An Application of Electron Energy Loss Spectroscopy to the Study of Residual Aluminum in Raney Nickel Catalyst

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The new technique of high resolution electron microscopy combined with the electron energy loss spectroscopy was applied to the study of the Raney nickel catalyst. The state and role of the residual aluminum in the developed catalyst have been revealed and discussed. It has been proved that the residual aluminum in Raney nickel catalyst is dispersing among the nickel crystal lattices. The crystal structure of the catalyst was also investigated by direct imaging of the crystal lattices and the unstable surface was observed.

The plasmon loss energies were measured for the Raney nickel and the Ni-Al alloys with various elemental ratios.

KEY WORDS: Raney nickel/ Plasmon loss/ Electron energy loss spectroscopy
(EELS)/ Residual aluminum/ High resolution electron
microscopy/

INTRODUCTION

The Raney catalyst which is obtained from an alloy by dissolving one element has been currently investigated both in the academic and industrial field since 1925[1]. The Raney nickel, for example, is prepared from Ni-Al alloy by dissolving most part of alminum in a solution. It has been considered that a small amount of aluminum still remains in the catalyst particles to exhibit the catalitic reactivity. However, the role of the residual aluminum as well as the state of remaining in the catalyst is not clear till now.

Recent development of electron energy loss spectroscopy combined with the high resolution electron microscopy[2] can realize the structure and elemental analysis of so small particles as a few nanometer in diameter. The electronic properties of such small specimens can also be investigated at the same time with this method by measuring the plasmon loss energy.

In the present work this method has been applied to the study of Raney nickel catalyst in order to elucidate the structure of the catalyst particles and the state of the residual aluminum in them.

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EXPERIMENTAL

The powdered Ni-Al alloys supplied by Kawaken Fine Chemicals Co. Ltd. were used as the starting materials. The alloys whose nickel contents were 42, 60 and 70 weight percents were examined. Each powder was dispersed in pure ethanol and a drop of the suspension was fixed on a microgrid for the observation with an electron microscope. Another part of the powder of 42 wt% Ni-Al alloy was developed by the following procedures. One gram of the powder was dispersed into 100 ml solution of 5% NaOH. After being heated at 100°C in a water bath for an hour, the powder was separated by decantation from the solution and washed several times with distilled water of 1000 ml in total amount. In order to remove the trace of water from the powder surface, dehydrated methanol and isopropanol of each 100 ml were used and the final product was kept in isopropanol. For the electron microscope study one drop of the product suspension was mounted on a microgrid and dried in the specimen exchange champer of the electron microscope so that the very reactive product, that is Raney nickel powder, can be observed without contacting to air.

The electron energy loss spectra were obtained with a JEM ASEA-2 energy analyzer of magnetic sector type which was attached to an electron microscope, JEM 100C. The high resolution work has been done with a JEM 200CX top entry electron microscope whose point-to-point resolution is 2.0 Å.

RESULTS AND DISCUSSION

The Ni-Al alloy containing 42 wt% of nickel (abbreviated as 42% Ni-Al) can be considered from the atomic ratio to be an intermetalic compound of $NiAl_3$. However, the x-ray powder diffraction pattern shown in Fig. 1 exhibits that the powder specimen
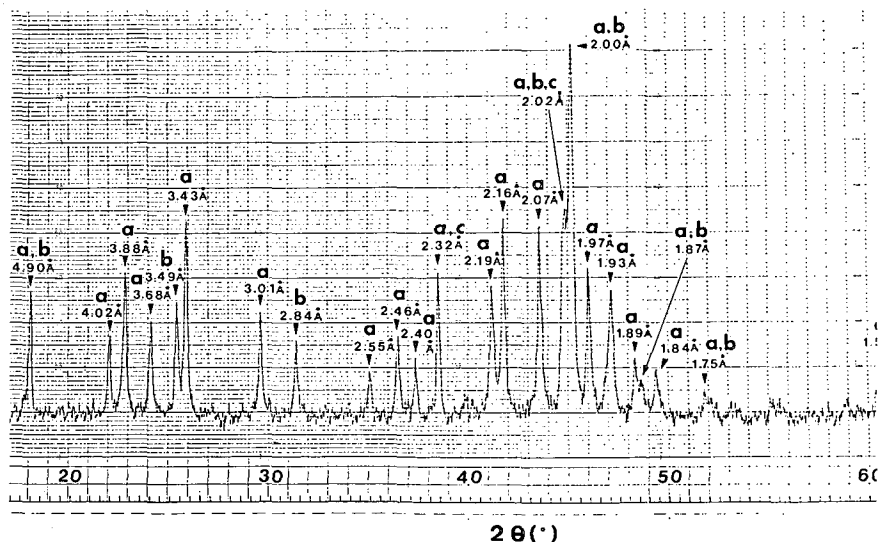

