

FORMATION AND TRANSPORT OF CaF IN DC ARC PLASMA*

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Received 13 December 1974

Abstract: A decrease in the Ca spectral line intensities and in the CaO molecular band intensity was observed in d. c. arc plasma, in the presence of fluorine. The transport properties of CaF were investigated. The cause for depressive effect of added fluorine on the Ca spectral line intensities might be explained by chemical reactions leading to the formation of CaF in plasma and by the change in the transport properties of calcium.

1. Introduction

The addition of fluorine into the d. c. free burning plasma arc changes also plasma temperature and plasma electron density¹⁾ besides plasma composition due to the formation of fluoride compounds. The effect of added fluorine on processes occurring in the plasma can be seen also in changes of transport velocities of investigated elements and their residence times.

In this paper, the formation and the transport of CaF radicals in free burning plasma arc, was observed. These radicals emit the band spectrum and the appearance of CaF bands proves undoubtedly the existence of CaF radicals in investigated plasma. Due to the formation of CaF in plasma, the reduction of the concentration

* This paper was presented in part at VII Yugoslav Symposium on the Physics of Ionized Gases, Rovinj 1974.

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of Ca atoms, Ca^+ ions and CaO molecules is expected entailing the reduction of atomic and ionic spectral line intensities of calcium and of CaO molecular band intensities.

2. Experimental

NH_4F was evaporating from the upper electrode (cathode), through a small hole at the bottom, Fig. 1. The probe, containing mixture of graphite powder and CaCO_3 , was put into the anode. This method of separate evaporation of the probe and NH_4F was used in order to diminish the effect of fluorine on the evaporation of calcium.

The emission spectra of Ca atoms and CaO molecules were photographed in the absence and in the presence of NH_4F . At the same time, the emission band spectrum of CaF radicals was observed, in the presence of fluorine. The arc current was 10 A and the electrode distance was 5 mm. From Table 1. the influence of NH_4F on Ca atomic spectral line intensity and on the intensity of the heard of CaO band can be seen (presence of F).

Transport of calcium in the presence of fluorine has been investigated. Fluorine, as $\text{CF}_2 = \text{CF}_2$, was evaporating from the lower electrode-anode (whose shape was the same as that of the upper electrode in Fig. 1).

$\text{Ca}(\text{NO}_3)_2$ has been injected in drops into the arc²⁾. The existence of CaF radicals due to the reaction $\text{Ca} + \text{F} \rightleftharpoons \text{CaF}$ in the plasma was confirmed by CaF emission band spectrum at 530 nm (transition $\text{B}^2 \Sigma \rightarrow \text{X}^2 \Sigma$) and at 600 nm (transition $\text{A}^2 \Pi \rightarrow \text{X}^2 \Sigma$). Microphotometric measurements of the arc spectrum, in the presence and in the absence of F, at 530 nm, have been carried out. Fig. 2. (a, b) represents transpance as the function of the wavelength in the presence and in the absence of F, respectively. From these microphotograms we can see that at 530 nm the interference of the arc band spectrum (CN, C_2) or CaO with CaF bands can be neglected. Neither strong atomic nor ionic spectral lines of calcium exist in this spectral region. The CaF radiation at 530 nm was selected using the interference filter.

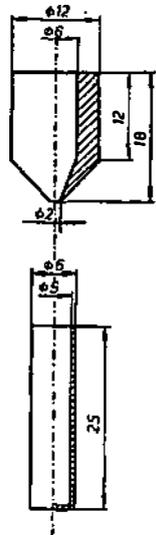


Fig. 1.
Shape of the
electrodes.

For the transport processes investigation the arc has been photographed by a high speed camera. By the method described in paper³⁾ diffusion coefficients were determined from the time dependence of changes in the spatial intensity distribution of CaF radiation. The spatial intensity distribution was determined by microphotometric measurements of pictures taken by a high speed camera. The axial transport velocities of the clouds of the excited substance were measured, too (Table 2.).

TABLE 1.

The influence of added fluorine on the Ca atomic spectral line intensity and on the intensity of the head of CaO molecular band

I CaI 6166 Å	I CaO 6097 Å
I* CaI 6166 Å	I* CaO 6097 Å
1.66 ± 0.27	1.60 ± 0.15

* means the addition of F.

TABLE 2.

Diffusion coefficients and axial transport velocities of CaF

N°	D (cm ² s ⁻¹)	pol. upper electrode	v_{ax} (cm s ⁻¹)
1	3.9	—	450
2	2.7	—	330
3	1.1	—	310

For the comparative consideration, the results of observation of CaO bands in the absence of F taken from paper⁴⁾ are shown in Table 3.

