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Microstructure of Oxide Layers Formed on Magnesium Surface at Elevated Temperature

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The microstructure of oxidizing magnesium at elevated temperatures has been studied using HR-TEM, SEM and EDS. Two kinds of thin magnesium specimen for TEM observation were prepared. One was oxidized after preparing TEM foil of magnesium, the other was prepared from an oxidized bulk magnesium for observing the cross-section of oxide/Mg interfacial region.

In the former, several oxides(MgO) morphologies were observed depending on the temperature and time of the oxidization. The growth of needle-like oxides formed at 573K and mottled oxides formed at 773K were recognized as a remarkable phenomenon belonging to the local oxidization. These oxides were composed of poly-crystal. The thin uniform oxidization layer was also observed in all conditions.

In the cross-sectional observation, the local oxide layer, nearly 300*nm* in thickness, on the matrix(Mg) were observed. The thin uniform oxidized layer of bulk samples was identified as a kind of modified layer ($\sim$ 40*nm* in thickness) in which the formation of HR-TEM lattice fringes were prevented by the strain due to the slight oxidization.

1. INTRODUCTION

The density of magnesium ($1.74 g/cm^3$) is the smallest one in the engineering metallic materials. It is only a quarter of steel and zinc, and two-third of aluminum. In addition, magnesium has good recycle nature. In recent years ,there is a great deal of demands for it in developing light-weight metal for all kinds of instrumental design. However, since single magnesium is very easy corrosive in humid[1] and high temperature atmosphere, it is hard to increase the mass utilization as structural materials. Therefore, the study on the structure of Mg/MgO interface is important to progress the corrosion-resistance of Mg.

By ultramicrotomy, J. H. Nodlien et al.[2] prepared thin foil cross-sectional specimens of interface between Mg and Mg oxide which was oxidized in air or distilled water at room temperature, and observed them by transmission electron microscopy (TEM). Their observation indicated that an amorphous and dense oxide was formed on pure Mg, when a freshly trimmed

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surface was exposed to air. However, because the observations were performed by a low magnification, the detail and fine structure of oxide/matrix interface had not been revealed.

We prepared TEM specimens by ion milling, different from J. H. Nodlien et al.'s method, and tried to obtain high resolution Mg/MgO interface images. The specimens in the present study were oxidized at the high temperature(573~773K) lower than the melting point of Mg. And then these specimens were observed by TEM and scanning electron microscopy (SEM) and their oxygen contents were analyzed by energy dispersive X-ray spectrometry (EDS).

2. EXPERIMENTAL PROCEDURES

Purity 99.98% magnesium was used as the starting material. Two types of specimens were prepared by the procedures as shown in Fig.1.

Type A (specimens oxidized in as-thin foil Mg): 10mm wide strip of magnesium was mechanically thinned to a thickness of 0.1mm. The TEM specimen was electro-polished by conventional window technique[3] and cleaned by ion milling for an hour at a voltage of 4kV using argon gas(Fig.1(a-1)). After high resolution TEM (HR-TEM) observation, specimen's surface was oxidized in air (oxidization condition, shown in Table.1-a). After this, we call these specimens (Fig.1(a-2)) by the numbers, such as i (i=①,②,⋯⑨) in Table1. We observed the same place by TEM method for Type A specimens.

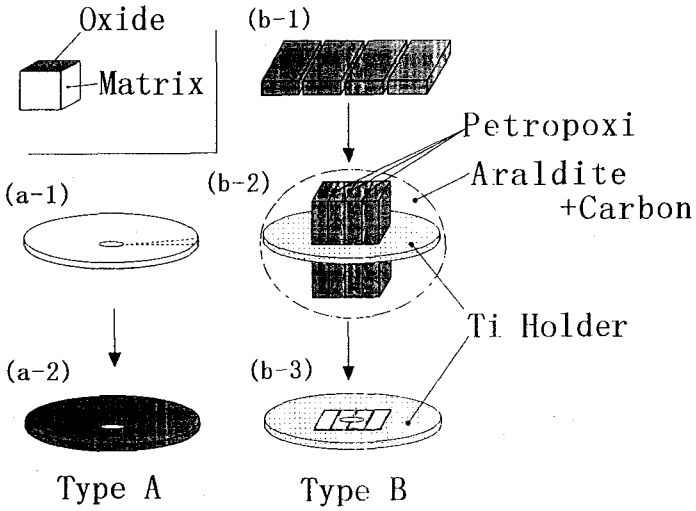


Fig.1.How to make specimens.

