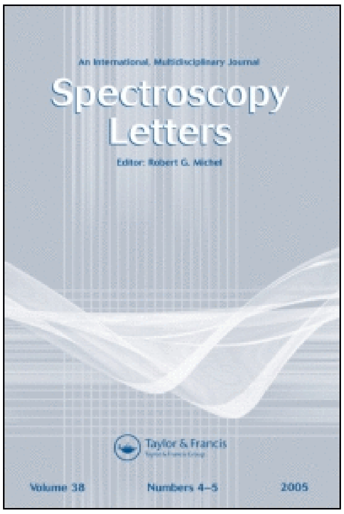

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SPECTROSCOPIC INVESTIGATION OF PLASMA COMPOSITION OF U-SHAPED ARGON STABILIZED D.C. ARC

KEY WORDS: U-shaped arc, plasma composition, molecular components, rotational temperature

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ABSTRACT

The spectroscopic analysis of emitted radiation from the U-shaped argon stabilized d.c. arc is performed when the arc was burning without and in the presence of water aerosol. The special attention is paid to the emission of molecular components. The radial distribution of rotational temperature is obtained from the OH band spectra. The arc plasma composition is also theoretically calculated supposing the state of local thermodynamic equilibrium and compared with experimental results.

INTRODUCTION

The U-shaped d.c. arc is a very stable plasma source characterized by a long horizontal column stabilized by the gas vortex technique.[1] It is possible to change easily the arc atmosphere (introducing different gases) i.e. the composition of the main components as well as of traces, thus affecting various chemical reactions which occur in a large plasma volume, under changeable physical conditions. Therefore, the gas plasma from the arc column can be used as a suitable excitation source of various species as well as a generator of free atoms, molecules and radicals. These characteristics enable its application in atomic emission and absorption spectroscopy as well as in plasma chemistry.

In this paper the plasma composition of the U-shaped d.c.arc is analyzed spectroscopically and theoretically for the arc burning in air and stabilized with argon and in the case when water aerosol is introduced into the plasma. Discussing these results it is possible to investigate the influence of the water on plasma characteristics and its composition. In all these considerations the radial distribution of temperature has to be taken into account.

EXPERIMENTAL

The experimental set-up of the U-shaped argon stabilized d.c. arc is described in detail elsewhere.[1] A relatively long horizontal arc column is formed between two vertical and parallel electrodes (a graphite anode and a carbon cathode). A stream of argon flows tangentially into the cavity of teflon segments, forming a gas vortex stabilizing the arc column. When the arc is used in analytical atomic spectroscopy, the argon stream introduces the sample aerosol, which has to be analyzed, into the plasma. The

TABLE 1

Experimental facilities and operation conditions

Polychromator	PGS-2 with order sorter
Grating	600 grooves/mm,
	blaze angle 49°
Order of diffraction	8th
Dispersion	0.05 nm/mm
Photo multiplier	Hamamatsu, R 212
Photo plate	Kodak, SA-1
Arc current	7.5 A
Argon flow	2 dm^3/min
Nebulizer	Meinhard concentric glass

experimental facilities and operation conditions are presented in Table. 1.

The radiation emitted from all the plasma column volume is spectroscopically analyzed in spectral region from 250 to 750nm applying observation in end-on direction. The emitted radiation is registered both photographically and photoelectrically. The U-shaped arc is a spatially inhomogeneous plasma source with relatively long cylindrically symmetric arc column. For the purpose of radial density distribution determinations, observation from side-on direction was performed. The lateral profiles were transformed to radial by means of the Abel integral inversion.

The radial distribution of rotational temperature is obtained from the corresponding distribution of rotational lines of the OH $A^2\Sigma$-$X^2\Pi$ band spectra. The temperature was determined applying the Boltzmann plot method to the rotational lines whose characteristics are given in Table 2.[2]

TABLE 2

Physical characteristics of rotational lines of 306.4 nm OH band

Wavelength(nm)	Excitation energy(cm^{-1})	gA
306.928	33949	28.8
306.918	33650	24.8
306.967	35912	49.1
307.114	36393	53.2
307.303	36903	57.2
307.437	32947	12.8
307.703	32778	8.9

The lateral intensity distribution was measured at each wavelength position, converted to a radial distribution and these data were used for temperature determination. Namely, the Boltzmann plots were constructed for different radial positions in plasma enabling the determination of temperature radial distribution.

CALCULATION OF PLASMA COMPOSITION

The experimentally determined results were compared with the computed plasma equilibrium composition. For that purpose, the method of minimizing the Gibbs free energy function was used taking into account the mass action law for dissociation, ionization and radiative capture and quasi neutrality condition.[3] The arc plasma was considered to be in LTE, existing as a single-phase system with a constant ratio of the main atomic components: argon, nitrogen, hydrogen, oxygen and carbon.

