Determination of manganese, chromium, nickel, molybdenum, tungsten, and copper in high manganese austenitic low-temperature steel by inductively coupled plasma atomic emission spectrometry

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ABSTRACT

As a new material, high manganese austenitic low-temperature steel has been widely used in the field of low-temperature pressure vessels due to its excellent low-temperature performance and low cost. The content of manganese, chromium, nickel, molybdenum, tungsten and copper is the basic parameter of high manganese austenitic low-temperature steel materials, and that is crucial for product quality control. In view of the fact that the current standards cannot cover the alloy composition range of high manganese austenitic low temperature steel, the analysis method for multi-element of high manganese austenitic low temperature steel was studied based on Inductively coupled plasma atomic emission spectroscopy. Optimize and determine instrument parameters and analytical spectral lines such as RF power, atomization gas flow rate, plasma gas flow rate and observation height. The specific parameters are as follows: RF power: 1.0 kW, atomization gas flow rate: $0.7 \text{ L} \cdot \text{min}^{-1}$, auxiliary gas flow: $1.0 \text{ L} \cdot \text{min}^{-1}$, plasma gas flow: $12.0 \text{ L} \cdot \text{min}^{-1}$, observation height.: 7mm, carrier gas: argon, pump speed: $12 \text{ r} \cdot \text{min}^{-1}$, stability time: 10 s, reading time: 6 s, lifting delay: 20 s, observation mode: radial direction, repetition number: 3 times, analysis spectrum line: Mn 260.568 nm, Cr 206.158 nm, Ni 231.604 nm, Mo 202.032 nm, Cu 327.395 nm, W 207.912 nm, Background correction method: fitting. Finally, a method for multi-elements of high manganese austenitic low temperature steel by inductively coupled plasma atomic emission spectrometry was established. The limitation of quantification, precision and accuracy can meet the actual inspection requirements.

Keywords: high manganese austenitic low-temperature steel; inductively coupled plasma emission spectroscopy; multi-elements; rapid determination

1. INTRODUCTION

To address global climate change and build a green, low-carbon and circular economic system, major economies such as China, the United States, Europe and Japan have successively released carbon peaking and carbon neutrality strategies. Natural gas is an important bridge and key element for achieving carbon peak at present. Liquefied natural gas (LNG) ships are the main carriers for cross-border transportation and trade of natural gas, and low-temperature steel is the main structural material for LNG storage tanks. High manganese austenitic low-temperature steel with a manganese content ranging from 22% to 25% combines advantages such as high strength, high toughness, and low cost. It has broad application prospects in the LNG storage tank market, and has received widespread attention from the shipbuilding and steel industries. In April 2022, China Classification Society issued the first domestic CCS certification for high manganese steel series products to Luoyang Ship Material Research Institute for high manganese steel welding materials, to Wuhan Steel Company for high manganese steel plates, and to CIMC Hongtu Company for high manganese steel storage tanks, that will provide technical paths and industry guidance for the next step in the application of LNG ship manufacturing[1-2].

Components such as manganese, chromium, nickel, molybdenum, tungsten and copper are the basic parameters of high manganese austenitic low-temperature steel plates and matching welding materials [3-4], which affect the microstructure, low-temperature strength and toughness, corrosion resistance, and welding performance of the materials. Therefore, the accurate and rapid determination of its composition has important guiding significance for the quality monitoring of high manganese steel and the safe service of LNG storage tanks. In recent years, inductively coupled plasma atomic emission spectroscopy has been widely used in the chemical composition analysis of low alloy steel and stainless steel due to its advantages of accuracy, efficiency, and simultaneous determination of multiple elements [5-7]. However, the current standards such as JIS G1258-2-2014 [8] stipulates that the determination range of manganese should not exceed 20%. The upper limit for manganese determination in standards such as SN/T 2718-2010[9], SN/T 3343-2012[10] and SN/T 3345-2012[11] is between 10% to 15%, and related research or applications are also focused on the range of 10% to 18% of manganese content [12]. Moreover, there are no literature reports on the determination of tungsten content in high manganese steel, so that all the standards could not meet the demand for composition analysis of high manganese austenitic low-temperature steel.

