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Mass-spectrometric investigation of $UO_3(g)$

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Abstract

Vaporization behavior of $UO_3(g)$ over $UO_{2+x}(s)$ coloaded with MgO(s) was investigated by means of a quadrupole mass spectrometer equipped with a Knudsen-cell up to 1923 K. The ion current behavior of UO_3^+ and X-ray diffraction analysis of the $UO_{2+x}(s)$ sample after the vapor pressure measurement suggested that magnesium negligibly dissolved into $UO_{2+x}(s)$. The partial pressures of $UO_3(g)$ and Mg(g) were determined in a modified integral method. The partial pressure of $O_2(g)$ was obtained indirectly from the partial pressures of $UO_3(g)$ and Mg(g). The Gibbs free energy of formation of $UO_3(g)$ was calculated from the partial pressures of $UO_3(g)$ and $O_2(g)$ in the temperature range of 1723–1923 K. It was found that the Gibbs energy of formation of $UO_3(g)$ obtained in this study was a little higher than the recommended values recently reported.

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1. Introduction

In spite of the importance of evaluating behaviors of volatile species in case of core disruptive accident, there are discrepancies among the values of partial pressures over hyperstoichiometric uranium dioxide, $UO_{2+x}(s)$, in the literature [1]. The reason for that is possibly due to inaccuracy of the standard Gibbs free energy of formation of $UO_3(g)$, $\Delta G_f^0(UO_3, g)$. The purpose of this study is to determine the partial pressure of $UO_3(g)$ over $UO_{2+x}(s)$ and evaluate $\Delta G_f^0(UO_3, g)$ by means of mass spectrometry.

Several mass-spectrometric studies have been conducted in the past to obtain such quantities [2,3]. Satisfactory results, however, have not been obtained because of the difficulties of maintaining the condensed phase in a sufficiently oxidized state during the measurement in vacuo as well as the uncertainty of the ionization cross-sections related to the mass-spectrometric measurement [4]. In this study the mass-spectrometric measurement of vaporization of uranium dioxide, $UO_2(s)$, coloaded with magnesium monoxide, MgO(s), which could function as an oxygen supplier, was carried out to overcome the former problem. MgO(s) is considered to be a suitable material as an oxygen supplier, for the calculation based on known thermochemical data [1,5] suggests that the coexistence with MgO(s) leads to the production of a sufficient amount of the vapor species of $UO_3(g)$ in the mass-spectrometric study. Further, it is reported that the solubility of magnesium in $UO_2(s)$ is only a few mol% when MgO(s) was heated with $UO_2(s)$ in vacuum at 2623 K [6]. For the latter problem a modified integral method was used, which does not require the ionization cross-section in determining the partial pressure of vapor species from the ion current [7].

2. Experimental

$UO_2(s)$ powder, of which the main impurities are listed in Table 1, and MgO(s) powder with 99.5% in

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Table 1
Impurity analysis of UO_2 powder

Element	Concentration (wt ppm)
Al	20
Ag	0.1
B	<1
Cd	<1
Cr	<50
Cu	3
Fe	130
Mg	<20
Mn	<10
Mo	3
Ni	100
Pb	2
Si	100
Sn	2

purity were supplied by Spencer Chemical, USA and Johnson Matthey, Germany, respectively. $UO_2(s)$ powder was reduced to stoichiometric composition by heating at 1100 K in a stream of Ar–8%H_2 mixed gas, while MgO(s) powder was heated at 1273 K in an Ar gas stream.

A quadrupole mass spectrometer (EXTREL, MEXM-1200) equipped with a Knudsen cell was used. An Ir Knudsen cell with an effusion orifice of 1.0 mm in diameter was employed in the measurement. A shutter is positioned above the Knudsen cell. $UO_2(s)$ powder put into the platinum container cup was placed on the MgO(s) powder, with which the inner bottom of the Knudsen cell is covered, to avoid the contact of $UO_2(s)$ and MgO(s) powders and the contact of the platinum cup and the Ir Knudsen cell. The sample masses of $UO_2(s)$ and MgO(s) powders are about 70 and 40 mg, respectively. Temperature was measured by two sets of W/Re 3–25 thermocouples inserted into the upper and lower positions of Ta holder containing the Knudsen cell, which was calibrated by the melting point of Pd. The highest temperature was restricted by use of Pt container cup and the lowest temperature by the ion-detection limit of $UO_3(g)$. The background pressure in the vacuum chamber was maintained to less than 2×10^{-4} Pa during the vapor pressure measurement. Samples after the measurement were subjected to the X-ray diffraction analysis.

