BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1010—1013 (1971)

The Spectroscopic Observation of the Selective Volatilization of Metal Solid Samples in a Nitrogen Plasma Flame[1]

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(Received June 5, 1970)

Some metal solid samples were burned in a nitrogen plasma flame, and the spectrum intensity-time curves were spectrographically observed. The curves indicated that the fractional distillation of alloying elements was caused by the reactions of the solid-alloy sample and nitrogen gas. The fractional distillation was explained in terms of the difference in the stabilities of the metal nitrides. The distribution of the emission species and the temperature of the flame suggested that there were few chemical reactions in the flame or that the chemical reactions in the flame had little effect on the spectrum intensities. In an appendix, the method of line-pair selections for obtaining the correct temperature is considered.

Many molecular species, such as MO, OH, and CN, are produced by the introduction of solution samples into a plasma flame; they cause the high background spectra. The use of a metal solid sample instead of the solution may eliminate some of them, but the difficulties of the use of a solid sample are present in the complications of sample charging, high-temperature physicochemical reactions in an electrode, and the evaporation process of electrode materials. Several excellent discussions of fractional distillation or selective vaporization have already been reported.[2-4] However, few papers have discussed the fractional distillation resulting from the reactions of elements in a metal electrode with gases which produce plasmas. In a previous report,[5] a burner which produced a current-free nitrogen plasma jet flame was used for the spectrographic analysis of metal solid samples. With it, satisfactory calibration curves were obtained

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[1] This paper was read at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] L. H. Ahrens and S. R. Taylor, "Spectrochemical Analysis," Addison-Wesley Publ. Co., Reading, Mass. (1961).

[3] O. Leuchs, *Spectrochim. Acta*, **4**, 237 (1950).

[4] E. Schroll, *Z. Anal. Chem.*, **198**, 40 (1963).

[5] K. Hirokawa and H. Goto, This Bulletin, **42**, 693 (1969).

for the determination of some alloying elements in iron alloys, but for the alloying elements in aluminum alloy the precision was not satisfactory because of the sputtering of aluminum as aluminum nitride. In this report, the evaporation process of aluminum alloy and iron alloy, the emission profiles for metallic species in the nitrogen plasma flame, and the flame temperature will be investigated.

Experimental

The apparatus was the same as that described in the previous report.[5] The spectra were photographed under the following conditions: sample, 15 mm in length and 5 mm in diameter; polarity, anode; condenser voltage, 230—250 V; arc current, 13—15 A; tangentially-introduced gas-flow rate, 1.4 *l*/min; atomizer gas-flow rate, 4.2 *l*/min; slit width of spectrograph, 30 μ. Fuji spectrographic plates were developed with F.D. 131 at 20°C for 5 min. In order to measure the distribution of spectrum intensities along the vertical axis of the nitrogen plasma flame, the flames were imaged on the spectrographic slit with a 10-sec exposure after a predischarge of 120 sec. The intensity-time curves were obtained by a focused image of the flames on a condenser lens and by repeating a 10-sec exposure and a 20-sec interval after a predischarge of 5 sec. A Shimadzu ARL electron X-ray microprobe analyser was used for microanalysis; it had an accelerating voltage of 20 kV.

Results and Discussion

The vertical emission profiles for metallic species in the nitrogen plasma flames produced by an aluminum alloy (Si, 0.75; Cu, 0.90; Mg, 2.32; Zn, 3.06; Fe, 0.09; Mn, 0.274; Pb, 0.40; Bi, 0.58; Cr, 0.177; Ti, 0.266%) and by an iron alloy (V, 1.72%) are shown in Figs. 1 and 2 respectively. The spectrum intensities are normalized to the intensity of the part, 0.3 to 0.9 mm above the top of the burner. There were no proper two lines for measuring the temperature for the aluminum alloy flame. Therefore, the temperature was measured only for the iron alloy flame with the line-pair of FeI 3214.40 and FeI 3219.59. The method of selecting line-pairs for obtaining the correct temperature will be considered in an appendix. The temperature distribution curve along the vertical axis of the plasma flame is shown in Fig. 3. The higher a position in the flame, the lower the temperature. This suggests that the flame is cooled by the surrounding air and has no exothermic reactions at least. Moreover, the monotonous and nearly uniform decrease in the spectrum intensities with the height of the flame indicates that there are few reactions in the flame or that the chemical reactions have little effect on the