In response to the issue that the current standard method of inductively coupled plasma emission spectroscopy is not applicable to the analysis of alloy composition in high manganese austenitic low-temperature steel, this article investigates the digestion method of high manganese austenitic low-temperature steel, optimizes instrument parameters such as radio frequency power, atomization gas flow rate, plasma gas flow rate, and observation height, determines the optimal analysis spectral line and interference elimination method, and conducts methodological evaluation from the perspectives of quantitative limit, precision, and accuracy. A method for rapid determination of multiple elements such as manganese, chromium, nickel, molybdenum, tungsten, copper, etc. in low temperature high manganese austenitic low-temperature steel using inductively coupled plasma emission spectroscopy is established, providing a method for rapid detection of high manganese austenitic low-temperature steel.

2. EXPERIMENTAL SECTION

2.1 Instruments and equipment

5110 SVDV Inductively Coupled Plasma Emission Spectrometer (Agilent Technology Co., Ltd.), with the following operating parameters: RF power: 1.0 kW, atomization gas flow rate: 0.7 L · min-1, auxiliary gas flow rate: 1.0 L · min-1, plasma gas flow rate: 12.0 L · min-1, observation height: 7 mm, carrier gas: argon, pump speed: 12 r · min-1, stable time: 10 s, reading time: 6 s, lifting delay: 20 s, observation method: radial, repetition rate: 3 times, analysis spectral lines: Mn 260.568 nm, Cr 206.158 nm, Ni 231.604 nm, Mo 202.032 nm, Cu 327.568 nm 395 nm, W 207.912 nm, background correction method: fitting. Electronic balance (d=0.01mg), graphite constant temperature electric heating plate.

2.2 Materials and reagent

Pure argon(φ(Ar)$\geq$ 99.99%). Hydrochloric acid(ρ= 1.18 g/mL, analytically pure), nitric acid(ρ= 1.42 g/mL, analytically pure), hydrofluoric acid(ρ= 1.42 g/mL, analytically pure). Manganese stock solution, chromium stock solution, nickel stock solution, molybdenum stock solution, tungsten stock solution, and copper stock solution. The experimental water is grade one water.

Standard sample: High manganese steel control sample (Zhengzhou Machinery Research Institute): YSBS 37344-13. Calibration samples for the automotive high manganese steel industry (Steel Research NAK Testing Technology Co., Ltd.): YSBS 11357-2019 (NCS 013020).

Calibration solution: Take 5 polytetrafluoroethylene beakers and add a certain amount of high-purity iron (accurate to 0.0001 g) as shown in Table 1. Then add 9 mL hydrochloric acid, 3 mL nitric acid, and 1 mL hydrofluoric acid. Place them on an electric heating plate and slowly heat until the solution is clear. Remove and cool to room temperature. Add each element's single standard solution separately, and the total amount added is shown in Table 1. Then transfer to a 250 mL plastic volumetric flask and mix well to obtain the calibration solution.

Table 1. Calibration solution configuration.

Elements	Total Addition/mg				
	B0	B1	B2	B3	B4
Fe	100	76.85	70.70	64.00	56.40
Mn	0	20.00	21.50	23.50	26.30
Cr	0	1.00	2.00	3.00	4.00
Ni	0	1.00	2.50	4.00	5.50
Mo	0	1.00	2.00	3.00	4.00
Cu	0	0.15	0.30	0.50	0.80
W	0	0	1.00	2.00	3.00

2.3 Experimental methods

Weigh (0.100 ± 0.001) g of the sample (accurate to 0.0001 g) into a PTFE beaker, add 9 mL of hydrochloric acid, 3 mL of nitric acid, and 1 mL of hydrofluoric acid respectively, and place them on an electric heating plate to slowly heat until the sample is completely dissolved. Remove and cool to room temperature, transfer to a 250 mL plastic volumetric flask for constant volume testing. Under the set working parameter conditions, sequentially measure the calibration solution and the test solution, establish a calibration curve, and calculate the mass fraction of each test element in the sample based on the spectral intensity of the test element and the sample mass.