3. Results and discussion

3.1. Ionization efficiency curve

As the ionic species, $U^+, UO^+, UO_2^+, UO_3^+, Mg^+$ and O_2^+, were identified by opening and closing the shutter, while MgO^+ ion was not detected. There is a possibility that the ion intensity of UO_2^+ originating from $UO_2(g)$ vapor instead of $UO_3(g)$ vapor reaches the detectable level at a higher temperature, while it is known that the fragmentation pattern of $UO_2(g)$ is different from that of $UO_3(g)$ and that, for $UO_2(g)$, the ratio of UO^+ fragment ion to UO_2^+ parent ion is 0.78 at 30 eV of electron energy [8]. Fig. 1 shows the relative ion intensities of U^+, UO^+, UO_2^+ and UO_3^+ at 1723 and 1923 K, normalized to that of UO_3^+ at 70 eV, as plotted against electron energy. As shown in this figure, the ionization efficiency curves for 1723 K agreed well with those for 1923 K and the ion intensity of UO^+ at 30 eV is very small compared to that of UO_2^+ at the same electron energy. Therefore, it is considered that the amount of $UO_2(g)$ vapor species was negligible compared to that of $UO_3(g)$. Fig 1 also shows that the ion intensity of UO_3^+ has already saturated at 70 eV. So, for convenience, the electron energy of 70 eV was chosen for all the vapor species in the measurement.

3.2. Time-dependence of the ion currents

Under the present experimental conditions there was a possibility that magnesium dissolves into $UO_2(s)$ because of the existence of magnesium in gaseous phase

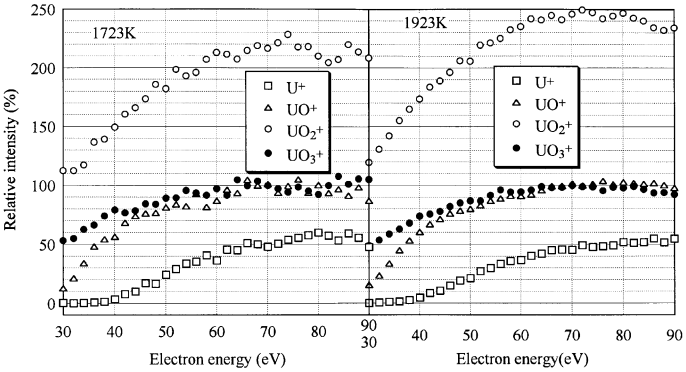

Fig. 1. Ionization efficiency curves of U^+, UO^+, UO_2^+ and UO_3^+ at 1723 and 1923 K.

[9]. Moreover, the O/U ratio of UO_{2+x}(s) will change at each temperature under the ambient oxygen pressure in equilibrium with MgO(s). In such cases the ion currents of the species vaporized from the sample should change with time. So the time-dependences of the ion currents of UO_3^+ and Mg^+ were checked at all the measurement points by holding the sample temperature which was initially raised from 1723 to 1923 K in the temperature interval of 50 K and then lowered to 1723 K in the same temperature interval. Figs. 2(a) and (b) show the time-dependences of these ion currents obtained at 1823 K, respectively, where these ion currents are plotted from the time when the sample temperature was considered to become constant. In the temperature range 1723–1923 K, at first the ion currents of UO_3^+ on heating stage gradually increase with time and those of Mg^+ decrease. On the other hand, these ion currents on cooling stage change in the opposite manner. However, these ion currents ultimately become constant. Therefore, it is considered that the time-dependence of the ion currents of UO_3^+ and Mg^+ is resulted from the shift of O/U ratio of UO_{2+x}(s) in response to change in the ambient oxygen pressure equillibrated with MgO(s). Further, these ultimate ion currents on heating stage almost agree with those on cooling stage although there is a tendency that the ion intensities of Mg^+ on heating stage are a little higher than those on cooling stage. So the agreement of the ion currents between on heating stage and on cooling stage suggests that dissolution of a significant amount of magnesium into uranium dioxide is not likely to occur during the measurement.