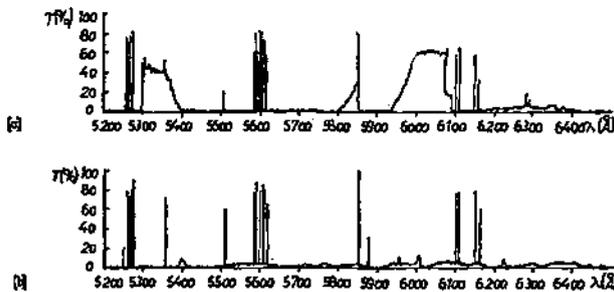


Fig. 2. Microphotograms of the arc spectrum; T -transparency; λ -wavelengths, a) in the presence of F, b) in the absence of F.

3. Discussion

The decrease in the Ca atomic spectral line intensities and in the CaO molecular band intensity, observed in experiment 1., might be caused by the following phenomena:

- the change in the excitation and ionization conditions due to the change in the plasma temperature and electron density,
- the higher transport velocities of calcium particles from the discharge zone, and

- the change in the concentration of Ca and CaO particles in the plasma due to chemical reactions leading to the formation of CaF radicals in the arc plasma.

It has been shown¹⁾ that the increase of plasma temperature which is expected on the basis of the plasma energy balance and has been observed, does not account for the depressive effect of added fluorine on spectral line intensities.

Somewhat lower values for the diffusion coefficients of CaF and higher values for axial transport velocities (Table 2) have been found, compared to the diffusion coefficients of CaO and its axial transport velocities, given in Table 3.

TABLE 3.
Diffusion coefficients and axial transport velocities of CaO

N°	D (cm ² s ⁻¹)	pol. upper electrode	T (K)	v_{ax} (cm s ⁻¹)
1	14.0	—	3500	210
2	6.3	+	3000	170
3	7.0	—	2500	220
4	4.3	+	2000	200
5	3.5	+	1500	200
6	1.6	—	1000	270

It may be assumed that the lower values of the diffusion coefficients of CaF refer to the lower temperature zone of the arc while higher axial transport velocities are mostly due to the higher convection velocity in the presence of F. The mean value of the convection velocity of carbon particles, determined independently with a high speed camera, is about 3 ms⁻¹ and 2 ms⁻¹⁵⁾ in the presence and in the absence of fluorine, respectively. The change in the convection velocity is probably due to the change in the spatial plasma temperature distribution. In the presence of halogen a plasma core of higher temperature is formed and the radial temperature gradient increases considerably⁶⁾.

The results of experiment 1. can be explained in terms of the transport properties investigated in experiment 2. It may be assumed that convection processes are independent of the mass and the kind of particles. The decrease in the Ca spectral line intensities and in the CaO band intensity, in the presence of F, can be due to the higher axial transport velocities of calcium particles, caused mostly by the higher convection velocity in the outer zone of the arc. On the other hand, the increase in the axial transport velocities leads to a decrease in the number of particles that leave the discharge zone, diffusing in radial direction, whereby the negative effect of the higher axial transport velocities on the spectral line intensities is to a certain extent compensated⁷⁾.

It may be assumed that the decrease in the Ca spectral line intensities and in the CaO molecular band intensity is at least in part caused by the formation of CaF in plasma.

We suppose that all forms of calcium (Ca, Ca⁺, CaO, CaF) have a common transport if the substance occupies a small region of the arc (experiment 2). But, under the conditions of experiment 1. when the substance to be investigated was spread throughout the discharge zone, it is likely that a process of separation of different calcium components occurs.

References

- 1) M. Tripković and V. Vukanović, *Spectrochim. Acta* 26B, (1971) 131;
- 2) V. M. Vukanović, M. S. Todorović, P. S. Todorović and T. S. Mihailidi, *Spectrochim. Acta* 30B (1995) 31;
- 3) M. N. Perić, P. S. Todorović and V. M. Vukanović, *Spectrochim. Acta* 30B (1975) 21;
- 4) M. N. Perić, P. S. Todorović, V. M. Vukanović, *Proc. XVII Coll. Spectr. Intern., Firenze 1973, Vol. 1., (1973) 186;*
- 5) P. S. Todorović, V. M. Vukanović, M. M. Simić and M. N. Perić, *Spectrochim. Acta B* (in Press)
- 6) N. Ikonomov and B. Pavlović and V. Vukanović, *Spectrochim. Acta* 26B (1971) 127;
- 7) P. W. J. M. Boumans and L. De Galan, *Analytical Chemistry, Vol. 38 5* (1966) 674.

OBRAZOVANJE I TRANSPORT CaF U PLAZMI LUKA

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Sadržaj

Zapaženo je smanjenje intenziteta spektralnih linija Ca i molekulskih traka CaO u plazmi luka, u prisustvu fluora. Ispitivane su transportne osobine CaF. Depresivni efekat dodatog fluora na intenzitete spektralnih linija Ca može se objasniti hemijskim reakcijama koje dovode do obrazovanja CaF u plazmi i promjenom transportnih osobina kalcijuma.