

고밀도 폴리에틸렌의 표면결정성과 그 산화속도

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Surface Crystallinity of High Density Polyethylene and its Oxidation Rate

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요약 : 고밀도 폴리에틸렌의 결정격자의 배열은 결정할 때 용융고분자물질과 접촉하는 물질의 영향을 크게 받는다. 플루오르수지를 접촉물질로 하면 접촉물질이 스테인레스철을 사용하였을 때 보다 적외선흡수파장의 비 $R_{A720\text{cm}^{-1}/A730\text{cm}^{-1}}$ 가 작게 나타난다. 그 흡수파장의 비가 작은 것은 고분자 필름의 결정도에 관계된다고 보다는 인-페이즈 메틸렌 록킹 진동이 플루오르수지와 접촉한 고분자물질의 표면과 나란하기 때문이다. 1720cm^{-1} 와 1640cm^{-1} 에서의 흡수 피크의 높이는 코로나방전 처리시간과 비례하며 1640cm^{-1} 에서의 흡수피크의 높이는 1720cm^{-1} 에서의 흡수 피크 높이와 거의 같은 속도로 증가한다. 플루오르수지와 접촉하고 급냉시킨 시료의 적외선 흡수파장의 비 $R_{A720\text{cm}^{-1}/A730\text{cm}^{-1}}$ 가 코로나방전 처리시간에 따라 일정시간 동안 감소하는데 이러한 현상은 서냉을 시키든지 혹은 스테인레스철을 접촉물질로 사용했을 때는 일어나지 않는다. 플루오르수지와 접촉하고 급냉시킨 시료의 표면은 다른 시료에 비해 결정성이 낮고 코로나방전 처리로 비결정성 부분이 빨리 산화 및 열화를 가져오기 때문이 아닌가 생각된다.

Abstract : Orientation of crystalline lattice in HDPE film is greatly influenced by contacting materials with polymer melt. The HDPE films prepared by contacting the melt with PTFE show weaker absorbance ratio $R_{A720\text{cm}^{-1}/A730\text{cm}^{-1}}$ than those films prepared by contacting stainless steel. The weaker absorbance is attributed not by a degree of crystallinity in the film but by the fact that in-phase methylene rocking vibration of the film made by contacting PTFE is parallel to the film surface. Absorbance at 1720cm^{-1} as well as 1640cm^{-1} increase linearly with time of corona treatment and the increase rate at 1640cm^{-1} is as high as that at 1720cm^{-1} . The absorbance ratio $R_{A720\text{cm}^{-1}/A730\text{cm}^{-1}}$ gradually decreases with time of corona treatment if the sample used is fast-cooled film on PTFE while slow-cooled film on PTFE or film on steel shows little change in the absorbance ratio. The result suggests that crystallinity in the surface of fast-cooled film on PTFE increases by corona treatment for a short time.

Introduction

Low density polyethylene (LDPE) oxidizes easily and becomes chemically active because of abundance of tertiary hydrogen or double bond which is prone to oxidation. Surface oxidation of LDPE increases the surface energy and lowers the contact angle. The result brings good adhesion as well as printability^{1~4}.

Surface energy of polyethylene (PE) is increased by chemical, flame, ozone or corona treatment, but the corona treatment is so simple and efficient that the method is used most widely. When LDPE is oxidized for an increase of surface energy, the treatment accompanies degradation to lose some of mechanical strength. Corona treatment of PE in nitrogen, however, enhances surface energy markedly without oxidation or degradation⁵.

Since oxidation rate of LDPE by corona treatment is controlled by square root of treatment time, the reaction is regarded as diffusion-controlled⁶. LDPE has about 60% of crystallinity and diffusion of a gas through a amorphous region is not prohibited⁷.

This study tries to show that orientation of methylene group in the crystal on the surface region depends markedly on crystallization condition, and oxidation mechanism on the surface of high density polyethylene (HDPE) by corona treatment in air differs greatly from that of LDPE by the same method.

Crystallization Mechanism of PE on the Surface

When HDPE is cooled from melt, nuclei are formed and spherulites grow until they contact with each other. While spherulites are growing, amorphous material is pushed away from the spherulites and stays between

spherulites when crystallization process is over⁸. Average size of spherulites depends on number of nuclei in a given volume of polymer melt.