Table1. The condition of oxidation

	Temperature(K)	Time(sec)
a	room temperature	① 2.6×10^5, ② 8.6×10^5
	573	③ 3.6×10^3, ④ 1.8×10^4, ⑤ 2.6×10^5
	673	⑥⑦ 3.6×10^3
	773	⑧ 6.0×10^2, ⑨ 3.6×10^3
b	673	⑩ 3.6×10^3

a: Type A, b: Type B

Type B (specimens oxidized in bulk): The strips of magnesium with 1mm in width were mechanically thinned to a thickness of 0.2mm and cleaned by electro-polishing for 5 minutes and subsequently ion milling for an hour. The specimens' surface were heated to be oxidized in air(Fig.1(b-1)) (oxidization condition, shown in Table.1-b). They were glued each other with Petropoxi, and the bundle of small samples was dried in globular shape buried and fixed in the

special titanium holder with mixed resin of Araldite and carbon black(Fig1(b-2)). And then, this disk sample, in which the Mg bundle was pinched by a titanium holder, was mechanically thinned to less than 0.1mm in thickness and was finally thinned by ion milling. After this, we call this specimen (Fig.1(b-3)) by the number, such as ⑩ in Table1. Subsequently it was observed by TEM. And the some other specimens before glued with Petropoxi were observed by SEM in order to investigate the situation of oxide on the bulk sample of Type B.

Ethanol solution with 3% perchloric acid in volume fraction was used for electro-polishing the Mg samples at 243K and 40V. HR-TEM images were taken using TOPCON EM-002B high-resolution transmission electron microscope operated at 200kV. SEM images were taken using JSM-6300 operated at 20kV. The measurement of composition was also performed both in TEM and SEM with EDS devices.

3. EXPERIMENTAL RESULTS

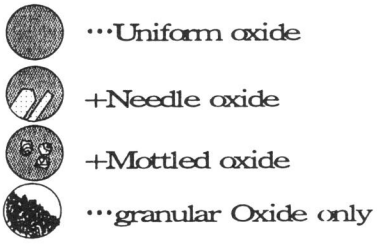
Figures2-(a) and (b), taken from the Specimen ① in the states before and after oxidization treatment for the same area respectively, show TEM images, the X-ray spectra of EDS and the selected area diffraction pattern (SADP). There was no remarkable change in TEM images. But oxygen peak in EDS was detected, and the ring pattern in SADP taken from the center of the image was identified as MgO pattern. Specimen ② showed the same result as Specimen ①.

TEM images obtained from Specimen ⑤ and ⑥ are shown in Figs.3-(a) and (b), respectively. Figure3-(c) shows HR-TEM image, the X-ray spectra of EDS, SADP and the micro-beam diffraction pattern (MBDP) taken from the area marked in Fig.3-(a). Some needle shape contrasts with about 10μm in size were observed in Specimen ⑤ and ⑥. According to the results subjected to EDS and MBDP analysis, formation of MgO was identified on the investigated area. The needle shape MgO crystals grown from edges of TEM sample were embedded along crystallographic low index plane of $(0001)_{Mg}$ or $(10\bar{1}0)_{Mg}$. The orientations of MgO crystals were different from place to place in the needle type oxide. In other words, these needles consist of poly crystal oxides. Specimen ③ and ④ showed no apparent change in microstructural characteristics.

Another Specimen ⑦ showed some bright contrasts of mottled shape, about 2μm in

Table2. Summarized experimental results of type A specimens.

	room temperature	573K	673K	773K
6.0×10^{2}sec				⑧
3.6×10^{3}sec		③④	⑥ ⑦	⑨
1.8×10^{4}sec				
2.6×10^{5}sec	①②	⑤		
8.6×10^{5}sec				



size, in spite of the same condition as the oxidization for Specimen ⑥. According to EDS and SADP, these mottled objects are also MgO. Specimen ⑧ showed the same morphology and structure of MgO as ones of specimen ⑦. Figures4-(a) and (b) show TEM images, the X-ray spectra of EDS and SADP obtained from the same area before and after oxidization treatment for Specimen ⑧. As shown in Fig.4-(b) MgO was formed preferably not only on edges but also on some line defects such as twin boundary. Figures5-(a) and (b) show TEM images and SADP taken from the same area before and after oxidization treatment for Specimen ⑨. The surface area was perfectly covered by micro-crystals of MgO formed during oxidization, because the ring pattern of MgO was only observed in the SADP. The experimental results obtained from specimens of type A mentioned above is summarized in Table2.

