THERMAL RADIATIVE PROPERTIES OF MAGNESIUM OXIDE AT HIGH TEMPERATURES

A.P. Chernyshev, V.A. Petrov, V.E. Titov, and A.Yu. Vorobyev

Institute of High Temperatures, Acad. of Sci. of Russia, 127412 Moscow, Russia

Keywords: radiation, absorption, scattering, reflectivity, effective temperature, optically infinite layer, wavelength.

ABSTRACT

Results are given, obtained from measurements of the normalhemispherical reflectivity of pure magnesium oxide at wavelengths of 0.488; 0.6328; 1.15; 3.39 and 5,4 μ m during its heating in air by CO₂ laser radiation from room temperature up to intensive

evaporation temperatures and during subsequent cooling. It was found that when there is a molten layer about 100 µm thick on the surface, an optically infinite layer is realized in the melt for the entire studied spectral range, and the value of the reflectivity is determined only by the refractive index. Comparison of the MgO radiation spectra in the wavelength range of 0.4-1.5 $\mu\text{m},$ measured during heating and cooling, and the radiation spectra of a blackbody model made it possible to calculate the "effective" brightness temperatures. This information enabled the nature of the spectral and temperature dependence of the absorption coefficient of MgO in both the solid and the liquid phase to be appraised. The brightness temperatures measured by a pyrometer at wavelengths of 0.55 and 0.72 μ m during the course of melting indicated a substantial change in the absorption coefficient.

The possible influence of radiation scattering by MgO condensate particles near the sample on the results of measuring radiative characteristics has been considered. This influence can be very appreciable in the visible and the nearest infrared region of the spectrum.

Observation of the melting and solidification plateaus enabled us to determine the melting point of the magnesium oxide more precisely, viz. 3215 ± 30 K, which is much higher than the generally accepted value.

INTRODUCTION

Magnesium oxide is a typical representative of semitransparent materials. At room temperature, the region of high

transparency in single MgO crystals extends approximately from 0.4 to 6 μ m, (Voronkova *et al.*, 1965; Touloukian and De Witt, 1972). The optical properties of both single crystals and dense polycrystalline samples of magnesium oxide at room temperatures have been studied quite well. But at high temperatures these properties have been the subject of relatively few studies, the maximum temperatures in these studies not exceeding 2300 K (Touloukian and De Witt, 1972; Sheindlin *et al.*, 1974). This can be explained, to a considerable extent, by the obstacles encountered in such measurements. They are associated with the need for indirect heating of the sample in an atmosphere of air but with the elimination of the effect of direct, scattered and reflected radiation from the heater on the results of the measurements.

In recent years, the possibilities for studying nonconducting semitransparent oxides have expanded quite considerably with the development of powerful lasers. The maximum temperatures now attainable in experimental studies have been significantly increased, but the specific nature of laser heating requires the detailed elaboration of the experimental procedure. To date, laser heating for studying the reflectivity of refractory oxides has been employed only by Bober and Karow (1977) and by Bober *et al.* (1980). The latter measured the reflectivity of magnesium oxide at a wavelength of 0.63 μ m (in the region of transparency) and at 10.6 μ m (in the region of opacity) in both the solid and liquid phases. However, the cited authors have not given adequate attention to important considerations such as the formation of a temperature field in the bulk of the samples being studied under conditions of laser heating, and to the problem of measuring the temperature itself.

The present work is a continuation and further development of studies of first results which were presented in an paper by Petrov and Chernyshev (1987). The objective of the present work is the experimental study of the normal-hemispherical reflectivity of magnesium oxide in the region of semitransparency at "laser" wavelengths of 0.488; 0.6328; 1.15; 3.39 and 5,4 μ m. The measurements were made during heating by CO₂ laser radiation up to

intensive evaporation temperatures and during the subsequent cooling of a sample. The relation between reflectivity and the formation of a temperature field in the melt and the solid ceramics was determined. In addition, the radiation emission spectra in the wavelength range from 0.4 to 1.5 μ m were studied during heating, during the quasi-steady temperature state, and during cooling of the sample.

