Determination of Gaseous Elements in Metals and Metal Powders

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Summary: Presence of gaseous impurities affect the mechanical and corrosion resistance properties of metals and alloys. Selected samples of metal and metal powder have been analyzed for the determination of gaseous impurities like hydrogen, oxygen and nitrogen by inert-gas fusion extraction technique. The accuracy of the method has also been verified for hydrogen, oxygen and nitrogen. All results data was statistically evaluated and compared with the literature values.

Introduction

Gaseous impurities are commonly present in trace amount in metals, alloys and metal powders, 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. One of the most critical problem in analytical chemistry of the metals has been the quantitative determination of the gaseous impurities, i.e., hydrogen, oxygen, and nitrogen. Tolerance levels for these impurities in many metallurgical materials has steadily reduced to the point where a concentration of 1 ppm or less is of current interest. This has been generated by the fact that concentration of these impurities in the range of 1-10 ppm exert significant effects on the physical, mechanical, corrosion resistance and electrical properties of many metals. Hydrogen impurity may induce swelling of the material whereas nitrogen and oxygen cause weld embrittlement and decrease in machinability [1]. For production control and metallurgical evaluation of such effects, accurate and precise analytical determinations on these impurity contents in metals and alloys are required. The importance of this problem has promoted extensive research on the determination of these elements in metals and alloys by conventional vacuum-fusion, inert gas fusion, emission spectrometric, neutron activation, isotope dilution, and wet chemical methods [2-5]. Comprehensive reviews are available in literature on other physicochemical and radioanalytical techniques for the assessment of gaseous impurities in metals and alloys [6]. Recently Ramakumar *et al.* [7] has measured hydrogen in zircaloy clad material by spark source mass spectrometry. The present work has been carried out for the evaluation of accuracy of inert gas fusion method for measurement of hydrogen, oxygen and nitrogen contents in some selected metals and metal powders.

Table-1: Gaseous contents in steels (ppm)

S.No.	Specimen Identification	Hydrogen	Oxygen	Nitrogen
1.	Steel Standard	6± 2	88 ± 5	74 ± 4
2.	11-B Steel turnings	48 ± 3	387 ± 32	118 ± 18
3.	12-A Steel turnings	19 ± 2	635 ± 42	83 ± 8
4.	9-E Steel turnings	17 ± 3	106 ± 8	40 ± 7
5.	24-01 Steel turnings	13 ± 2	547 ± 24	48 ± 17
6.	24-20 Steel turnings	11 ± 3	1398 ± 49	345 ± 2

Table-2: Gaseous contents in Titanium metal (ppm)

No.	Specimen Identification	Hydrogen	Oxygen	Nitrogen
1.	Titanium - 01	107 ± 20	32 ± 3	2014 ± 87
2.	Titanium - 02	262 ± 18	38 ± 9	1256 ± 101
3.	Titanium - 03	189 ± 7	45 ± 8	1987 ± 57
4.	Titanium - 04	98 ± 5	113 ± 6	1190 ± 77
5.	Titanium - 05	502 ± 17	104 ± 5	1582 ± 101
6.	Titanium - 06	263 ± 8	124 ± 8	2109 ± 157
7.	Titanium - 07	189 ± 6	98 ± 4	2039 ± 83
8.	Titanium - 08	83 ± 2	191 ± 6	1017 ± 81

Table-3: Oxygen contents in Copper, Iron, Nickel and Tungsten metal powder (ppm).

No.	Sample Condition	Sample Identification	Oxygen
1.	Copper Powder	Cu-1A	412 ± 15
		Cu-2B	418 ± 19
		Cu-2A	756 ± 15
		Cu-3B	773 ± 13
		Cu-4A	1094 ± 23
		Cu-5B	1488 ± 16
2.	Iron Powder	Fe-1A	1060 ± 127
		Fe-2B	1076 ± 139
		Fe-3C	1176 ±10
3.	Nickel Powder	Ni-1A	527 ± 23
		Ni-2A	554 ± 23
		Ni-3A	674 ± 12
		Ni-4B	993 ± 20
		Ni-5A	1043 ± 43
		Ni-6B	1056 ± 15
		Ni-7A	1419 ± 13
		Ni-8A	1775 ± 33
4.	Tungsten Powder	W1-W9	328 ± 13
		W10-W15	530 ± 36
		W16-W20	670 ± 22
		W21-W25	759 ± 16
		W25-W27	868 ± 19
		W28-W29	910 ±12
		W-30	1098 ± 18
		W-31	1253 ± 16
		W-32	1474 ± 11

Results and Discussion

The effect of oxygen, hydrogen, and nitrogen impurities on the mechanical and physical properties of metals and alloys are of considerable interest over the past several years. Using the optimum conditions, metal and metal powder samples were analyzed for gaseous impurities, except for a few isolated samples, all of the data reported in Table-1-3 represent the average of three determinations. To assess the accuracy of the results obtained, all the data was statistically analyzed. The standard deviations quoted refer to three measurements. Co-efficient of variation (CV) was measured for each sample, which is the percentage of standard deviation to the mean [8].

