Profiling of Redox Index During Combustion to Monitor C/C Composite Degradation in Flames

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It is often important to know if the local area in a flame is in reducing or oxidizing environmental conditions during combustion. In this study, a new reducing/oxidizing (redox) index parameter has been introduced. The value of this parameter has been determined experimentally by a *chemical seeding technique*. A solution of chromium was sprayed into a premixed acetylene–air flame supported on a slot burner. The flame temperature was determined as an excitation temperature by comparing the spectral intensities of two triplet lines emitted from chromium atoms. The redox index is defined as the ratio of experimentally determined and theoretically calculated degrees of atomization. The degree of atomization for the reaction $CrO \rightarrow Cr + O$ has been determined by comparing the spectral intensity of CrO band emission with the Cr triplet lines. Theoretically, the degree of atomization was calculated by assuming that a simple thermal dissociation takes place in the reaction. Two-dimensional distributions or profiles of the excitation temperature have been determined experimentally. The degree of atomization and redox index has been measured using a charge-coupled device camera fitted with an optical bandpass filter. The output from the camera was coupled to a personal computer for data acquisition and data processing. This diagnostic tool has been successfully used to determine the degradation processes of high-temperature materials, such as carbon/carbon composites, using an air–acetylene flame.

Introduction

A WIDE variety of physical properties have to be measured in flames to determine the desired important aspects of combustion using the relevant key diagnostics.[1] Temperature and flow velocity are among the important properties for many of the combustion systems. In material processing, it is necessary to know the properties of environment surrounding the material because these properties directly affect the processed material quality. In harsh combustion environments, the material surface is greatly affected in the combustion atmosphere. The reducing environment has a different effect on the processed material than the oxidizing atmosphere. It is, therefore, a challenge to determine whether the flame has a reducing environment or an oxidizing environment during the processing of materials such as steel and other metals. In practical flames, the reducing/oxidizing (redox) atmosphere is not uniform throughout the combustion zone. The entire material processing region often has spatial distributions as well as temporal variation. It is very difficult to illustrate the behavior by theoretical modeling because a large number of chemical species provide the role of reducing and oxidizing agents in complex schemes.

In this study, a new reductive-oxidative index (**redox index**) has been introduced. A *chemical seeding technique* has determined this index experimentally. The determination of this redox index requires information on temperature and the degree of atomization.

The flame temperature was experimentally determined as the excitation temperature by comparing spontaneous emission intensities of two chromium triplets. In the experiments, a low concentration of chromium solution was continuously sprayed into the premixed acetylene–air flat flame for the short duration of the experiments. Note that iron can also be used as seed material in place of chromium. The degree of atomization from chromium monoxide to atomic chromium was determined by comparing spectral intensities of spontaneous emission from chromium monoxide and chromium atoms. The determination of the degree of atomization also requires information on the temperature. In flames, metal molecules, such as chromium and iron monoxide, mostly exist as atoms at high temperatures. The degree of atomization can change with temperature and redox atmosphere of the flame. To remove the temperature effect on the redox index, the experimentally determined degree of atomization has been normalized with the theoretically calculated value assuming the simple thermal dissociation of chromium monoxide. The redox index thus obtained gives a measure of the redox atmosphere in the combustion field. The combustion field is oxidative, neutral, and reductive when this number is, respectively, smaller, equal, and greater than unity.

The two-dimensional distribution or profiles of the excitation temperature, the degree of atomization, and the **redox** index have been obtained for the acetylene–air flame using a charge-coupled device (CCD) camera fitted with an optical bandpass filter. This method has been applied to monitor the degradation of carbon/carbon composites in a flame.

