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Microstructures of SiO_2 scales formed on $MoSi_2$

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Abstract. The microstructures of oxide scales formed on $MoSi_2$ at medium-high temperatures in air were observed by TEM. Based on the observation, relationships between oxidation temperature and formation of MoO_3 and crystallization of amorphous SiO_2 scales were investigated. At 1273 K and 1373 K, the oxide scales had a structure consisting of amorphous SiO_2 with small amounts of fine MoO_3 particles. The oxide scales at 1573 K and 1773 K had a structure consisting of amorphous and crystalline SiO_2. Growth rate of the oxide scale formed at 1773 K appreciably increased due to crystallization of amorphous SiO_2. It was thought that the increase in the oxidation rate at 1773 K was caused by a change in the diffusion mechanism from O_2 diffusion to lattice diffusion of O^{2-} through SiO_2. In addition, the diffusion coefficient of oxygen was estimated from the growth rate of SiO_2 scale.

Introduction

In the field of advanced jet engines and gas turbines, development of ultra-high temperature structural materials is indispensable. Molybdenum disilicide ($MoSi_2$) has a high melting point (2303 K) and a relatively low density (6.24 g/cm^3), undergoes brittle-to-ductile transition at a temperature of about 1173 K, and has excellent resistance to oxidation at temperatures above 1073 K. Therefore, $MoSi_2$ is a promising candidate material for ultra-high temperature applications. It is well known that the excellent resistance of $MoSi_2$ to oxidation at temperatures above 1073 K is attributed to the formation of a protective SiO_2 scale due to selective oxidation of Si. On the other hand, at low temperatures, especially at temperatures as high as 773 K, $MoSi_2$ shows accelerated oxidation behavior due to simultaneous oxidation of Mo and Si. Oxide scales formed on $MoSi_2$ at low temperatures have been extensively investigated [1-7], but there were few studies on microstructures of oxide scales formed at high temperatures. Such situation leads to ambiguous understanding of oxidation mechanism of $MoSi_2$. In the present study, the microstructures of oxide scales formed on $MoSi_2$ at medium to high temperatures, with focus on relationship between oxidation temperature and formation of MoO_3 and crystallization of amorphous SiO_2, were investigated using TEM-EDS.

Background

It is known that $MoSi_2$ shows accelerated oxidation behavior at low temperatures (673-1073 K) due to simultaneous oxidation of Mo and Si, while it has excellent resistance to oxidation at high temperatures (1073-1873 K) due to selective oxidation of Si (passive oxidation). Therefore, oxidation reactions at low and high temperatures can be expressed as

$$2\ \mathrm{MoSi_2(s)} + 7\ \mathrm{O_2(g)} \rightarrow 2\ \mathrm{MoO_3(s)} + 4\ \mathrm{SiO_2(g)} \qquad (673\mathrm{K}\sim1073\mathrm{K}) \qquad (1)$$

$$5\ \mathrm{MoSi_2(s)} + 7\ \mathrm{O_2(g)} \rightarrow \mathrm{Mo_5Si_3(s)} + 7\ \mathrm{SiO_2(s)} \qquad (1073\mathrm{K}\sim1873\mathrm{K}) \qquad (2)$$

A chemical potential diagram of a Mo-Si-O system at 1773 K is shown in Figure 1, which was constructed by using a thermodynamic soft ware, MALT 2. As can be seen in this figure, the stable oxide on $MoSi_2$ is SiO_2. Such thermodynamic stability of SiO_2 scale on $MoSi_2$ holds even at low temperatures. Nevertheless, reaction mechanism at high temperatures is different from that at low temperatures, as expressed in above equations. In oxidation at high temperatures, vaporization of MoO_3(g) probably plays an important role for formation of a protective SiO_2 scale, because MoO_3(g) possesses high vapor pressure. The predicted oxidation mechanism is stated below.