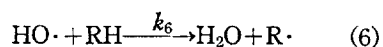
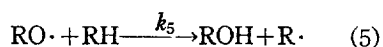
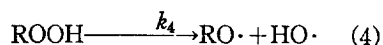
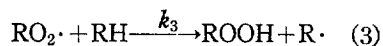
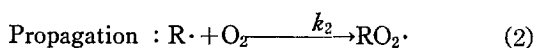
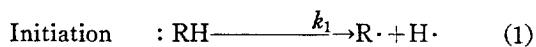
Since nuclei can be part of polymer molecules or any other materials which contact with polymer molecules, number of nuclei on the surface of a contacting material with the polymer depends on surface energy of the material.

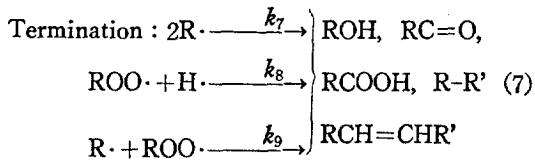
When polymer melt contacts with a material with high surface energy, a great deal of nuclei are formed on the contacting surface and spherulites grow to meet each other on the surface and no further development at the contact is expected. The spherulites, however, grow deep into melt where crystallization process is slow. The surface crystalline region is called trans-crystalline¹⁰ and the thickness reaches 25-50 μ ¹¹.

If the polymer melt is quenched, it is expected that crystallinity is poor specially on the contacting surface whether the surface energy of contacting material is high or low⁹.

Oxidation of PE

Corona discharge in oxygen produces active particles such as oxygen atoms, excited oxygen molecules, ozone, ions, electrons, etc^{12,13}. The active particles react with PE molecules and oxidize them. Mechanism of oxidation of organic chemicals has been proposed by Bolland and Gee¹⁴, and that is successfully applied to polymers¹⁵.





Initiation rate, k_1 , is low at room temperature in a dark place but the rate is enhanced by heat, ultraviolet light, electrical discharge or mechanical shear force¹⁶.

Propagation reaction of autooxidation of hydrocarbons is controlled by radical combination as well as hydrogen abstraction. Since hydrogen abstraction rate, k_3 , is much lower than peroxy radical formation rate, k_2 , overall propagation rate depends on the former¹⁷. Oxidation rate of polymer molecules is proportional to k_4 in equation (4)¹⁸.

Decomposition of each hydroperoxide radical after oxidation induction period produces two free radicals and accelerates oxidation.

Hydrogen Abstraction Mechanism of HDPE

Oxidation of HDPE in a corona discharge has a different mechanism from that of LDPE because there is much less tertiary hydrogen or double bond which is the main site for oxidation in LDPE. The main chain is broken or a hydrogen is abstracted from the molecule by active particles in the corona discharge to produce free radicals which immediately react with oxygen molecules.

Since the polymer has high crystallinity, the active particles hardly move into the bulk polymer and the reaction occurs mostly on the polymer surface. HDPE is highly crystalline material of which molecules have chain folding structure. The probable site for free radical production is the segment of chain folding or a loose chain.

Once hydroperoxide is formed on the polymer surface, the reaction follows propagation and

termination mechanism proposed on oxidation of organic chemicals¹⁴. At the same time free radical transfer causes C=C formation by abstracting hydrogen intramolecularly or intermolecularly¹⁹.

Reaction Rate

Rate of double bond formation or of oxidation reaction is obtained from rate of increase on infrared absorption at 1720cm^{-1} and 1640cm^{-1} , respectively, for carbonyl group and double bond by infrared spectroscopy.

According to Lambert-Beer's law,

$$A = \log(I_0/I) = \epsilon dc \quad (8)$$

where A is absorbance or optical density, I_0 , incident intensity, I, light intensity after passing the sample, c, concentration of chemical group, ϵ , extinction coefficient, and d, sample thickness.

If sample thickness and extinction coefficient are assumed to be constant, absorbance is a function of the concentration, which is a function of treatment time. The absorbance is expressed as

$$A = \log(I_0/I) \propto k't \quad (9)$$

where k' is reaction rate.