The observation for the specimen of type B was done in order to investigate a Mg/MgO interfaces prepared by oxidization at 673K (see Table1-(b)). During the ion milling treatment, we found that the specimen was shaved in order from Petropoxi to oxide via Mg because of their difference between their spattering rate. Figure6-(a) shows TEM image taken from the Mg/MgO cross-section of Specimen ⑩. Figure6-(b) also shows HR-TEM image and SADP taken from a small area marked in Fig.6-(a). According to SADP, the narrow band contacted with the upper side of the edge of Mg was oxide, and the lower dark part was matrix(Mg). The oxide is about 300*nm* in thickness. We could observe spotted pattern as a kind of substructure inner area near the edge of Mg in Fig.6-(a). HR-TEM image and SADP obtained from Mg/MgO cross-section of Specimen ⑩ are shown in Fig.7. The left side part of the photograph was a modified layer corresponding to uniform surface oxidization. Because notwithstanding a certain oxide layer was not observed clearly in the bright field image, the faint ring pattern of MgO and the spot pattern of Mg in SADP taken from the modified layer was observed, and on the other hand SADP taken from Mg matrix showed only spot diffraction pattern of Mg. The lattice fringes of Mg matrix of the specimen were observed in HR-TEM micrograph, but they became to disappear near the modified layer of about 40*nm* in thickness at left side of the arrows marked in Fig.7. It was obvious that there were micro-oxides dispersively in the surface layer, and HR-TEM lattice fringes were prevented by the strain introduced from a certain dispersive micro-oxides. Figure8 shows SEM image and X-ray spectra of EDS for the surface obtained from Specimen ⑩. A noticeable oxygen peak in the X-ray spectra of EDS was obtained from the white island area pointed with an arrow A in the center of the picture of Fig.8. According to quantitative analysis, oxygen content in this area was 23.1 at. %. The oxygen content at the other place denoted by an arrow B was 1.3 at. %, and 1.5 at. % at the dark cavity denoted by C.

4. DISCUSSION

4.1. Uniform Oxidization and Local Oxidization

As magnesium is very easy oxidizable material, it can be considered from the results mentioned above that Mg will be oxidized uniformly at once if it is set in air at elevated temperatures, and especially, it will be also remarkably oxidized at some defected area of Mg surface. In this paper, the former is called the uniform oxidization. the latter is called the local oxidization belonging to the needle or the mottled type oxide in Fig.3 or 4. The local oxide of the surface in Fig.6 is also considered to be such the white island (A) in Fig.8, and on the other hand the Mg surface area except the white island in Fig.8 may be considered to be covered by the

uniform oxide.

No oxygen is detected by EDS from the uniform oxide of the surface part(Fig.3 and 8), but formation of oxide is detected as diffraction pattern obtained from the cross section part of the uniform oxide(Fig.7). The reason can be regarded that X-ray spectrum of Mg obtained from the specimen must be detected much stronger than that of oxygen obtained from the thin uniform oxide.

4.2.Needle and Mottled Type Oxides

As the oxidization temperature is elevated, the local oxidization is remarkably recognized. We can observe some different morphologies of oxide in spite of the same condition as heating at 673K for 3.6×10^3sec (Type A specimen ⑥ and ⑦). But roughly, we can expect for Type A specimens as summarized in **Table2** that needle type oxide is formed during heating for about one hour among temperature range of 573~673K and mottled type oxide at 673~773K. And their thin film is covered totally with micro-crystal of granular oxide(MgO) at more than 773K as shown in **Table2**. Through increasing oxidization temperature, the oxidization area is preferentially spread from the edge of thin film to the whole specimen via the particular portion at defects, such as twin, segregation and/or inclusion.

It can be regarded that the needle type oxides in **Fig.3** may be formed at relatively low temperature because the oxidization rate is slow, and moreover the growth rate of oxide is influenced by the anisotropy of matrix(Mg). On the other hand, the mottled type oxides are formed under the condition of the high oxidization rate and less anisotropy effect of Mg at high temperature(673,773K).

