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Transient Behaviors in Thermal Radiation Characteristics of Heat-Resisting Metals and Alloys in Oxidation Processes[1]

T. Makino,[2] O. Sotokawa,[2] and Y. Iwata[2]

A high-speed spectrophotometer system is developed to study radiation characteristics of materials. The system allows measurements of the spectra at wavelengths of 0.35–10 μm repeatedly with a period of less than 1 s. It is applied to the study of transient behaviors in reflection characteristics of heat-resisting alloys and the constituent transition metals in air-oxidation processes at high temperatures. An interference phenomenon due to the multiple reflection at the upper and lower boundaries of the oxide film is observed in the diffuse reflection spectra of oxidizing rough-finished surfaces as well as in the specular reflection spectra of oxidizing specular-finished surfaces. The phenomenon is found to be fairly reproducible and consistent over all the materials investigated. It is attributed to the interference and diffraction of radiation at three-dimensional nonparallel film elements of the polycrystalline oxide grains. A possibility is suggested for the theoretical modeling of radiation characteristics of real surfaces in the actual environments of industry.

KEY WORDS: heat-resisting alloy; high-speed spectroscopy; oxidation; radiation property; transient behavior; transition metal.

1. INTRODUCTION

Knowledge of radiation characteristics of metallic materials is important for thermal designs of engineering systems and also for developing measurement techniques of the surfaces. The characteristics have origins in the electronic properties and the surface conditions. The electronic properties have been investigated extensively [1]. The radiation characteristics

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[2] Department of Engineering Science, Kyoto University, Kyoto 606, Japan.

may depend strongly on the surface conditions. There are various surface roughness and oxide films, which may change depending on the actual environments of industry. Values of radiation characteristics found in data books [2] scatter over a wide range. A systematic investigation should be made to deal with the complicated phenomenon. We developed a high-speed spectrophotometer system as an experimental method to study the radiation phenomenon of real surfaces [3, 4]. The system was used to investigate the transient behavior of reflection spectra of copper oxidizing at high temperatures. It was found that the measured spectra are characterized clearly by the interference and diffraction of radiation, which are reproduced well.

The present paper describes the recent development in the spectrophotometer system. An extended investigation is made on heat-resisting alloys and their constituent transition metals. The possibility of a general theoretical modeling of the radiation characteristics of real surfaces of metallic materials is suggested.

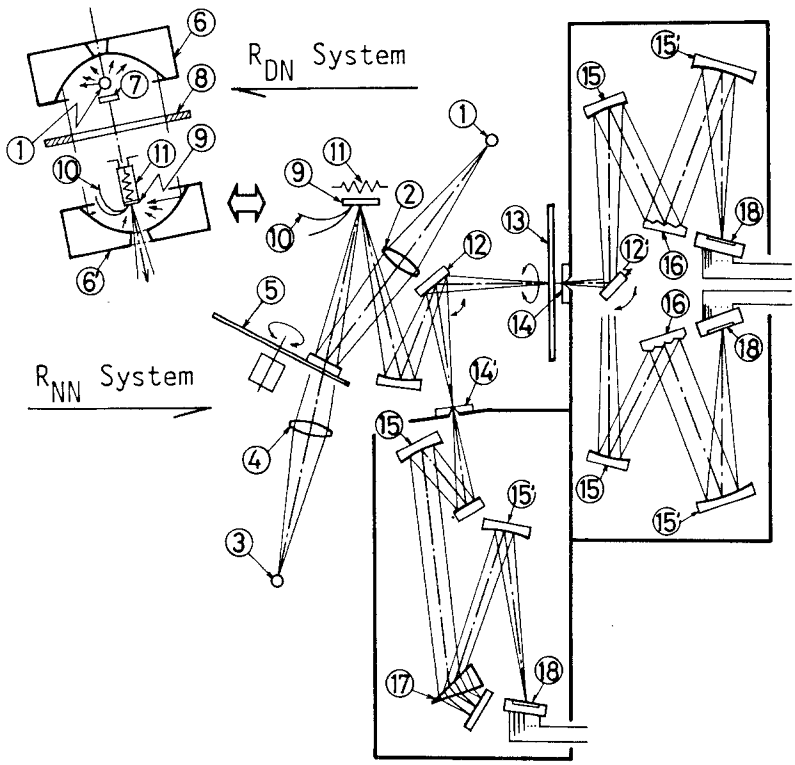
2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1. High-Speed Spectrophotometer