The absorbance is measured with a multiple internal reflection (MIR) device. The beam penetration, P, is expressed as

$$P = \frac{\lambda}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}} \quad (10)$$

where λ is wave length of incident light, θ , incident beam angle, and n_{21} , ratio of refractive index of PE to refractive index of the crystal used²⁰.

Experimental

Sample

HDPE used is Hizex 2-200J from Mitsui Co. and has density, 0.970g/ml , weight average molecular weight, 40,000 and melt index, 5.5,

respectively.

Preparation of Film

HDPE film with thickness of 0.05 mm was formed by using a hot press of which mold was made of stainless steel with (called film on steel) or without (called film on PTFE) Teflon-sheet covering. The polymer was preheated at $160 \pm 1^\circ\text{C}$ for five minutes and then pressed under stress of $32\text{kg}/\text{cm}^2$ for 10 minutes. After the polymer was pressed under the hot press, the mold was cooled either by dipping into a cold water bath (11°C) (called fast-cooled) or moving into a dry oven with temperature of $130 \pm 2^\circ\text{C}$ and keeping there for 15 minutes (called slow-cooled).

Treatment of HDPE in a Corona Discharge

The power generator is originally built to use for a neon sign and can generate 15,000 volts if it is connected to a 100 volt power source. The stainless steel electrodes are covered by 2mm glass plates and four spacers with thickness of 5mm were inserted between the electrodes. Sample of $18 \times 50 \times 0.05$ (mm) was put on the bottom electrode and treated at temperature of $11\text{--}14^\circ\text{C}$.

Infrared Spectroscopy and MIR Accessory

Infrared spectrometer used is Perkin Elmer 521 with a constant voltage regulator which fixes the input voltage at 115v. The MIR attachment is a model No. 186-0382 from Perkin Elmer and a KRS-5 plate ($20 \times 50 \times 2$ mm) is used as the reflection crystal.

Results and Discussion

Crystallinity

Figure 1 shows transmission and MIR IR spectra around $730\text{--}720\text{cm}^{-1}$ from the sample made by the slow cooling method with stainless steel. The band at 730cm^{-1} is assigned as in-phase

methylene rocking of PE repeat unit which is parallel to a-axis of the crystal lattice and the band at 720cm^{-1} shows up when out-of-phase methylene rocking is parallel to b-axis in the lattice²¹, as shown in Figure 2²². The band at 720cm^{-1} is also assigned as bending vibration of methylene in an amorphous region because the band at 720cm^{-1} is the only one remaining when crystallinity in PE disappears by heating²³.

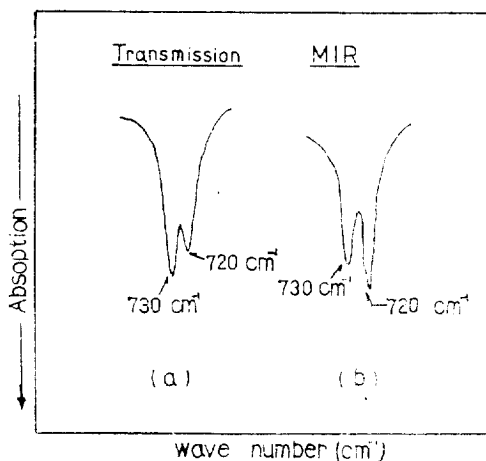


Figure 1. Infrared absorption of slow-cooled film nucleated against PTFE in the region 720cm^{-1} , $\sim 730\text{cm}^{-1}$.

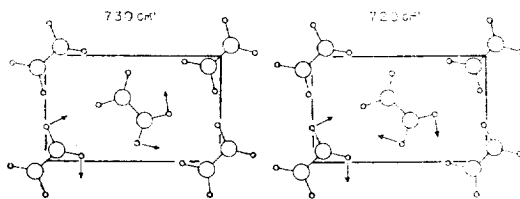


Figure 2. Methylene rocking modes of PE at 730cm^{-1} and 720cm^{-1} .

The absorbance ratio $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ for transmission and MIR IR spectra of films made by different ways are listed in Table I.

