A novel gas analysis system for metallurgical materials based on time-of-flight mass spectrometry

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ABSTRACT

A new analyzing system for gas analysis from metallurgical materials was developed by coupling a home-made electron ionization time-of-flight mass spectrometer (EI-TOFMS) with an inert gas fusion unit. A description of principle, configuration along with key features of the system especially the EI-TOFMS was presented. The properties of the EI-TOFMS were checked by the indoor air and standard gas sample, and the initial results for the system measuring of the steel samples show that oxygen, nitrogen, hydrogen and argon could be measured simultaneously and quantitatively at a detection limit of μg/g level.

1. Introduction

Oxygen, nitrogen, hydrogen and argon dissolved in metallurgical materials in the form of metal compounds, solid solutions, pinholes and blowholes have a vital influence on the characteristics of the metal, and the understanding of the concentration of these elements in metal is very important [1]. Presently, the popular oxygen, nitrogen and hydrogen analytical method is the inert gas protection-inert gas fusion-infrared absorption and thermal conductivity method [2–5], but there exist several drawbacks, such as low sensitivity, too complex, large time-consuming. In 2004, a probe combined with a quadrupole mass spectrometer was developed to simultaneously measure H, N and O in molten metal, and was assembled in a multi-gas analysis system at Midwest Instrument Co [6]. About the argon in metal, as far as we know, neither analytical method nor equipment is reported till now. This paper proposes a new analytical method for metallurgical materials which is an Electron Ionization Time-of-flight Mass Spectrometer (EI-TOFMS) [7–9] coupled with a pulse heating inert gas fusion unit.

It could simultaneously analyze multiple components including argon in one sample at high sensitivity.

2. Experimental

The new system mainly consists of a pulse heating inert gas fusion unit and an EI-TOFMS. The pulse heating inert gas fusion unit connects with the EI-TOFMS through a branch capillary, and only a little sample gas can enter the MS analyzer which could keep the vacuum pressure better than 10^{-3} Pa. In this experiment, the pulse heating inert gas fusion unit, ONH3000, is provided by Beijing NCS Analytical Instruments Co. Ltd. (China), and the EI-TOFMS is homemade.

2.1. Pulse heating inert gas fusion unit

Fig. 1 shows the structure of a pulse heating inert gas fusion unit. The carrier gas, purified by filter, can flow through the whole analysis system. The graphite crucible is located between the upper and lower electrodes of the pulse heating furnace and can be heated to over 3000 °C in 10 s by high current. The sample is dropped in and fused instantly after heating. The O in the sample is deoxidized into CO by reacting with graphite (which can be changed into CO_2 through CuO catalyst furnace or by Schutz reagent), and the N, H

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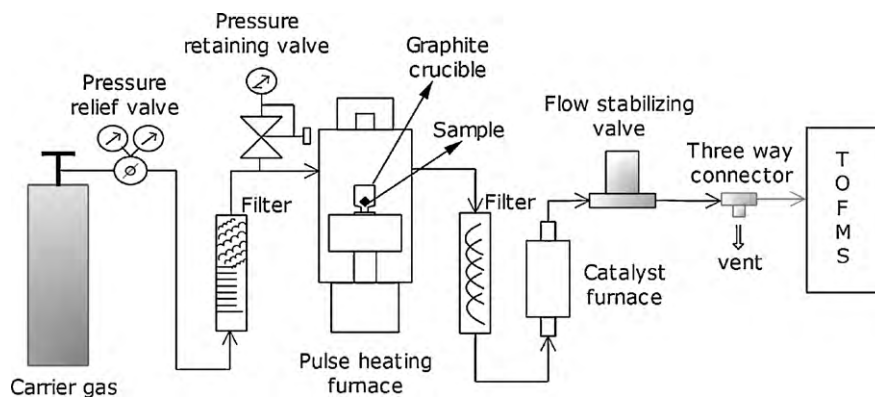E-mail address: zhouzhen@shu.edu.cn (Z. Zhou).