EXPERIMENTAL

The experimental apparatus is shown schematically in Fig. 1. The experimental procedure was based on the high-speed measurement of radiation reflected by the sample from a probing laser with the required wavelength during heating by a continuous wave CO_2 laser (maximum power 1.5 kW), operating at a wavelength of 10.6 μ m, and during subsequent cooling of the sample after switching off the heating radiation. A helium-neon (0.6328; 1.15 and 3.39 μ m), argon (0.488 μ m) and CO laser (the probing radiation near 5.4 μ m was selected by a narrow bandpass filter with a half-width of 0.2 μ m)



Fig. 1. Schematic view of experimental apparatus: 1 - probing laser; 2 - digital voltmeter; 3 - laser radiation power meter; 4 - chopper; 5 - optoelectronic coupler; 6 - CO_2 heating laser; 7 - mirror; 8 - heating radiation shatter; 9 - crate CAMAC; 10 - beam splitter; 11 - small integrating sphere; 12 - radiation detector; 13 - ZnSe lens; 14 - 4-channel transient recorder; 15 - pyrometer; 16 - spectrometer; 17 - integrating sphere; 18 - sample; 19 - lock-in amplifier.

were employed as the probing lasers.

Each sample was put into the integrating sphere, and its reflection was compared with that from a reference sample at room temperature. To obtain a highly diffused reflection from the sphere walls within the entire spectral range being studied, interchangeable inserts in the form of aluminium hemispheres were put into the sphere. The inner surfaces of the inserts were sand-blasted, and highly reflective coatings of barium sulfate, gold, or aluminium were applied to them. Photodiodes of silicon, germanium, lead selenide, and cadmium-mercury telluride were used as the radiation detectors. The temperature of the sample was measured on the basis of its radiation at the wavelengths of 0.55 and 0.72 µm by a single-range two-channel photodiode pyrometer with logarithmic amplifiers. The choice of pyrometer wavelengths was based on making them as short as possible, within the sensitivity limits of a silicon photodiode while, at the same time, sufficiently far from the wavelengths of the probing lasers. The radiation spectra were recorded by a scanning high-speed spectrometer ROFIN-6000 (spectral range, 0.4 to 1.5 μ m; resolution, 10 nm; spectrum recording time, about 10 ms; period between successive spectra, about 90 ms). The pyrometer and spectrometer were calibrated according to the radiation from a blackbody by comparison with the readings of a reference disappearing filament pyrometer.

Usually the heating of refractory oxides by CO_2 laser radiation is considered to affect only the surface, but this is not completely correct for magnesium oxide. The temperature dependence of the absorption coefficient for the infrared region of the spectrum was studied by Cabannes and Billard (1987) and by Jasperse et al. (1966). By extrapolating the data in these publications to a wavelength of 10.6 μ m, we can estimate the absorption coefficient at 2000 K to be about 300-400 cm⁻¹. We shall show below that for such a value of the absorption coefficient the heating cannot be considered as surface heating.

The typical values of the heating radiation flux were $q = 3 \cdot 10^{3}$ W/cm². Such flux values ensured heating of the sample up to 3500 K, while, at the same time, they were insufficient to cause a breakdown and formation of a plasma of air and MgO vapor. The duration of heating was about two seconds, and a quasi-steady state temperature was essentially achieved. The diameters of the heating radiation and probing radiation spots were 6-8 and 0.5-1 mm, respectively, and those of the sighting areas of the pyrometer and spectrometer were 0.25 and 0.5 mm, respectively. The homogeneity of the temperature field in a sample over the area of the probing radiation spots was confirmed indirectly after an experiment. For this purpose, transverse sections of the sample were made across the crater, and the constancy of the temperature field.

It should be noted that magnesium oxide is very refractory, but it also has a very high vapor pressure. According to Glushko (1981), its melting point is $T = 3100\pm70$ K, while the total equilibrium pressure of the vapor components is 10 N/m² at about 3600 K. Hence, to prevent strong evaporation, the maximum possible temperature of the melt surface when studying the radiation characteristics must not exceed the melting point by more than 400-500 K.

Our earlier studies of how the condensation of magnesium oxide vapor affects the results of measuring radiation characteristics (Vorobyev *et al.*, 1991) showed that when there is a melt on a surface, the scattering of radiation by the condensate particles may introduce appreciable errors into the measurements. The magnitude of the scattering depends on the wavelength and on the distance from the sample surface. Scattering increases the values of the reflectivity and lowers the values of the spectral intensities of the radiation measured by the pyrometer and spectrometer.

Biberman et al. (1985) and Brykin (1989) showed theoretically, and Vorobyev et al. (1991) experimentally that in the action zone of the heating laser radiation, the growth of the particles may be retarded, and their size limited. To reduce the influence of scattering by condensate particles on the results of measuring reflectivity in the present studies, the probing laser radiation was directed into the integrating sphere at an angle close to the normal to the sample surface (about 7°). This was done so that the probing radiation would enter the action zone of heating radiation at a sufficient distance from the sample, beyond the limits of the air stream of free convection with condensate droplets rising at its vertical surface.