3. RESULTS AND DISCUSSION

3.1 Digestion system

Firstly, the digestion system (hydrochloric acid and nitric acid) recommended in GB/T 20125-2006 for carbon steel and low alloy steel was used to digest low-temperature high manganese austenitic low-temperature steel samples. The results showed that there were particles of insoluble substance at the bottom of the solution, and after analysis, the insoluble substance was mainly tungsten. According to MSDS, tungsten is soluble in a mixed acid of nitric acid and hydrofluoric acid, so it is recommended to use a mixed acid of aqua regia and hydrofluoric acid to dissolve the sample. Experiments have shown that 12 mL of aqua regia and 1 mL of hydrofluoric acid can completely digest 0.10 g of the test sample, and the solution is clear and transparent. Firstly, the digestion system (hydrochloric acid and nitric acid) recommended in GB/T 20125-2006 for carbon steel and low alloy steel was used to digest low-temperature high manganese austenitic low-temperature steel samples. The results showed that there were particles of insoluble substance at the bottom of the solution, and after analysis, the insoluble substance was mainly tungsten. According to MSDS, tungsten is soluble in a mixed acid of nitric acid and hydrofluoric acid, so it is recommended to use a mixed acid of aqua regia and hydrofluoric acid to dissolve the sample. Experiments have shown that 12 mL of aqua regia and 1 mL of hydrofluoric acid can completely digest 0.10 g of the test sample, and the solution is clear and transparent.