3.3. X-ray diffraction analysis

X-ray diffraction patterns of UO_2(s) and MgO(s) after the vapor pressure measurement are shown in Fig. 3. This figure shows that no phases other than UO_2(s) and MgO(s) exist. However, it was found that the deposition of UO_2(s) on MgO(s) sample occurred during the vapor pressure measurement. However, the change in lattice parameter of UO_2(s) due to the vapor pressure measurement suggests that dissolution of a significant amount of magnesium did not occur during the measurement [9].

3.4. Vapor pressures

In the present experiment condition, the predominant uranium-bearing vapor species is considered to be UO_3(g) as mentioned in Section 3.1. Then, the number of uranium atoms, N_U, effused through the orifice in the time interval of $\Delta t = t_2 - t_1$, during which the tempera-

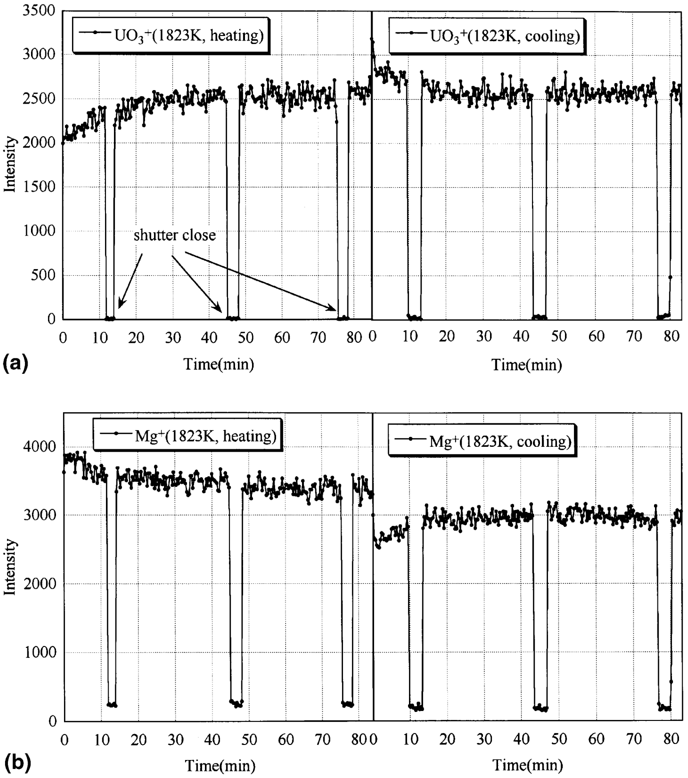

Fig. 2. Time-dependence of the ion currents of (a) UO_3^+ and (b) Mg^+ at 1823 K.

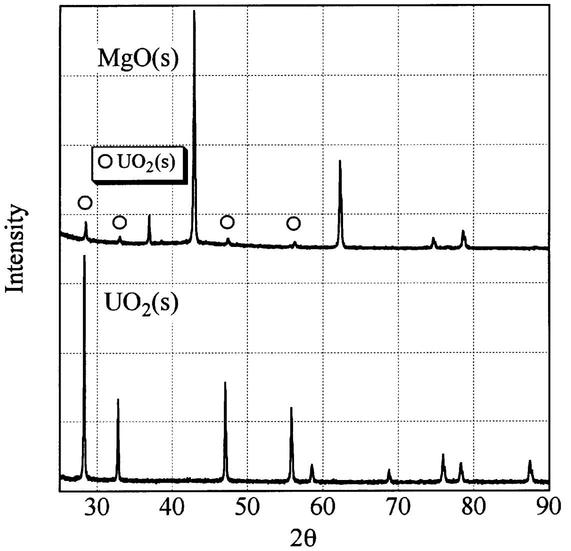

Fig. 3. X-ray diffraction patterns of $UO_2(s)$ and MgO(s) after the mass-spectrometric measurement.

ture is T_i, can be calculated in the modified integral method [7] with the following equation:

$$N_U(T_i) = \frac{\Delta W(UO_2)\ N_A}{\gamma_{235}M(^{235}UO_2) + \gamma_{238}M(^{238}UO_2)} \times \frac{\int_{t_1}^{t_2} I(UO_3)\sqrt{T_i}\,dt}{\int_0^{t_{end}} I(UO_3)\sqrt{T}\,dt}, \tag{1}$$

where ΔW is the weight difference before and after the mass-spectrometric measurement, M the mass number, γ the isotopic abundance ratio, N_A Avogadro constant, I the ion current and t_{end} the time when the measurement is completed.