The ceramic samples of pure magnesium oxide were fabricated by cold pressing with subsequent sintering in the form of disks, 10 mm in diameter and 4 mm thick, with a porosity of about 15%. The grain sizes were within very broad limits from a few to hundreds of micrometers. Admixtures of other oxides, chiefly of calcium and aluminium, did not exceed 0.4% by mass. As a result of porosity, the radiation characteristics in the spectral region corresponding to the high transparency of a single crystal MgO are



Fig. 2. Change in the effective temperatures and reflectivity when heating MgO ceramics with a radiation flux of $3.1 \cdot 10^3$ W/cm². 1 - $R_{0.48}$; 2 - $R_{1.15}$; 3 - $R_{5.4}$; 4 - $T_{ef,1}$; 5 - $T_{ef,2}$; A - melting period; B - solidification period.

determined both by the spectral and temperature dependence of the absorption coefficient and by the scattering coefficient. The thickness of 4 mm was sufficient to allow a sample to be considered as optically infinite because of intensive scattering even at room temperature (at the smallest values of the absorption coefficient). The transmissions at 0.63 μ m was under 0.5% at room temperature. Before an experiment, the samples were heated in air at 1200 K for two hours and were then held under room conditions for three days. The values of the reflectivity at room temperature at wavelengths of 0.488; 0.6328; 1.15; 3.39, and 5,4 μ m were 0.91; 0.93; 0.95; 0.68, and 0.72, respectively.

RESULTS OF EXPERIMENT

Figure 2 shows, as an example, the results of measuring the reflectivity at wavelengths of 0.488; 1.15, and 5,4 μ m (R_{0.48}; R_{1.15}; R_{5.4}) when MgO sample was heated with a flux of $q = 3.1\cdot 10^3$ W/cm² for the first time. The time was measured from the instant of opening the heating radiation shutter. Recording of the pyrometer signal was started at the instant when the temperature reached about 2200 K. The temperature values T and T eff, and T eff, and 0.72 μ m do not give the true temperature of the sample's surface, as was shown earlier by Petrov and Chernyshev (1987). The value of the temperature to that of a blackbody radiation which, at the wavelengths of the temperature temperature to the sample's surface, as the wavelengths of the temperature temperature for each wavelength is equivalent to that of a blackbody radiation which, at the wavelengths of the temperature temperature temperature temperature when the temperature temperature temperature for each wavelengths of the temperature temperature temperature temperature temperature for each wavelength temperature temperature temperature temperature temperature temperature temperature for each wavelength temperature temperature temperature temperature temperature temperature for each wavelength temperature temperature temperature temperature temperature temperature temperature temperature for each wavelength temperature te

pyrometer, has the same intensity as the radiation emitting from a nonisothermal near-surface layer of a sample of a certain thickness depending on the temperature level. This is why we called the temperatures measured by the pyrometer effective temperatures.

Heating is manifested by an increase in the effective temperatures, the rate of increase decreasing with time. There is a break in the time dependence of the temperature associated with melting (time period A). At the instant corresponding approximately to t = 1.6 s, the temperatures almost reach quasi-steady values, though the thickness of the melt with further heating continues to increase (Galaktionov and Stepanov, 1990). It should be noted that during the initial heating stage

It should be noted that during the initial heating stage after the instant of opening the shutter, the reflectivity at all three wavelengths does not change significantly and corresponds to the values at room temperature. The value of R begins to decrease earlier at a wavelength of 0.488 μ m, which is connected with a shift in the electron absorption edge. The decrease in $R_{5.4}$ begins

later than in $R_{0.48}$, but earlier than in $R_{1.15}$. The decrease in R

throughout the entire spectral range before the beginning of melting must be due to an increase in the absorption coefficient since the scattering coefficient depends chiefly on the porosity and the refractive index does not change substantially with elevation of temperature, up to the appearance of the melt. When the latter appears, the value of $R_{0.48}$ begins to decrease more

slowly. The appearance of a melt does not substantially affect the change in reflectivities $R_{1.15}$ and $R_{5.4}$, and they continue to decrease at about the same rate. At temperatures below their

quasi-steady values, the reflectivities $R_{1.15}$ and $R_{5.4}$ attain constant values and are 0.10 and 0.05, respectively, whereas for $R_{0.48}$ an increase from about 0.12 to about 0.15 is observed due to the increase in scattering of the probing radiation by the condensate particles.