3.2 Instrument parameters

RF power, atomization gas, plasma gas, and observation height are the main parameters to be considered during the method establishment process. They can affect the distribution of plasma temperature, atomization efficiency of the test solution, and aerosol residence time, thereby affecting the intensity of emission spectra of each element. Based on the parameters set in Section 1.1, using the method of controlling a single variable, taking standard solution B3 as an example, the influence of the above parameters on spectral intensity and signal-to-noise ratio was investigated. The results are shown in the following figures 1 and 2.
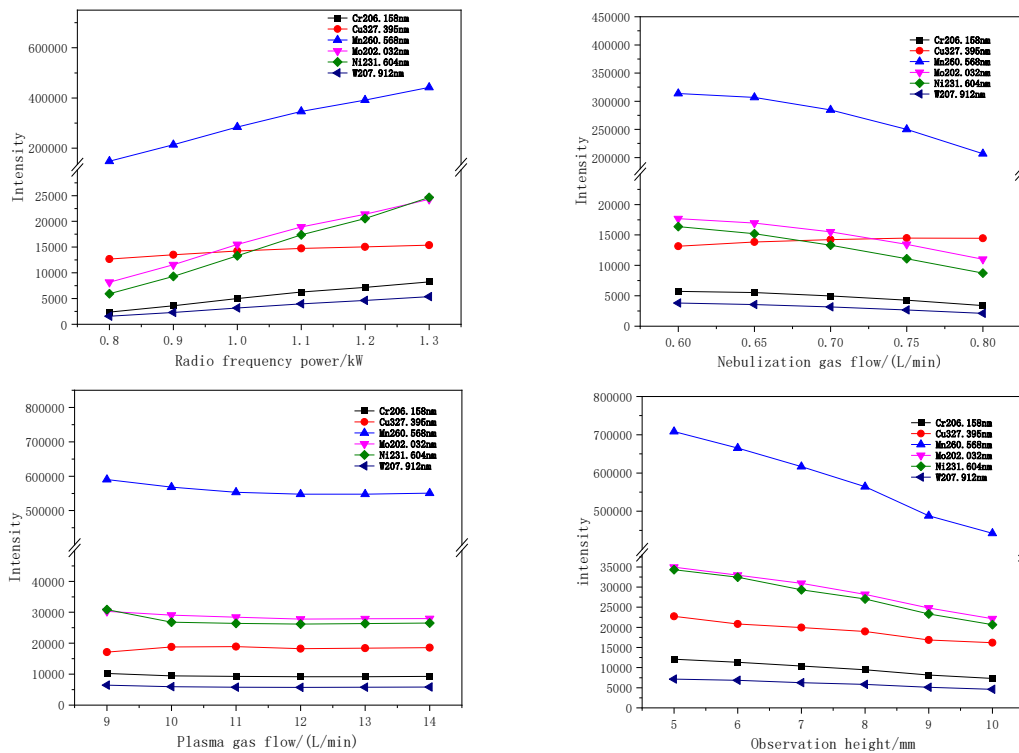
Figure 1. Effect of spectral parameters on intensity. (a): Radio frequency power; (b): Nebulization gas flow; (c): Plasma gas flow; (d) Observation height.
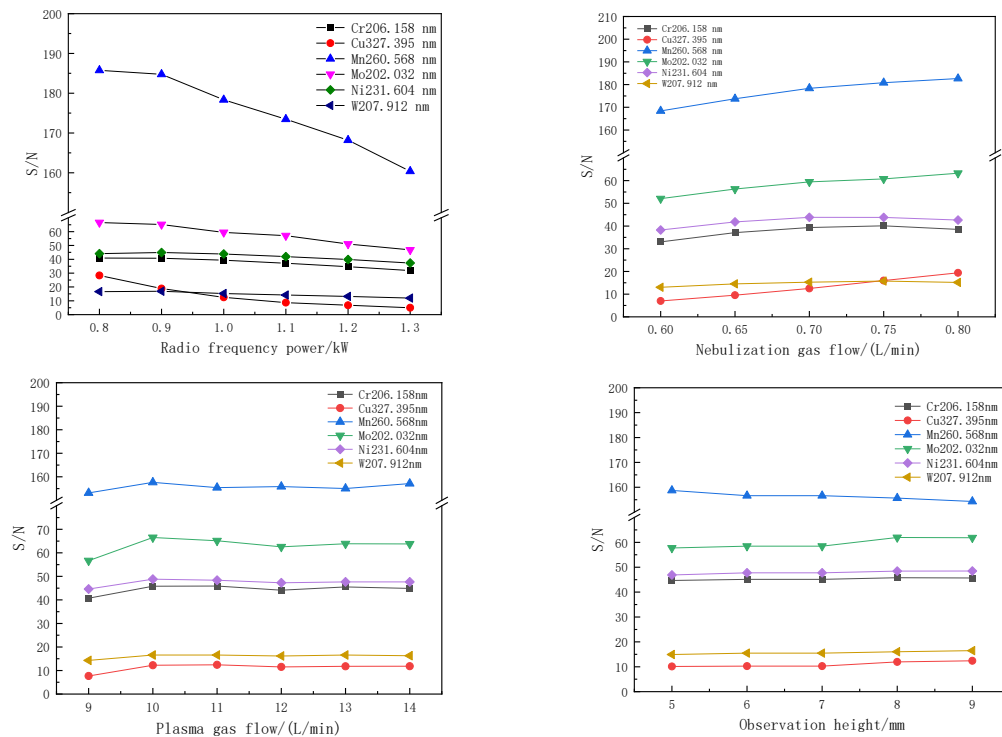

Figure 2. Effect of spectral parameters on S/N. (a): Radio frequency power; (b): Nebulization gas flow; (c): Plasma gas flow; (d) Observation height.

The experiment found that radio frequency power and atomization gas flow rate have a significant impact on spectral intensity and signal-to-noise ratio; As the RF power increases, the spectral intensity of each element approximately increases linearly, while the signal-to-noise ratio decreases linearly; As the atomization gas flow rate increases, the spectral intensity of copper remains almost unchanged, while the spectral intensity of other elements gradually decreases, while the signal-to-noise ratio of each element gradually increases. The influence of plasma gas flow rate on spectral intensity and signal-to-noise ratio is relatively weak. The radial observation height has a significant impact on spectral intensity but a weaker impact on signal-to-noise ratio. As the radial observation height increases, the spectral intensity of each element decreases, while the signal-to-noise ratio remains unchanged. Based on the relationship between spectral intensity and signal-to-noise ratio, and taking into account the balance between high spectral intensity and low signal-to-noise ratio, the middle value is more suitable for all four parameters, which is: RF power of 1.0 kW, atomization gas flow rate of 0.7 L/min, plasma gas flow rate of 12.0 L/min, and observation height of 7 mm.