The arc plasma burning at atmospheric pressure with no aerosol ("dry" plasma) is considered to contain argon (95%),

TABLE 3.

The physical characteristics of some of the atomic lines identified from the U-shaped arc

Element	Wavelength(nm)	Excitation energy(eV)	Ionization energy(eV)
H	486.13	12.74	13.60
O	436.83	12.36	13.61
Ar	426.63	14.53	15.76
C	247.86	7.68	11.26

nitrogen (3.4% from air), oxygen (1.1% from air), hydrogen (0.4% from air) and carbon (0.1% from electrodes). In another case when water aerosol is introduced into the plasma the system consists of 96.5% of Ar, 0.35% of N, 1.1% of O, 2.0% of H and 0.05% of C. The choice of components was made in accordance with spectroscopic investigations. Needed data on free energy was taken from Refs.4 and 5 or calculated .

RESULTS AND DISCUSSION

The very important characteristics of the emission spectra of the U-shaped d.c. arc is the simultaneous appearance of atomic lines of the main and trace plasma components and molecular bands. In both cases, when arc is burning without and in the presence of water aerosol, the atomic spectral lines of the main components such as argon, hydrogen, oxygen and carbon appear in the spectra as it is presented in Table 3.

The radial density distribution experimentally measured for Ar, C and continuum are presented in Fig.1.

Considering the measurements of the same distributions of other main components as well as of trace elements added to the

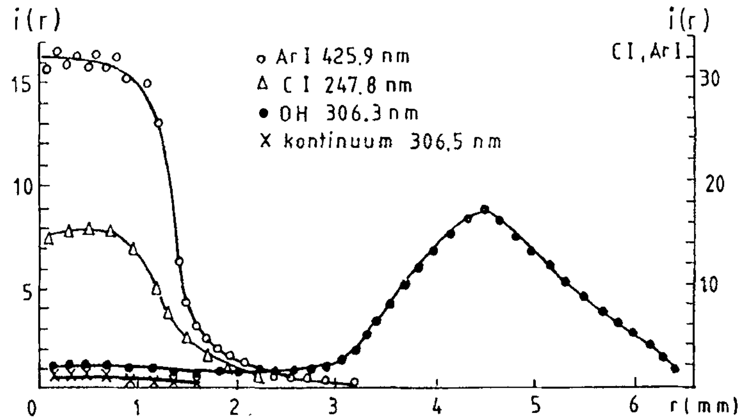

Fig. 1. Radial intensity distribution of ArI, CI lines, OH band head and continuum

water solution, it can be concluded that all the components with high ionization potential are excited in the central part of plasma column, i.e. in plasma core.

The previous measurements have shown that the temperature in this zone is between 7000 and 8000K.[6] Fig.1. also shows the radial density distribution of OH 306.4 nm band head. It is evident that radial density distribution of OH component is quite different in shape in comparison with atomic components, i.e. this component is excited in the plasma periphery where the temperature is suitable for this process.

In order to obtain the temperature conditions in this peripheral plasma zone, the Boltzmann plot method was applied to the chosen rotational lines from OH band spectra (Table 2.). The results obtained for radial temperature distribution are presented in Fig.2. It can be concluded that in this zone the temperature is lower in comparison with plasma core while the temperature gradient is relatively broad.

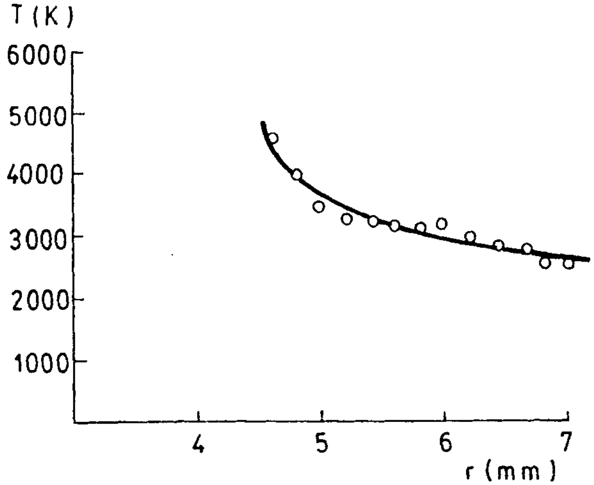

Fig.2. Radial distribution of rotational temperature

The spectral analysis of emitted radiation registered in side-on direction has shown quite a different molecular composition of the main plasma components for the arc burning without water aerosol and in the presence of water aerosol.

The emitted spectra of the "dry" plasma is characterized by simultaneous appearance of spectral lines of elements with high ionization potentials and of bands of various components such as CN, N_2^+, OH, NO and NH. The list of the main band systems observed in the emission spectra is given in Table 4.