Fig. 1. X-ray diffraction pattern of 42% Ni-Al powder alloy. a, b and c denote the diffraction lines from $NiAl_3$, Ni_2Al_3 and Al respectively.

employed here was composed of NiAl$_3$, Ni$_2$Al$_3$ and pure aluminum crystals. In the figure, the letters a, b and c are inserted with the interplanar spacings which correspond to the diffraction lines from NiAl$_3$, Ni$_2$Al$_3$ and Al, respectively. These observed spacings agree well with those calculated on the basis of the following lattice constants assigned for each crystal[3];

Al; a＝b＝c＝4.049Å, face centered cubic.

NiAl; a＝6.598Å, b＝7.352Å, c＝4.802Å, orthorhombic.

Ni$_2$Al$_3$; a＝4.028Å, b＝4.028Å, c＝4.891Å, hexagonal.

The electron micrograph of this material is reproduced in Fig. 2 which shows that the alloy particles have irregular shapes and that their edges are partly thin enough for the 100 kV electrons to transmit. Such a thin area of 0.5-5 μm in diameter was selected by an aperture of electron microscope and the electron diffraction patterns (SAED) from these small areas were observed with each of many particles. The SAED patterns most frequently observed are exhibited in Fig. 3. They show that some particles can be assigned on the basis of their diffraction patterns to be NiAl$_3$ and others to Ni$_2$Al$_3$ which assume various orientations.

When the powdered alloys were developed in aqueous solution of 5% NaOH, they turned into the Raney nickel catalyst where the most part of the aluminum has been dissolved into the solution. The particles of Raney nickel thus obtained retained the original shapes but the texture has remarkably changed as can be seen in Fig. 4. The salient feature of the crystal is its dendroid structure composed of many fine crystallites. The SAED from the crystal (Fig. 4(b)) clearly shows that these fine crystallites have a defenite orientation as if the particles assumed a single crystal as a whole. The lattice
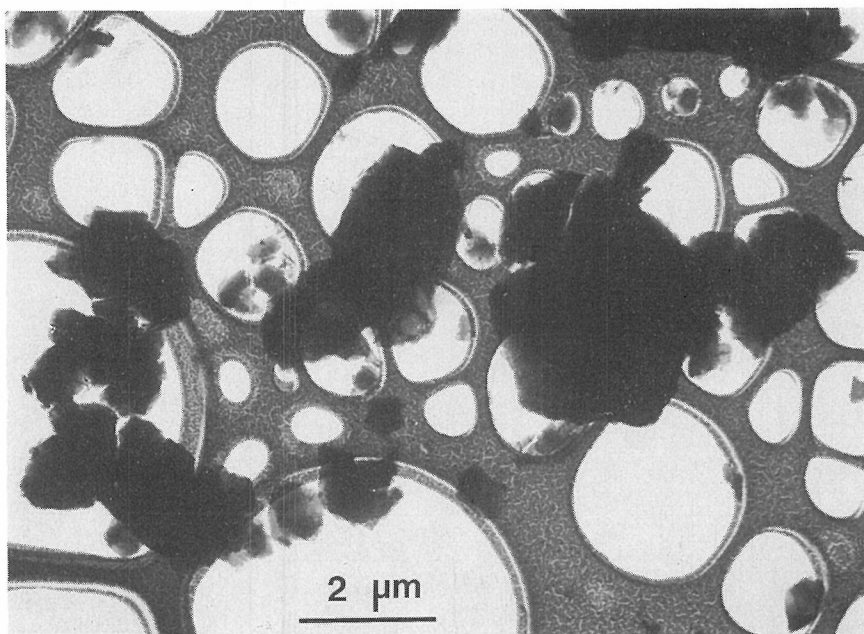

