EFFECT OF THICKNESS OF OXIDE FILM ON THE EMISSIVITY AND REFLECTIVITY OF HEAT-RESISTANT METALS AND ALLOYS

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Emissivity and reflectivity data have been obtained for nickel, chromium, Cr18Ni10Ti steel, and CrNi78Ti nickel alloy in the oxidized state at oxide-film thicknesses on the range from 300 Å to 45 μ. It has been found that there are three distinct regions of oxide-film thicknesses within which the radiation flux is differently formed.

In many cases the economical use and reliability of high-temperature apparatus depend on the stability of the emissive properties of the heated elements; hence the importance of being able to estimate the emissivity and reflectivity of metal surfaces in an oxidizing medium.

Under natural conditions the surface of a metal is always covered with an oxide film several tens of angstroms thick. After heating in air and in a slightly rarefied atmosphere it is possible to observe a broad range of oxide-film thicknesses at which radiation can still escape from the metal [1]. In this case the formation of the outward flux must be considered in relation to the "metal–natural transparent oxide-film" system, under conditions which include reflection at the metal–film boundary and scattering and interference involving both the oxide's own emission and the metal emission passing through the film. In the case of a nontransparent film the outward radiation is determined solely by the oxide phase.

Recent publications examine the emission of oxidized metals and alloys over relatively broad temperature ranges [1-4]. It has been noted that temperature [1] and a rarefied atmosphere [3] affect the emission of metal surfaces with an oxide film.

However, the important practical problem of establishing the film thicknesses that permit broad control over the integral emissivity of a metal-oxide film system has not been adequately studied.

We have determined the integral normal emissivity on the temperature interval 100-800°C (Table 1) and the spectral reflectivity at room temperature (Table 2) for nickel, chromium, Cr18Ni10Ti steel and CrNi78Ti nickel alloy at oxide film thicknesses from 300 Å to 45 μ. The formation of the radiation flux in the oxide layer has been examined.

The integral normal emissivity was investigated by the radiation method on the apparatus described in [5], the specimens being heated in air; the spectral reflectivity was investigated in the UR-20 spectrophotometer on the spectral interval from 2 to 25 μ, the specimen being supplied with a nonmonochromatic radiation flux at an angle of 20° to the normal. On the interval 300-2000 Å the thickness of the oxide film was estimated from the interference colors, and at values of more than 5 μ by micrometry. Thicknesses lying between these limits were determined by the method described below.

The error in determining the integral normal emissivity was 4.5%, the error in determining the spectral reflectivity 2%, the corresponding errors for the thickness of the oxide film were 20% up to 2000 Å and 10% above 5 μ.

Before oxidation the surface of the specimens was given a class ∇10 finish. A full set of film thicknesses was obtained on the same specimen by stepwise heating in air and holding, for two hours in each case, at the temperatures indicated in Table 1. The emissive and reflective characteristics and the thickness of the oxide films were determined between oxidation steps.

It should be noted that after each oxidation step the specimens were investigated at a temperature interval on which the film thickness in question was preserved. This was checked with respect to the reproducibility of the results obtained on heating and cooling the specimens.

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TABLE 1. Integral Normal Emissivity (ε_n) of Nickel, Chromium, Cr18Ni10Ti Steel, and CrNi78Ti Nickel Alloy at Different Oxide-Film Thicknesses