Affinity of Mo for oxygen is very high, hence SiO_2 and MoO_2(s) and/or MoO_3(s) are tend to be simultaneously produced according to reaction (1). Here, although MoO_2(s) is more stable than MoO_3(s), only the latter has been detected. As a result, at low temperatures, MoO_3(s) and SiO_2(s) remain on $MoSi_2$ substrate, resulting in the formation of a mixed oxide scale. Also in the early stage of

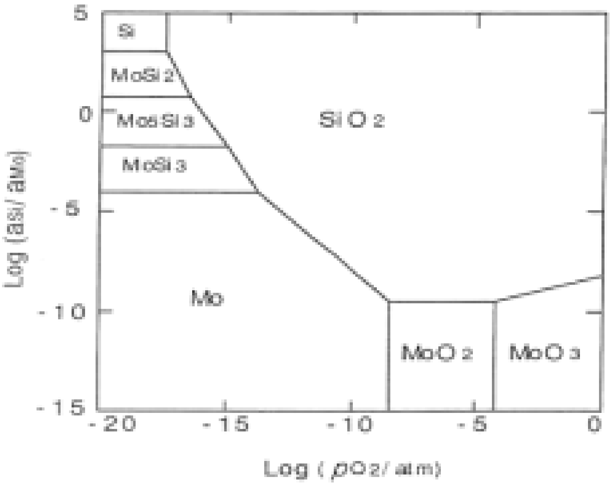

Fig. 1 Chemical potential diagram of a Mo-Si-O system at 1773K

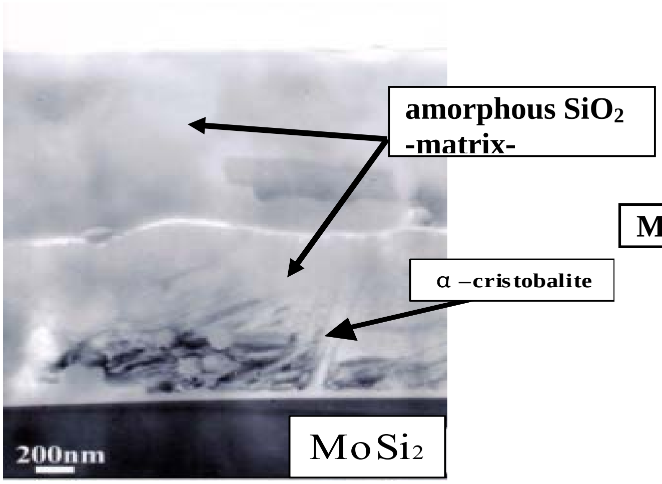

Fig. 2 Cross-sectional microstructures of scales formed on $MoSi_2$ during oxidation at 1773 K for 36 ks.

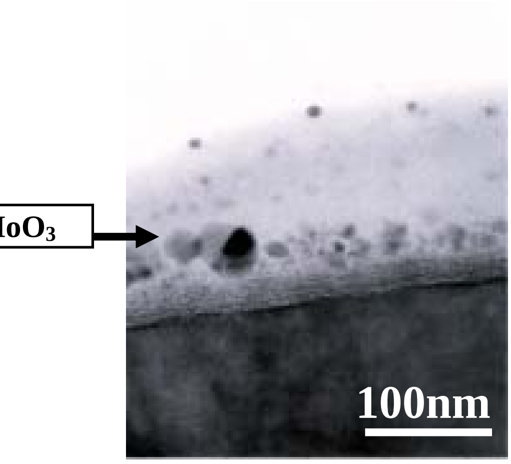

Fig. 3 Cross-sectional microstructures of scales formed on $MoSi_2$ during oxidation at 773 K for 360 ks.

oxidation at high temperatures, such simultaneous oxidation mechanism could be also established. However, since $MoO_3(g)$ possesses high vapor pressures at higher temperatures, $MoO_3(s)$ vaporizes at the same time as it is produced. Consequently, only SiO_2 remains on the surface of $MoSi_2$. Once a continuous SiO_2 scale has been formed by this mechanism, $MoSi_2$ undergoes the reaction according to reaction (2). In fact, the oxide scales formed at high temperatures are consisting of only SiO_2, as shown in Figure 2. On the other hand, the oxide scale formed at a low temperature is consisting of SiO_2 and $MoO_3(s)$, as shown in Figure 3[7] which shows an oxide scale formed in an early stage of oxidation (before accelerated oxidation behavior). However, microstructures of oxide scales formed in a transition temperature region from accelerated oxidation (low temperature) to passive oxidation (high temperature) have not still been clarified. Especially, information on existence of $MoO_3(s)$ in the oxide scale has not been obtained.

