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ASSESSING THE SAMPLE TEMPERATURE EFFECT ON NITRIDATION IN A HIGH-FREQUENCY DISCHARGE*

VÁCLAV KREJČÍ**, JARMILA KODYMOVÁ**, Praha

The effect of temperature on the nitridation rate of magnesium samples placed in a hf discharge nitrogen plasma has been investigated. It follows from all experimental results that although the thermal effect cannot be neglected, decisive for the nitridation rate in plasma is the production of chemically active particles.

ОЦЕНКА ВЛИЯНИЯ ТЕМПЕРАТУРЫ ОБРАЗЦА НА НИТРАЦИЮ В ВЫСОКОЧАСТОТНОМ РАЗРЯДЕ

В работе исследовано влияние температуры на скорость нитрации магниевого образца, помещённого в высокочастотном разряде. Из всех экспериментальных данных следует, что решающее влияние на скорость нитрации в плазме имеет продукция химически активных частиц, если даже учитывать влияние температуры.

It is welll known that rate of heterogeneous chemical reactions like oxidation or nitridation of metal surfaces in an oxygen or nitrogen atmosphere can be considerably increased by the application of a hf electric field which changes the originally neutral gas into a hf plasma containing various particles in ionized or excited states (e. g. [1]). The mechanism of this effect has not yet been quite explained. However, it is evident that the hf field causes directly or indirectly (e. g. by accelerating charged particles bombarding the metal surface) a rise of the substrate temperature and thus enhances the reaction yield. In the present paper we have tried to assess the contribution of the temperature effect to the total increase of the reaction rate in plasma. The results presented here have been included into the thesis of J. Kodymová[2].

The discharge was excited by a 4 MHz generator in a flow of nitrogen (about 1 m/s) in a quarz tube with an external active electrode (viz. electrode connected to the unearthed plug of the generator). For the first experiments (results presented in Fig. 1) the discharge tube was in a vertical position and the magnesium sample had

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** Institute of Physics Czech. Acad. Sci., Na Slovance 2, CS-180 40 PRAHA.

the form of a long tape hung in the axis of the tube as suggested by V. Hermoch. Later we used magnesium samples in the shape of disks fixed in a special holder and placed in the horizontal discharge tube. Only one side of the sample was exposed to the influence of the discharge plasma. From its opposite side the aluminium block was applied. In some experiments a small electric oven (18 W) was placed in this block which made an additional heating of the sample possible. The temperature of the sample was measured by an iron-constantan thermocouple

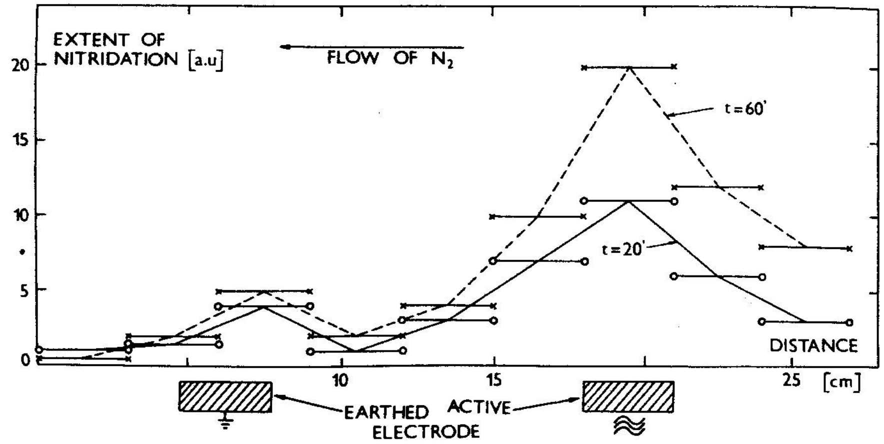

Fig. 1 The extent of magnesium nitridation in different places of a hf discharge (p = 185 Pa, I = 0.5 A).

