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INFLUENCE OF METAL IMPURITIES ON THE TRANSPORT PROPERTIES OF MULTICOMPONENT PLASMA OF UNDERWATER DISCHARGES

The influence of metal impurities on the transport properties of multicomponent thermal plasma at the ambient atmosphere of water vapor has been considered. The calculations are carried out on the basis of the Grad method. It is shown that a small amount of metal impurities can substantially change the magnitude of transport coefficients in comparison with the case of pure water vapor. The influence of the model for the cross-section of electron collisions with a metal atom on the transport properties of thermal plasma is analyzed.

Keywords: multicomponent plasma, underwater discharge, arc discharge, pulsed discharge, thermal conductivity of plasma, plasma conductivity.

1. Introduction

In the last decade, the attention to the study of discharge plasma in water was enhanced [1–10, 14]. Discharges of this kind are widely used in electro-discharge technological processes such as welding, punching, fettling of castings, rock crushing, and so forth. Underwater discharges find their application in shipbuilding, metallurgy, and oil-gas industry. In addition, the attention to the study of discharges in water becomes stronger due to the development of technologies associated with the application of a water-vapor arc plasma for the gasification of carbon-containing raw materials [1, 2] and, as a whole, for the waste processing, as well as for new technologies of water purification [3].

Copper, iron, and tungsten belong to substances that are widely used for electrodes. Therefore, they often become a component of the underwater discharge plasma. In particular, the influence of copper vapor considerably changes the characteristics of arc discharges [11, 12].

In the case of multicomponent medium, due to a considerable number of particle-to-particle interactions of different types, the scenario of occurring processes becomes substantially complicated. For partially ionized plasma, the processes of interaction between electrons and neutral particles are very important. The electron scattering by copper atoms is the most completely studied process. In work [15], various models for the cross-section of electron-copper atom collisions and the results of their application to simulate a low-temperature plasma were discussed in detail. The most widespread models for the cross-section of low-energy electron scattering by a copper atom are the following ones: the resonance model [16], which is characterized by the presence of a resonance near 0.1 eV, and the non-resonance one [17]. However, the results of calculations in the framework of a new alternative model were reported recently [18]. This model is also characterized by the presence of a resonance, but shifted toward higher energies. It will also be considered below.

This work was aimed at studying how the physical characteristics of the plasma medium that arises at underwater discharges – this is a mixture of water vapor and metal atoms (copper, iron, and tungsten) – affect the transport properties of plasma.

2. Component Composition Formation in Underwater Discharge Plasma

The evaporated material of electrodes and conductors that are used to maintain the plasma current or to initiate discharges because of high insulating properties of water inevitably gets into water, in addition

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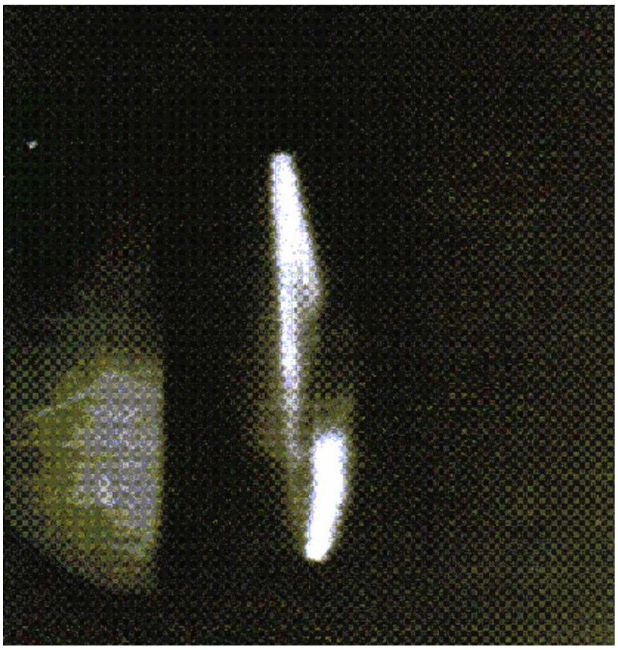