After heating is switched off, the reflectivity at each wavelength increases rapidly and in a few seconds has reverted to its initial values, as may be seen in Fig. 2. A typical break associated with solidification of the MgO melt can be seen on the cooling curves $T_{\rm of,1} = f(t)$ and $T_{\rm of,2} = f(t)$ (time period B). The results for the change in reflectivity at the wavelength of 3.39 μ m are not shown in Fig. 2. In this case, a noticeable increase in the reflectivity, from 0.68 to 0.78, was observed during the initial 0.1 s of the first heating. Konovalova *et al.* (1988) have shown that adsorbed water, Mg(OH)₂, and MgCO₃, formed on the surface of the samples as a result of being held in the

room atmosphere, yield a broad absorption band extending from 2.5 to 4.0 μ m. During the initial heating stage, the adsorbed water is removed, the Mg(OH)₂ and MgCO₃ decompose, magnesium oxide forms again, and therefore R_{3.39} increases at the beginning of heating. When the sample is cooled, R_{3.39} reverts to about 0.72. Within a few seconds as a result of the formation of magnesium hydroxide and carbonate on the surface of a sample, the value of the reflectivity again begins to decrease.

The properties of the surface layer of MgO, during the first heating, may change irreversibly. To establish the existence of these changes, we ran experiments with repeated and multiple



Fig. 3. 1, 2 - $R_{0.63}$ vs. $T_{ef,2}$ when heating with flux of $q_1 = 3.0 \cdot 10^3 \text{ W/cm}^2$ and $q_2 = 3.2 \cdot 10^3 \text{ W/cm}^2$, 3, 4 - $R_{0.63}$ vs. $T_{ef,2}$ in cooling of samples 1, 2.

heatings. Though the overall nature of the change in R and $T_{\rm ef}$ in the first and repeated heating is similar, some distinctions are nevertheless observed. The effective temperatures in repeated heating increase more rapidly because the expenditure of energy for the evaporation of the adsorbed water and the decomposition of the Mg(OH)₂ and MgCO₃ is considerably lower than in the first heating. Moreover, it has been shown in special experiments that the value of the reflectivity at the wavelength of the heating radiation also changes after the first heating. The temperatures acquire quasi-steady values after only 0.8 s of heating. Accordingly, a more rapid decrease in R is observed at all wavelengths.

Figure 3 compares the dependencies of $R_{0.63}$ on $T_{ef,2}$ obtained both during heating by various fluxes and during subsequent cooling. It can be seen that at the same effective temperatures during heating, smaller values of R are obtained with smaller flux of heating radiation. Petrov and Chernyshev (1987) considered in detail why the value of reflectivity depends on the flux of the heating radiation throughout temperature interval being studied . They showed for the first time that the reflectivity and emissivity under the conditions of laser heating of oxides are not physical constants that can be related to the surface temperature, but depend on the temperature field in the near-surface layer of a sample. This field, in turn, depends on the heating radiation flux.

The curves $R = f(T_{ef})$ for heating diverge because the quantity R (which for an optically infinite layer equals $1 - \lambda$, where λ is the absorptivity) is determined by the temperature dependence of the absorption coefficient k, whereas the magnitude of the temperature being measured is affected by the increase in

volume density of radiation j arising from the increase in intensity I_p of the Planck equilibrium radiation in each elemental layer, since $j = kn^2 I_p(T)$, where n is the refractive index. There is little scattering in the liquid phase, whereas the absorption coefficient increases to very high values, so that beyond a certain temperature, the melt layer becomes optically infinite. In this case, the reflectivity is identical for all heating radiation flux because it is determined only by the refractive index. If a sample cools to below the solidification point, but at

If a sample cools to below the solidification point, but at temperatures where absorption is substantial, the thickness of the solidified melt is the determining factor affecting the magnitude of R. At a lower heating radiation flux, the melt thickness is also smaller. Hence, when a sample cools, the optically infinite layer vanishes earlier, the probing radiation attenuates less reaching the highly scattering (reflecting) layers of the porous ceramics and thus, the magnitude of the reflectivity is greater at the same values of T_{ef} than with a thicker layer of solidified melt.

Figure 4 illustrates, on an expanded scale, the change in the reflectivity R_{λ} and the effective temperatures, shown in Fig. 2

during the quasi-steady state, and also when the sample cools during and near the solidification plateaus. Fig. 5 shows a similarly expanded plot of these characteristics for heating near the melting point. Examination of Fig. 4 reveals that supercooling of the melt is observed before the solidification plateau. The magnitude of the supercooling below the solidification temperature was generally 60-100 K. The supercooling is due to the intensive loss of energy by radiation and to the required formation of a sufficient number of nuclei of the crystalline phase for homogeneous nucleation.