This number can be also obtained from the partial pressure of $UO_3(g)$ by the Langmuir equation [10]:

$$N_U(T_i) = \left(\frac{\gamma_{235}P(UO_3)}{\sqrt{2\pi M(^{235}UO_3)RT_i}} + \frac{\gamma_{238}P(UO_3)}{\sqrt{2\pi M(^{238}UO_3)RT_i}}\right) \times N_A \Delta t s L, \tag{2}$$

where s is the cross-section of orifice, L Clausing factor and R the gas constant.

From Eqs. (1) and (2), the partial pressure of $UO_3(g)$ can be calculated with the following equation:

$$P_{UO_3}(T_i) = \frac{\Delta W(UO_2)}{\gamma_{235}M(^{235}UO_2) + \gamma_{238}M(^{238}UO_2)} \times \frac{\sqrt{2\pi RT_i}}{\Delta t\ sL}\left\{1\Big/\left[\frac{\gamma_{235}}{\sqrt{M(^{235}UO_3)}} + \frac{\gamma_{238}}{\sqrt{M(^{238}UO_3)}}\right]\right\}\frac{\int_{t_1}^{t_2} I(UO_3)\sqrt{T_i}\,dt}{\int_0^{t_{end}} I(UO_3)\sqrt{T}\,dt}. \tag{3}$$

In the same way, the partial pressure of Mg(g) can be calculated with the following equation:

$$P_{Mg}(T_i) = \frac{\Delta W(MgO)}{\gamma_{24}M(^{24}MgO) + \gamma_{25}M(^{25}MgO) + \gamma_{26}M(^{26}MgO)} \times \frac{\sqrt{2\pi RT_i}}{\Delta t\ sL}\left\{1\Big/\left[\frac{\gamma_{24}}{\sqrt{M(^{24}Mg)}} + \frac{\gamma_{25}}{\sqrt{M(^{25}Mg)}} + \frac{\gamma_{26}}{\sqrt{M(^{26}Mg)}}\right]\right\} \times \frac{\int_{t_1}^{t_2} I(Mg)\sqrt{T_i}\,dt}{\int_0^{t_{end}} I(Mg)\sqrt{T}\,dt}. \tag{4}$$

On the other hand, the partial pressure of $O_2(g)$ was obtained from the balance of the numbers of atomic magnesium and oxygen effused through the orifice of the Knudsen cell. The oxygen supplied by MgO(s) could be consumed to oxidize the $UO_2(s)$ sample or to form $UO_3(g)$ and $O_2(g)$. However, when equillibrium reaches, the composition of the condensed phase becomes constant and the oxygen supplied by MgO(s) could be used for formation of $O_2(g)$ and $UO_3(g)$ apparently. Thus, the number of atomic oxygen supplied by MgO(s) becomes equal to the sum of twice the number of $O_2(g)$ and that of $UO_3(g)$. Then, the following equation holds:

$$\left(\frac{\gamma_{24}}{\sqrt{M(^{24}Mg)}} + \frac{\gamma_{25}}{\sqrt{M(^{25}Mg)}} + \frac{\gamma_{26}}{\sqrt{M(^{26}Mg)}}\right)P_{Mg} = \frac{2P_{O_2}}{\sqrt{M(O_2)}} + \left(\frac{\gamma_{235}}{\sqrt{M(^{235}UO_3)}} + \frac{\gamma_{238}}{\sqrt{M(^{238}UO_3)}}\right)P_{UO_3}. \tag{5}$$