Fig. 1. The schematic flow chart of the pulse heating-inert gas fusion.
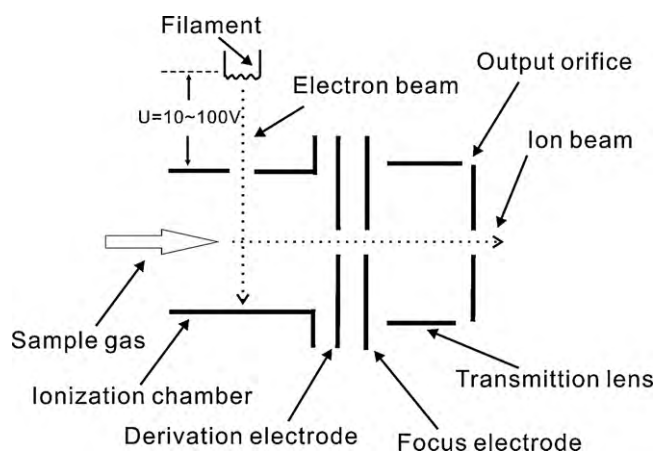

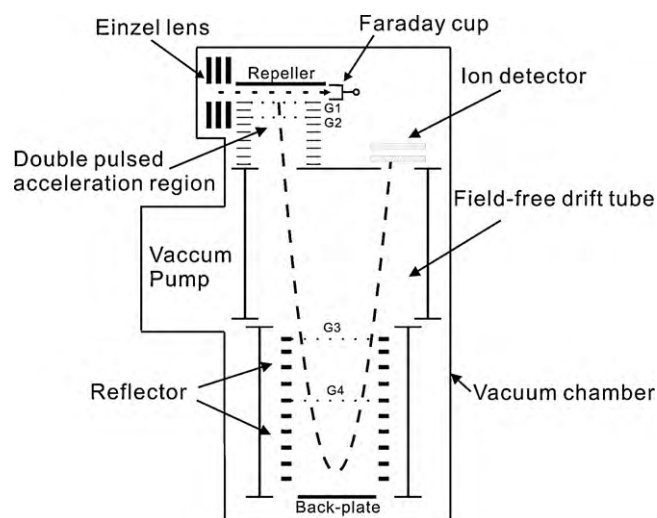Fig. 2. The Structure of the home-made EI source.

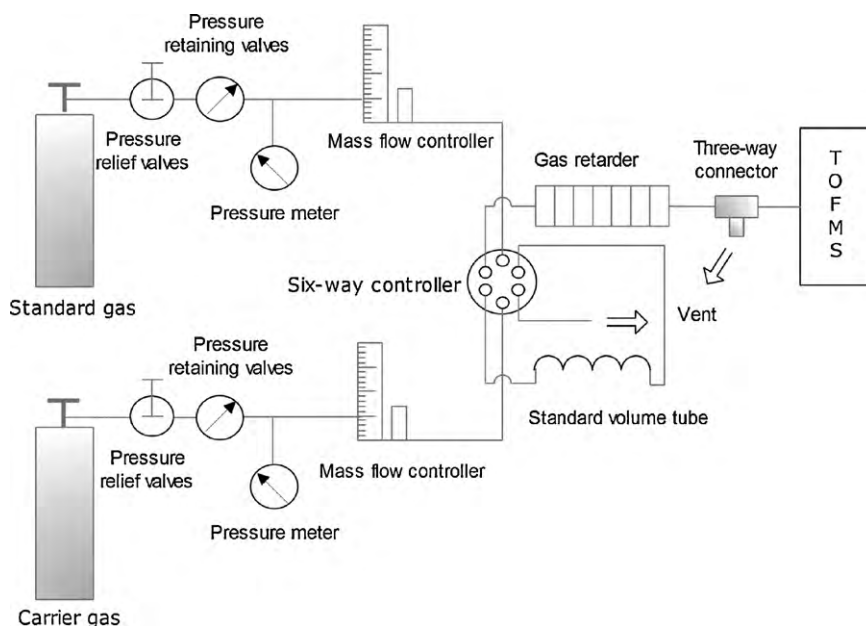Fig. 3. The schematic of orthogonal acceleration TOFMS.