Steels

Results of hydrogen, nitrogen and oxygen contents measured in steels are presented in Table-1. The results were compared with literature values ascertained by different techniques and was found to be consistent [9-11]. The most preferred method for the estimation of hydrogen in steels appears to be extraction from the sample in the solid state, in vacuum, or in an inert gas techniques. Hydrogen in steels comes mainly from moisture in iron, from ferro-alloys, from rust on scrap, and from the combustion of fuel if the steel is made by gas-fired process [9]. Hydrogen can have a deleterious effect on the mechanical properties of steel. Steel generally have hydrogen concentration ranging from 1-10 ppm [10]. In concentrations greater than 2 ppm, hydrogen plays an important role in a phenomenon known as flaking. This is manifested as internal cracks or bursts usually occurring during cooling from rolling or forging and is more pronounced in heavy sections and in higher carbon steel [11]. Such defects have resulted in the disintegration of large rotors used in power plants because of the internal stresses. All steels contain nitrogen, the amount present depends on the method of steel production; type, amount, and manner of addition of alloying elements; how the steel was cast or poured; and finally whether nitrogen was purposely added. Nitrogen may be present in steel interstitially, as a metal nitride, or as nitrogen dissolved in a second phase, such as a metal carbide. Nitrogen soluble in solid steel exists in the iron lattice and at dislocations [12]. Interstitial nitrogen imparts many of the same properties, such as hardening to iron that interstitial carbon does. In alloyed iron, the effect of interstitial nitrogen is not as clearly defined, because of the presence of alloying metals. Oxygen in steel can originate from a variety of sources such as air, moisture in the air or in the addition agents, and oxide in scrap [13]. Lesser concentrations come from broken or eroded refractories. Usually the particles from these sources are relatively so large. They rapidly rise to the surface of the molten metal in the ladle of mould and can be separated. Oxygen, like hydrogen, can affect the mechanical properties of steel deleteriously. The oxygen concentration is not only important in this regard but also the number, type, size, and distribution of the oxygen-bearing inclusions namely metal oxides, silicates, aluminate, oxysulfides and similar second-phase inclusion compounds [14]. Steels and cast-iron generally have oxygen concentrations varying from 10 to 800 ppm, the value depending upon whether the steel is the rimmed, semiskilled, or killed type and the method by which the steel is made (e.g., basic oxygen process, vacuum induction consumable electrode remelting). It is desirable to remove oxygen from steel, caused during solidification, carbon and oxygen in solution react to give carbon monoxide, which can cause blowholes. Also, on cooling, oxygen can come out of solution as FeO, MnO, and other oxide inclusions that may impair the hot and cold workability and the ductility, toughness, fatigue resistance, and machinability of steel. Oxygen, along with nitrogen and carbon, can cause aging or a spontaneous increase in hardness at room temperature, which is accelerated by raising the temperature. In cast iron, oxides may react with carbon while the casting is solidifying, thus causing porosity and weakness in the product [11]. The results of present determination of nitrogen and oxygen in steels were found to be closely comparable with those obtained by Well [14] and Kirshenbaum [15-16].

Titanium metal

Table-2 portrays the results of hydrogen, nitrogen and oxygen contents of titanium metal and was found to be similar with isotopic dilution technique [17]. Because of their position in the periodic table of the elements, titanium and zirconium are in general, similar in behaviour toward 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 favourable or unfavourable effect on the physical and mechanical properties of the metals. Hydrogen is of great concern mainly because in sufficient concentration, it causes embrittlement [18]. This is true for two metals (Zr, Ti), but the susceptibility to embrittlement varies considerably from alloy to alloy. Titanium reacts with nitrogen to form nitride at elevated temperatures. In general, nitrogen causes an increase in hardness and strength. In the case of titanium and zirconium nitrogen has been found to be very detrimental to the corrosion resistance of the metal [19]. Ashley and Denovan [20] measured hydrogen in titanium 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 vacuum extraction or fusion methods. Oxygen has a very pronounced strengthening effect on these metals (Ti and Zr) 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 react very rapidly with titanium and zirconium 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.