The measured magnitude of supercooling can also be affected by other factors, however. In particular, switching off the heating radiation may be followed by the rapid growth in size of the condensate particles in the action zone near the sample. The particles grow less, prior to switching off the heating, because they are being heated by the CO_2 laser radiation. However these

particles are carried off by convective streams of air, while the supply of newly formed vapor diminishes sharply because of cooling of the sample. As shown earlier by Vorobyev et al. (1991), the time duration required for the removal of the particles from the zone of action after their formation is about 0.01 s. Although these experiments involved heating by a different laser with a different flux density and a smaller heating spot, their results suggest that by the time the solidification process begins the condensed particles will affect the measurement of temperature only slightly. However, this matter requires further study.

only slightly. However, this matter requires further study. The crystallization of a melt, depending on its thickness, which is determined by the heating radiation and the duration of its action, may require anywhere from several to hundreds of milliseconds.

Within the entire studied spectral range from 0.48 to 5.4 μ m, an optically infinite layer is realized in the melt after two seconds of action with a flux q 3.0·10³ W/cm². This follows from the fact that, after switching off the heating radiation with a drop in the effective temperatures by 200-400 K, the values of reflectivities at all wavelengths do not change, i.e. the magnitude of reflectivity is independent of the temperature, but is determined only by the refractive index. These results enable



Fig. 4. Change in R and T_{ef} in cooling a sample (Section B in Fig. 2): 1 - $R_{0.48}$; 2 - $R_{0.63}$; 3 - $R_{1.15}$; 4 - $R_{3.39}$; 5 - $R_{5.4}$; 6 - $T_{ef,1}$; 7 - $T_{ef,2}$.

us to appraise the nature of the spectral dependence of the absorption coefficient k_{λ} of MgO in the solid phase at temperatures close to the melting point. The first to increase is immediately after the solidification R_{1.15} because this in the (1.15 μm) lies region of the maximum wavelength transparency of MgO. The value of $R_{0.48}$ begins to increase later in time (i.e. at lower temperatures) than either $R_{0.63}$ or $R_{1.15}$. The wavelength of 0.48 μm is nearer to the long-wave edge of electron absorption and the absorption coefficient at this wavelength is higher than at $\lambda = 0.63 \ \mu m$. The wavelength of 5.4 μm is closer than the others to the phonon edge of absorption, and the optically infinite layer vanishes here later than at $\lambda = 3.39$ μ m. This signifies that the absorption coefficient at 5.4 μ m is higher than at 3.39 μ m.

During the melting period for the first heating of the sample, it can be seen from Fig. 5 that the beginning of melting and the subsequent growth in the thickness of the melt are associated with a sharp change in the rates of temperature variation and the relevant change in the magnitude of reflectivity (Fig. 5 shows the reflectivity for $\lambda = 0.48 \ \mu\text{m}$). When a definite amount of melt is built up (corresponding to the duration of the plateau from 0.61 to 0.68 s), a very steep, almost jump-like change in both effective temperatures occurs, after which they merge with further heating.

Figure 6 shows the wavelength dependence of the effective temperatures as determined from the MgO emission radiation spectra recorded at various times during heating with a heating radiation flux of $q = 3.1 \cdot 10^3$ W/cm² and during subsequent cooling of the sample. The spectrometer was calibrated according to the radiation from a blackbody model at a temperature of 3150 K. The spectrum used to calculate curve 1 was recorded during the time interval of



Fig. 5. Change in R and T_{ef} in melting of MgO ceramics (Section A in Fig. 2): $1 - R_{0.48}$; $2 - T_{ef,1}$; $3 - T_{ef,2}$.



Fig. 6. Change in $T_{\rm ef} = f(\lambda)$ calculated from spectra recorded during the heating and cooling of MgO at different times: 1 - t = 0.56 s; 2 - t = 2.06 s; 3 - t = 2.15 s.