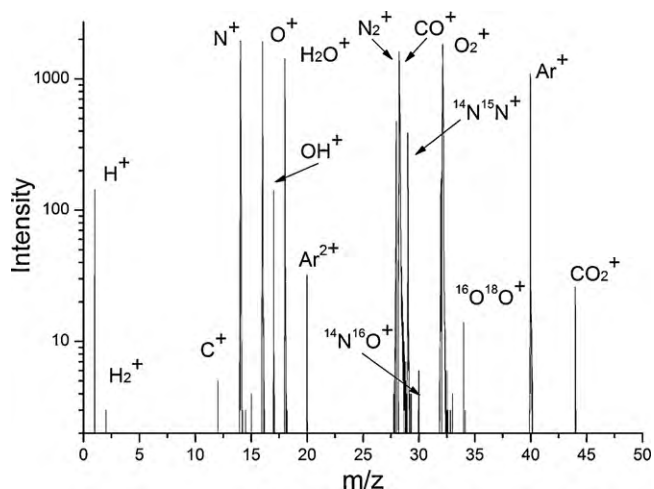Fig. 4. The schematic of the standard gas injection system.

Fig. 5. The EI-TOF mass spectrum of the indoor air components.

and A_r contained in the sample are released as N_2, H_2 and A_r, respectively. Then the released gases, CO, N_2, H_2 and A_r are flown away by the carrier gas and only a small quantity is sampled through a diffusion capillary into the TOF-MS analyzer.

2.2. Electron ionization time-of-flight mass spectrometry (EI-TOFMS)

2.2.1. EI source

Electron ionization source [10–12] is one of the most widely used ion sources for its many great advantages. The design of our homemade EI source is shown in Fig. 2. It consists of filament, ionization chamber, derivation electrode, focus electrode, transmitting lens and output orifice. The filament is made of WRe20 alloy, more flexible than pure tungsten, with the diameter 0.25 mm and effective length 10 mm. When heated to 1500 K, the filament will emit electrons continuously with the electron current (Ie) as high as 5 mA, and electron energy adjustable from 10 to 100 eV. In the ionization chamber, the sample molecules are bombed by the electron beam and turn into ions. Then the ions are pulled out and focused

by the derivation electrode and the focus electrode. The transmitting lens is a DC-only quadrupole, which can guide the ion beam in certain direction to compensate the mechanism error. The output orifice can reduce the background signal by blocking the dispersed ions, in addition to its focusing property. The ion source is floating at a certain positive potential, (18–24 V), to provide the necessary velocity in the horizontal direction to adjust the ion arrival time at the test region.

2.2.2. TOFMS

The schematic of the home-made TOFMS is presented in Fig. 3. It consists mainly of einzel lens and mass analyzer. The TOFMS is developed originally from the system created by Dodonov et al. [13,14] and the similar structures are presented in our previously publications [7,8]. In this paper only the vital mechanical and electrical parameters are introduced.

The einzel lens can adjust the angular divergence of the ion beam to improve mass resolving power as well as to compensate the unavoidable misalignment about mechanical assembling.