4.3.Relation of Orientation between Magnesium and Magnesia(MgO).

The existence of misfit in the interface between Mg and MgO can be considered as the reason why the needle type oxide didn't grow to a single crystal as shown in Fig.3. The volume per one Mg atom is calculated in Mg and MgO as follows.

Mg(HCP, a=0.321 *nm*, c=0.521 *nm*)

$$V=\frac{(0.321)^2\times\frac{\sqrt{3}}{2}\times3\times0.521}{6}=0.023(nm^3).$$

MgO(FCC NaCl model, a=0.421 *nm*)

$$V=\frac{(0.421)^3}{4}=0.019(nm^3).$$

When Mg is oxidized, its volume becomes 0.83 times as large as that before oxidization. Therefore, when MgO grows, tensile stress acts on MgO and compressive stress acts on Mg matrix. MgO could lose epitaxial coherence with Mg and could grow to poly-crystal. This can also explain that the oxide particles are formed dispersively in the layer of the uniform oxidization.

4.4.The Oxide Grown on the Specimen of Type B(Bulk)

A mechanism of the high temperature oxidization in the bulk specimen is basically same as in a thin film. The island type oxides growing on the bulk specimen are same as the mottled type oxide in the respect of that they grow irrespective of crystallographic relation between MgO and matrix(Mg). But the preferential sites for oxidization are much less in comparison with the thin

film specimen because there is no thin film effect in the bulk specimen. Therefore the morphology of the local oxidization of type B is different from type A in spite of the same condition 673K(3.6×10^3sec). In specimen of type B, needle type and mottled type oxides are not found as in specimen of type A, but only the island oxides detected through the SEM observation. In other words, it is assumed that the formation of needle and mottled type oxides is a phenomenon of thin foil specimens.

5. CONCLUSIONS

The Mg/MgO interface structures were investigated by HR-TEM and EDS. When the temperature was elevated for thin specimens, the needle type($10\mu m$) and mottled type($2\mu m$) oxides were produced. The needle type oxides tended to grow along crystallographic low index plane of $(0001)_{Mg}$ and $(10\bar{1}0)_{Mg}$, and the internal structure of these oxides consisted of a poly-crystal, not a single crystal. It can be regarded that the needle and mottled type oxides are formed as a phenomenon of thin specimens. In the bulk specimen, not the needle and mottled type oxides, but the local oxide layers which construct about $300nm$ in thickness on the Mg matrix were observed. The uniform oxide layers of about $40nm$ in thickness were of Mg matrix including dispersive micro-oxides which disturbed the formation of HR-TEM lattice fringes of Mg.