It is worth mentioning that while the CN and OH band spectra readily occurred in carbon arcs in air, the band systems corresponding to the other mentioned species such as N_2, N_2^+, NO and NH are not typical for this kind of discharge.

The radial distribution of the radiation density of the band heads of all the components except of OH are similar. The radial distribution of emitted radiation of CN and N_2^+ are given in Fig. 3. as illustration. The intensity of band heads of N_2, N_2^+, CN NO and NH decreases radially from the plasma center to the periphery.

TABLE 4

The main band systems observed in emission spectra of the "dry" plasma

Species	System	Transition
CN	violet	$B^2\Sigma_u^+ - X^2\Sigma_g^+$
N_2	2nd positive	$C^3\Pi_u - B^3\Pi_g$
N_2^+	1st negative	$B^2\Sigma_u^+ - X^2\Sigma_g^+$
NO	γ, 3rd positive	$A^2\Sigma^+ - X^2\Pi$
NH	336.0 nm	$A^3\Pi - X^3\Sigma^-$
OH	306.4 nm	$A^2\Sigma^+ - X^2\Pi$

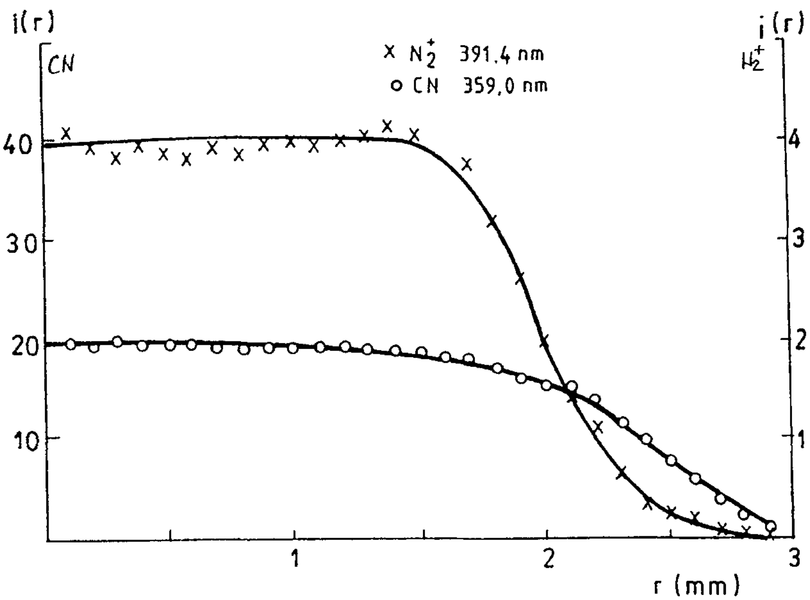

Fig. 3. Radial intensity distribution of CN and N_2^+ band heads

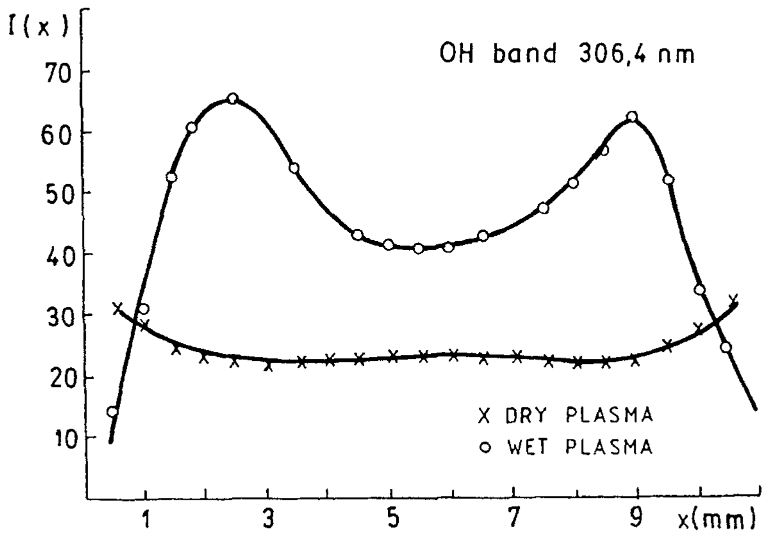

Fig. 4. Lateral profile of OH band head without and with water vapor

It is evident that these species are emitted from the plasma core which expands up to 3mm from the axis. The maximal intensity of the band head in the center is higher in the case when air is introduced instead of water aerosol with argon flow into the plasma column. The intensity is reduced when nitrogen, oxygen and hydrogen come only from argon (as impurity) or from the outer atmosphere which was realized by shutting the system for introduction of aerosol. But it is evident that under this condition the molecular components are still formed in the plasma.

When water aerosol is introduced into the plasma, which is the ordinary practice in spectrochemical analysis, the emission of all the mentioned molecular bands disappears except of OH bands which are certainly stronger. In the case of OH, the maximum of the intensity of emission is in the plasma periphery so there were difficulties to apply the Abel inversion to such profiles when water was not introduced into the plasma. The lateral profiles of OH bands without and in the presence of water aerosol are presented in Fig. 4.