The mass analyzer consists of a double pulsed acceleration region, a field-free drift tube, a reflector and an ion detector. The length of the double pulsed acceleration region is 52 mm. When the space between the Repeller and grid G1 is filled with ions, a push-out pulse +500 V and a pull-out pulse −500 V are respectively applied to the Repeller and the grid G2 simultaneously to guide the ions into the field-free drift tube. The extraction pulse, with a rise time less than 50 ns, has a width 13 μs and frequency 12 kHz. The grid G1 is grounded and a small DC voltage 10 V is applied onto G2 to compensate the penetration of the accelerating electrical field. The faraday cup is used to monitor the ion beam intensity. The field-free drift region is 300 mm in length and held at an electrical potential 2200 V where the ions could fly at a constant speed. The reflector is separated into two stages with different field strengths by grid G4 at a ground potential. The first stage is 90 mm in length and the second is 35 mm. The potential of the Back-plate is 350 V. For the ion detector, two micro channel plates (MCP) assembled with chevron-type are used. Each MCP features an area of 30 mm × 30 mm, a channel diameter of 5 μm and a bias angle of 8°. The signals generated from the MCP are recorded by a Time-to-Digital Converter (TDC) [15] with a sampling rate 2.5 G/s and provided by Guangzhou Hexin Analytical Instrument Co. Ltd. (China).
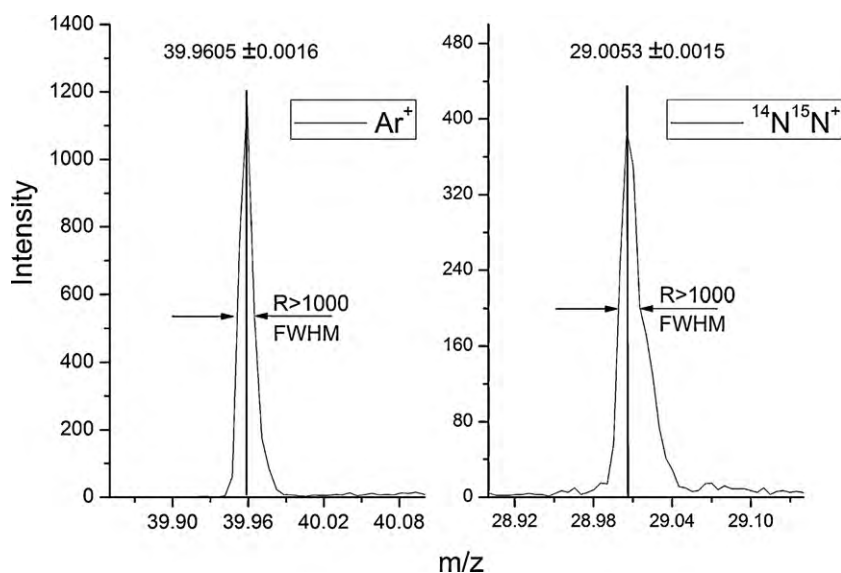

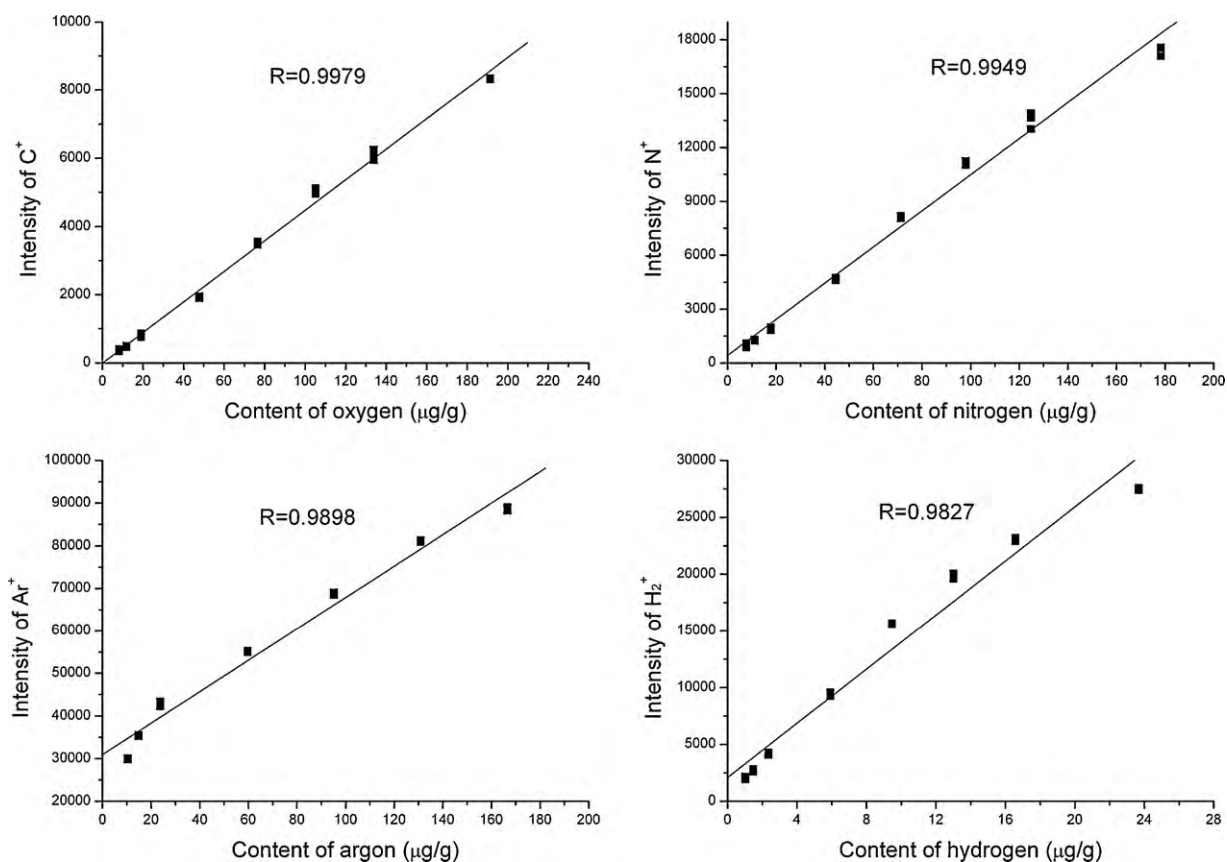**Fig. 6.** Mass precision and resolution of A_r^+ and $^{14}N^{15}N^+$.