Theoretical

The excitation temperature T is given by the following well-known two-line method when the Boltzmann distribution law is applicable to an observed small region. Such a local thermal equilibrium is the case for most cases in the field of combustion at temperatures below 2500 K. However, in some combustion cases this is not true when the chemiluminescence due to C_2 radicals takes place due to exothermic reaction enthalpy:

$$I_1/I_2 = (g_1 A_1/g_2 A_2) \exp\{(E_2 - E_1)/kT\} \quad (1)$$

where I is the spectral intensity of spontaneous emission of radiation from atoms, g the statistical weight of the excited state, A the Einstein's transition probability for spontaneous emission, E the excitation energy, and k the Boltzmann constant. The subscripts in the preceding equation indicate the properties at the two lines. In this study, spectrally integrated intensities were measured for the two chromium triplets because the spectral bandpass of the optical filter fitted to the CCD camera was not narrow enough to separate each component line of the triplets. Equation (1) can, therefore, be modified as:

$$\frac{I_1}{I_2} = \frac{\sum_{i=1}^3 g_i A_i \exp(-E_i/kT)}{\sum_{j=1}^3 g_j A_j \exp(-E_j/kT)} \quad (2)$$

where the subscripts i and j represent the two triplets.

The degree of atomization β_{exp} can be obtained from Eq. (3) by taking the ratio of intensities of atomic and molecular emission, as reported in previous studies[2]:

$$\frac{I_{Cr}}{I_{CrO}} = \frac{\beta_{exp} g_{Cr} A_{Cr} q_{e,CrO}(T)}{(1-\beta_{exp}) g_{CrO} A_{CrO} q_{e,Cr}(T)} \exp\left(\frac{E_{CrO}-E_{Cr}}{kT}\right) \quad (3)$$

where $q_e(T)$ is the partition function for the electronic excitation system, or the state sum

$$\sum g_k A_k \exp\left(-\frac{E_k}{kT}\right)$$

representing all of the energy levels involved. Thus, by the use of the excitation temperature determined from Eq. (2), the degree of atomization can be experimentally determined.

On the other hand, the theoretical degree of atomization β_{theo} can be calculated as follows from the equilibrium constant $K(T)$ and is based on simple thermal dissociation,[3]

$$\frac{\beta_{theo}^2}{1-\beta_{theo}} N_{m,o} = K(T) \quad (4)$$

where $N_{m,o}$ is the total number density of the species introduced into the flame by spraying the chromium solution. This gives a value on the simple thermal dissociation in the chemical equilibrium and is used as the reference. This value is compared with the experimental value that deviates due to the redox environment or nonchemical equilibrium effects. The equilibrium constant is given by the following equation:

$$K(T) = \frac{Q_{Cr}(T) Q_O(T)}{Q_{CrO}(T)} \quad (5)$$

The overall partition function $Q(T)$ for Cr and CrO is expressed as a product of the partition functions involved for the system:

$$Q_{Cr}(T) = q_{tr,Cr}(T) q_{e,Cr}(T), \qquad Q_O(T) = q_{tr,O}(T) q_{e,O}(T)$$

$$Q_{CrO}(T) = q_{tr,CrO}(T) q_{vib,Cr}(T) q_{rot,Cr}(T) q_{e,CrO}(T) \quad (6)$$

where the subscripts tr, vib, rot, and e represent translational, vibrational, rotational, and electronic systems, respectively. These partition functions are given in most textbooks on physical chemistry[4] except for the last one (electronic). The electronic partition functions have been given as a polynominal function for atomic systems.[3] In a previous study, $q_{e,CrO}(T)$ has been calculated directly from the definition, or the state sum

$$\sum g_k A_k \exp\left(-\frac{E_k}{kT}\right)$$

using the known spectroscopic levels.[3] Finally, the redox index, η_{rdx} can be obtained by taking a ratio of the experimentally and theoretically determined obtained degree of atomization, that is,

$$\eta_{rdx} = \beta_{exp}/\beta_{theo} \quad (7)$$

Table 1 Spectral lines observed

Wavelength nm	Excitation energy, 10^{-19} J	gA value, 10^8 s^{-1}	Ref.
357.869[a]	5.51	8.3	5
359.349[a]	5.53	7.0	5
360.533[a]	5.55	5.2	5
425.435[b]	4.67	2.0	5
427.480[b]	4.65	1.5	5
428.972[b]	4.63	0.95	5
605.34	3.28	0.18	1