Figures 1 and 2 show schematic diagrams of the developed high-speed spectrophotometer system. The system consists of an incident optical system, a monochromator/detector system, and a signal-processing/electric-control system. Although various kinds of incident systems may be chosen, Fig. 2 includes the two systems normally used: a system for the near-normally incident specular reflectance R_{NN} and a system for the diffuse component of the perfectly diffuse near-hemispherically incident normal reflectance R_{DN}. The R_{NN} system has two light sources (1 and 3) for the visible/near-infrared and the infrared regions, respectively. By rotating a sector disk (5), which involves a plane mirror, an aperture, and a black surface, any one of the two light sources and the black part may be chosen. The measurement using the black part may provide data for the compensation of the effect of self-emission by the specimen at high temperatures. The monochromator system consists of two grating systems for the visible/near-infrared ($\lambda = 0.35$–$1.11\ \mu$m; λ is the wavelength of radiation in vacuum) and the infrared ($\lambda = 1.2$–$4.6\ \mu$m) regions and a prism system for the far-infrared region ($\lambda = 4.8$–$10\ \mu$m). The three systems are linked by two rotating mirors (12 and 12′). A filter disk (13) with five cut-on filters is used for the grating systems. The detectors (10) are three sets of linear sensor arrays: a 35-Si-photodiode array for the visible/near-infrared region, a 4-Ge-photodiode/10-PbSe element array for the infrared region, and a

16-PZT-pyroelectric element array for the far-infrared region. By scanning these elements electronically, fast detection is realized.

The R_{NN} system covers the wavelength region of 0.35–10 μm. We measure a reflection spectrum which is affected by the self-emission of the specimen, and we measure the self-emission spectrum just after the



1	tungsten-halogen lamp	10	thermocouple (K)
2	lens (BK-7)	11	heater
3	SiC light source	12,	12' rotating mirror
4	lens (KRS-5)	13	filter disk
5	sector disk	14,	14' entrance slit
6,	6' paraboloidal mirror	15,	15' collimator
7	mask	16	diffraction grating
8	iris	17	KRS-5 prism
9	specimen	18	optical detector array

Fig. 1. Schematic diagram of the high-speed spectrophotometer system—incident-optical system and monochromator/detector system.

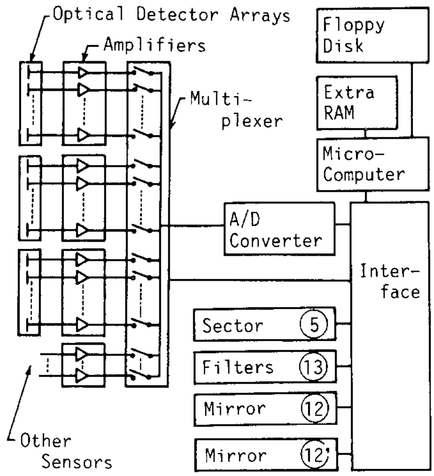


Fig. 2. Schematic diagram of the high-speed spectrophotometer system—signal-processing/electric-control system.

reflection measurement. Thus we obtain an R_{NN} spectrum. This process is repeated with a period of less than 1 s. Most of the 1 s is devoted to the time for the motor drive. The R_{DN} system has only a light source (1) of a tungsten lamp. The emission of the source is transformed to a perfectly diffuse near-hemispherical incidence by two paraboloidal mirrors (6 and 6′). The normal component of the hemispherical reflection at the specimen (9) is measured. The iris (8) is prepared for the measurement of angular characteristics of reflection but is not used in the present work. Provided that the specimen is less than 600 K, the R_{DN} system may be used at wavelengths of 0.35–3.7 μm. The period of this spectrum measurement is 330 ms. At higher temperatures the long-wavelength limit is shortened, because the R_{DN} system has no attachment for the compensation of the self-emission of the specimen.