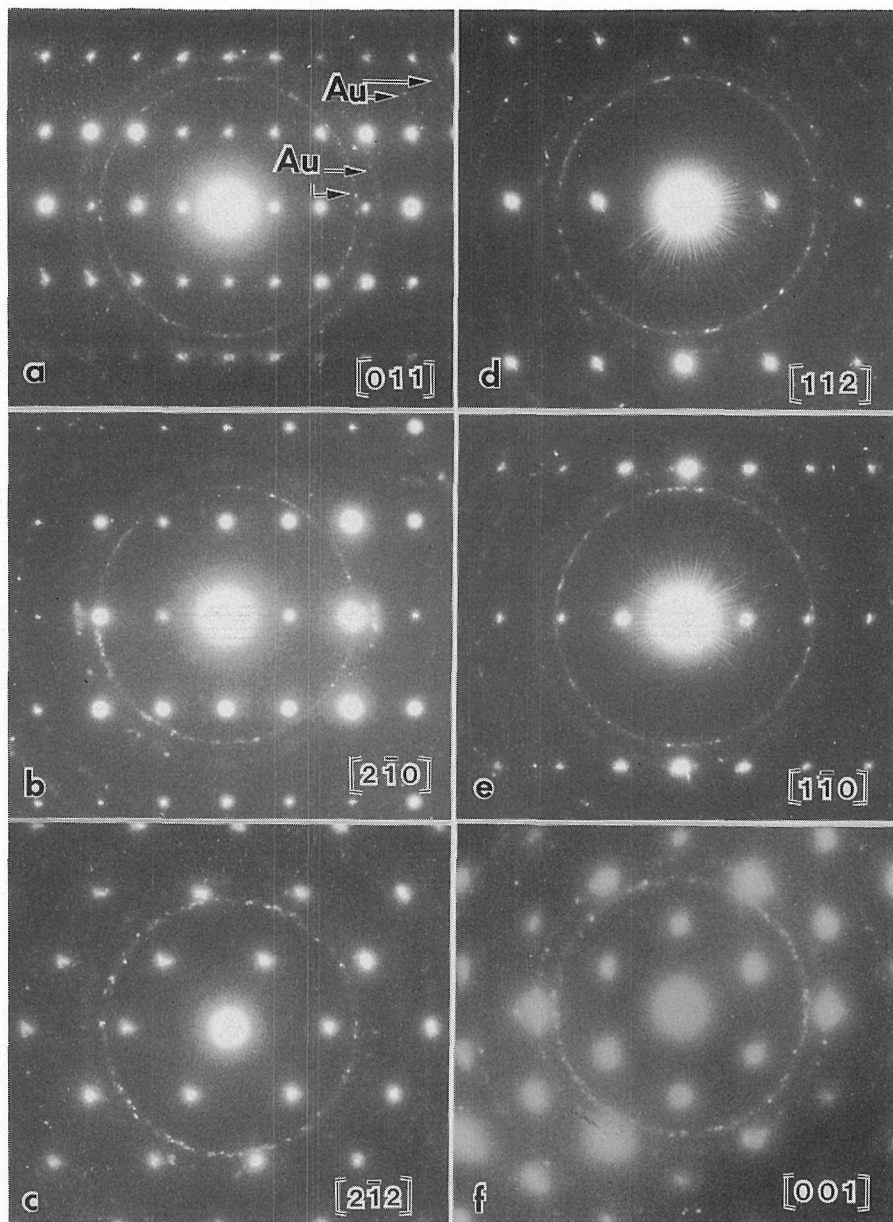Fig. 2. Electron micrograph of the powder of 42% Ni-Al on a gold-coated microgrid.

Fig. 3. Selected area electron diffraction patterns of 42% Ni–Al alloy particles. (a) − (c) and (d) − (f) correspond to those of Ni_2Al_3 and $NiAl_3$ respectively.

spacings obtained from the SAED pattern coincide well with those of pure nickel in (111) orientation, although each spot is very diffuse. The cause of the diffuseness of the spots is that the crystallites forming the dendrite have very small sizes. Many lattice imperfections or lattice irregularities they contain are also the origine of the diffuseness.