[a]The sum of intensity I_2 in Eq. (2).
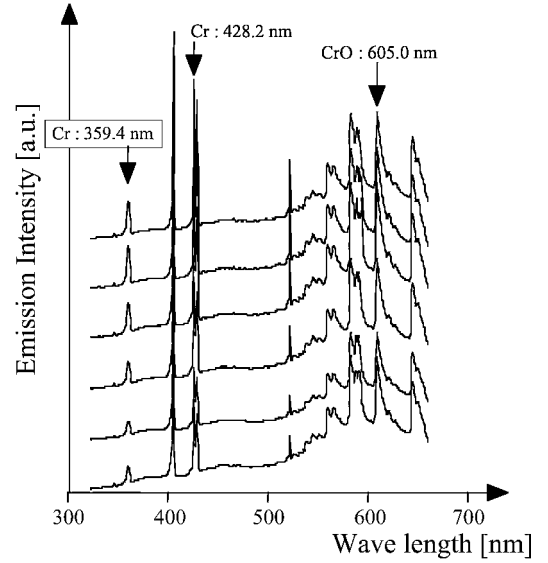[b]The sum of intensity I_1 in Eq. (2).

Fig. 1 Spectra of Cr triplets and CrO band; chemical seeding: solution of 10,000 ppm Cr.

If the combustion field is of neutral atmosphere in terms of redox, the degree of atomization is totally controlled by the simple thermal dissociation. Consequently, $\beta_{exp} = \beta_{theo}$ and $\eta_{rdx} = 1$. The redox index η_{rdx} becomes higher if the atmosphere during combustion is reductive because the degree of atomization becomes higher because more atoms are produced through reducing reactions than those expected by the simple thermal dissociation. In contrast, η_{rdx} becomes less than unity for the oxidative atmosphere.

In the acetylene–air flame examined here, chromium was selected as the chemical seeding element because it concurrently gave adequate spectral intensities of atomic and molecular spontaneous emission. Less toxic iron is an alternative element, though the atomic and molecular emission intensities are weaker. For flames at lower temperatures, such as methane–air flames, calcium would be a suitable choice for the chemical seeding element. Such selection is closely associated with the dissociation energy of the oxide, as well as the excited level energies of the atomic and molecular spontaneous emission.

The spectral lines observed in this study by the CCD camera, as well as the relevant physical properties at various wavelengths (lines), are listed in Table 1. Figure 1 shows typical spectra of the chromium triplets and the CrO band emission. Emission intensity peaks for Cr occurs at 359.4 and 428.2 nm, whereas that for CrO occurs at 605.0 nm. Cr solutions of other concentrations show similar spectra, although their peak intensity will be different.

Experimental

Figure 2 shows a schematic diagram of the experimental apparatus. This is basically the same as that developed in a previous study.[6] The system consists two main parts. The first part consists of a premixed acetylene–air flame supported on a conventional slot burner incorporating a concentric nebulizer for atomic

Table 2 Experimental conditions and instrument specifications

| Specifications	Conditions
Flame	Flat flame of premixed acetylene–air
Burner slot	100×0.25 mm
Flow rate of C_2H_2	2.3 lmin^{-1}
Flow rate of air	12.5 lmin^{-1}
Equivalence ratio	2.3
Chemical seeding	Potassium dichromate solution (100, 1000, and 10,000 ppm Cr)
Spray uptake rate	2.0 ml min^{-1}
Spray efficiency	1.5%
Sample material	Noncoated and coated C/C composites (coating layers: SiC of 0.05 mm and glass of 0.02 mm thickness)
Size	Disk of 6 mm diam and 4 mm thickness
Momochomator	JASCO CT-10
Focal length	10 cm
Grating	1200 grooves mm^{-1} and blaze wavelength of 250 nm
Slit width	1.0 mm (entrance and exit)
Bandpass	7.5 nm (nominal)
Wavelength setting	Cr 359.4 and 428.2 nm
	B.G. 375.0 and 445.0 nm
	CrO 605.0 nm
	B.G. 620.0 mn
CCD camera	Santa Barbara Instrument Group, ST-6B
Exposure time	1.0 s
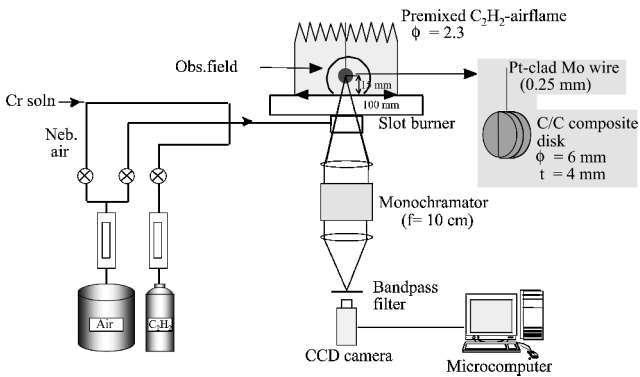
Fig. 2 Experimental apparatus.