2.2. Specimens and Experimental Procedure

The present experiments are made on seven kinds of heat-resisting alloys [iron-based SUS 304, SUS 316, Incoloy 800; cobalt-based X-40 (Stellite 31); nickel-based Hastelloy X, Inconel 600, Inconel 617] and their constituent transition metals (chromium, iron, cobalt, nickel). These materials are chosen because the spectra of optical constants are known over wide temperature regions [1]. Two kinds of surfaces are prepared for each material: a buffed specular-finished surface and a rough-finished surface hand-ground randomly on an emery paper of JIS mesh-180. These surfaces are heated in air with a heating rate of $3.3\ \mathrm{K \cdot s^{-1}}$ up to 800 K for metal elements except for chromium, and up to 1000 K for chromium and the other materials, and held at the temperatures. Transient behavior in the reflectances R_{NN} and R_{DN} is measured.

3. RESULTS AND DISCUSSION

The transition of the reflection spectra of the above materials investigated has been found to have the same principal tendencies. Accordingly, we discuss the typical results and make a general consideration.

3.1. Specular Reflectance Spectra of Specular-Finished Surfaces

Figures 3 and 4 show the behaviors of the specular reflectance spectrum of the specular-finished surfaces of chromium and the nickel-based alloy Hastelloy X, respectively. The reflectance R^*_{NN} is a relative reflectance normalized by the value of the original clean specular surface, t is the time after the start of heating, and T is the surface temperature. The spectra are

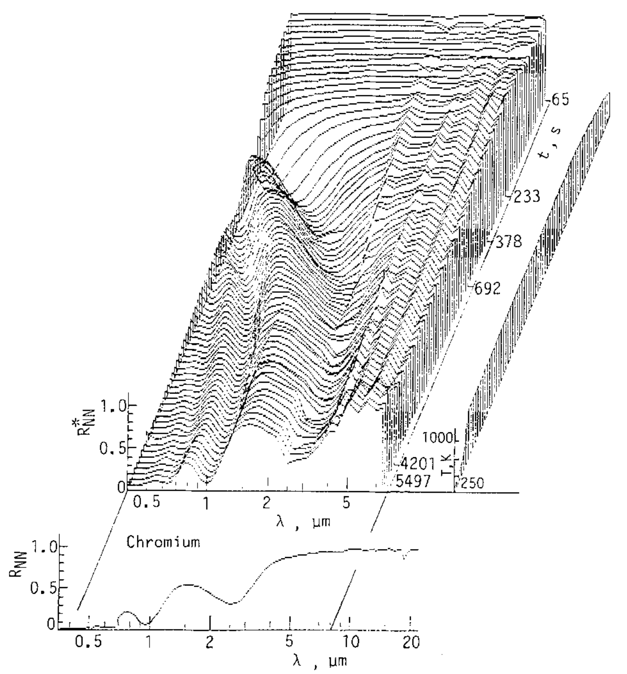


Fig. 3. R^*_{NN} spectra of an oxidizing specular-finished chromium.