3.3 Selection of analytical spectral lines and interference elimination

The interference effects of inductively coupled plasma atomic emission spectroscopy mainly include spectral interference and physical interference. Choosing appropriate analytical spectral lines is an important way to reduce spectral overlap interference. For each element to be tested, select the first, second and third spectral lines recommended by the instrument and list them in Table 2 below.

Table 2. Analytical spectral lines.

Element	Wavelength/nm	Intensity	Interference spectral lines
	257.610	222170	W 257.617 nm
Mn	259.372	176940	W 259.369 nm, Mo 259.371 nm, Cr 260.560 nm,
	260.568	68540	Fe 260.565 nm
	267.716	33439	W 267.715 nm, Mn 267.725 nm
Cr	205.560	11435	Ni 205.549 nm, W 205.557 nm,
	206.158	6817	/
	231.604	9024	Mo 231.610 nm
Ni	216.555	6350	W 216.555 nm, Mn 216.560 nm
	221.648	7884	Cr 221.663 nm, W 221.641 nm
	202.032	9730	Cr 202.033 nm
Mo	204.598	5931	Cr 204.591 nm
	203.846	2745	Mn 203.853 nm, Cr 203.868 nm
	327.395	53785.0	/
Cu	324.754	41390.0	Mo 324.761 nm
	213.598	9470.0	Mo 213.591 nm, Cr 213.603 nm,
	207.912	2624.2	/
W	209.475	946.4	Ni 209.512 nm
	220.449	2925.8	Cr 220.387 nm, W 220.399 nm

According to the information provided in the table, select spectral lines based on the principles of no coexisting component spectral interference, high signal intensity values, and not reaching signal peak saturation.

For manganese element, there are three interfering elements, tungsten, molybdenum, and iron, at Mn 259.372 nm, which is the highest among the three recommended spectral lines. At the same time, due to the manganese content in the tested samples being above 20%, considering that Mn 257.610 nm has the highest intensity, there is a possibility of saturation of the detection intensity peak. Therefore, it is recommended to analyze the spectral line as Mn 260.568 nm.

For the chromium element, although Cr 267.716 nm and Cr 205.560 nm have high intensity, they both have multiple interfering spectral lines. There is no relevant interference spectrum at Cr 206.158nm, so it is recommended to choose Cr 206.158nm as the analysis spectrum.

For the four elements of nickel, molybdenum, copper, and tungsten, the spectral interference elements with the highest spectral intensity are also the least. Therefore, four spectral lines are recommended: Ni 231.604 nm, Mo 202.032 nm, Cu 327.395 nm, and W 207.912 nm, respectively.

For all elements, the matrix matching method and background fitting correction were used simultaneously to eliminate the matrix background interference and physical interference caused by the iron matrix and digestion medium.

3.4 Calibration curve and limitation of detection and quantification

Measure the series of calibration solutions using experimental methods, and plot the calibration curve with spectral intensity (I/cps) as the y-axis and mass fraction (w/%) as the x-axis. The fitting equation and correlation coefficients are shown in the table below. According to the experimental method, the blank test solution was measured 10 times in parallel. The detection limit and quantification limit were calculated at 3 and 10 times the standard deviation of the blank, respectively. The results are shown in Table 3.

Table 3. Calibration curve and limitation of detection and quantitation.

Element	Wavelength /nm	Fitting equation	Correlation coefficient	Detection limit.	Quantization limit.
Mn	260.568	$y=22527.57x+61.86$	0.99991	/	/
Cr	206.158	$y=3004.39x+7.61$	0.99996	0.0030	0.0099
Ni	231.604	$y=6366.58x+48.59$	0.99999	0.0017	0.0056
Mo	202.032	$y=9056.97x+32.48$	0.99996	0.0006	0.0020
Cu	327.395	$y=34523.95x+32.02$	0.99994	0.0009	0.0029
W	207.912	$y=2768.83x+5.77$	0.99999	0.0020	0.0068

Note: This method determines that the content of Mn element is greater than 20%, so the detection limit and quantification limit are not calculated.