Oxide-film thickness	ε_n at a temperature (°C) of								Oxidation temperature
	100	200	300	400	500	600	700	800	
Nickel (electrolytic, 99.98%)									
⩽500 Å	0,07	0,08	0,09	0,1					440
650	0,08	0,10	0,12	0,14	0,16				475
900	0,09	0,13	0,17	0,21	0,25				520
1600	0,15	0,22	0,29	0,36	0,43	0,48			670
2700	0,21	0,275	0,34	0,405	0,47	0,51	0,55		700
1,5 μ	0,36	0,46	0,44	0,48	0,52	0,55	0,58	0,61	900
2,5	0,44	0,47	0,50	0,53	0,56	0,59	0,62	0,65	950
15	0,52	0,54	0,56	0,58	0,60	0,62	0,64	0,66	1050
35	0,62	0,61	0,60	0,60	0,60	0,62	0,64	0,69	1200
Chromium (99.7%)									
⩽500 Å	0,05	0,065	0,08	0,095	0,11				530
540	0,06	0,075	0,09	0,105	0,13	0,145			615
660	0,08	0,11	0,14	0,17	0,20	0,23	0,26		700
750	0,10	0,14	0,18	0,22	0,26	0,30	0,34		720
3800	0,45	0,48	0,51	0,54	0,57	0,60	0,62	0,64	900
2,0 μ	0,66	0,675	0,69	0,705	0,72	0,735	0,75	0,76	950
8	0,73	0,73	0,73	0,74	0,74	0,74	0,75	0,77	1050
45	0,76	0,76	0,76	0,76	0,76	0,76	0,77	0,81	1200
Cr18Ni10Ti Steel									
⩽400 Å	0,12	0,135	0,15	0,17	0,19				440
470	0,13	0,16	0,19	0,22	0,25	0,28			680
550	0,14	0,175	0,21	0,245	0,28	0,325	0,35		710
1200	0,18	0,25	0,32	0,39	0,46	0,53	0,60		770
1400	0,33	0,40	0,47	0,54	0,61	0,68	0,70	0,71	820
2 μ	0,61	0,625	0,64	0,655	0,67	0,685	0,70	0,715	900
5	0,74	0,75	0,76	0,77	0,78	0,79	0,81	0,81	950
22	0,76	0,77	0,78	0,79	0,80	0,81	0,82	0,83	1050
45	0,80	0,81	0,82	0,83	0,84	0,84	0,84	0,84	1200
CrNi78Ti Nickel alloy									
⩽450 Å	0,13	0,14	0,15	0,16	0,175				550
540	0,15	0,175	0,20	0,225	0,25	0,275	0,30		730
2000	0,23	0,28	0,33	0,38	0,43	0,48	0,53	0,58	900
2,5 μ	0,52	0,56	0,60	0,63	0,65	0,67	0,69	0,71	950
12	0,67	0,71	0,75	0,76	0,77	0,78	0,79	0,80	1050
18	0,78	0,81	0,84	0,84	0,83	0,82	0,83	0,85	1200

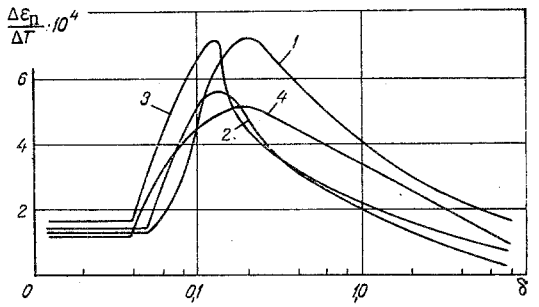

Fig. 1. Slope of the temperature dependence of the integral normal emissivity as a function of the thickness δ of the oxide film: 1) nickel; 2) chromium; 3) Cr18Ni10Ti steel; 4) CrNi78Ti nickel alloy. $\Delta\varepsilon_n/\Delta T$, 1/deg; δ, μ.

The temperature dependences of the integral normal emissivity at film thicknesses up to 5 μ can be approximated by a linear dependence. It is interesting to note the change in the slope of the temperature dependences of the integral normal emissivity as the thickness of the oxide film increases (Fig. 1). It is clear from Fig. 1 that on the film thickness range of up to several hundreds of angstroms $\Delta\varepsilon_n/\Delta T$ remains unchanged. In the region of thicker oxide films the $\Delta\varepsilon_n/\Delta T = f(\delta)$ curves take a bell-shaped form. It is important to note

TABLE 2. Spectral Normal Reflectivity ($R_{\lambda n}$) of Nickel, Chromium, Cr18Ni10Ti Steel, and CrNi78Ti Nickel Alloy