Fig. 7. Dependence of ion intensity on the corresponding content of O, N, H and A$_r$ for the standard gas sample measured by EI-TOFMS.

Table 1
(a) Standard metal samples of H. (b) standard metal samples of O, N.

Number	Certified value of H (%)	Sample weight (g)	Theoretical amount of H (µg)	Company
(a)				
AR546	0.000063	0.9817	0.62	ALPHA, USA
AR546	0.000063	0.9944	0.63	ALPHA, USA
BS HON-T	0.00027	1.0193	2.75	Brammer, USA
BS HON-T	0.00027	1.0161	2.74	Brammer, USA
AR557	0.00037	1.0688	3.95	ALPHA, USA
AR558	0.00037	1.0686	3.95	ALPHA, USA
AR556	0.00058	1.0038	5.82	ALPHA, USA
AR556	0.00058	1.0052	5.83	ALPHA, USA
YSBC20601-2007	0.00088	1.0588	9.3	NCS, CHINA
YSBC20601-2007	0.00088	1.0596	9.32	NCS, CHINA

Number	Certified value of O (%)	Certified value of N (%)	Sample weight (g)	Theoretical amount of O (µg)	Theoretical amount of N (µg)	Company
(b)						
15#-1	0.00062	0.0087	0.5000	3.10	43.50	NCS, CHINA
15#-1	0.00062	0.0087	0.5000	3.10	43.50	NCS, CHINA
GBW02617a	0.00085	0.0068	1.0076	8.56	68.52	NCS, CHINA
GBW02617a	0.00085	0.0068	1.0077	8.56	68.52	NCS, CHINA
AR557	0.0018	0.0425	1.0700	19.26	454.75	ALPHA, USA
AR557	0.0018	0.0425	1.0700	19.26	454.75	ALPHA, USA
JSS GS 1D	0.00354	0.0200	0.7849	33.39	156.98	Aichi, Japan
JSS GS 1D	0.00354	0.0200	1.0433	36.90	208.66	Aichi, Japan
JSS GS 1D	0.00354	0.0200	0.7470	26.44	149.40	Aichi, Japan
501-644	0.0037	0.0092	1.0010	37.00	92.01	LECO, USA
501-644	0.0037	0.0092	1.0000	37.00	92.00	LECO, USA
BS HON-T	0.0044	0.0365	1.0165	44.88	372.30	Brammer, USA
BS HON-T	0.0044	0.0365	1.0143	44.88	372.30	Brammer, USA
GSB03-1065-99	0.0064	0.0165	0.9968	63.79	164.47	NCS, CHINA
GSB03-1065-99	0.0064	0.0165	0.9968	63.79	164.47	NCS, CHINA