absorption spectrometry. The second part is a spectrovideo CCD camera that was developed in a previous study and consists of a small size monochromator and a CCD camera. The flame image is made monochromatic with the use of the monochromator. The CCD camera detects the resulting image after passing the light signal through a narrow bandpass filter. Further details of the spectrovideo camera are provided in Ref. 6. The specifications of the instrument, as well as the measurement conditions employed in this study, are given in Table 2.

The chemical seeding was obtained by introducing Cr solution of known concentration into the flame. Iron can also be used in place of chromium solution. When a solution of potassium dichromate is sprayed into the flame, the image of spontaneous emission is acquired with the CCD camera for a time duration of several seconds. The time-averaged images thus obtained with different optical filters are recorded using a personal-computer-based computer data acquisition system. Further data processing is then conducted on the recorded images to reconstruct the profiles of the excitation temperature, the degree of atomization, and the redox index. To examine the effect of initial number density of chemical species containing chromium on the redox index, potassium chromate solutions of three different concentrations of 100, 1000, and 10,000 ppm were examined. These solutions were prepared by dissolving an analytical grade reagent in micropore filtration grade pure water just before use.

Carbon-reinforced carbon composites are selected as the test materials because they are promising advanced materials for many energy conversion systems and are also used for applications in aerospace science. However, drawbacks of this material are that they suffer from oxidation in the combustion environment. Two types of C/C composites (noncoated and double-layer-coated) were tested for their degradation in the flame. The coating layers assist to prevent the C/C substrate from being oxidized by the active species in flames.

Results and Discussion

The profiles of the spectral intensities of the chromium triplets, and the CrO band emitted from the premixed acetylene–air flame, are shown in Fig. 3. Data are also presented in Fig. 3 when a disk of noncoated C/C composite was located in the flame. Data are presented at an exposure time of 0.5 and 20 min, as well for the flame alone. The flow direction is from the bottom to the top in all of the profiles shown in Fig. 3. Note from the two profiles (shown in the upper and left in Fig. 3) that chromium emission becomes stronger in upstream regions of the flame. This shows a greater number density of chromium atoms being produced in this region and suggests that this region is more reducing. The CrO emission is also more intense in the upstream region. This suggests that more CrO molecules are produced from molecules of Cr in their higher oxidation states, such as CrO_3. Also note from the other profiles obtained with disk of C/C composite placed in the flame that higher emission intensities of Cr and CrO are found around the peripheral region of the disk. These intensities become even higher at an exposure time of 20 min. These results suggest that the peripheral region is more reductive due to the reaction of the C/C disk near its surface with the combustion field.

Figure 4 shows typical temporal changes in the profiles of spectral intensity peaks of Cr and CrO obtained when a C/C composite disk coated with SiC/glass was exposed in the flame for longer time duration. The results shown in Fig. 4 are for three exposure times of 0.5, 60, and 120 min. In contrast to the results obtained for
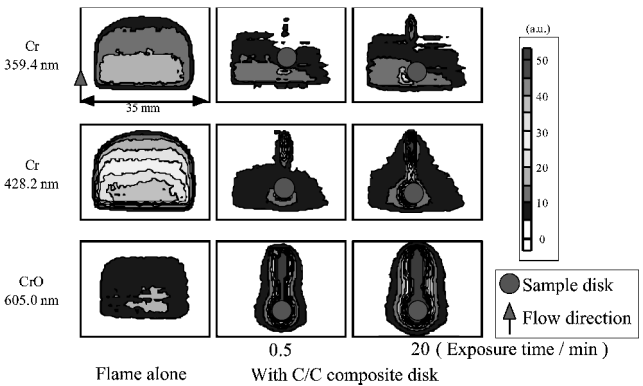