0.56-0.57 s before there was a melt on the surface of the sample. The pyrometer readings at $\lambda = 0.55 \ \mu m$ during the time of spectrum recording increased from 3050 to 3078 K. The effective temperatures monotonically diminish with increasing wavelength from 3180 K at $\lambda = 0.4 \ \mu m$ to 2970 K at $\lambda = 1.5 \ \mu m$. This indicates that in the solid phase up to the melting point in the visible and near infrared region of the spectrum, the absorption coefficient substantially diminishes with an increase in wavelength. The between effective temperatures measured discrepancy by spectrometer (curve 1 in Fig. 6) and that of the pyrometer (Fig. 5) at 0.55 μ m and 0.72 μ m is within the limits of their inaccuracy. The spectrum used to calculate curve 2 was recorded during the quasi-steady state when a melt layer about 100 μ m thick formed on the surface of the sample and an optically infinite layer was observed for the entire spectral interval. Here the nature of the curve $T_{ef} = f(\lambda)$ is different. From 0.4 μ m to 0.7 the effective temperature decreases, and then begins to μm, increase with an increasing wavelength. Curve 3 corresponds to the radiation spectrum recorded during melt solidification; the spectrum was recorded during the time interval 2.14-2.15 s, the $T_{\rm of,1} = 3180$ K and $T_{\rm of,2} = 3181$ K at and $\lambda = 0.72$ μ m, respectively. The pyrometer readings were wavelengths of $\lambda = 0.55$ relation $T_{i} = f(\lambda)$ is essentially independent of wavelength in the spectral range from 0.4 to 1.35 μm , while at larger wavelength a monotonic decrease in $T_{\rm ef}(\lambda)$ is observed. This is probably due to the vanishing of the optically infinite layer for wavelengths exceeding 1.35 μ m.

ANALYSIS OF RESULTS

According to Fig. 4 the values of the reflectivities $R_{0.48}$, $R_{0.63}$, $R_{1.15}$, $R_{3.39}$, and $R_{5.4}$ with the presence of an optically infinite layer of the melt are 0.15, 0.12, 0.10, 0.04, and 0.05, respectively. Because of scattering by particles of the magnesium oxide vapor condensate, the values of the reflectivity in the visible and beginning of the infrared region of the spectrum may be too large. We ran special experiments in which the specular component of the reflectivity was removed from the integrating sphere and, consequently, the amounts by which the values of R could be too large because of scattering were determined. The corrected values of $R_{0.48}$, $R_{0.63}$, and $R_{1.15}$ are 0.07, 0.06, and 0.06, respectively. No scattering was observed at the wavelengths of 3.39 and 5.4 μ m. We estimated the accuracy of determining R to be ± 0.02. If we calculate the specular component of reflectivity indices at room temperature taken from the reference book by Voronkova *et al.* (1965), the results of the calculations coincide with our data on R within the error indicated above. Consequently, the refractive indices store to the reflective indices of the reflective indices

Our studies made it possible to define more precisely the melting point of magnesium oxide. As noted above, in the reference book by Glushko (1981), the melting point of pure magnesium oxide is given as 3100 ± 70 K. This value is based on the results reported by McNally *et al.* (1961) which were taken as the most authentic ones among limited available information.

We performed over 50 experiments involving the heating of MgO ceramics by laser radiation with observations made during the first, repeated, and multifold heatings; in each experiment, the temperature at the solidification plateau was measured. The values

of $T_{\text{of,1}}$ and $T_{\text{of,2}}$ coincided at the solidification point, and the difference between them did not exceed ± 5 K. The average value of the effective temperatures in solidification was 3190 ± 10 K. Scattering of the radiation by particles of the MgO vapor condensate can only lower the temperature, but as indicated above, by the time solidification occurs most of the condensate particles were apparently carried off by the convective flows of air. If we consider that in the course of crystallization of the melt a temperature gradient over the thickness of the melt is absent and adopt an emissivity value of $\varepsilon = 1 - R = 0.94$, we can appraise the solidification point of magnesium oxide to be $T = 3215 \pm 30$ K.

The stated value of error was obtained by summing the systematic and random errors (inaccuracy and imprecision) as proposed by Rabinovich (1978).

McNally at al. (1961) and Rilei (1966) determined the melting point of MgO at the moment of melting of a specimen when heated in graphite furnaces in an inert atmosphere (N_2 , Ar). A visual

optical pyrometer ($\lambda = 0.65 \ \mu m$) was sighted vertically on a sample. The magnesium oxide vapor could rise into the colder zone and condense there. Particles of the magnesium oxide condensate could be lifted by the convective stream and screen the pyrometer from the surface of the sample. Owing to the considerable distance from the pyrometer to the sample surface being sighted, the melting point values for MgO obtained by these authors could be appreciable understated because of scattering and absorption of radiation by the condensate particles. No attention was given to the possible influence of the condensate particles on the results of measuring the temperature obtained by these authors.

The electron microphotographs of the structure of a cross section of the sample through crater show that there is a layer of crystallized melt with a thickness δ of about 100 μ m near the surface. Below it, is a compacted layer about 300 μ m thick with a finely crystalline structure in which there was apparently a transition two-phase zone with a solid phase concentration varying in depth.