Fig. 1. General view of a discharge channel at the final stage of a pulsed discharge. The voltage $U_0 = 10$ kV, the discharge gap $l_0 = 4$ cm, and the inductance of the discharge contour $L_0 = 0.47$ μH

to the substances that have already been dissolved in it. Atoms of those impurities can substantially affect the properties of underwater discharge plasma. In particular, they induce changes in the distributions of current and released power in the discharge channels and influence the formation of their structures and development dynamics.

The accumulation of electrode material impurities was studied experimentally by monitoring the dynamics of variations in the radiation spectrum distributions along and across the discharge channels of pulsed discharges. The complete opacity of plasma channels at the initial discharge stages did not allowed the process of metal arrival into plasma to be traced in detail at those stages. However, the analysis of reabsorbed Cu lines in the radiation spectrum unequivocally testified to an intensive arrival of the copper electrode material into the channel and its presence in both the internal and external channel regions. The attention was attracted by the fact that, in a certain time interval, the electrode material reached the central part of the channels, which was the most remote from the electrodes, even if the studied dimension of the discharge gap was maximum. The observation of the discharge development during later periods, when plasma became transparent, allowed the mechanism of accelerated transport of the electrode material into plasma to be elucidated. For the discharges examined in this work (the oscillatory discharge of a reservoir capacitor through a water gap at the voltages $U_0 = 2 \div 40$ kV and the currents $I_0 = 10 \div 200$ kA), torch-like ejections of the substance evaporated from the electrodes were observed along the discharge channel axis. The results reported above were typical, when “thin” conductors smaller than 20 μm in diameter were used to initiate discharges. This was the only case where the hydrogen lines were the brightest in the plasma spectrum before the electrode material vapor arrived into the observation zone. When the diameter of conductors was increased to 70 μm, the lines of the conductor material dominated in the radiation emission spectrum near the H_β line.

Hence, the evaporation and erosion of the material of discharge electrodes were the main source of the uncontrollable arrival of impurities into the plasma of researched pulsed discharges. In the arc discharges, the component composition of plasma is determined not only by the discharge medium material, but also the material of evaporated electrodes. The amount of an evaporated material is usually proportional to the electric charge that crossed the electrode contact area during the discharge and depends on the specific energy required to melt and evaporate the electrode material. In pulsed discharges in liquids, owing to the contraction of the anode and cathode spots, the current density reaches so high values that the evaporation is accompanied by the ejection of jets of a molten metal and its vapor from the overheated sections of discharge spots on the electrodes in the direction normal to the electrode surface plane. In our previous spectrometry researches, we found that copper reached the middle of discharge gaps within several tens of microseconds. This propagation velocity considerably exceeded the diffusion one. A direct observation of the propagation of an electrode material at the active discharge stage was impossible owing to the opacity of the plasma channel. We could only monitor the results of this process.

In Fig. 1, a photo of the discharge channel at the time moment, when it became transparent owing to its expansion, so that its medium became cooled down, is depicted. The cathode and anode jets, which are propagating along the channel, are well distinguished. The shape of the jets may testify to a subsonic velocity of their propagation: higher densities at the jet ends are inherent to supersonic jets (the so-called Mach jumps are absent). A diffusion-smeared darkening, the trace of the tungsten wire, is observed along the channel axis. No features testifying to the appearance of large-scale perturbations are observed. The anode and cathode jets are also not deformed by vortex fluxes.

3. Transport Properties of Plasma

Let us consider plasma in the state of local thermodynamic equilibrium [25]. Owing to high concentrations of neutrals and electrons, the collision processes in such plasma play a much more important role than the particle transport and radiation processes.