Experimental Procedure

Dense $MoSi_2$ was fabricated by using a spark plasma sintering equipment. In the sintering method, $MoSi_2$ powder (average grain size: ~3 μm) was packed into a graphite die under a compressive stress, and then a pulsating current was passed through the specimen in an evacuated chamber. The sintering conditions used in this study were compressive stress of about 40 MPa, heating rate of 0.17 K/sec and maximum sintering temperature of 1673 K, and holding time at the temperature was 600 s.

Specimens for oxidation were cut from the sintered body into 14mm × 3mm × 1mm pieces. The surfaces were polished to a 1-μm diamond finish and then cleaned ultrasonically in acetone. Isothermal oxidation of $MoSi_2$ was carried out in air at 1273, 1373, 1573, and 1773 K for 36-360 ks. The oxidation kinetics was evaluated by measuring the thickness of the oxide scale formed on $MoSi_2$.

Cross sections of the oxidized $MoSi_2$ were observed using transmission electron microscopy (TEM) with energy dispersive X–ray spectroscopy (EDS). The specimens for TEM were cut into 2.5mm × 1.0mm × 0.3mm pieces. Each piece was bonded on a ring made of stainless steel for thinning by the focused ion beam (FIB) method and then coated with tungsten (W) to protect the oxide scale. Finally, a selected area of each piece was thinned to a thickness of less than 100 nm by gallium (Ga) - ion sputtering.

Results and Discussion

Temperature-induced change in structure of oxide scale. Temperature-induced changes in microstructures of oxide scales formed on $MoSi_2$ during oxidation in medium-high temperature region were examined by TEM-EDS. Figure 4 (a)-(c) show TEM bright-field images of cross sections of oxide scales formed on $MoSi_2$ during oxidation at 1273, 1373 and 1573 K, respectively. Top black layers in the upper images are deposited W layers for protection of the surfaces of scales, and it can be seen that a dense oxide scale of 200-400 nm in thickness is formed on each $MoSi_2$ substrate.

The oxide scale formed at 1273 K consists of amorphous SiO_2 with a small amount of dispersed fine gray-colored $MoO_3(s)$ particles. In the case of oxidation at 1373 K, $MoO_3(s)$ particles exist in the vicinity of the scale/substrate interface. In these oxide scales, SiO_2 was confirmed by electron diffraction to be an amorphous phase.

These results indicate that oxide scales formed at 1273 K and 1373 K are protective but that the oxygen partial pressure in the oxide scale and at the scale/substrate interface is higher than the dissociation pressure of $MoO_3(s)$ ($MoO_3(s) \rightarrow MoO_2(s) \rightarrow Mo(s)$). However, as the formed $MoO_3(s)$

vaporizes, it does not remain in top surface area of the oxide scale. A relationship between oxidation temperature (vapor pressure of metal oxide) and formation of a SiO_2 scale has discussed in our previous work [8, 9]. The results demonstrated that when the vapor pressure of metal oxide reaches about 10^{-4} atm, an oxide scale consisting of SiO_2 is formed and shows protective behavior. In the case of $MoSi_2$, the corresponding temperature was estimated to be about 1073-1173 K. This estimation roughly agrees with the present results; formation of almost complete SiO_2 scale at 1273 K.

Oxidation at higher oxidation temperature leads to formation of a complete SiO_2 scale. The oxide scale at 1573 K consists of only SiO_2 (amorphous SiO_2 with some α-cristobalite SiO_2 grains at the scale/substrate interface). The oxide scale at 1773 K consisted of SiO_2 with an α-cristobalite SiO_2 layer of about 400 nm in thickness near the scale/substrate interface (see Fig. 2). These results demonstrate that formation of MoO_3(s and g) is completely suppressed at oxidation temperatures above 1573 K, probably except for a very short initial stage of oxidation.