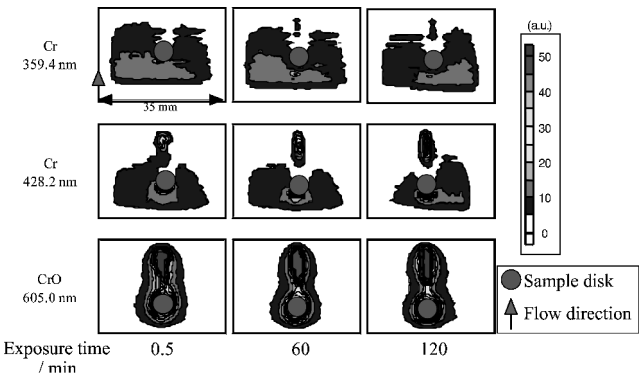**Fig. 3 Intensity profiles of Cr triplets and CrO band.**

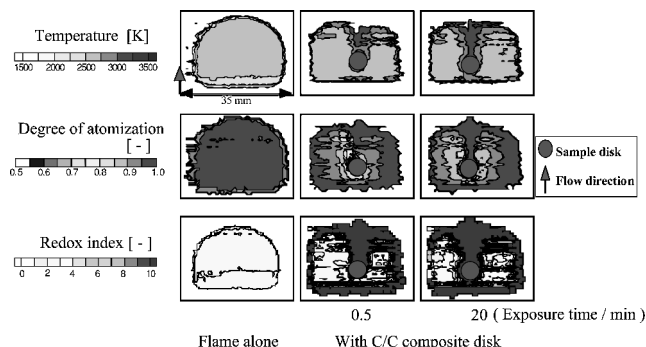**Fig. 4 Profiles of Cr triplets and CrO band; sample: coated C/C composite.**

Fig. 5 Profiles of degree of atomization and redox index.

Fig. 6 Profiles of degree of atomization and redox index; sample coated-C/C composite.

the noncoated C/C composite, the temporal changes are negligibly small. This indicates that the coated layer effectively prevents the C/C composite surface from being oxidized.

The results provided on the spectral intensities alone makes it difficult to determine quantitatively the redox atmosphere of the flame. It is also difficult to determine its temporal change because the spectral emission intensity depends on the flame temperature.

The excitation temperature, degree of atomization, and redox index has been calculated according to the procedure given in the theoretical section. Figure 5 shows the profiles of excitation temperature, degree of atomization, and the redox index, as well as their observed temporal changes when a noncoated C/C composite disk is placed in the flame. Note that the excitation temperature is fairly uniform within the observed field, except for the upstream flame region having a bright blue color. This region corresponds to the hotter region of the flame. The measured temperature profiles also clearly illustrate the elevated temperature at the downstream region behind the sample disk. This region is mainly due to the enthalpy accumulation caused by flow eddies.

In the flame alone, the numeric values on the degree of atomization and the redox index were found to lie in the range of 0.95–1.00 and 3–4, respectively. These values for both degree of atomization and redox index became smaller in the downstream region. The value of redox index greater than unity indicates that the combustion field produced by the flame is of a reducing atmosphere (reductive). This result is in agreement with the equivalence ratio of 2.3 utilized for the flame, which lead to the fuel-rich combustion conditions. The two-dimensional profiles of the redox index quantitatively illustrate the degree of the reductive atmosphere in the flame. This diagnostics can, therefore, be used to determine the local equivalence ratio in practical flames.