For low-temperature plasma, in which the local thermodynamic equilibrium is maintained, the electron concentration at a given discharge point is related to the concentration of ions and neutral particles by means of the Saha equation. For the molecular gas plasma, the law of mass action, which reflects the reaction processes, has also to be taken into account. We included 16 sorts of particles into consideration. In particular, for a mixture of water vapor with copper, the following set of particles was used: e^-, H_2O, H_2O^+, H_2, H_2^+, OH, OH^+, O_2, O_2^+, H, H^+, O, O^+, Cu, Cu^+, and Cu^{2+}. Similar sets of particles were used for mixtures containing iron or tungsten.

It should be noted that, unlike the case of atomic gas, the processes of molecular dissociation and atomic association are typical of the molecular gas plasma. In addition, in comparison with the atomic gas, its molecular counterpart has additional internal (vibrational and rotational) degrees of freedom. Owing to those factors, the properties of the molecular gas plasma are substantially different from those of the atomic gas plasma.

The determination of the plasma composition allows the transport properties of plasma to be calculated. In calculations, we used the Grad method [19–21]. Note that, in work [21], the applicability of the Grad method to the problems of partially ionized plasma was demonstrated, and a comparison with a more widespread Chapman–Enskog method was carried out.

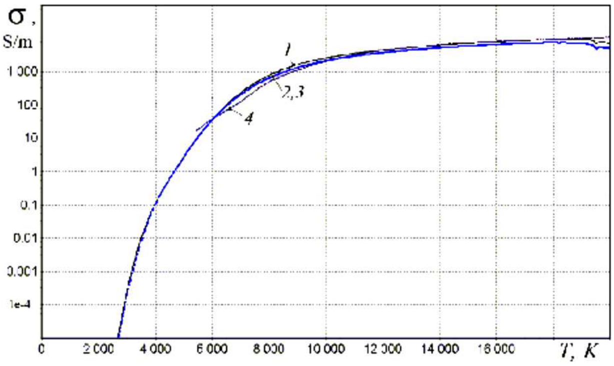

Fig. 2. Temperature dependences of the conductivity of water-vapor plasma (the pressure $p = 1$ bar) in various models: Lorentz model (LM) (*1*), zero-density model (ZM) (*2*), dense model (DM) (*3*), and data of work [22] (*4*)

The conductivity of thermal plasma is mainly determined by electrons:

$$\sigma = \frac{3}{2} n_e^2 e^2 \left(\frac{2\pi}{m_e kT}\right)^{1/2} \frac{|q'|}{|q|}, \tag{1}$$

where m_e and e are the electron mass and charge, respectively; k is the Boltzmann constant; T the temperature; n_e the electron concentration; and the elements of determinants q and q' are complicated functions of the transport integrals (see works [20, 21]).

The thermal conductivity of plasma is governed by several factors:

$$\lambda = \lambda_h + \lambda_e + \lambda_{\text{int}} + \lambda_{rd} + \lambda_{ri}, \tag{2}$$

where λ_h is the thermal conductivity of heavy particles, λ_e the electron thermal conductivity, λ_{int} the thermal conductivity associated with internal degrees of freedom, and λ_{rd} and λ_{ri} are the coefficients of thermal conductivity due to the effects of dissociation and ionization, respectively. It should be noted here that, in addition to the influence of dissociation owing to the heat transfer by means of vibrational and rotational degrees of freedom, the gas component of the thermal conductivity for the molecular gas considerably exceeds the corresponding contribution for the atomic gas.