Oxide-film thickness	$R_{\lambda n}$ at wavelength (μ) of											
	2	4	6	8	10	12	14	16	18	20	22	24
	Nickel (electrolytic, 99.98%)											
Before oxidation	0,77	0,85	0,90	0,94	0,95	0,95	0,95	0,95	0,95	0,95	0,94	0,92
900 Å	0,19	0,76	0,90	0,94	0,95	0,95	0,95	0,95	0,95	0,95	0,91	0,87
1600	0,08	0,63	0,85	0,90	0,94	0,95	0,95	0,95	0,95	0,95	0,91	0,87
2700	0,33	0,30	0,73	0,85	0,91	0,94	0,95	0,95	0,95	0,95	0,91	0,84
1,5 μ	0,09	0,19	0,40	0,36	0,30	0,70	0,84	0,86	0,81	0,90	0,87	0,78
2,5	0,11	0,12	0,24	0,27	0,19	0,62	0,50	0,54	0,48	0,84	0,89	0,76
15	0,07	0,10	0,13	0,10	0,11	0,24	0,36	0,16	0,38	0,75	0,76	0,64
35	0,02	0,03	0,04	0,05	0,05	0,05	0,02	0,01	0,08	0,14	0,18	0,20
	Chromium (99.7%)											
Before oxidation	0,76	0,93	0,95	0,96	0,96	0,96	0,97	0,97	0,97	0,97	0,98	0,98
540 Å	0,71	0,92	0,95	0,96	0,96	0,96	0,97	0,97	0,97	0,97	0,98	0,98
750	0,56	0,47	0,84	0,93	0,95	0,96	0,94	0,92	0,78	0,94	0,94	0,90
3700	0,04	0,03	0,10	0,22	0,39	0,56	0,50	0,20	0,47	0,05	0,46	0,54
2 μ	0,02	0,01	0,02	0,04	0,12	0,21	0,16	0,16	0,33	0,05	0,24	0,24
8	0,01	0,01	0,02	0,03	0,04	0,14	0,07	0,05	0,13	0,05	0 05	0,06
45	0,01	0,01	0,01	0,01	0,01	0,02	0,03	0,02	0,05	0,01	0,02	0,02
	Cr18Ni10Ti Steel											
Before oxidation	0,64	0,75	0,80	0,83	0,86	0,87	0,88	0,89	0,88	0,88	0,85	0,83
470 Å	0,45	0,71	0,79	0,83	0,86	0,87	0,88	0,89	0,88	0,88	0,85	0,80
550	0,21	0,66	0,79	0,83	0,86	0,87	0,88	0,89	0,88	0,88	0,85	0,78
1400	0,06	0,02	0,38	0,67	0,78	0,85	0,88	0,88	0,84	0,82	0,80	0,78
5 μ	0,01	0,10	0,04	0,22	0,06	0,34	0,64	0,69	0,72	0,43	0,25	0,16
22	0,02	0,02	0,03	0,04	0,02	0,12	0,25	0,25	0,32	0,25	0,24	0,19
45	0,01	0,01	0,01	0,01	0,02	0,02	0,04	0,07	0,06	0,05	0,05	0,07
	CrNi78Ti Nickel alloy											
Before oxidation	0,72	0,80	0,82	0,84	0,85	0,86	0,88	0,90	0,90	0,89	0,88	0,88
450 Å	0,62	0,74	0,81	0,84	0,85	0,86	0,88	0,90	0,90	0,89	0,88	0,84
540	0,35	0,66	0,78	0,80	0,80	0,84	0,85	0,88	0,88	0,88	0,85	0,83
2000	0,03	0,36	0,67	0,77	0,80	0,84	0,85	0,90	0,90	0,89	0,85	0,78
2,5 μ	0,02	0,10	0,10	0,16	0,43	0,82	0,71	0,71	0,80	0,30	0,55	0,66
12	0,02	0,03	0,04	0,16	0,20	0,20	0,50	0,50	0,63	0,46	0,24	0,08
18	0,02	0,02	0,02	0,02	0,02	0,10	0,20	0,20	0,28	0,27	0,18	0,18

that for all the oxidized metals and alloys it was possible to observe the same type of law of variation of $\Delta\varepsilon_n/\Delta T$ with increase in the thickness of the oxide film, despite the differences in composition. With increase in temperature the composition of the oxide film on Cr18Ni10Ti steel is known to vary as [1]

$$(Fe, Me)_2O_3 \rightarrow Fe(Cr, Me)_2O_4 \rightarrow Cr_2O_3,$$

where Me are the other metallic components.