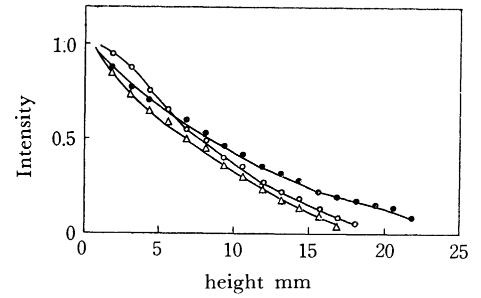

Fig. 1. The vertical emission profile for metallic species in the nitrogen plasma flame produced by Al-alloy.
○, TiI 3642.68; ●, CrI 3020.67; △, MgI 3096.90

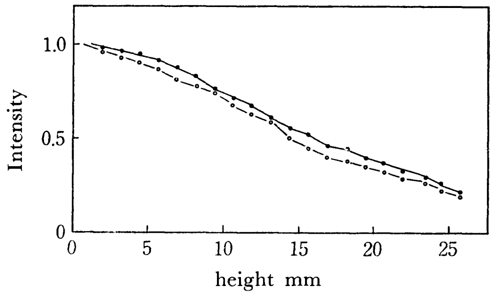

Fig. 2. The vertical emission profile for metallic species in the nitrogen plasma flame produced by Fe-alloy.
●, VI 3185.40; ○, FeI 3184.90

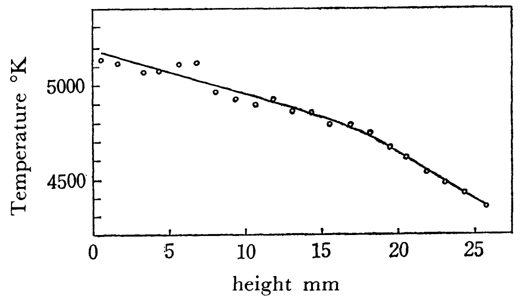

Fig. 3. The temperature curve along the vertical axis of iron-nitrogen plasma flame.

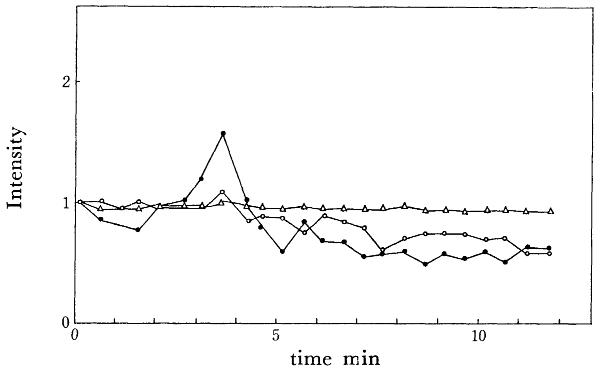

Fig. 4. Intensity-time curve for Cr, Si, Al in Al-alloy.
△, CrI 3593.49; ●, SiI 2881.58; ○, AlI 2567.99

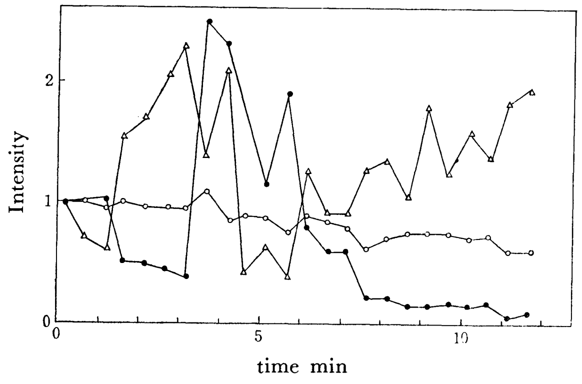

Fig. 5. Intensity-time curve for Mn, Ti, Al in Al-alloy.
△, MnII 12605.69; ●, TiI 3642.68; ○, AlI 2567.99.

spectrum intensities.

For some elements in aluminum alloy, the intensity-time curves are shown in Figs. 4 and 5. Aluminum, magnesium, silicon, chromium, nickel, zinc, and lead make one group. Their intensities decreased with the time, though the rates of decrease were small. However, the intensity of manganese had risen in the early stage, and then, after a diminution, increased gradually again. The spectral intensity of titanium had decreased at first and then after an increase, decreased again. The intensity-time curve of a solid sample was not, of course, the same in each discharge, but the patterns of the curves appeared similar.