It is obvious that the introduction of water aerosol increases the intensity of OH band head. But also it can be concluded that in the presence of water, the maximum of band head intensity is moved towards the center of plasma column. This can be taken in connection with the fact that intensity of spectral line of Ar is increased in the presence of water. From the energy balance considerations for the d.c. arc plasma it is shown that the introduction of water vapor to the plasma leads to the formation of the narrow plasma core of higher temperature.[7,8] A very steep gradient of the radial temperature distribution is formed towards the zones in which chemical reaction occurs. This means that in this high temperature zone excitation of argon is improved. As OH radical is formed in low temperature zone, its optimal excitation in the presence of water will be nearer to the plasma center. When plasma is burning without water, the plasma core is wider and of lower temperature and conditions optimal for the formation of OH are away from the plasma center.

In order to explain all these results, the plasma composition for the conditions corresponding to the U-shaped d.c. arc stabilized with argon is calculated and presented for neutrals in Fig. 5a and for ions in Fig 5.b. The calculated results are in accordance with experimental one. The conditions for the formation and excitation of the identified molecular components are convenient when the arc is burning with no water aerosol.

The difference in the shape of lateral profiles of OH band heads compared to other molecular bands can be explained considering their particle density distributions in dependence of temperature. OH component is preferably formed in a low temperature region which is in accordance with radial density distributions obtained. With the introduction of water aerosol the plasma composition is slightly changed. Namely, the quantity of nitrogen introduced into the plasma is decreased while the quantity of hydrogen is

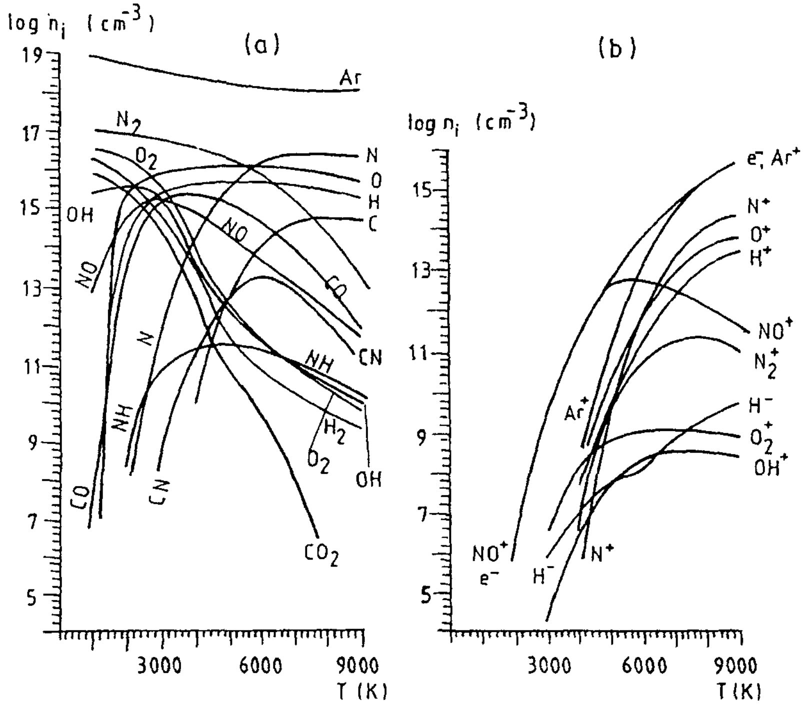

Fig. 5. Equilibrium composition of (a) neutral and (b) charged components

increased. Consequently, the plasma conditions are altered and the maximum of band head intensity of OH is moved toward the plasma center. With the temperature increase the quantity of other molecular species formed decreases and there are not enough of them to be detected in emission. It should be added that the disappearance of the most molecular bands from the emission spectra when water aerosol is introduced into the plasma is of importance for the practical spectrochemical analysis of various materials.

CONCLUSION

The U-shaped d.c. arc stabilized with argon is investigated as a medium suitable for the formation of various molecular components. The experimentally obtained radial radiation density distributions of different species are in accordance with their particle density distributions calculated supposing the LTE conditions. Various components such as CN, N_2, N_2^+, NH, NO and OH are formed in plasma. It is of interest to point out that some of these species are not typically emitted from the d.c. arc plasma. The disappearance of all the mentioned components except of OH when water aerosol is introduced into the plasma can be explained considering energy balance calculations for this type of discharge. Namely due to chemical reactions occurring in plasma, the narrow high temperature core is formed in the presence of water. Therefore, the changed plasma conditions affect the appearance of various species. The results of these investigations are of importance for spectrochemical analysis as well as for plasma chemistry.

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