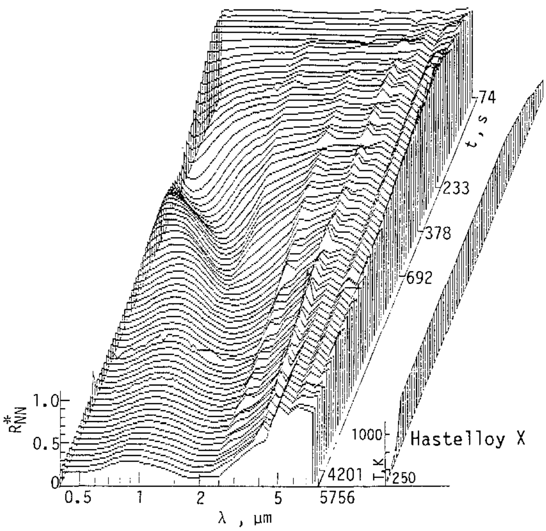


Fig. 4. R^*_{NN} spectra of an oxidizing specular-finished Hastelloy X.

selected from the many measured ones and are shown at regular time intervals in each period between the times indicated on the time axis. The precision of the measurement is not good at long wavelengths, because of the poor performance of the infrared arrays and the influence of the infrared-active gases in the experimental system. The structure in the spectra at the long wavelengths has its origin in these causes.

The spectrum has a valley at the shorter wavelengths. It is caused by the interference of radiation at the upper and lower boundaries of an oxide film formed on the surface. With the growth of the film, the valley shifts to the longer wavelengths, and the spectrum has the first-order hill of the interference. In the case of chromium, the higher-order valleys and hills of the interference are observed. Also, besides the waviness of the intereference, the specular reflectance decreases with the growth of the film, particularly at the shorter wavelengths. Since the film grows on each crystal grain of the polycrystalline substrate, the difference in the orientation of growth makes a microroughness. The decrease in R^*_{NN} contributes to the diffuse reflection and to the absorption of the surface system.

The oxidation rate becomes low at the later stage of the experiment. At this stage the specimen was cooled with measuring the R^*_{NN} spectra. The spectrum was found to be stable in this process. The temperature dependence of optical constants of the films is considered to be weak. Figure 3 includes an R_{NN} spectrum of the cooled surface at room temperature. It was measured by using commercial spectrophotometers. An absorption band of the lattice vibration is observed in the far-infrared region. If the wavelength region of the high-speed spectrophotometer system is extended to this region, the identification of the chemical compositions of the films may be possible.

3.2. Diffuse Reflectance Spectra of Specular-Finished Surfaces

Figure 5 shows the behavior of the diffuse reflectance spectrum of the specular-finished surface of chromium. The reflectance R^*_{DN} is a relative reflectance normalized by the value of the above-mentioned rough-finished surface. The spectra are shown at the wavelengths free from the effect of self-emission of the specimen.

The R^*_{DN} spectrum becomes observable with the formation of an oxide film. It has a hill at the shorter wavelengths when the oxide film growth reaches a stage at which the appearance of the valley in the R^*_{NN} spectrum is observed. The hill grows and shifts to the longer wavelengths, and the spectrum has hills and valleys of the higher order. This process is caused by the film growth and the microroughness formation. It is a phenomenon of interference with the roughness effect. The manner of the coherent diffuse reflection is the same as that found in the oxidation process of copper [3]. Although the phenomenon seemed to be strange, it is reproduced generally over all the materials investigated.

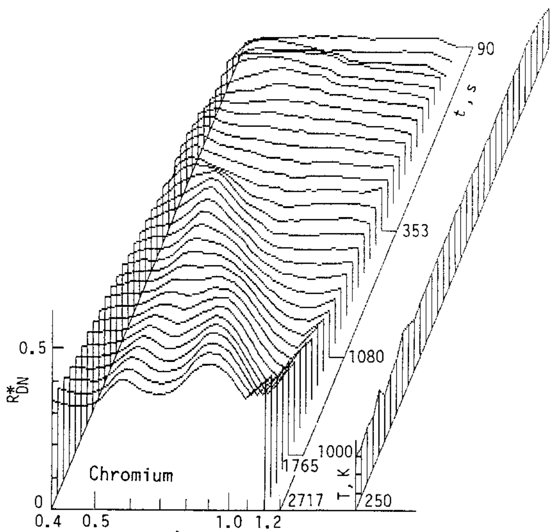


Fig. 5. R^*_{DN} spectra of an oxidizing specular-finished chromium.