Metal powders

Hydrogen and oxygen are the gases of primary interest in copper, since nitrogen has a very limit solubility in copper and forms no stable nitrides. In present study, only oxygen gas was measured in certain metal powders like Cu, Fe, Ni, and W. Results of oxygen contents in copper metal powder are presented in Table-3. Oxygen contents were determined in different samples of copper metal powder in range of 412-1488 ppm with Coefficient of variation (CV) of 2-5%. Kirshenbaum *et al.* [17] reported as little as 0.01% oxygen in copper using isotope-dilution methods. Harris and Hickam [21] measure oxygen in copper by vacuum-fusion technique in the range of 0.01-0.5 %. Nickel has been used extensively as an alloying element in steels, high temperature alloys, and magnetic materials and constitutes the matrix for a distinguished series of alloys. The wider scope of applications for high purity, particularly in the electronics industry, has made it necessary to evaluate with great care the inherent variables affecting the determination of gases in the parts-per million range [22]. Table-3 also shows the results of oxygen contents in nickel and tungsten metal powders. Results of oxygen contents in nickel and tungsten were measured in range of 527-1775 ppm and 328-1098 ppm with Co-efficient of variation of 2-4% and 2-7% respectively and were found to be in good agreement as obtained by Dallman and Fassel [23] for several base-metals. Although inert-gas fusion methods have been used extensively for oxygen in nickel, but most investigations have used the vacuum-fusion approach. It permits a wide variety of samples geometries and composition ranges and simultaneously yields the three major gases of interest [24].

Experimental

Selected samples of metal and metal powder like steels, titanium metal and copper, iron, nickel, tungsten powders were obtained from the Alloy Development Group, NMD, PINSTECH. Strohlein H-mat 251, Dinimat-450 and O-mat 350 were used for determination of hydrogen, nitrogen and oxygen respectively. Standard samples were also analyzed to ascertain the precision and accuracy of the particular method.

Procedure for hydrogen and nitrogen

The experimental approach used in this study was based on the standard ASTM [25], single sample per crucible technique for the quantitative determination of gaseous impurities in metal and metal powder samples. Approximately 0.5 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 the 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, high purity 99.999% helium for nitrogen) through the microprocessor. All graphite crucibles were degassed before analysis.

Procedure for oxygen

In case of oxygen analysis, metal or metal powder samples were placed in tin capsules and heated in the graphite crucible at about 200°C higher than the metling point of the sample. Nitrogen and oxygen are released from the sample as N_2 and CO (carbon monoxide). These gases together with a chemically inert carrier gas (argon) pass out of the furnace through an infrared analyzer for selective evaluation of CO. The resulted analogue signal produced by IR. absorption was amplified and integrated which provides a unique measure of quantity of oxygen contents (as carbon monoxide) of the sample as shown in Figure 1.

Conclusions

Inert-gas fusion technique possesses several advantages over vacuum fusion. Analysis by inert-

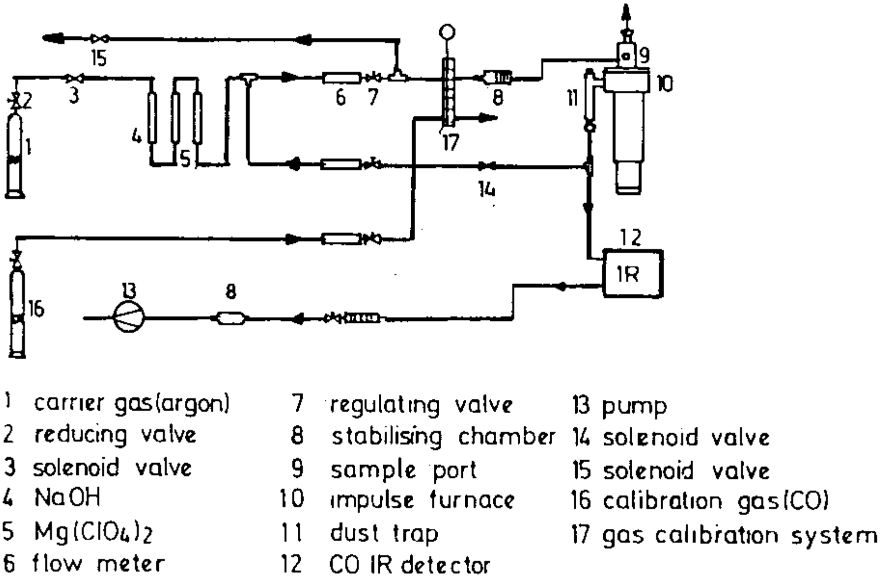

Fig.1: Block diagram for oxygen gas analysis.

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. The inert gas fusion is more versatile technique for the samples that can not be analyzed by vacuum fusion.

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