4. Calculation Results and their Discussion

The results of calculations are shown in Figs. 2 to 9. One can see that the properties of the water-vapor discharge plasma with metal impurities substantially

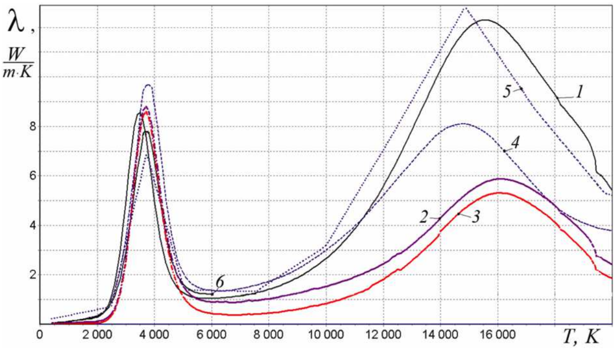

Fig. 3. Temperature dependences of the thermal conductivity of water-vapor plasma (the pressure $p = 1$ bar) in various models: LM (*1*), ZM (*2*), DM (*3*), data of work [22] (*4*), data of work [23] (*5*), and data of work [24] (*6*)

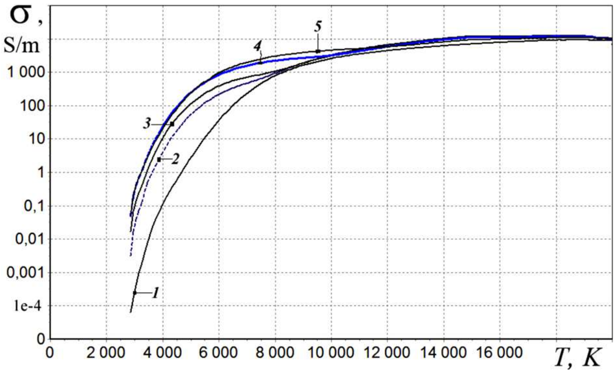

Fig. 4. Temperature dependences of the conductivity of the water-copper mixtures with various H_2O : Cu molar ratios (the pressure $p = 1$ bar): pure water (ZM) (*1*), 99.99 : 0.01 (*2*), 99.7 : 0.3 (*3*), 95 : 5 (*4*), 70 : 30 (*5*). The alternative model of $e^- + Cu$ cross-section [18] was applied

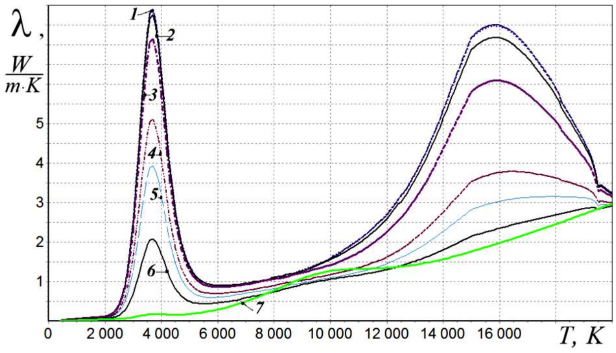

Fig. 5. Temperature dependences of the thermal conductivity of the water-copper mixtures with various H_2O : Cu molar ratios (the pressure $p = 1$ bar): 99.99 : 0.01 (a slight difference from the pure water case (ZM) (*1*), 99.9 : 0.1 (*2*), 99.7 : 0.3 (*3*), 99 : 1 (*4*), 95 : 5 (*5*), 70 : 30 (*6*), and 10 : 90 (*7*). The alternative model of $e^- + Cu$ cross-section [18] was applied

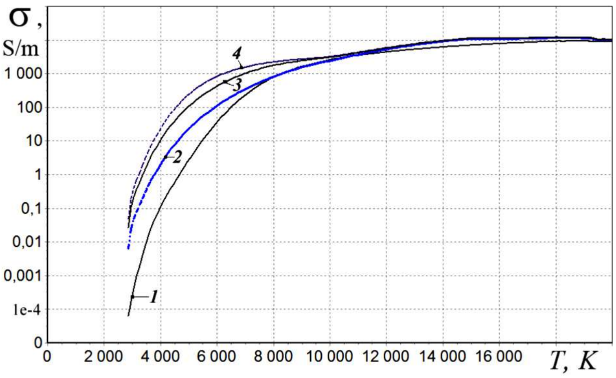

Fig. 6. Temperature dependences of the conductivity in pure water in the ZM (*1*) and in various water-metal mixtures with a constant molar ratio of 95 : 5 (the pressure $p = 1$ bar): H_2O : Fe (*2*), H_2O : Cu (*3*), and H_2O : W (*4*). The alternative model of $e^- + Cu$ cross-section [18] was applied