A high resolution electron micrograph of the Raney nickel catalyst is shown in Fig. 5. The fringes with 2.04 Å spacing correspond to the (111) lattice plane of nickel
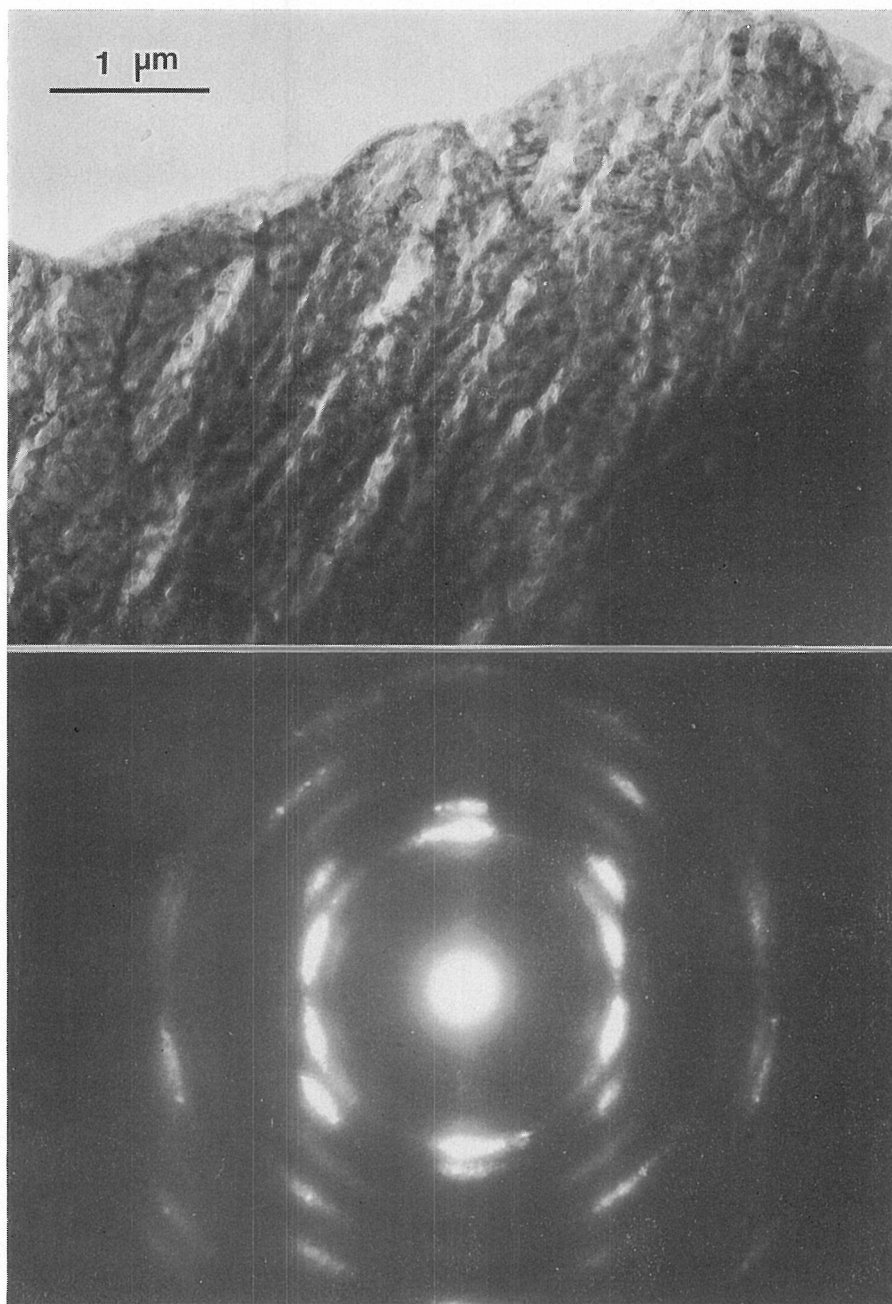
Fig. 4. Electron micrograph of Raney nickel developed in 5% NaOH solution and its selected area diffraction pattern.