The film made from polymer melt contacting with stainless steel (high surface energy) shows

Table I. $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ by Transmission and MIR IR Spectroscopy

Contacting material with melt	PTFE		Steel	
Cooling method	fast-cooled	slow-cooled	fast-cooled	slow-cooled
Transmission	0.901 ± 0.020	0.852 ± 0.023	0.941 ± 0.018	0.936 ± 0.018
MIR	1.232 ± 0.036	1.120 ± 0.024	1.048 ± 0.030	1.032 ± 0.026

lower value of $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ than the film by contacting with PTFE (lower surface energy) in MIR IR, but the ratio becomes opposite in transmission IR. Spherulites formed by using PTFE must have disc shape and show anisotropic behavior with respect to IR²⁴. Transcrystalline structure develops when the polymer melt crystallizes on a surface with high surface energy²⁵. Spherulites in the transcrystalline structure appear long bars with small diameter and contain random orientation of methylene group²⁴. The orientation of methylene group in the film on PTFE favors in-phase methylene rocking in transmission IR to result lower ratio $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$, which, however, does not mean that the crystallinity is higher than that of the film on steel.

Figure 1a has a stronger peak at 730cm^{-1} than at 720cm^{-1} due to presence of more crystalline a-axis parallel to the surface of the film than b-axis. Figure 1b shows the weaker peak at 730cm^{-1} than the one at 720cm^{-1} . The stronger peak at 720cm^{-1} means that methylene segments are in amorphous region as well as in crystalline state with dipole moment parallel to the b-axis. The film on steel also shows stronger absorption in transmission IR and weaker in MIR IR at 720cm^{-1} than at 730cm^{-1} (Table I).

Small difference in the ratios of the fast-cooled and the slow-cooled films on steel is expected because of the same effect on IR absorption by random orientation of methylene groups in transcrystalline region and small spherulites. Since the incident beam in MIR

IR penetrates the film surface by only 2μ according to equation (10), aggregation of spherulites on the surface of film on steel would show the same effect as a transcrystalline region in IR absorption.

The ratio of fast-cooled film on PTFE is higher than that of slow-cooled film on PTFE but difference between the ratios of transmission and MIR IR of the fast-cooled film on PTFE is larger than that of the slow-cooled film on PTFE. The probable reason is more presence of amorphous methylene groups in the fast-cooled than the slow-cooled, especially on the film surface.

Corona Treatment

Figure 3 shows a part of transmission IR spectrum (dotted line) of 5-minute treatment

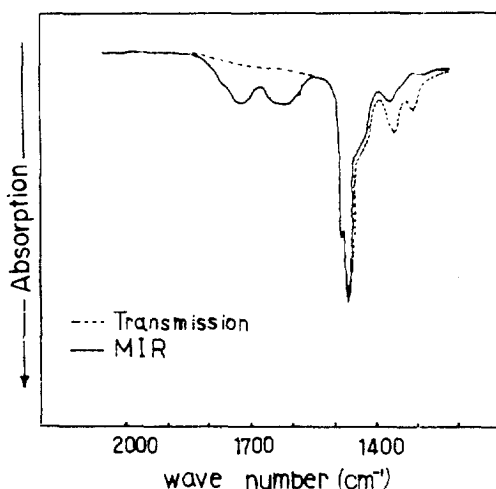


Figure 3. Transmission and MIR IR spectra of fast-cooled film on PTFE, dotted line; transmission IR, solid line; MIR IR.

and MIR IR spectrum (solid line) of 1-minute treatment in the corona discharge. The 5-minute treatment shows little change in the IR spectrum but the 1-minute treatment reveals a large change. It explains that the reaction occurs exclusively on the surface.

The bands at 1720cm^{-1} and 1640cm^{-1} are assigned as $\text{C}=\text{O}$ and $\text{C}=\text{C}$, respectively²⁶. The base line method²⁷ has been applied to measure the intensities for $\text{C}=\text{C}$ and $\text{C}=\text{O}$ quantitatively. The absorbance vs corona treatment time are shown in Figures 4-7. Figure 4 shows that absorbance at 1720cm^{-1} for $\text{C}=\text{O}$ produced on the surface of PTFE film increases linearly with time of corona treatment.