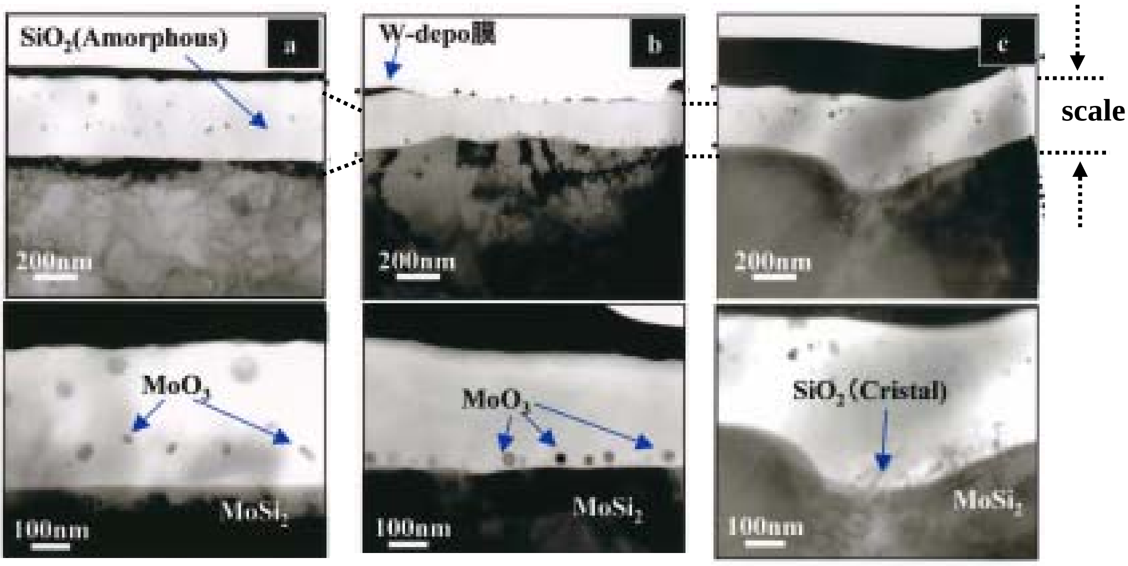

Fig. 4 Cross-sectional microstructures of scales formed on $MoSi_2$ during oxidation for 36 ks at (a) 1273 K, (b) 1373 K, and (c)1573 K.

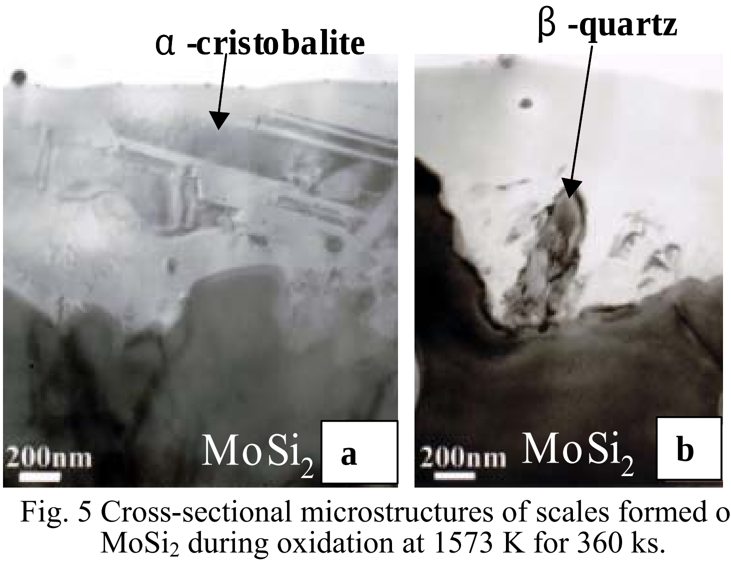

Fig. 5 Cross-sectional microstructures of scales formed on $MoSi_2$ during oxidation at 1573 K for 360 ks.

Time- and temperature-induced crystallization of SiO_2. Oxidation time- and temperature-induced changes in SiO_2 phase were examined by TEM-EDS. Figure 5 shows TEM bright-field images of a oxide scale formed on $MoSi_2$ during oxidation at 1573 K for 360 ks. The images shown in (a) and (b) are cross-sectional views of different sites of the same specimen. The image shown in figure 5(a) shows that the oxide scale consists of amorphous SiO_2 mixed with some α-cristobalite SiO_2 grains. The volume ratio of crystalline SiO_2 to total SiO_2 scale is greater than that in the scale formed during oxidation at 1573 K for 36 ks (see Fig. 4(c)). Figure 5(b) shows a cross-sectional view of a different site in the same specimen. The oxide scale consists of amorphous SiO_2 near the surface and β-quartz SiO_2 at the substrate/oxide scale interface.