The excitation temperature becomes higher with an increase in exposure time. The heat produced from the oxidation reactions that occurs on the surface of the C/C composite primarily causes this effect. The redox index is also greater. This suggests that with the carbon species evolving from the surface of the C/C composite at high temperatures, the peripheral region of the disk becomes more reductive.[6]

Figure 6 shows the results obtained for the coated C/C composite. The temporal changes in the excitation temperature are negligibly small. This suggests that no surface reaction takes place near the disk. Both the degree of atomization and the redox index increase with an increase in exposure time. This is caused by the very small amount of carbon-containing reductive species that evolves though cracks and/or pores of the coating layers. These are most likely to be produced during the long exposure time of the disk placed in the flame. Note that the observed change is related to the heat evolved. Thus, it is possible to detect slight degradation of the coating layer with the change in the redox index.
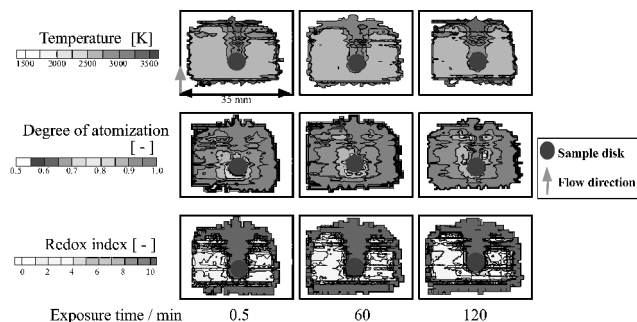
The dependence of the measured redox index on the concentration of the chromium solution was also examined, and it was found that at concentration of 100 and 1000 ppm of Cr, the relative errors in the redox index were within 15%. Thus, the localization of the chemical seed in the flame may not give significant errors. Further studies should be conducted to evaluate the accuracy and precision of this effect and the diagnostics. However, the redox index proposed in this work is the first promising parameter that quantitatively determines the local environment (reductive or oxidative) in flames and combustion fields.

Conclusions

A new **redox index** parameter has been introduced here whose values have been determined experimentally using a chemical seeding technique. The redox index gives a measure on the reducing/oxidizing conditions and allows one to determine whether the combustion field is oxidative, neutral, or reductive. The three conditions correspond to the case when the redox index is smaller, equal, and greater than unity, respectively. The results of redox index obtained with the diagnostics presented here have been confirmed experimentally with the acetylene–air flames of known stoichiometry. Two-dimensional distributions or profiles of the excitation temperature, the experimentally determined degree of atomization, and the redox index have been measured in high-temperature flames. The new diagnostic technique has been successfully applied to examine the degradation processes of high-temperature materials such as carbon/carbon composites in an air–acetylene flame. The technique can be applied to other materials, flames, and combustion systems.

References

[1]Gupta, A. K., and Lilley, D. G., *Flowfield Modeling and Diagnostics*, Abacus Press, Tunbridge Wells, England, 1985, pp. 185–323.

[2]Kitagawa, K., Yanagisawa, M., and Takeuchi, T., "Spectroscopic Study of Atomization Processes and Inter-Element Effects on Flame Emission of Chromium and Iron in an Air-Acetylene Flame," *Analytica Chimica Acta*, Vol. 115, No. 121, 1980, pp. 121–131.

[3]Moore, W. J., *Physical Chemistry*, 1st ed., Lowe & Brydone, London, U.K., 1950, pp. 358, 359.

[4]De Galan, L., Smith, R., and Winefordner, J. D., "The Electronic Partition Functions of Atoms and Ions Between 1500° K and 7000° K," *Spectrochim. Acta*, Vol. 23B, No. 521, 1976, pp. 521–524.

[5]Corliss, C. H., and Bozmann, W. R., "Experimental Transition Probabilities for Spectral Lines of Seventy Elements," *National Bureau of Standards (NBS) Monograph 53*, U.S. Government Printing Office, Washington, DC, 1994, pp. 101–104.

[6]Kubota, K., Tsuge, S., Kitagawa, K., Arai, N., Ushigome, N., and Kato, T., "Analysis of Degradation Processes of Carbon/Carbon Composites in a High Temperature Chemical Flame by a Spectrovideo Camera," *Carbon*, Vol. 36, No. 928, 1998, pp. 1783–1790.