For some elements in iron alloys, the intensity-time curves are shown in Figs. 6 and 7. Nearly constant spectral line-intensity ratios with time were obtained for manganese, molybdenum, and vanadium in iron. On the other hand, the spectrum intensity ratios aluminum and titanium to iron decreased with the time. These patterns were also similarly maintained in each discharge.

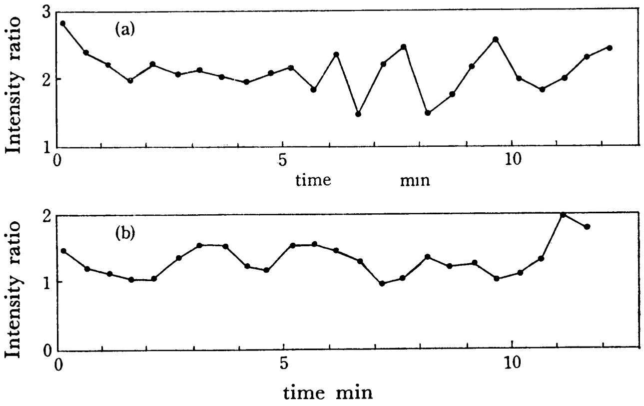

Fig. 6. Intensity-time curve for Mn in Al-Mn-Steel, MnI 2801.06/FeI 2840.42 (a); and Mo in Mo-Steel, MoI 3864.11/FeI 3805.34 (b).

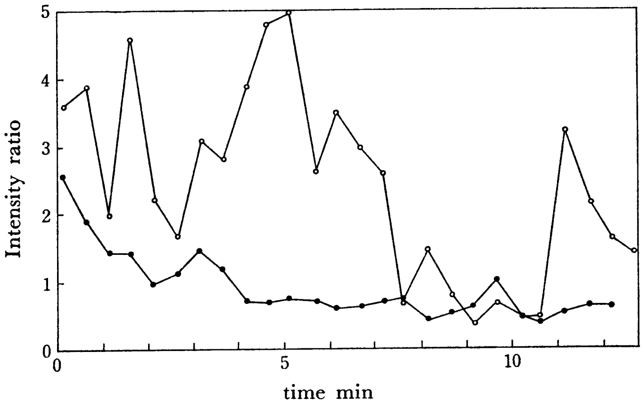

Fig. 7. Intensity-time curve for Ti, in Ti-Steel, and Al in Al-Mn-Steel.
○, TiI 3653.50/FeI 3451.92; ●, AlI 3092.71/FeI 3142.45

The flame temperature of titanium-iron alloy was around 4600—4900°K during the burning period. The flame used was current-free, so that violent change in the excitation conditions of the plasma during the burning period is not considered. Since the emission-spectral-line intensities from the flame under constant conditions are proportional to the concentration of the elements in the flame, the intensity-time curves are considered to be equivalent to the evaporation rate-time curves. The evaporation rates may depend to a considerable degree upon the chemical reactions on the electrode. Figures 4 to 7 may, consequently, indicate that there is a relationship between the intensity-time curves and the reactions on the electrode. The equilibrium between metals and the corresponding nitrides have been represented graphically by Darken and Garry.⁶⁾ The equilibrium is represented:

$$xM_{(solid)} + N_{2(gas)} = M_xN_{2(solid)}$$

Iron nitride decomposes at a low temperature, and titanium nitride is more stable at a high temperature. The partial pressure of the nitrogen of other metal system comes between the partial pressure of the iron system and that of the titanium system at the same temperature, as in Darken and Garry's graph. In the case of the aluminum matrix, the evaporation-rate ratio of aluminum to metal, which forms not so stably as aluminum, is nearly constant. Titanium is concentrated on the electrode surface of the electrode, titanium may intermittently evaporate in large quantities; then a second decrease is observed. In the case of the iron matrix, aluminum and titanium behave similarly. In electron-microprobe analysis, the intensity of Ti$K\alpha$ on the discharged surface of the sample was higher than that of other parts, and N$K\alpha$ was observed in the same places. These findings indicated that titanium was concentrated as titanium nitride there. Titanium nitride was observed even in the heated area of the bulk sample. However, the behavior of manganese could not be explained.

Conclusion

The reactions of solid-sample metal with nitrogen gas, which produces an arc plasma, cause a fractional distillation of the elements in samples. It indicates that a nitrogen plasma flame may not be adequate for the determination of titanium and zirconium in some alloys because of the higher stabilities of their nitrides. The differences in the stabilities of metal nitrides cause a fluctuation in the emission spectral intensity ratios.