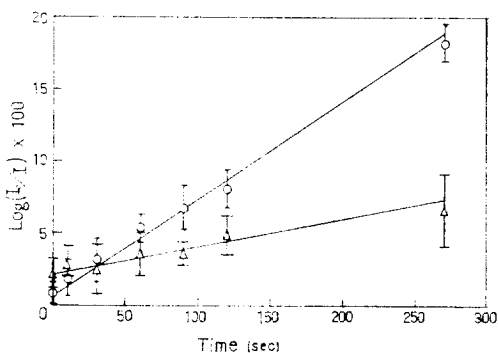


Figure 4. Rate of increase of $\text{C}=\text{O}$ absorbance by MIR IR at 1720cm^{-1} with corona treatment of film on PTFE. Circle; fast-cooled, triangle; slow-cooled.

The fast-cooled film shows much higher oxidation ratio. It is feasible to assume that crystallization is incomplete when polymer melt contacting PTFE is quenched, and oxidation occurs easily on the molecular chains which are in amorphous state.

Formation of $\text{C}=\text{C}$ group, as shown in Figure 5, increases with time of corona treatment and the increase rate is larger in the fast-cooled film than in the slow-cooled. Slow-cooled film shows positive initial absorbance of $\text{C}=\text{O}$ or

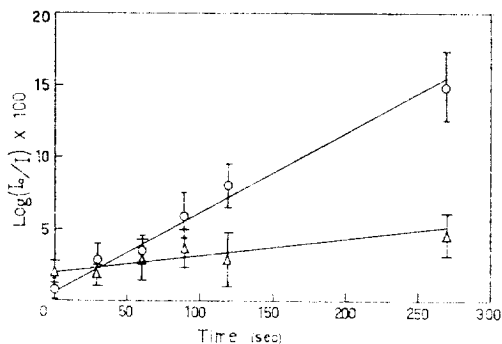


Figure 5. Rate of increase of $\text{C}=\text{C}$ absorbance by MIR IR at 1640cm^{-1} with corona treatment of film on PTFE. Circle; fast-cooled, triangle; slow-cooled.

$\text{C}=\text{C}$, which tells that oxidation already occurs while the specimen is prepared.

Figures 6 and 7 show a linear increase of the absorbance with time of corona treatment. The reaction rate is almost the same each other and the probable explanation is that there is little difference on the surface crystallinity of films of the fast-cooled and slow-cooled if the contacting material is stainless steel.

The present results show that the intensity at 1640cm^{-1} is as strong as that at 1720cm^{-1} . It is interesting to note that LDPE has $\text{C}=\text{C}$ group as well as tertiary hydrogens on the

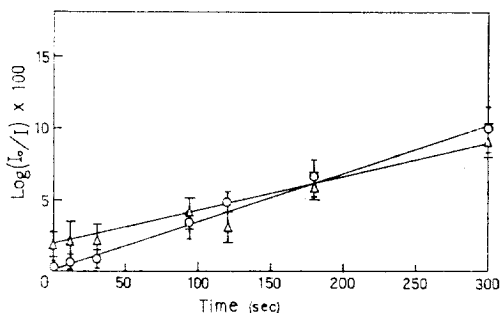


Figure 6. Rate of increase of $\text{C}=\text{O}$ absorbance by MIR IR 1720cm^{-1} with corona treatment of film on steel. Circle; fast-cooled, triangle; slow-cooled.

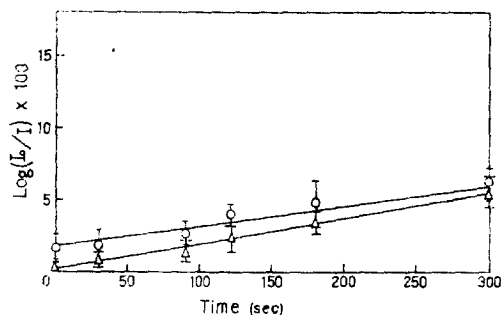


Figure 7. Rate of increase of C=C absorbance by MIR IR at 1640cm^{-1} with corona treatment of film on steel. Circle; fast-cooled, triangle; slow-cooled.

chain and the intensity by C=C group changes little when the polymer is oxidized²⁸. HDPE, in this study, seems to have oxidation reaction mainly at methylene on loose chains or at chain folding segments to produce C=C group as much as C=O group.