Knowing the thickness of the melt and considering that in the reflection measurement the probing radiation must pass through the melt twice to reach the higher reflecting layer of the two-phase zone and emerge into the integrating sphere, we can estimate the value of the absorption coefficient of the melt corresponding to the instant when the optically infinite layer for the discrete layer vanishes at a value of $k \cdot 2\delta = 5$, we find that k should be 250 cm⁻¹.

Since the temperature drop of the melt layer in cooling is not very large, the effective temperatures can be related to the the competatures by assuming that $\varepsilon = 1 - R$. The true temperatures at which the absorption coefficient is 250 cm⁻¹ for various wavelengths are given below: true temperatures by assuming that $\varepsilon = 1 - R$. The various wavelengths are given below:

0.63 3.39 λ, μm 0.48 1.15

5.4 2790 2940 3175 2915 2830

т, к Of course, the temperatures at which the absorption coefficient is obtained in this way are only approximate. Their error 250 cm may reach 3-4%.

We have already noted that the only other investigation of the thermal radiation characteristics of magnesium oxide at temperatures above its melting point was that of Bober *et al.* (1980). They measured the spectral reflectivity of MgO at a wavelength of 0.63 μ m within the temperature range 1000 to 4000 K.

Their measurements were conducted in an integrating sphere in an Ar atmosphere at a pressure of about two bars. The flux of the heating CO_2 laser radiation was of the order of 10^5 W/cm², while

the duration of heating was varied from 1 to 100 ms. The emissivity was evaluated by the formula for an isothermal optically infinite layer assuming that $\varepsilon = 1 - R$.

The data obtained by Bober et al. (1980) differ substantially from our results. The reason, in our opinion, is that the melt when heated using such a high flux is very thin, while the temperature gradient in the near-surface layer is very high. It may be shown easily by numerical calculation of combined radiation and conduction heat transfer for laser radiation heating of ceramics (Galaktionov and Stepanov, 1990). Though Bober et al. do not indicate the melt thickness, we can judge from a similar melt thickness for uranium oxide studied by them (a melt thickness of 20 μ m) that the melt was much thinner than in our work. It is not surprising that Bober et al. obtained a greatly understated value of the melting point of MgO (2870 K), because their pyrometer measured radiation not only from the melt but also from the nonisothermal colder near-surface layer of the ceramics. The nature of their observed temperature dependence of $R_{0.63}$ up to

melting, at which $R_{0.63}$ is essentially constant, does not agree with our results (Fig. 3).

The fact is that, with such a high flux of the heating radiation as used by Bober et al., the reflectivity should not depend on the temperature up to the melting point because the contribution of the absorption in the thin heated layer is negligible.

Our more detailed analysis of the melting process reveals (Fig. 5) that, with our appreciably lower flux than those employed by Bober *et al.*, the beginning of melting corresponds to effective temperature of about 3160 ± 10 K. This lower value of the melting point in comparison with the solidification temperature is associated with the absence of an optically infinite layer upon melting. The radiation of the CO₂ laser is absorbed, not on the

surface as is customarily considered, but in a certain near-surface layer whose depth is of the order of magnitude of the reciprocal of the absorption coefficient, i.e. 30 μ m. With such bulk melting in this layer, a two-phase zone appears in which the change in the ratio of the volumes of the liquid and solid phase in melting does not apparently change the thermal radiation characteristics to an appreciable extent.

The slight reduction in reflectivity during the melting plateau is due to the lower scattering in the two-phase region. The sharp jump in the effective temperatures after the melting plateau shown in Fig. 5 may be due to the jump-like increase in the absorption coefficient of the liquid phase after the completion of melting of this near-surface layer. After the jump in the absorption coefficient, the values of the two effective temperatures measured by the pyrometer approach each other, while with further heating they merge completely because of the growth in the absorption coefficient.

It should be noted that the volume absorption of heating radiation causes the formation of a temperature distribution such that in the quasi-steady state with the presence of ablation, it has a maximum within the melt at a certain distance from the surface. This can be seen clearly in the spectrum of radiation shown by curve 2 in Fig. 6. Beginning from 0.4 μ m, the decrease of $T_{\rm ef}$ with increasing λ is due to the prevalent influence of the reduction in absorption coefficient on the intensity of the radiation outgoing from the sample. With further increase of λ after the minimum in $T_{\rm ef}$ at $\lambda = 0.6 \ \mu m$, the higher temperature of the deeper layers has the prevalent influence on the intensity of radiation since at these wavelengths the deeper layers begin to contribute noticeably to the radiation.