2.3. Gas injection system

In order to simplify the analysis, the standard gas with known contents was used through a standard gas injection system (Fig. 4) to simulate the actual gas released from the metal samples in pulse heating inert gas fusion unit. The carrier gas is set at a constant flux about 400 mL/min with certain pressure. A certain volume of standard gas will be injected into the carrier gas flow by the six-way valve. The flow rate of the sample gas through the capillary to the EI-TOFMS is about 6 μL/min.

3. Experimental results and discussion

3.1. Real time indoor air monitor by EI-TOFMS

The performance of the EI-TOFMS was checked by the indoor air, and the mass spectrum is shown in Fig. 5. The peaks in the mass spectrum can be identified as H^+, H_2^+, C^+, N^+, O^+, OH^+, H_2O^+, Ar^{2+}, N_2^+, CO^+, $^{14}N^{15}N^+$, $^{14}N^{16}O^+$, O_2^+, $^{16}O^{18}O^+$, Ar^+, CO_2^+. Due to the characteristic of TDC, the ions like N^+, O^+, N_2^+ and O_2^+ were saturated and the peak area cannot present the ion intensity normally. Fig. 6 shows the mass spectra of Ar^+ and $^{14}N^{15}N^+$. From this figure, we can see that the mass accuracy is better than 1×10^{-4} and mass resolution is over 1000 (FWHM) based on $R = m/\Delta m$.

3.2. Standard gas samples measurements

In order to simplify the analysis of the sample materials and make more tests about the EI-TOFMS, a gas injection system (Fig. 4) was introduced to simulate the pulse heating inert gas fusion unit, and the experiments were conducted with known contents standard gas.

The relationship between injected volume of the standard gas and the content of O, N, H and Ar could be determined by the formula (1).

$$W = \frac{M_n \times P_n \times V_j}{V_m} \tag{1}$$

where W (μg) is the content of each component in a sample; V_j (μL) is the volume of injected standard gas; P_n is the percentage of certain gas by volume; M_n (g/mol) is molar mass of the component; V_m (L/mol) is the molar volume of an ideal gas at 1 atmospheric pressure.

H_2 and Ar can be measured directly based on the peak area of H_2^+ ($m/z = 2$) and Ar^+ ($m/z = 40$), but for CO and N_2, C^+ ($m/z = 12$) and N^+ ($m/z = 14$) peaks were selected. The reason is that the interference exists between the peak CO^+ ($m/z = 28$) and peak N_2^+ ($m/z = 28$). In the experiment, high purity He (99.999%) was used as carrier gas with pressure 0.1 MPa and flow rate 400 mL/min. The contents of the five-component mixed standard gas include H_2: 1.01%, CO: 1.0%, N_2: 1.03%, Ar: 0.5%, He: 96.46%. Here it was assumed that the components were released from the metal sample weighed 1 g.

Fig. 7 shows that variation of the ion intensity with the element content of O, N, H and Ar measured for the standard gas sample. It is quite clear that there is a linear dependence between the ion intensity and element content, and the regression coefficients for the four elements are all better than 0.98 which indicate that the homemade EI-TOFMS can be used as an analyzer to simultaneously and quantitatively measure the multiple components in standard gas sample.