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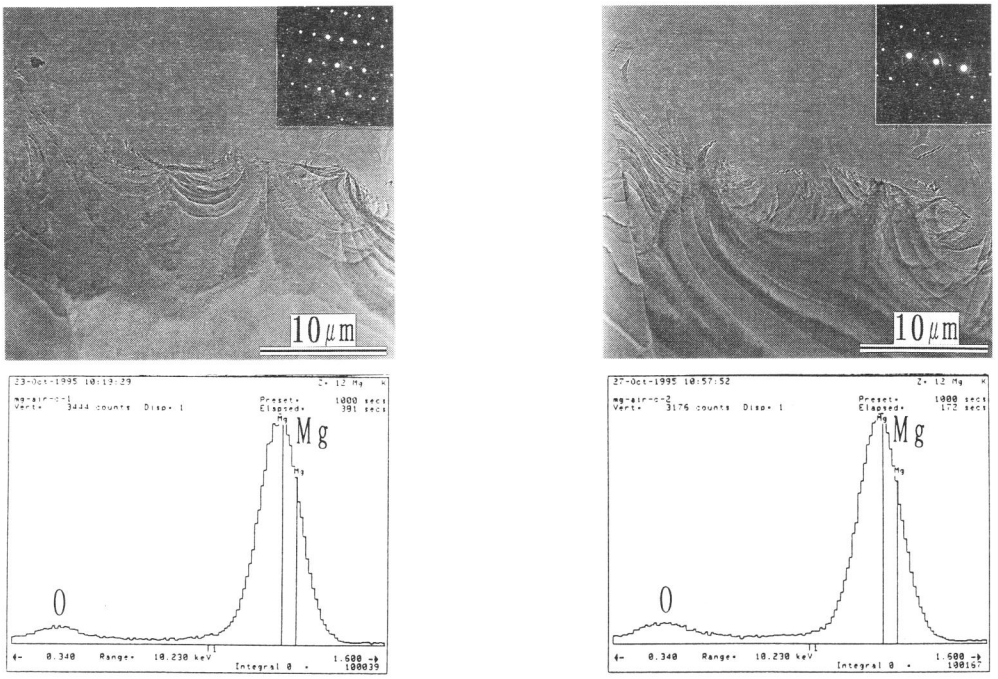
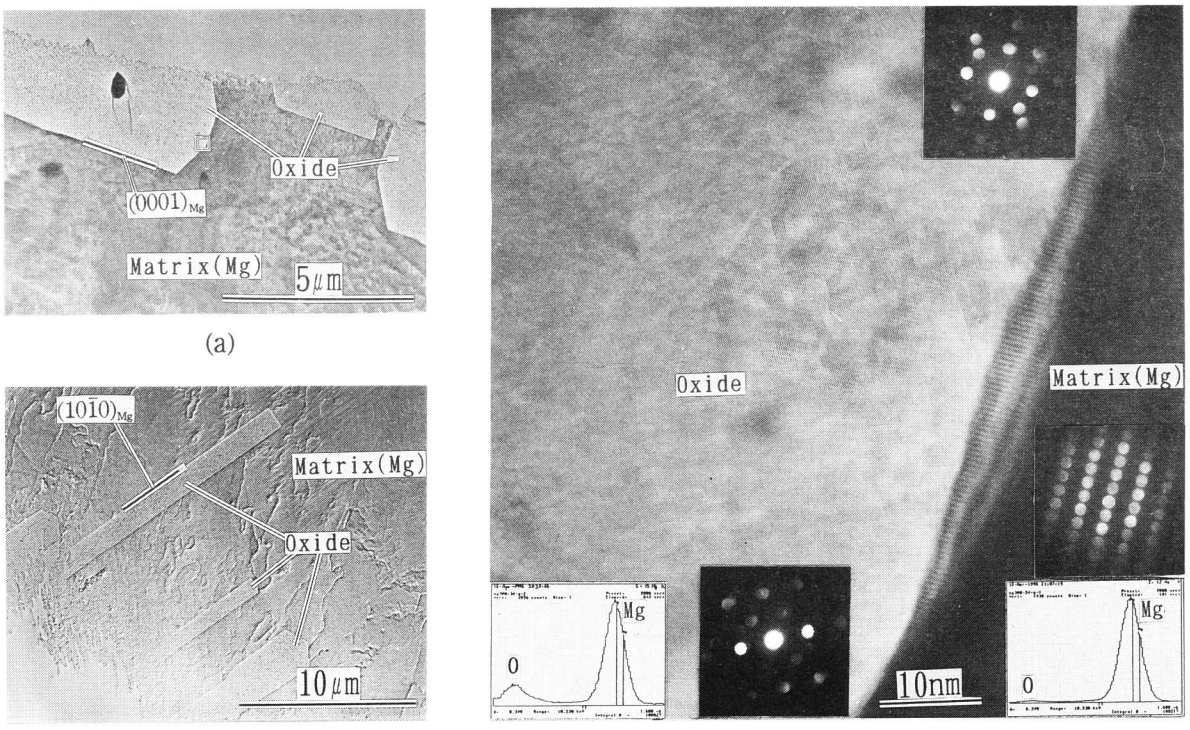