CONCLUSION

The present investigation has shown the necessity of taking into account (i) the specific nature of the heating of refractory oxides, in particular, magnesium oxide heated by CO_2 laser radiation, when determining the thermal radiative characteristics and optical properties up to the temperatures of intensive evaporation, and (ii) the influence of the heating radiation flux and possible scattering by the condensate droplets on the indicated characteristics and the temperatures being measured. The solidification point of magnesium oxide was determined more precisely and was found to be somewhat higher than the currently adopted value. A nonmonotonic change in the absorption coefficient of magnesium oxide in the visible region of the spectrum has been shown to occur in the melt. The vanishing of the optically infinite layer when the melt layer cools made it possible to appraise the value of the absorption coefficient of magnesium oxide for some wavelengths.

REFERENCES

- Biberman, L.M., Brykin, M.V., and Khrapak, A.G., 1985. Gomogennaya condensatsiya v pole electromagnitnogo izlucheniya. *Teplofizika Vysokikh Temperatur*, 23:446-455 (in Russian).
- Bober, M., Karow, H.U., 1977. Measurement of spectral emissivity of UO₂ above the melting point. In: A. Cezairliyan (Editor), Proc. 7th Symp. on Thermophysical Properties, ASME, New York, pp. 344-350.
- Bober, M., Karow, H.U., and Muller, K., 1980. Study of the spectral reflectivity and emissivity of liquid ceramics. High Temperatures High Pressures, 12:161-168.
 Brykin, M.V., 1989. Pogloschenie lazernogo izlucheniya dispersnoy
- Brykin, M.V., 1989. Pogloschenie lazernogo izlucheniya dispersnoy fazoy produktov razrusheniya materialov, obrazuyuschikhsya pri spontannoy gomogennoy kondensatsii para. Teplofizika Vysokikh Temperatur, 27:312-320 (in Russian).
- Cabannes, F. and Billard, D., 1987. Measurement of infrared absorption of some oxides in connection with the radiative transfer in porous and fibrous materials, Int. J. Thermophysics, 8:97-118.
- Galaktionov, A.V. and Stepanov, S.V., 1990. Vozdeystvie izlucheniya na silno rasseivayuschie keramiki. Teplofizika Vysokikh Temperatur, 28:124-130 (in Russian).
- Glushko, V.P. (Editor), 1981. Termodinamicheskie svoystva individual'nykh vestchectv. Vol.3, part 2, Nauka, Moscow, (in Russian).

Jasperse, J.R., Kahan, A., Plendl, J.N., and Mitra S.S., 1966. Temperature Dependence of Infrared Dispersion in Ionic Crystals

Lif and MgO. Physical Review, 146:526-542. Konovalova, O.P. et al., 1988. Opredelenie opticheskikh konstant vakuumnykh tonkoplenochnykh kondensatov na metall iz spektrov IK-otrazheniya. Optiko-Mekhanicheskaya Promyshlennost, 7:14-16 (in Russian).

McNally, R.N., Peters, F.I., and Ribbe, P.H., 1961. Laboratory Furnace for Studies in Controlled Atmospheres; Melting Points of MgO in N₂ and of Cr_{2O_3} in N₂ and Air Atmospheres. J. Amer. Ceramic Soc., 44:27 - 29.

Petrov, V.A., and Chernyshev, A.P., 1987. Eksperimentalnoye issledovanie poverkhnostnogo nagreva keramiki iz oksida migniya lazernym izlucheniem. 25:361-368 (in Russian). Teplofizika Vysokikh Temperatur,

Rabinovich, S.G., 1978. Pogreshnosti izmereniy. Energiya, Leningrad, (in Russian).

Rilei, B., 1966. The determination of melting points at temperatures above 2000 Celcius. Rev. Hautes Temper. et Refract., 3:327-336.

Sheindlin, A.E., (Editor), 1974. Izluchatel'nye svoystva tverdykh
materialov. Energiya, Moscow, (in Russian).

Touloukian, Y.S. and de Witt, D.P., 1972. The properties of matter. Vol.8. IFI/Plenum, New York. Thermophysical

Voronkova, E.M., Grechushnikov, B.N., Distler, G.I., and Petrov,

I.P., 1965. Opticheskie materialy dlya infrakrasnoy tekhniki. Nauka, Moscow, (in Russian). Vorobyev, A.Yu., Petrov, V.A., Titov, V.E., and Chernyshev, A.P., 1991. Eksperimentalnoye issledovanie kondensatsii parov tugoplavkikh oksidov pri poverkhnostnom nagreve misheni v vozdukhe lazernym izlucheniem. Teplofizika Vysokikh Temperatur, 29:981-987, (in Russian).