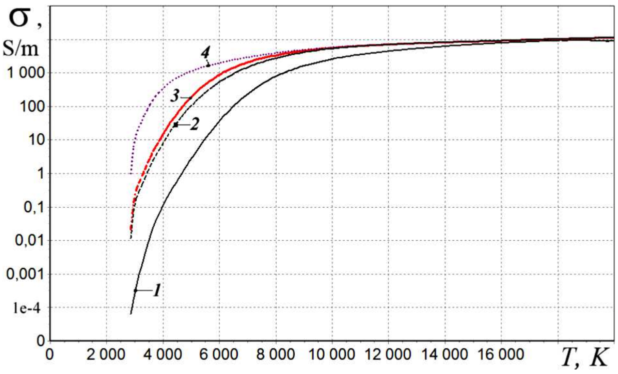

Fig. 7. Temperature dependences of the conductivity in pure water in the ZM (*1*) and in the H_2O : Cu water-metal mixture with a constant molar ratio of 10 : 90 in various models (the pressure $p = 1$ bar): resonance model of $e^- + Cu$ cross-section [16] (*2*), alternative model [18] (*3*), and non-resonance model [17] (*4*)

depend on the plasma composition. As a rule, the appearance of metal impurities gives rise to the growth of conductivity and energy density in plasma.

First, let us consider the characteristic features of transport properties of thermal plasma in the case of water-vapor thermal plasma without impurities. In Figs. 2 and 3, the results of calculations obtained, on the one hand, with the use of the Grad method – both not taking non-ideality effects into account (the zero density model (ZM) model) and making allowance for plasma non-ideality (the dense model (DM)) [26], – and, on the other hand, on the basis of Lorentz models (LM) [13, 14] and following the Chapman–Enskog method [22, 23] are compared. The results of calculations agree well with the data reported in works [14, 22–24]. The attention should be paid to the fact that the temperature dependences of the thermal conductivity have characteristic maxima, which are associated with the dissociation and ionization processes (in the case of atomic gas, the first "dissociative" maximum is absent). The attention should also be paid to the fact that, in the case of water vapor, the "dissociative" maximum looks like a single peak, although water molecules dissociate in a number of ways. Such a scenario is characteristic, generally speaking, of two-atomic gases, in particular, hydrogen. Taking into consideration that the magnitude of indicated maxima for water vapor is mainly determined by the mobility of hydrogen atoms and ions, as the lightest atomic particles available in the mixture, a conclusion can be drawn concerning the similarity of properties for the hydrogen thermal plasma and the water-vapor one. As a consequence, a similarity of discharge properties for the indicated media should also be expected.

Hence, let us consider characteristic features of transport properties for the water-vapor thermal plasma with metal impurities (Fig. 4 to 9). It is evident that the introduction of an insignificant amount of copper admixtures results in an increase of the conductivity and a reduction of the thermal conductivity (Figs. 4 and 5). The latter effect is connected with the difference between the thermal conductivity of molecular and atomic gases, which was mentioned above.

For the mixtures of water vapor with iron or tungsten, the picture is similar. A comparison with the copper impurity within the alternative model for the e^- + Cu scattering cross-section [18] demonstrates that the additiona of tungsten and iron should give a higher and lower conductivities, respectively, in the case of 5% molar fraction of the impurities (Fig. 6).

Now, let us consider the difference of plasma properties, if we assume that the cross-sections of electron scattering by the copper atom are different. For the thermal conductivity, the change of the electron-atom collision cross-section is insignificant, because there are many other factors that remain invariable. However, for the electric conductivity, this variation is substantial (Fig. 7). One can see that, in the framework of the alternative model, the conductivity occupies an intermediate place between the resonance and non-resonance ones.