Now, if the Clausing factor, L, is obtained, these partial pressures are determined. The mass-spectrometric measurement of silver was carried out to determine the Clausing factor from the following equation by using the reference data, $P_{ref.}$ [11]:

$$L = \frac{\Delta W(Ag)}{\gamma_{107}M(^{107}Ag) + \gamma_{109}M(^{109}Ag)}\frac{\sqrt{2\pi RT_i}}{\Delta t s P_{ref.}} \times \left\{1\Big/\left[\frac{\gamma_{107}}{\sqrt{M(^{107}Ag)}} + \frac{\gamma_{109}}{\sqrt{M(^{109}Ag)}}\right]\right\} \times \frac{\int_{t_1}^{t_2} I(Ag)\sqrt{T_i}\,dt}{\int_0^{t_{end}} I(Ag)\sqrt{T}\,dt}. \tag{6}$$

The value of the Clausing factor obtained in this way was larger than that calculated from the shape of the orifice [12]. As the reason for that, it was considered that a small amount of the vapor species might effuse from other than the effusion orifice. However, the Clausing factor calibrated with the mass-spectrometric measurement of silver is considered to be applicable for the determination of vapor pressure, for this apparent factor can cancel out the effect of such a leakage.

But, unfortunately, the weight differences, $\Delta W(UO_2)$ and ΔW(MgO) in Eqs. (3) and (4) could not be obtained from the weight differences of UO_2(s) and MgO(s) samples since the X-ray diffraction analysis indicated that UO_3(g) condensed to UO_2(s) on MgO(s) powder. So the standard Gibbs free energy of formation of MgO(s), ΔG_f^0(MgO,s), was utilized to obtain these weight differences. $P(O_2)$ can be expressed as a function of $\Delta W(UO_2)$ and ΔW(MgO). ΔG_f^0(MgO,s) at a higher temperature than boiling point of magnesium can be derived from the following equation:

$$\Delta G_f^0(\mathrm{MgO,s}) = RT\ln(P(\mathrm{Mg})P(\mathrm{O_2})^{1/2}), \quad (7)$$

while, the total weight difference of the sample, ΔW:

$$\Delta W = \Delta W(\mathrm{UO_2}) + \Delta W(\mathrm{MgO}) \quad (8)$$

can be obtained from the weight difference of the Knudsen cell containing the sample before and after the mass-spectrometric measurement assuming the negligible contribution of the Pt cup and the Ir Knudsen cell because both the vapor pressures of Ir(g) and Pt(g) are much lower than that of UO_3(g) [11]. Thus, $\Delta W(UO_2)$ and ΔW(MgO) were calculated from the simultaneous equations of Eqs. (7) and (8) by using the ΔG_f^0(MgO,s) given by Ref. [5]

The determined partial pressures of UO_3(g), Mg(g) and O_2(g) are plotted in Fig. 4 in the temperature range of 1723–1923 K. This figure also includes the O/U ratio of UO_{2+x}(s) in equilibrium with the oxygen pressure obtained in this study, which was calculated based on Blackburn's model [13] with the following equation:

$$\ln P(\mathrm{O_2}) = 2\ln\frac{x(2+x)}{1-x} + 108x^2 - 32700/T + 9.92. \quad (9)$$

3.5. Standard Gibbs energy of formation of $UO_3(g)$

For the following equilibrium reaction:

$$\mathrm{UO_2(s)\ in\ UO_{2+x}(s)} + 1/2\mathrm{O_2(g)} = \mathrm{UO_3(g)}. \quad (10)$$

$\Delta G_f^0(UO_3,g)$ can be calculated with the following equation:

$$\Delta G_f^0(\mathrm{UO_3,g}) = -RT\ln\left[\frac{P(\mathrm{UO_3})}{P(\mathrm{O_2})^{1/2}a(\mathrm{UO_2})}\right] + \Delta G_f^0(\mathrm{UO_2,s}), \quad (11)$$

where $a(UO_2)$ is the activity of UO_2(s) in UO_{2+x}(s). The activity was obtained from the relationship between the partial pressure of O_2(g) and the O/U ratio based on Blackburn's model by using the Gibbs–Duhem equation. This formula provided in ref. [1] is expressed as the following equation:

$$\ln a(\mathrm{UO_2}) = -x + 2\ln(1 + x/2) + \ln(1 - x) - 36x^3. \quad (12)$$

$\Delta G_f^0(UO_3,g)$ determined from Eq. (11) using $\Delta G_f^0(UO_2,s)$ given by Cordfunke and Koning's table [14] is plotted in Fig. 5 as a function of temperature. The least-squares treatment of the data gives the following equation:

$$\Delta G_f^0(T)(\mathrm{UO_3,g})(\mathrm{J/mol}) = -841000 + 94.6T \quad (1723\text{–}1923\ \mathrm{K}). \quad (13)$$