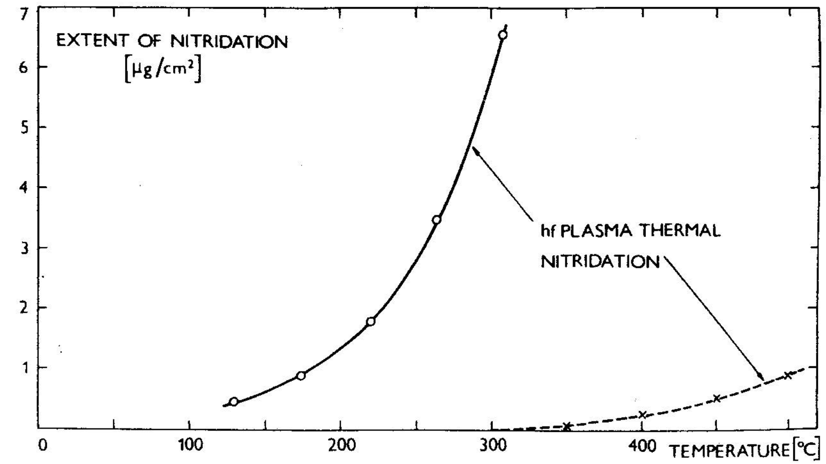

Fig. 2 Dependence of nitridation on sample temperature (p = 67 Pa, I = 0.3to 0.8 A, t = 30').

passing through the aluminium block to the sample surface. The temperature gradient across the 0.4 to 0.7 mm thick magnesium disk could result in a temperature difference of less than one degree Centigrade only. Also the effect of the hf field on the reading of the thermometer could be neglected: there was no considerable difference between the deflections of the thermometer indicator in the presence and in the absence of the hf field.

From the diagram in Fig. 1 it can be seen that the extent of nitridation depends strongly on the distance from the active electrode and hence on the intensity of the hf electric field causing the two above mentioned effects. In Fig. 2 the intensity of the nitridation in dependence on the metal temperature is given (full curve). The comparison with the pure thermal nitridation (dotted curve) shows that in both cases the dependence is exponential in form, however, in plasma the chemical reaction proceeds much quicker.

Finally in Fig. 3 nitridation of three samples of the same diameter and surface quality, exposed 60 minutes to a hf plasma, is compared. The first sample placed 5 cm from the active electrode attained the temperature of about 150 °C and a nitridation $\Delta m = 0.45$ μg of nitrogen chemicaly bound on 1 cm² of the magnesium surface. The most intensive nitridation ($\Delta m = 3.15$ μg/cm²) was obtained in the case of sample 2 placed in the region of the maximum electric field. The final temperature of this sample reached almost 300 °C. The third sample placed in a hf field of the same intensity as sample 1 attained a more than three times higher nitridation ($\Delta m = 1.65$ μg/cm²) due to the fact that its temperature had been

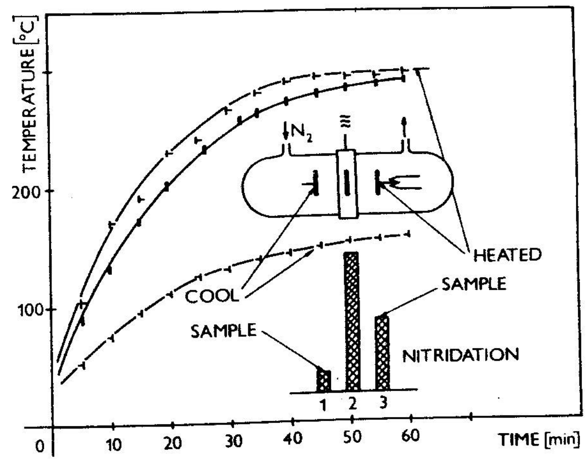

Fig. 3. Temperature course of three samples in a hf discharge (p = 130 Pa, I = 0.5 A) measured by an iron-constantan thermocouple and the resulting relative nitridation. The right-hand sample was heated by an electric heater.

maintained by heating slightly higher than the temperature of sample 2 (see diagram in Fig. 3).

From these results, especially from the last mentioned experiments, it can be seen that although the nitridation rate increases exponentially with temperature, the factor decisive for the growth of the nitride film in plasma is the presence of the chemically active particles created here. Their concentration has a maximum at the place of the active electrode and is controlled by the plasma parameters only. However, the sample temperature is not a negligible factor because of the fact that it influences to a certain extent the processes in the solid state.

This conclusion has also been confirmed by additional experiments not included in this paper. We can mention, e. g. those concerning a pure thermal nitridation, a superimposed hf discharge and nitridation in different places of a dc discharge [3, 4, 5].

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