3.3. Standard metal samples measurements

Based on the result of standard gas, the tests of standard metal samples were also implemented using the EI-TOFMS analyzing system (Fig. 1). High purity He (99.999%) was used as carrier gas with a
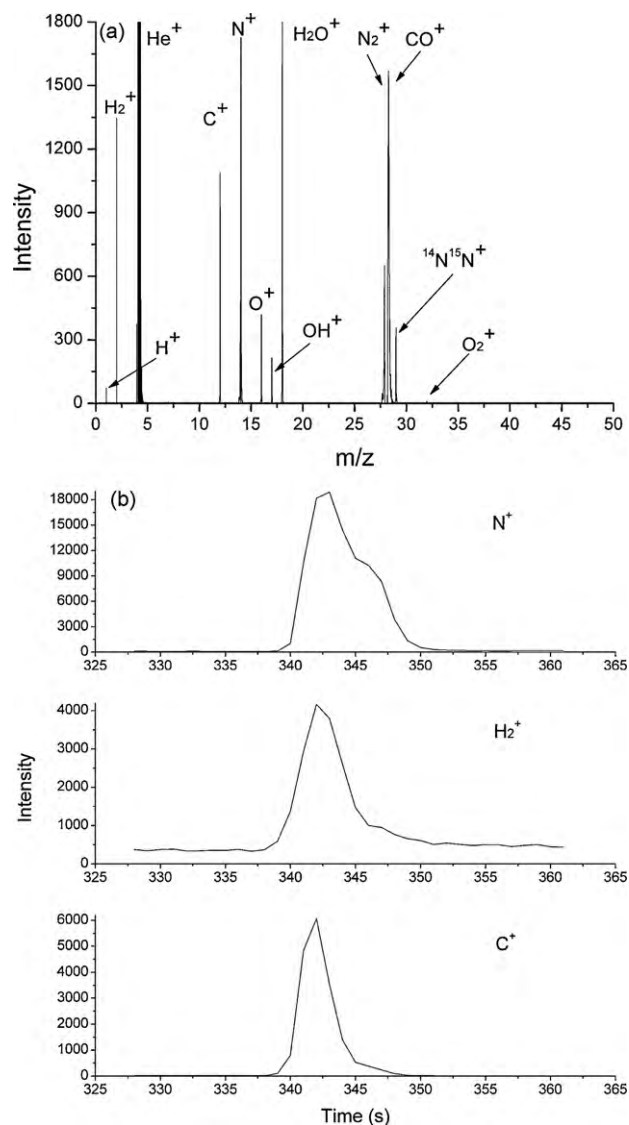

Fig. 8. (a) The EI-TOF mass spectrum of the standard metal sample. (b) The ion count curves of H_2^+, C^+ and N^+ which show the actual gas releasing progress from the standard metal sample fused by the pulse heating inert gas fusion unit.

pressure 0.1 MPa and flow rate 400 mL/min. Fig. 8(a) shows the EI-TOF mass spectrum of a standard metal sample. Fig. 8(b) is the ion count curves of H_2^+, C^+ and N^+ which show the actual gas releasing progress from the standard metal sample fused by the pulse heating inert gas fusion unit. From Fig. 8(a), we can see that besides the huge high peak He^+, there also exists other peaks, including H^+, H_2^+, C^+, N^+, O^+, OH^+, H_2O^+, N_2^+, CO^+, $^{14}N^{15}N^+$ and O_2^+. With the same method as we did for the standard gas sample, the H, N and O contents were measured based on the peak area of H_2^+ ($m/z = 2$), C^+ ($m/z = 12$) and N^+ ($m/z = 14$). The signal intensity of each component is the integral area of the ion count curves as shown in Fig. 8(b). The absolute mass content of components in the sample is calculated with formula (2):