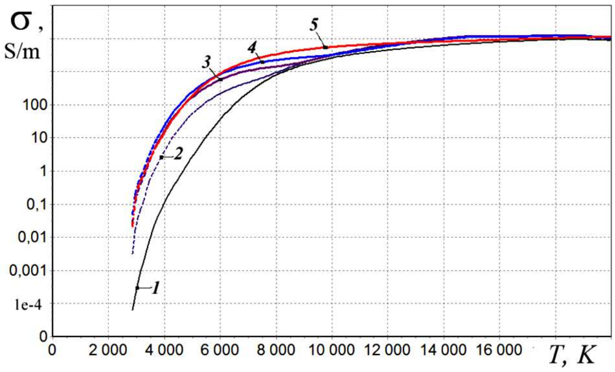

Fig. 8. Temperature dependences of the conductivity in pure water in the ZM (*1*) and in the H_2O : Cu water-metal mixtures with various H_2O : Cu molar ratios (the pressure $p = 1$ bar): 99.99 : 0.01 (*2*), 95 : 5 (*3*), 70 : 30 (*4*), and 10 : 90 (*5*). The alternative model of e^- + Cu cross-section [18] was applied

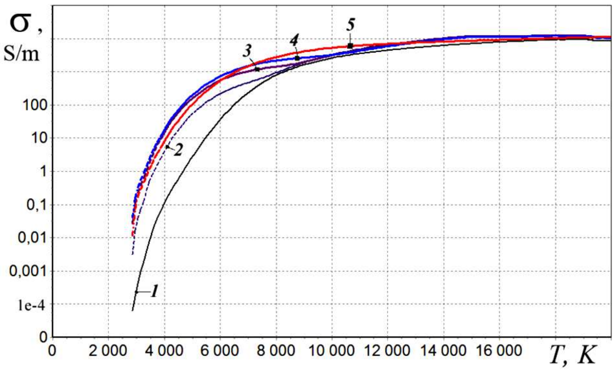

Fig. 9. The same as in Fig. 8, but with the resonance model for the e^- + Cu cross-section [16]

Finally, let us analyze the conductivity of a mixture with a high content of metal (Figs. 8 and 9). As one can see, the conductivity can even decrease, if the metal content grows substantially. However, the character of this phenomenon depends considerably on the electron-atom interaction. Note that, for the resonance model of interaction, a reduction of the conductivity at high concentrations of a metal impurity is more substantial.

5. Conclusions

To summarize, small amounts of metal impurities can give rise to considerable changes in the magnitude of transport coefficients for the underwater discharge plasma in comparison with the discharge in the aqueous medium free of impurities. The properties of a multicomponent discharge plasma with metal impurities substantially depend on the cross-section of the electron scattering by metal atoms. At present, there are considerable discrepancies between the magnitudes of transport properties for multicomponent plasmas calculated in the framework of various models for the transport cross-section of electron scattering by a copper atom. Therefore, the properties of a discharge plasma containing the copper impurity have to be studied further.

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ВПЛИВ МЕТАЛЕВИХ ДОМІШОК НА ТРАНСПОРТНІ ВЛАСТИВОСТІ БАГАТОКОМПОНЕНТНОЇ ПЛАЗМИ ПІДВОДНИХ РОЗРЯДІВ

Резюме

Розглянуто вплив домішок металів на транспортні властивості багатокомпонентної плазми в атмосфері водяної пари. Проведені розрахунки ґрунтувалися на методі моментів Ґреда. Показано, що невелика кількість металевих домішок може суттєво змінити величини транспортних коефіцієнтів порівняно із випадком чистої водяної пари. Розглянуто вплив моделі перерізу зіткнень електрона з атомом металу на транспортні властивості термічної плазми.