Appendix

The fundamental equation for temperature measurement according to the two-line procedure is:

$$I_a/I_b = (gA)_a/(gA)_b \cdot \nu_a/\nu_b \cdot \exp(-(V_a - V_b)/\boldsymbol{k}T).$$

if the lines are labelled a and b (I, relative intensity; g, statistical weight; A, relative transition probability; ν, frequency; V, excitation potential). Boumans⁷⁾ discussed the effect of $V_a - V_b$ and the $(gA)_a/(gA)_b$ ratio upon the relative error ($\Delta T/T$) of the temperature. The error, however, depends not only on them but also on the value of the I_a/I_b ratio.

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6) L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals," McGraw-Hill Book Co., Inc., New York, Tront, London (1954).

7) P. W. J. M. Boumans, "Theory of Spectrochemical Excitation," Plenum Press, New York (1966).

Experimentally measurable temperature ranges by two-line procedure[a]

Table 1. 2.00 eV $< V_a - V_b <$ 2.50 eV

V_a-V_b	(eV)	2.32	2.28	2.27	2.14
$(gA)_a/(gA)_b$		28.1	100	268	635
λ_a	(Å)	3265.62	3760.05	3956.46	4282.41
λ_b	(Å)	3440.99	3683.06	3940.88	4216.41
A	(°K)	4800—12000	3900—11000	3400—8000	2900—5900
B	(°K)		3900— 5100	3400—5200	2900—5000

Table 2. 2.50eV $< V_a - V_b <$ 3.00 eV

V_a-V_b	(eV)	2.70	2.73	2.67	2.72
$(gA)_a/(gA)_b$		34.2	200	382	745
λ_a	(Å)	2887.81	3638.30	3684.11	3677.63
λ_b	(Å)	2969.36	3707.82	3683.06	3683.06
A	(°K)	5400—15000	4200—10000	3800—8500	3600—7300
B	(°K)		4200— 6200	3800—6200	3600—6100

Table 3. 3.00 eV $< V_a - V_b <$ 3.50 eV

V_a-V_b	(eV)	3.35	3.37	3.30	3.27
$(gA)_a/(gA)_b$		94.1	250	473	945
λ_a	(Å)	3553.74	3805.34	3738.31	3586.11
λ_b	(Å)	3443.88	3922.91	3906.48	3683.06
A	(°K)	5800—17000	5000—12000	4500—9800	4200—8200
B	(°K)		5000— 8100	4500—7600	4200—7000

Table 4. 3.50 eV $< V_a - V_b$

V_a-V_b	(eV)	3.93	3.75	3.84	3.75
$(gA)_a/(gA)_b$		62.7	308	763	2160
λ_a	(Å)	5292.52^{+}	3282.33^{++}	3353.03^{+++}	3345.02^{++}
λ_b	(Å)	5105.54	3075.90	3351.97	3075.90
A	(°K)	7200—23000	5500—13000	5000—10000	4400—8200
B	(°K)		5500—8500	5000— 8500	4400—8200

a) In lines A and B the ratio $\Delta I/I$ ($I=I_a/I_b$) is larger than 4% and 10% respectively when the ratio $\Delta T/T$ is 2%. The combinations were made by atomic spectra line-pairs of iron expect Table 4. $^{+}$, CuI; $^{++}$, ZnI; $^{+++}$, CrI.

In experiments, especially with photographic plates, the range of the intensity ratio, $I(I_a/I_b)$, may be restricted to that between 0.1 and 10.0. The usual relative standard deviation of the spectrum intensity is larger than 2 per cent. Thus, if the $\Delta I/I$ is smaller than 4 per cent when I varies from I to $I+\Delta I$, the calculated temperature is not reliable. Since the small standard deviation in the temperature by the plotting method is 110°K at 5100°K,[8] temperature ranges where where determination errors are within 2 per cent are presented in the tables. Tables 1—4 show the combination of V_a-V_b, $(gA)_a/(gA)_b$, the corresponding temperature ranges. The values of gA are based on the measurement of Corliss and Bozman.[9] In the A and B lines, the $\Delta I/I$ ratios are larger than 4 per cent and 10 per cent respectively when the $\Delta T/T$ ratios are 2 per cent.

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8) C. H. Corliss, *J. Research NBS*, **66A** (Phys. and Chem.), 5 (1966).

9) C. H. Corliss and W. R. Bozman, "Experimental Transition Probabilities for Spectral Lines of Seventy Elemests," NBS Monograph 53, Washington, D.C. (1962).