At high temperatures the surface layer of the oxide film on CrNi78Ti nickel alloy is also enriched in chromium oxide [6]. Evidently, the shape of the $\Delta\varepsilon_n/\Delta T = f(\delta)$ curve is not much affected by re-emission associated with surface irregularities resulting from the growth of the oxide film, since in the first approximation it makes an additive contribution to the total emissive power of the system [1].

We have used the descending branch of the $\Delta\varepsilon_n/\Delta T = f(\delta)$ curve to estimate oxide film thicknesses of the interval from 3000 Å to several microns.

It is possible to distinguish three regions of oxide film thicknesses within which the formation of the radiation flux in the metal–transparent oxide-film system follows a specific characteristic course.

1. Films 400-500 Å Thick. The integral normal emissivity of the metal surface does not change with growth of the oxide film on this thickness range. There is a certain loss of loss of reflectivity at wavelengths of less than 4 μ only. At T > 400°C this leads to the temperature dependence of the integral normal emissivity becoming nonlinear as a result of the shift of the emission spectrum into the region of shorter wavelengths, with the inclusion of wavelengths $\lambda < 4\mu$. However, this deviation is reversible and does not affect the general trend, i.e., $\Delta\varepsilon_n/\Delta T = \text{const}$ at T < 400°C.

2. Films from 400-500 to 2000 Å Thick. The loss of reflectivity at room temperature extends to wavelengths of 6 μ.

At near-room temperatures the integral normal emissivity changes only slightly, but its temperature dependences fan out as the slope increases with the growth of the film. This situation is reflected in the left ascending branch of the $\Delta\varepsilon_n/\Delta T = f(\delta)$ curves.

A comparison of the spectral and integral characteristics reveals that in practice little long-wave emission is generated in films up to 2000 Å thick. At the same time, the considerable increase in the integral normal emissivity of the system at the same oxide film thickness with increase in temperature is associated with intensified scattering in the oxide film as a result of the excitation of the crystal lattice and the shift of the emission spectrum into the region of shorter wavelengths. Consequently, on this thickness interval broad variation of the integral emissivity is possible only as a result of thermal excitation of the system (temperature factor).

3. Films More Than 2000 Å Thick. The loss of reflectivity associated with the thickening of the film continues to spread into the region of longer wavelengths and at $\delta > 3000$–5000 Å embraces the whole of the spectral interval considered. The $R_{\lambda n} = f(\lambda)_\delta$ curves develop a series of alternating peaks and troughs, reflecting the interference of the nonmonochromatic radiation incident on the oxidized surface. At film thicknesses of more than 5 μ the reflectivity is very low over the entire spectrum; the interference pattern is smoothed out. Concurrently with the loss of reflectivity, in the long-wave part of the spectrum there is a sharp increase in the integral normal emissivity at low temperatures. This leads to a decrease in $\Delta\varepsilon_n/\Delta T$, which is reflected in the right descending branch of the $\Delta\varepsilon_n/\Delta T = f(\delta)$ curves.

Maximum emissive power is possessed by a system with a nontransparent oxide film. Nontransparency develops when the generation of radiation is confined to the oxide layer. At maximum thicknesses the oxide films investigated are still to some extent transparent, since the integral normal emissivity continues to increase with the thickness of the film, especially at low temperatures. Moreover, the emissive power of the system is affected by the structural characteristics of the films, developed during formation under different temperature conditions.

NOTATION

ε_n, integral normal emissivity; $R_{\lambda n}$, spectral normal reflectivity; δ, thickness of oxide film; λ, wavelength; T, temperature.

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