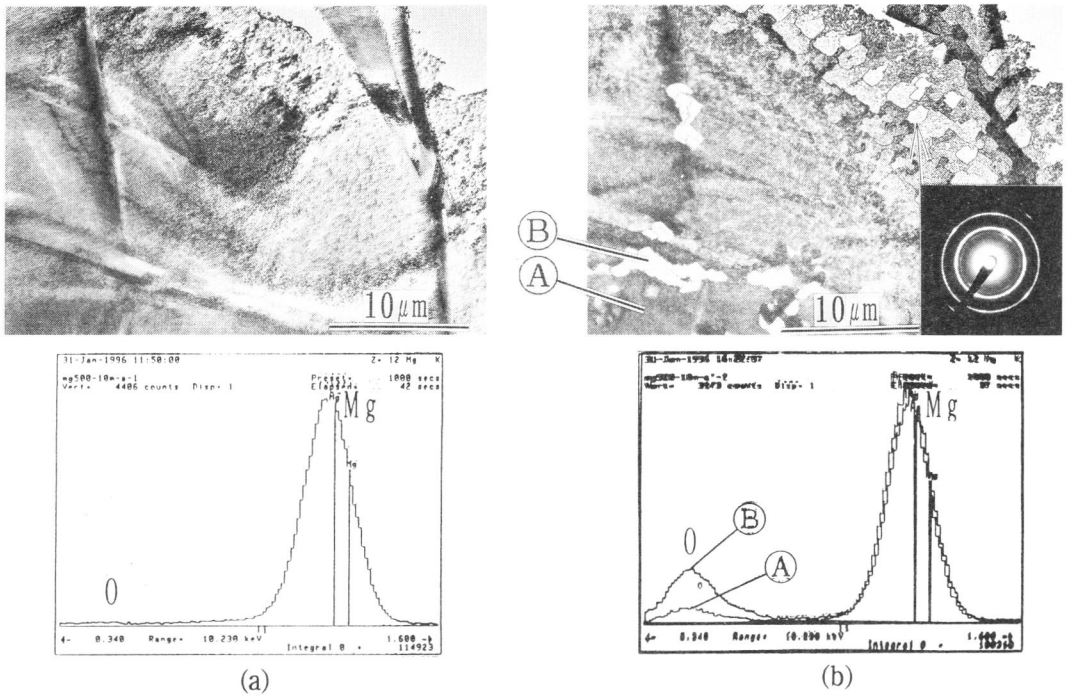
(a) (b)

Fig.2. TEM images and X-ray spectra obtained from Specimen ① oxidized in as-thinned TEM specimen. (a):Before oxidization. (b):After oxidization. A ring pattern of MgO is observed. No topographical changes between (a) and (b) is observed.



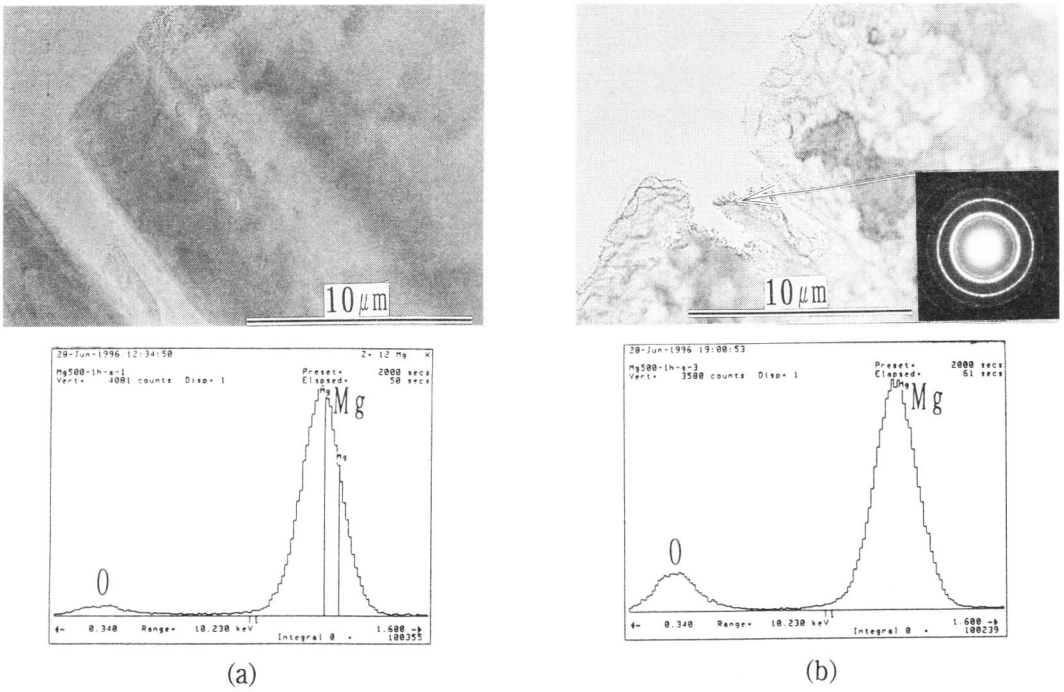
(a) (b) (c)

Fig.3. TEM images of needle type oxide formed in as-thinned TEM specimen. (a):TEM image obtained from Specimen ⑤. (b): TEM image obtained from Specimen ⑥. (c): HR-TEM image, X-ray spectra of EDS and MBDP taken from the rectangular region marked in Fig.3-(a). The needle type oxides grow along crystallographic low index plane of $(0001)_{Mg}$ or $(10\bar{1}0)_{Mg}$. These needles consist of poly crystal oxides.