Crystallization of SiO_2 becomes more pronounced when the oxidation temperature is further increased. Figure 6 (a) and (b) show TEM images of cross-sectional microstructures of oxide scales formed during oxidation for 3.6 ks and for 180 ks at 1773 K, respectively. As can be seen in figure 6(a), crystallization of SiO_2 has already started in oxidation for only 3.6 ks, and the oxide scale consists of a mixture of tridymite SiO_2 and amorphous SiO_2. As shown in figure 6(b), a thick layer of α-cristobalite SiO_2 has formed in oxidation for 180 ks.

The oxidation products are summarized in Table 1. In oxide scales formed at oxidation temperatures of 1273 K and 1373 K, some MoO_3 grains were observed inside the amorphous SiO_2 and no SiO_2 crystallization was observed even after a long period of oxidation. The crystallization of SiO_2 began at 1573 K and proceeded gradually with increases in oxidation temperature and time, finally reaching the stable α-cristobalite phase via quartz and tridymite phases.

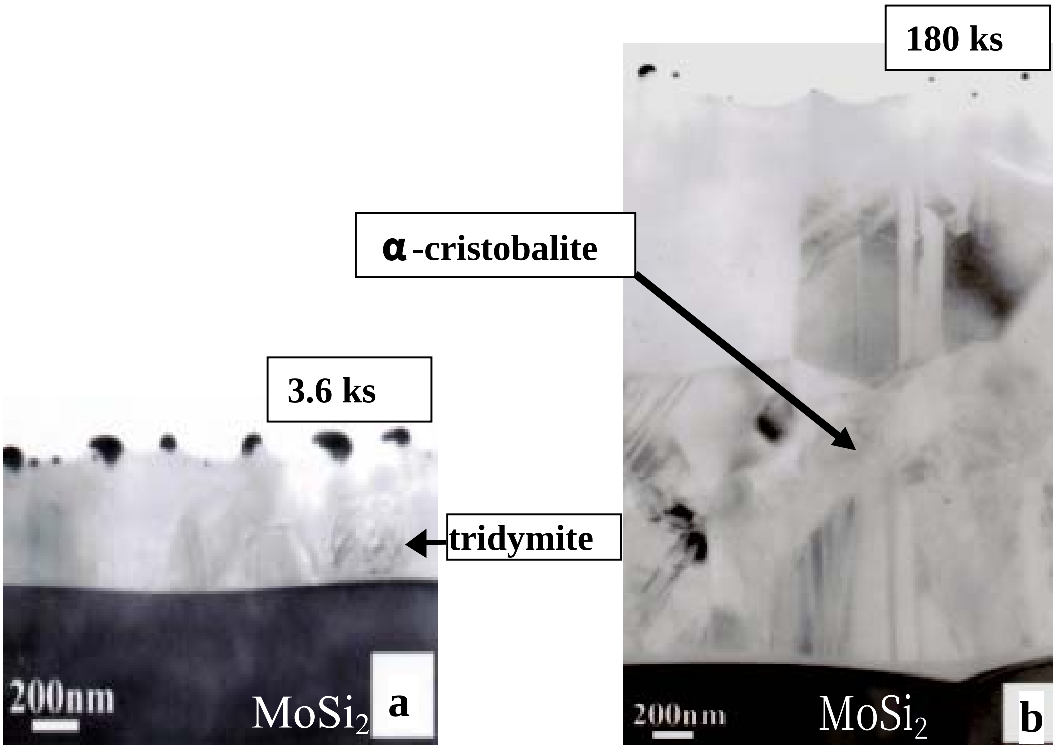

Fig. 6 Cross-sectional microstructures of scales formed on $MoSi_2$ during oxidation at 1773 K.

Growth rate of an oxide scale on $MoSi_2$. Figure 7 shows the relationship between thickness of the

Table 1 Oxidation products at medium-high temperatures.