Absorbance ratio of $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ are plotted against corona treatment time as shown in Figures 8 and 9. The fast-cooled film on PTFE shows a fast decrease in the absorbance (Figure 8) while the slow-cooled film on PTFE does little change. Since there is a considerable amount of amorphous region in the fast-cooled film on PTFE, oxidation occurs exclusively on

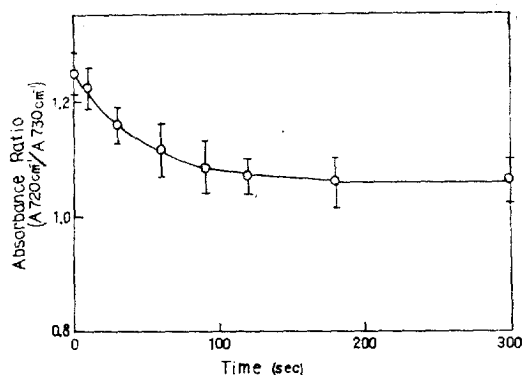


Figure 8. Change in MIR IR absorbance ratio $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ of fast-cooled film on PTFE with time of corona treatment.

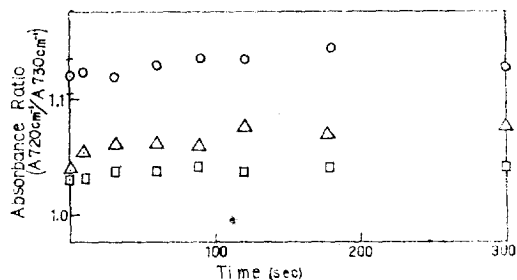


Figure 9. Change in MIR IR absorbance ratio $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ with time of corona treatment. Circle; slow-cooled film on PTFE, triangle; fast-cooled film on steel, rectangle; slow-cooled film on steel.

unaligned molecules to give an effect of increase in crystallinity. The slow-cooled film on PTFE shows very little change as does the slow-cooled film on steel (Figure 9). Oxidation might develop in the crystalline region to attack in-phase and out-of-phase methylene with even probability. The fast-cooled film on steel shows some increase in the absorbance ratio with time of corona treatment as shown in Figure 9. It may be assumed that the size of spherulites in this film is much smaller than those in the slow-cooled. Part of the crystallinity might be destroyed in corona treatment while loose molecules, too, are attacked. Change in the absorbance ratio in transmission with time of corona treatment is not detected.

Conclusion

In-phase methylene rocking vibration is predominant IR absorption mechanism in transmission IR spectroscopy of thin HDPE film made by contacting PTFE or steel. The result suggests that more methylene groups in the film on PTFE are aligned parallel to a-axis of the crystal lattice in transmission IR than those on steel are.

The fast-cooled film on PTFE shows higher

ratio $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ in MIR IR than the slow-cooled, which probably tells poor crystallinity on the film surface. There is little difference in the ratios between the fast-cooled and the slow-cooled films on steel in MIR IR.

The absorbance at 1720cm^{-1} and 1640cm^{-1} increase linearly with time of corona treatment in this experiment while oxidation rate of most polyolefinic materials is controlled by diffusion mechanism. It seems apparent that HDPE has high crystallinity and diffusion of reactive material into the crystalline region is almost prohibited. It is interesting to note that C=C formation rate on a HDPE film is as fast as C=O formation in corona treatment. Oxidation and C=C formation on HDPE surface by corona treatment develops much faster in the fast-cooled film on PTFE than in any other films experimented, and that could be a result of poorer crystallinity on the surface.

The absorbance ratio $R_{A720\text{cm}^{-1}}/A_{730\text{cm}^{-1}}$ decreases with time of corona treatment of fast-cooled PTFE film for a short time. Changes of the absorbance ratios and the oxidation rates would be related to degrees of crystallinity on the polymer surface. Crystallinity on the surface should be further examined by other means to clarify correlation of the oxidation rate with surface crystallinity in the future.

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