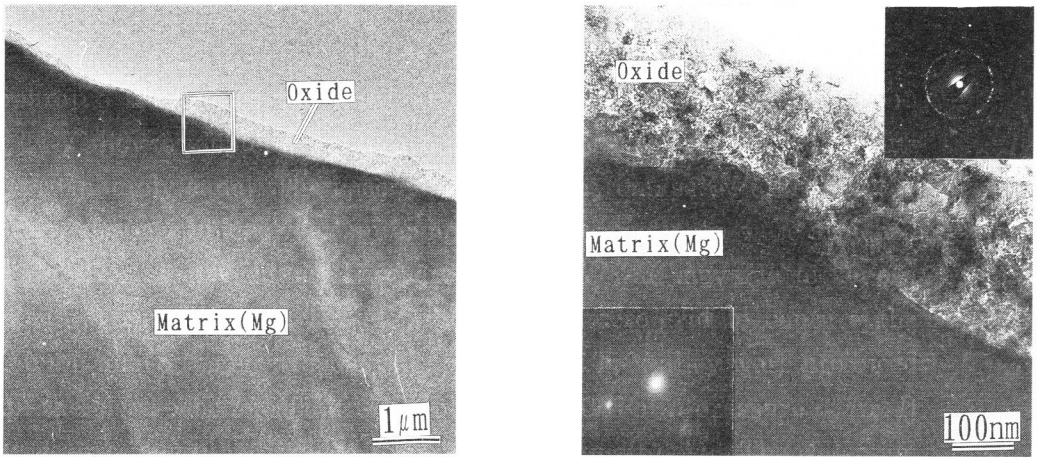
(a) (b)

Fig.4. TEM images, X-ray spectra of EDS and SADP obtained from Specimen ⑧ oxidized in as-thinned TEM specimen. (a):Before oxidization. (b):After oxidization with the mottled type oxide. Topographical changes and oxygen content increase are observed. MgO formed preferred not only on edge but also on some line defects.



(a) (b)

Fig.5. TEM images, X-ray spectra of EDS and SADP obtained from Specimen ⑨ oxidized in as-thinned TEM specimen. (a):Before oxidization. (b):After oxidization. Topographical changes and oxygen content increase are observed. All of the surface area are covered by micro-crystals of MgO formed during oxidization.



(a) (b)

Fig.6. (a):TEM image obtained from the cross section of "local oxide" layer of specimen ⑩. (b):HR-TEM image and SADP obtained from a small area marked in Fig.6-(a). The local oxide is about 300nm in thickness.

