hydrogen and nitrogen analysis.

Procedure for Oxygen

In case of oxygen analysis, hydrogen, nitrogen and oxygen gases along with carrier gas (argon) were pumped where carbon monoxide absorbs infrared radiation because of its molecular structure. The resulting change in the output signal of the infrared detector provides a unique measure of the quantity of oxygen (as carbon monoxide) contents of sample.

Conclusions

Melt extraction and inert-gas fusion technique possesses several advantages over vacuum fusion. Analysis by melt extraction or inert-gas fusion is faster and in general less expensive than vacuum fusion. Also, because the inert carrier gas suppresses the rate of vaporization of metals that may act as getters for oxygen. This method can be applied to

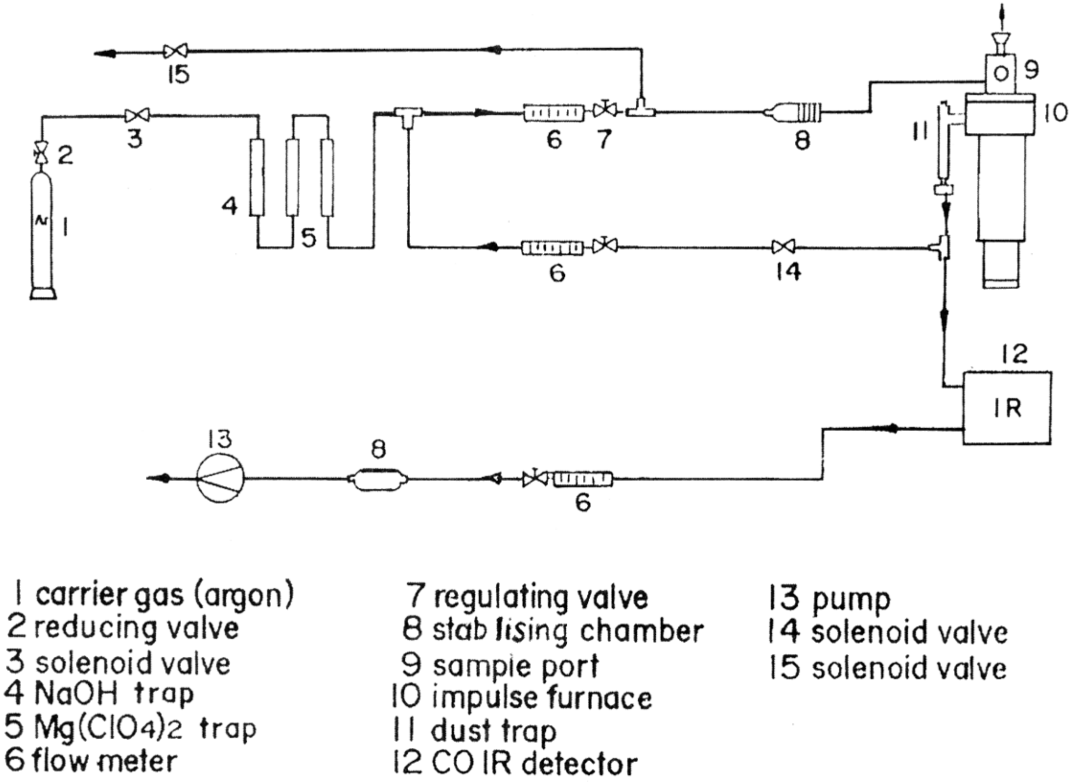

Fig. 2: Block diagram of instrument for oxygen analysis

samples that can not be analyzed by vacuum fusion. Carrier gas melt extraction method is suitable for successful analysis of zirconium and its alloys on routine basis as well as for end product.

Zirconium is rare transition metal. Pure metal is soft, ductile and weak, however its strength can be greatly improved by alloying. It is used in alloys, abrasive and flame proofing compounds. Zirconium of the highest purity is obtained by refining sponge. The zirconium produced, called “crystal-bar” zirconium, is low in all impurities especially in nonmetallic ones. Zirconium material containing as little as 50 ppm of nitrogen is noticeably less corrosion resistance in water at 600 °F than material containing 10 to 20 ppm nitrogen. Zirconium and its alloys react readily with hydrogen, oxygen and nitrogen at elevated temperatures. The annealing of fabricated shapes in commercial facilities often causes large pickup of these containments. The corrosion resistance of zircaloy-2,or -4 is adversely affected by increased nitrogen content and the fabricationability is adversely affected by increased oxygen, nitrogen, or hydrogen content. Therefore, the exposure of zirconium to furnace atmospheres should be minimized.