3.5 Precision and accuracy

According to the experimental method, the standard and actual samples of high manganese steel were measured, and the results are shown in Tables 4 and 5 below. The bias of the determination results of each element in the standard sample is within the extended uncertainty range provided by the standard sample. The relative standard deviation (RSD, n=10) of the determination results of all samples is not greater than 3%, indicating that the method has good accuracy and precision.

Table 4. Determination results of reference materials.

Sample	Element	Results/% (n=10)	average vavlue/%	Reference value /%	Bias/%	Extended uncertainty (k=2)/%	Standard deviation/%	Relative standard deviation /%
YSBS 11357-2019	Mn	24.15, 23.99, 23.89, 24.05, 24.02, 24.05, 24.04, 24.13, 23.98, 24.13	24.04	24.00	+0.04	0.08	0.080	0.33
	Cr	3.38, 3.41, 3.44, 3.39, 3.37, 3.40, 3.38, 3.39, 3.45, 3.41	3.40	3.37	+0.03	0.03	0.026	0.77
	Ni	0.019, 0.019, 0.020, 0.020, 0.020, 0.020, 0.019, 0.019, 0.019, 0.019	0.019	0.020	-0.001	0.001	0.0005	2.66
	Mo	0.206, 0.205, 0.204, 0.205, 0.204, 0.204, 0.205, 0.203, 0.205, 0.205	0.205	0.205	0.000	0.005	0.0008	0.41
	Cu	0.575, 0.574, 0.571, 0.569, 0.567, 0.570, 0.571, 0.571, 0.580, 0.568	0.572	0.571	+0.001	0.007	0.0038	0.67
YSBS 37344-13	Mn	22.21, 22.28, 22.26, 22.41, 22.36, 22.44, 22.24, 22.46, 22.39, 22.48	22.35	22.39	-0.04	0.04	0.098	0.44
	Cr	1.25, 1.24, 1.24, 1.24, 1.25, 1.24, 1.25, 1.25, 1.25, 1.24	1.24	1.23	+0.01	0.02	0.0053	0.42
	Ni	1.70, 1.70, 1.71, 1.71, 1.71, 1.71, 1.71, 1.72, 1.71, 1.72	1.71	1.69	+0.02	0.02	0.0067	0.39
	Mo	0.584, 0.586, 0.587, 0.587, 0.586, 0.588, 0.586, 0.585, 0.589, 0.588	0.587	0.580	+0.007	0.02	0.0015	0.26
	W	0.483, 0.481, 0.484, 0.484, 0.480, 0.486, 0.484, 0.485, 0.484, 0.486	0.484	0.490	-0.006	0.01	0.0019	0.40

Table 5. Determination results of actual samples.

Sample NO.	Element	Relative standard deviation /%
1#	Mn	0.46
	Cr	1.15
	Ni	0.41
	Mo	1.11
	W	0.38
2#	Mn	0.36
	Cr	0.73
	Ni	0.25
	Mo	0.44
	W	0.55
3#	Mn	0.43
	Cr	0.54
	Ni	0.28
	Mo	0.63
	Cu	2.38

4. CONCLUSION

This article establishes a method for determining the content of manganese, chromium, nickel, molybdenum, copper, and tungsten in high manganese steel using inductively coupled plasma emission spectroscopy. The effects of radio frequency power, atomization gas flow rate, plasma gas flow rate, and observation height on spectral intensity and signal-to-noise ratio were investigated, and methods such as calibration curve linear relationship, blank test, precision test, and standard substance verification were evaluated. The linear correlation coefficients of the calibration curves for all elements are greater than 0.999, and except for manganese, the quantification limits for all other elements are less than 0.010%. The relative standard deviation (RSD) of the actual sample and standard sample determination results is not more than 3%, and the bias of the standard sample determination results is within the uncertainty range of the standard sample. This has developed a new method for the chemical composition detection of high manganese austenitic low-temperature steel.

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