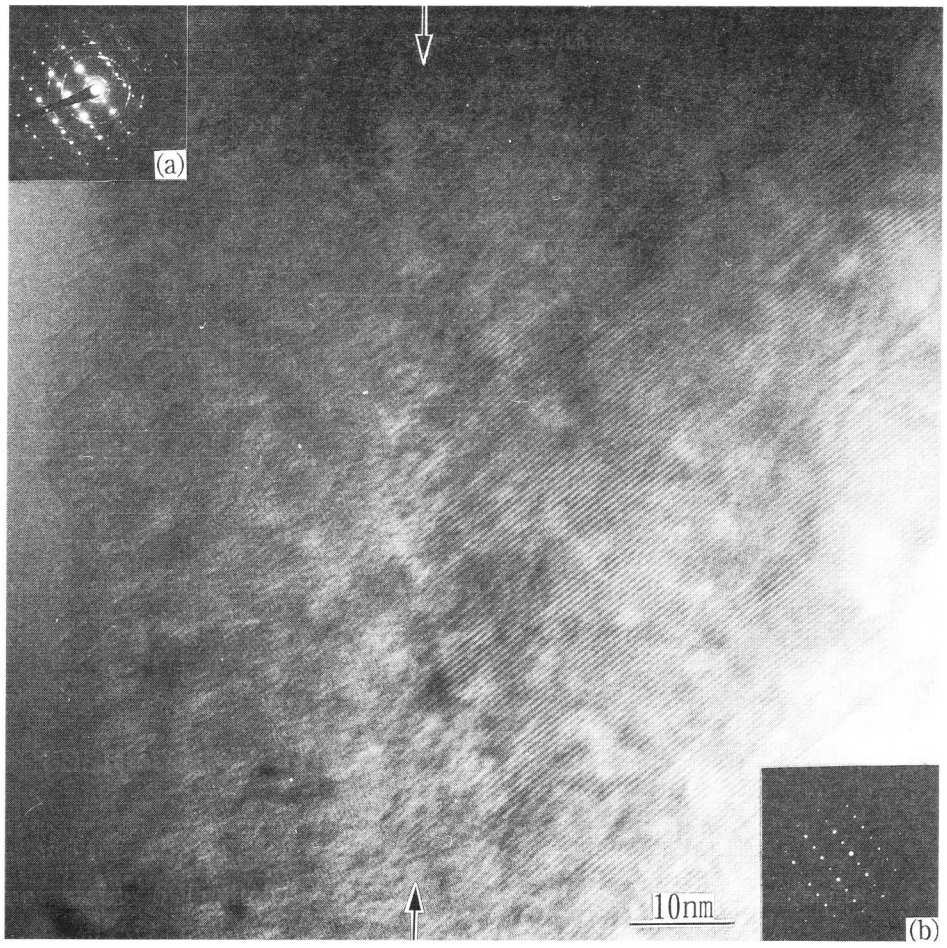


Fig.7. HR-TEM image and SADP obtained from the cross section of "uniform oxide" layer of Specimen ⑩. SADP(a) and (b) are obtained from the surface (the left hand side of this photograph) and inside (the right hand side) respectively. The ring pattern in SADP(a) is MgO pattern. But the oxides morphology is not obvious. No ring pattern was recognized in SADP(b).

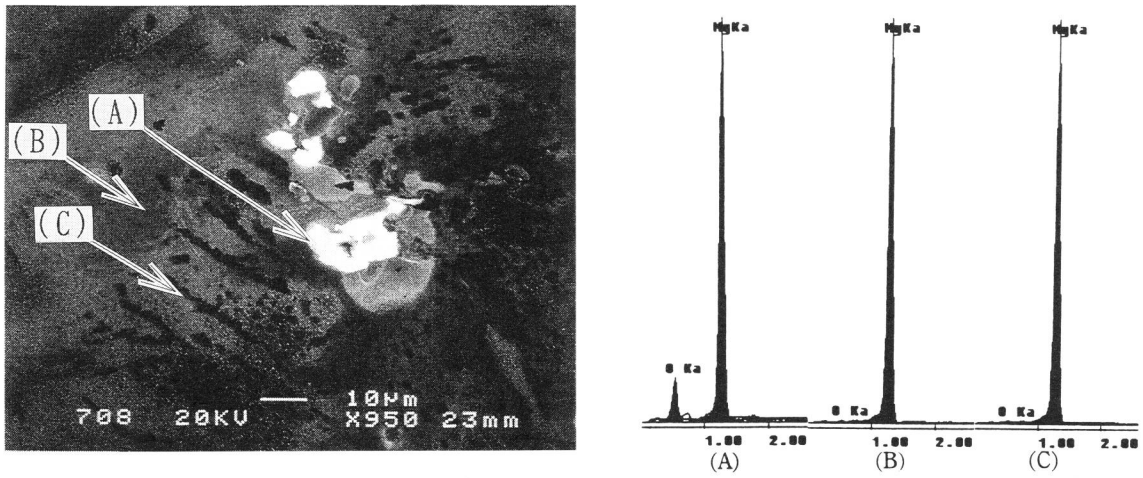


Fig.8. SEM image and X-ray spectra of EDS obtained from the surface area of bulk Specimen ⑩. (a):The white object like (A) is one of local oxide. The uniform oxidization is considered to form on area(B). Area(C) is considered to be surface cavity. (b):Relatively high oxygen content is detected from area(A), but only low oxygen content is detected from area(B) and (C).