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References

1. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* , Pergamon Press Inc., Maxwell House, Fairview Park, Elmford, New York, USA, pp. 112 (1986).
2. M. M. Laben, L. L. Lynn and D.H. Ben, *Determination of Gaseous elements in Metals,* John Wiley and Sons, New York, (1974).

3. S.H. Avner, *Introduction to Physical Metallurgy*, International Student Edition, McGraw-Hill International Book Company, Tokoyo, Japan, (1982).
4. A. Giovagnoli, M. Valladon, C. Koemmerer, G. Blondizux and J. L. Debrun, *Belg. Anal. Chim. Acta.,* **90**(2), 411-16, (1979).
5. H. Foerster, *J. Radioanal. Chem*., **58**(1), 205, (1980).
6. J. C. Gosset and C. Grumet, *J. Radioanal. Chem.,* **28**(1-2), 185 (1975).
7. K. Strijckmans, C. Vandecastcle and J. Hoste, *Belg. Anal. Chim. Acta.,* **89**(2), 255 (1977).
8. J. C. Barbour, B.L. Doyle and S. M. Myers, *Physical-Review, B: Condensed Matter.* **38**(10), 7005, (1988).
9. Z. Tao, D. E. Alburger, K. W. Jones, Y. D. Yao and Y. H. Kao**,** *Applied Physics Letters.* **53**(15), 1440 (1988).
10. F. C. Matacotta, G. Nobile, G. Serrini, M. D. Giardina and A. E. Merlini, *Symposium on high temperature superconductors***.** Boston, MA (USA). 1987, Edited by M.B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L.Tuller, High-temperature superconductors. Pittsburgh, PA (USA). Materials Research Society. pp.561 (1988).
11. H. Yasuhara, M. Shimura, K. Yoshioka, K. Abiko, *Mater. Trans JIM,* **41**(1), 71 (2000).
12. K. L. Ramakumar, V. A. Raman, V.L. Sant, P.M. Shah and V.D. Kavimandan, *Anal. Letters,* **19** (21-22**),** 2147 (1986).
13. K. Zhang, *Metall. Anal (China),* **19**(5), 24 (1999).
14. R. W. Ashley and A. S. Denovan, Atomic Energy of Canada, CRDC-1212, Chalk River, Ontario, (1965).
15. J. Akhtar, S. K. Durrani, N. A. Chughtai and K. A. Shahid, *J. Chem. Soc. Pak.,* **18**(1), 14 (1996).
16. W. Mitsuyoshi and A. Narukawa, *Bunseki Kagaku (Jpn),* **49**(10), 771, (2000). English Absract in Chemical Abstract, 133:343936x, 133 (24), (2000).
17. T. Li and S. Liu, *Metal Anal (China),* **19**(6), 35 (1999).
18. C. G. Paradine and B. H. Rivettt, *Statistical methods for technologists,* Published by The English Universities Press, lTD., St. Paul's House Warwick Lane, London, (1968).
19. A. D. Kirshenbaum and A.V. Grosse, *Anal. Chim. Acta,* **16**, 255 (1957).
20. C.R. Jr. Tipton, *Reactor Hand Book, Vol.1,Materials,* Interscience Publishers, Inc, New York, (1960).
21. T.L. Chang, L.W. Tsay and C.Chen, *Mater. Sci. Eng.A.,* **A31691-2,** 153(2001).
22. J. P. Mislan, H.D. Herrington, K.D. Wright and L. F. Junop, *In Progress Report, Chemistry and Materials Division,* Atomic Energy of Canda, Chalk River Nuclear Lab. Ontario, Canada, (1982).
23. T.Lyman, *Metals Hand Book,* **Vol.1,** 8th edition, American Society for Metals, Metals Park, Ohio USA, (1974).
24. W. Thomich, *Technical Report, Form No. 510-E,* Strhlein Intruments, Duesseldorf, West Germany, (1967).
25. ASTM annual Book of Standards, Part 32, *American Society for Testing and Materials,* Chemical Analysis of Metals, Philadelphia, (1973).