$$W = C \times W_{sample} \tag{2}$$

where W (μg) is the content of component in a sample. C is the percentage content of component while W_{sample} (μg) is the sample weight. Since the standard metal sample with known Ar content is very rare, Fig. 9 only shows the ion intensity variations about element content for H, N and O. Table 1 shows the information of standard metal sample of H, N and O. It is quite clear that there
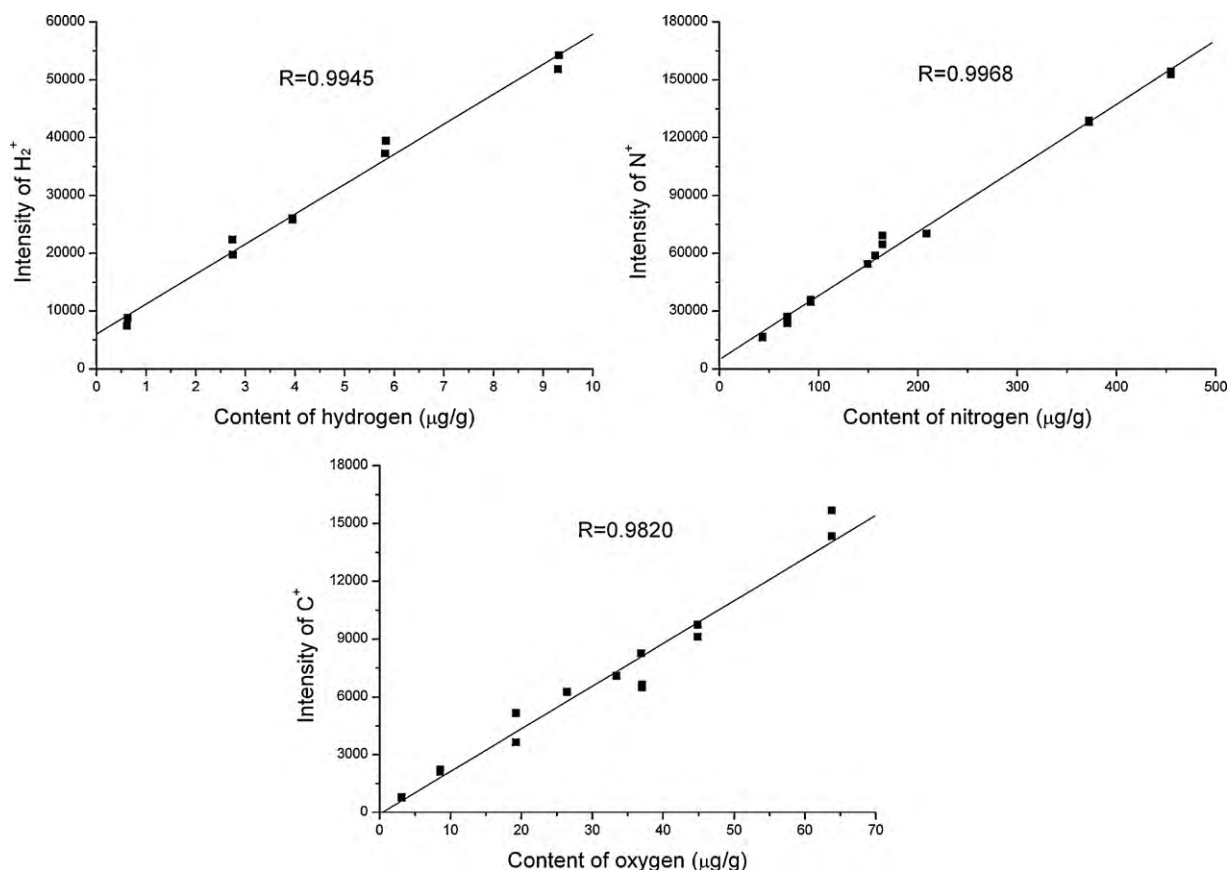
Fig. 9. Dependence of ion intensity on the corresponding content of O, N and H measured for the standard metal sample.

is a linear relationship with regression coefficient bigger than 0.98 between the ion intensity and element content for H, N and O. The result shows that the new analyzing system by coupling the EI-TOFMS with the pulse heating inert gas fusion unit can be used to analyze the element content of H, N, O and A_r in metallurgical materials simultaneously and quantitatively with the detection limit around μg/g level.

4. Conclusions

A new analyzing system for gas analysis from metallurgical materials was developed by coupling a homemade EI-TOFMS with an inert gas fusion unit. The EI-TOFMS measurement results of the standard gas sample and the emission from standard metal samples show that there is a good linear relationship between the ion intensity and element content for H, O, N and A_r and it indicates that the new analyzing system can be used to analyze the element content of H, O, N and A_r in metallurgical materials simultaneously and quantitatively with a detection limit at μg/g level.

Acknowledgements

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