As shown in this figure, $\Delta G_f^0(UO_3,g)$ obtained in this study is a little higher than the recommended value given

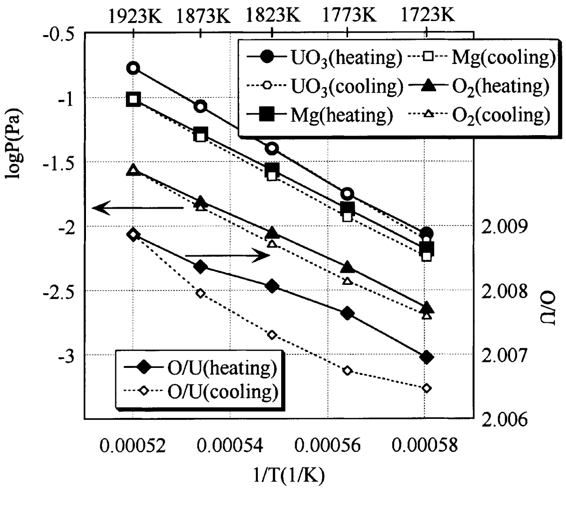

Fig. 4. Vapor pressures over UO_{2+x}(s) coloaded with MgO(s) and the O/U ratio of UO_{2+x}(s) based on Blackburn's model [13].

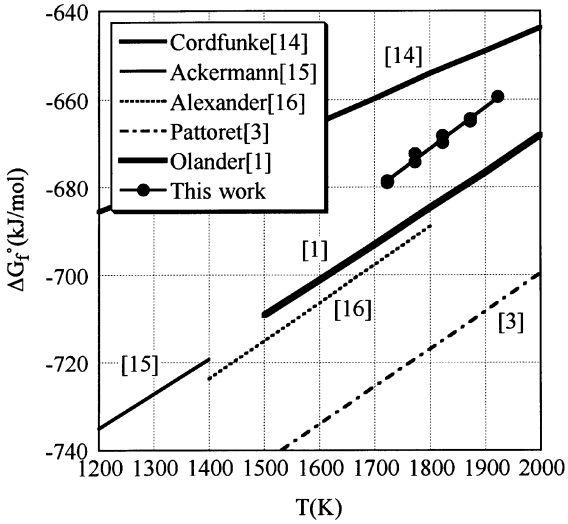

Fig. 5. Standard Gibbs free energy of formation of UO_3(g).

by Olander [1]. Most Gibbs free energies of formation of UO_3(g) reported in the past have been obtained from the transpiration experiment of U_3O_8(s) [1,15,16]. However, the traspiration technique at higher temperature has a difficulty of establishment of the equilibrium condition due to temperature gradient in the sample region. Furthermore, the thermodynamic data of U_3O_8(s) at higher temperature is not well established compared to that of UO_2(s). The other two $\Delta G_f^0(UO_3, g)$ reported in ref. [3] and [14] are obtained from mass-spectrometric data and from molecular parameters and spectroscopic data, respectively. As mentioned in the introduction, for ref . [3], there is the uncertainty of the ionization cross-sections related to the mass-spectrometric measurement. While, for ref. [14], there is the uncertainty of contribution of the electronic partition function to the free energy function of UO_3(g) which is required in the evaluation of $\Delta G_f^0(UO_3, g)$, as mentioned in this reference. Therefore, it is considered that the data of $\Delta G_f^0(UO_3, g)$ obtained directly from the vapor pressures of UO_3(g) and O_2(g) over UO_{2+x}(s) at high temperatures are more reliable.

4. Conclusion

The mass-spectrometric measurement of UO_2(s) coloaded with MgO(s) was carried out. The vapor pressures of UO_3(g) and Mg(g) were determined in a modified integral method and $\Delta G_f^0(UO_3, g)$ in the temperature range of 1723–1923 K was obtained. It was found that $\Delta G_f^0(UO_3, g)$ obtained in this study was a little higher than the recommended values.

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