

POSTER

Sorin D. Anghel · Tiberiu Frentiu · Ana-Maria Rusu
Lucia Bese · Emil A. Cordos

The analysis of conductive solid samples by r.f. capacitively coupled plasma at atmospheric pressure

Received: 25 September 1995/Revised: 14 November 1995/Accepted: 26 November 1995

Abstract A radiofrequency capacitively coupled plasma (rf CCP) with tip-ring electrode geometry has been used for the analysis of Al, Co, Cr, Cu, Mn, Mo, Ni, and V in low and medium alloyed steel. The sample is used as one of the electrodes of the plasma torch. The influence of plasma power, argon flow rate and distance between the electrodes on the analytical signals has been studied. The limits of detection are in the range of 0.001 to 0.048%. The dynamic range is three orders of magnitude.

The radiofrequency discharges at atmospheric pressure have been used for the analysis of solid samples, usually by combining the electrothermal atomisation with excitation in an r.f. plasma. [1–3]. With an r.f. capacitively coupled plasma (rf CCP) in tip-ring electrode geometry the two phases of the analytical process could be accomplished in one step on solid, conductive samples [4]. In the present paper the analysis of 8 elements in steel samples by spectrometry with rf CCP is examined along with the optimisation of the main instrumental parameters.

Experimental

The method is based on the sputtering of atoms from the tip of the lower electrode by positive ions accelerated in the zone of the plasma close to the electrode surface. Because of the electrode shape this zone exhibits all characteristics of a normal cathodic voltage drop. In the r.f. field alternation, when the tip of the lower electrode is

negative relative to the ring electrode, the positive ions are accelerated toward the electrode by the cumulated effect of the r.f. field and the field of cathodic voltage drop. The sputtered atoms are transported by the argon flow into the plasma core and are subsequently excited. The tip of the lower electrode is constructed as a separate piece made out of the steel sample.

Instrumentation. The experimental set-up is similar to that of reference [4], except for the lower electrode of the torch. The rf CCP with tip ring electrode geometry uses a unipolar discharge, in direct contact with a water cooled electrode, placed inside a quartz tube. The second electrode consists in a ring, situated at a certain height (H) relative to the lower electrode and outside the quartz tube. The water-cooled electrode of the plasma torch has a flat top which is placed on the steel sample with a tip machined in conical shape. The experiments were carried out with calibrated steel standards provided by the Romanian Research Institute for Metallurgy (ICEM).

Results and discussion

The emitted signal depends on plasma power, argon flow rate and distance between the electrodes. The measurements were carried out at a power of 135 W where the plasma stability is not influenced by the sputtering of the atoms by thermal effects. The influence of the Ar flow rate is shown in Fig. 1a. The maximum at 0.6 l min^{-1} corresponds to the gas flow rate at which the plasma core is well defined and the residence time of the atoms in the observation area is longer. At argon flow rates less than 0.2 l min^{-1} the air could diffuse in the upper part of the quartz tube and as a result a decrease of the plasma volume and the disappearance of the core is observed. The emitted signal reaches its maximum at a 60 mm distance of the electrodes (Fig. 1b). When the argon flow rate or the electrode distance are in the optimum range the relative standard deviation (RSD) of the emitted signal is minimal. The plasma shape changes little for electrode distances of 40 to 70 mm. For an electrode distance smaller than 40 mm the divergence of the electric field in the tip area is high and the absorbed power decreases. With electrodes at distances larger than 70 mm

T. Frentiu · A.-M. Rusu · E.A. Cordos (✉)
University of Cluj, Chemistry Department and Research Center
for Analytical Instrumentation, 3400 Cluj-Napoca, Romania

S.D. Anghel
University of Cluj, Physics Department, 3400 Cluj-Napoca,
Romania

L. Bese
Silcotub Co., 4700 Zalau, Romania

Table 1 Analytical results, SBR and LODs of low and medium alloyed steel

Element	Wavelength, nm	S.B.R.	LOD%	Certified value, %	Determined value, %
Al	396.15	0.25	0.003	0.016 ± 0.002	0.012 ± 0.001
Co	345.35	0.24	0.001	0.008 ± 0.001	0.010 ± 0.001
Cr	425.43	0.03	0.008	0.210 ± 0.010	0.170 ± 0.008
Cu	324.75	0.34	0.006	0.180 ± 0.004	0.200 ± 0.005
Mn	403.07	0.31	0.048	1.170 ± 0.070	1.220 ± 0.020
Mo	386.41	0.32	0.012	0.040 ± 0.002	0.030 ± 0.001
Ni	352.45	0.30	0.031	0.130 ± 0.010	0.160 ± 0.005
V	437.92	0.28	0.001	0.220 ± 0.010	0.190 ± 0.009

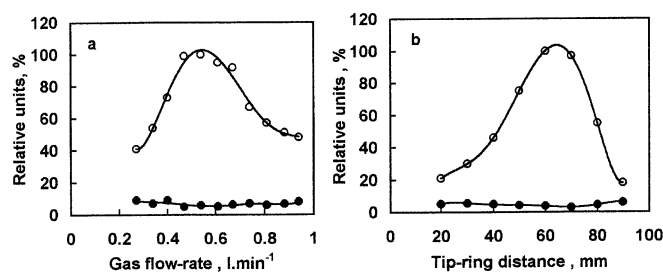


Fig. 1a, b The line intensity and RSD of 0.29% Mn in steel, as a function of argon flow rate (a) and distance between electrodes (b). ○ MnI 403.07 line intensity, ● RSD. Plasma power 135 W; a electrode distance 60 mm, b argon flow rate 0.60 l min⁻¹

the electric field intensity is not sufficient to maintain a plasma with core. These suppositions are supported by the increase of both the argon excitation temperature (9300 K) and the electron number density in the superficial luminescence zone when the electrode distance increases from 40 to 70 mm. The analytical re-

sults on a certified steel sample for 8 elements, along with SBR (signal to background ratio) and LODs (limits of detection) are shown in Table 1. The calibration was performed on 8 certified standards. The SBR were determined at a concentration 10 times the LOD. The SBRs, are surprisingly similar except for Cr, which proves the uniformity of the sputtering process. The calibration curves are linear over 3 orders of magnitude, starting from a concentration 5 times the LOD. The analytical results are in a good agreement with the certified values.

References

1. Blades MW, Banks P, Gill C, Huang D, Le Blanc C, Liang DC (1991) IEEE Trans Plasma Sci 19:1090
2. Liang DC, Blades MW (1989) Spectrochim Acta 44B:1049
3. Liang DC, Blades MW (1989) Spectrochim Acta 44B:1059
4. Cordos EA, Anghel SD, Frentiu T, Popescu A (1994) J Anal Atom Spectrom 9:635