	3.6 ks	36 ks	180 ks	360 ks
1273 K	-	MoO_3 Amorphous SiO_2	-	MoO_3 Amorphous SiO_2
1373 K	-	MoO_3 Amorphous SiO_2	-	MoO_3 Amorphous SiO_2
1573 K	-	Amorphous SiO_2 Crystalline	-	Amorphous SiO_2 α -Cristobalite, β -Cristobalite β -Quartz
1773 K	Amorphous SiO_2 Tridymite	Amorphous SiO_2 α -Cristobalite	Amorphous SiO_2 α -Cristobalite	-

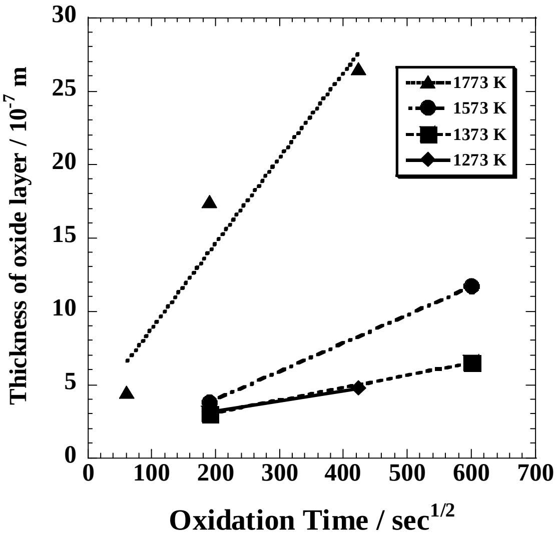

Fig. 7 Kinetics of oxide layer growth.

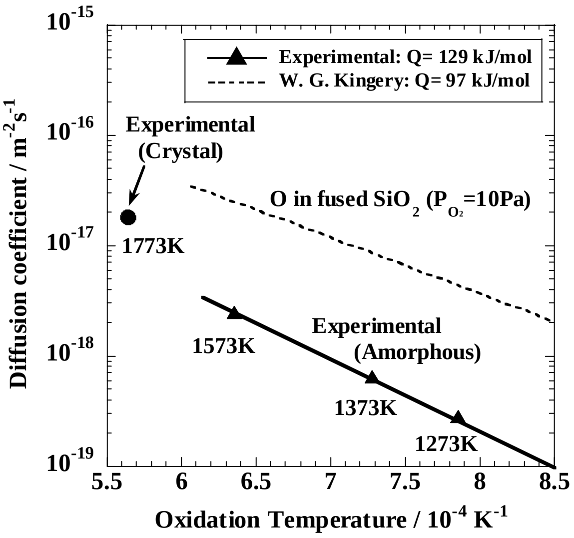

Fig. 8 Temperature dependence of oxygen diffusion coefficient.

formed oxide scale and oxidation time at each oxidation temperature. The thickness of the oxide scale increases linearly as a function of the square root of oxidation time, indicating that the oxide scale grows in accordance with the parabolic rate law.

The oxygen diffusion coefficient could be roughly obtained using the following equation, if it is assumed that growth of a SiO_2 scale proceeds due to preferential diffusion of oxygen:

$$x = (2Dt)^{1/2} \qquad (3)$$

where x is the thickness of the SiO_2 layer, D is the chemical diffusion coefficient and t is oxidation time. Figure 8 shows oxygen diffusion coefficients in the SiO_2 layer estimated from the rate of oxidation, which was calculated from data on oxidation kinetics shown in figure 7. Diffusion coefficients of oxygen in fused SiO_2 obtained in a study by Kingery et al. are shown for comparison[10]. Except for the oxidation temperature of 1773 K, at which a SiO_2 layer with a high degree of crystallization is formed, the calculated values of D can be joined by a straight line, and the activation energy is 129 kJ/mol. The diffusion coefficients obtained in this study are about one order lower than those obtained in the study by Kingery et al., but the activation energies are similar. The value at 1773 K is higher than the extrapolated value on the line. This indicates that lattice diffusion of oxygen ions in crystalline SiO_2 is greater than diffusion of O_2 in an amorphous SiO_2.

Conclusions

The microstructures of oxide scales formed on $MoSi_2$ at high temperatures in air were observed by TEM. The following results were obtained in this study.

(1) Formation of MoO_3 in an oxide scale is entirely suppressed above 1573 K.
(2) Crystallization of SiO_2 begins at 1573 K and proceeded gradually with increases in oxidation temperature and time.
(3) Crystallization of SiO_2 occurs more easily at the scale/substrate interface.
(4) Diffusion coefficient of oxygen in a growing SiO_2 scale was estimated.

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