3.3. Diffuse Reflectance Spectra of Rough-Finished Surfaces

Figure 6 shows the behavior of the diffuse reflectance spectrum of the rough-finished surface of chromium. The reflectance R^*_{DN} is a relative reflectance normalized by the value of the original surface.

The behavior of R^*_{DN} is very similar to that of R^*_{NN}, although the waviness is somewhat rounded. Even the diffuse spectrum of an oxidizing rough-finished surface is characterized by the interference. It is interesting that the regularity of an order of the electromagnetic radiation is observed in the diffuse reflection spectrum of a hand-ground surface and to the incidence of thermal radiation of the tungsten lamp. The oxide film is considered to grow by tracing the rough surface. The film is considered to have crystal grains of oxide film with nonparallel boundaries. The reflectance spectra include the information of the interference and diffraction at the structure. Since both spectra of R_{NN} and R_{DN} are characterized by the interference, the phenomenon may be found in the spectra of the normal emittance ε_N, which is equal to $(1 - R_{NN} - R_{DN})$ [3]. The phenomenon has been found in the ε_N spectra of some metals in oxidation processes [5]. The thermal emission of the substrate is affected by the interference in the semitransparent oxide film.

3.4. Possibility of Modeling of the Radiation Phenomenon of Real Surfaces

The above-mentioned tendencies in the spectrum transition are consistent over all the materials investigated. The oxidation of the metal

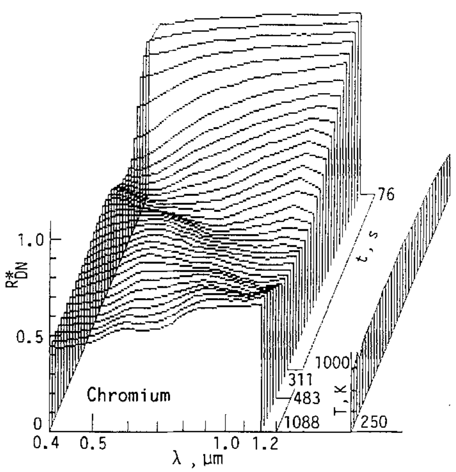


Fig. 6. R^*_{DN} spectra of an oxidizing rough-finished chromium.

elements continues until the higher-order interference is observed, while the oxidation of the heat-resisting alloys in the present temperature range ceases at the earlier stage of the first-order intereference. Comparing the interference behaviors in the present spectra with those of copper in a similar process [3, 4], it is noted that the amplitudes of the waviness are smaller, and the decrease in R_{NN} of the specular-finished surfaces is faster. It is particularly the case in the spectra of the heat-resisting alloys. It is considered to be the mechanism of the film formation.

In the present study, the principal manner of the spectrum transition has been clarified. The phenomenon has been found to be general and reproduced well. It may be the subject of a theoretical modeling. Interference and diffraction at the three-dimensional nonparallel film element model [6] may be investigated on the basis of an electromagnetic theory. It characterizes the phenomenon at the facet-type film grains. A statistical model of a rough surface [7] may be investigated to describe the three-dimensional roughness of the substrates. The present results suggest the possibility of a general model of the radiation phenomenon of the real surfaces.

4. CONCLUSIONS

A high-speed spectrophotometer system has been developed, and transient behaviors in radiation characteristics of heat-resisting metals and alloys in the oxidation processes have been investigated. The results are summarized below.

The radiation phenomenon of the real surfaces of metallic materials is characterized generally by the interference and diffraction of radiation at facet-type film grains at the surfaces. The phenomenon is reproduced well. It may be investigated on the basis of an electromagnetic theory. The high-speed spectroscopy is a good experimental technique for the investigation.

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