Fig. 5. High resolution electron micrograph of Raney nickel particle developed in 5%
         NaOH solution.

crystal. The lattice disorders can be clearly observed as discontinuity of the fringes.
Edge dislocations are also clear in the micrograph. Especially the non-uniformity of the
edge of the particle is notable. The sharp-pointed parts on the edge seems to be
unstable and they may show a high activity in the catalytic reaction. Because the
electron diffraction from the developed alloy is like a single crystal pattern it can be
concluded that the formation of Raney nickel catalyst occurred topotatic, though the
axial correlation between the original and the developed crystal could not be determined.

The electron energy loss spectra from such small selected area can be obtained
with an electron microscope equipped with an electron energy analyzer. The electron
energy loss spectrum from the catalyst particle of the dendroid shape is shown in Fig. 6
for the energy loss range of 0 through 100 eV. The absorption edge energy of two
peaks are 68 eV and 74 eV which are due to the core electron excitations of Ni and
Al. That is, the former is due to the excitation of Ni–3p electrons and the latter is that
of Al–2p electrons to the higher energy level than their respective Fermi energy. Thus
the existence of Al in the Raney nickel has been directly confirmed by this energy loss
spectrum. It seems unlikely that the residual alminum in Raney nickel catalyst exists as
the oxide because the energy loss due to the core electron excitations of oxygen did not
appear in the spectrum. This can also be confirmed by the plasmon loss energy of the
catalyst. In general it is said that the bulk plasmon loss occurs by collective excitation
of valence or conduction electrons in a solid and the energy of the plasmon excitation

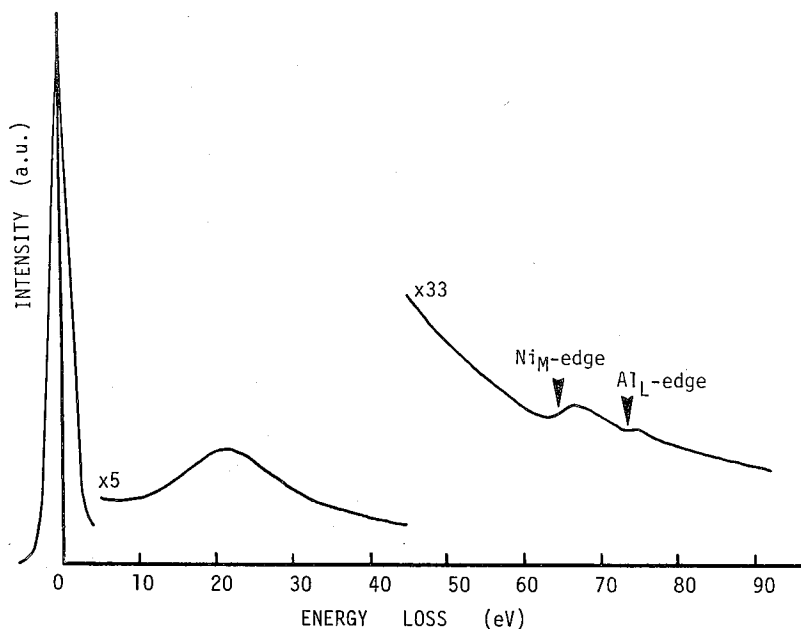H. KASANO, H. KURATA, T. KOBAYASHI and N. UYEDA

Fig. 6. The electron energy loss spectrum of Raney nickel catalyst showing the existence of Al in the same particle shown in Fig. 4.

is proportional to the square root of the conduction or valence electron density[4]. The width of the plasmon loss varies depending on the scattering relaxation time which is related to the electron conductivity. A good conductor with long relaxation time results a narrow sharp plasmon. In this report a series of Ni–Al alloys with different compositions were examined in advance for comparison. Fig. 7 shows the plasmon loss spectra from the alloys and the evaporated thin films of Ni and Al. Except for the case of Ni film the plasmon loss shows a single peak in the energy range of 15–25 eV. Their peak energies and full width at half maximum (FWHM) values are summarized in Table 1. The peak energies and FWHM both increase with the increase in the content of Ni in the alloy. This dependence of energy values and FWHM of plasmon peaks on the atomic ratio of Ni to Al can be used to characterize the chemical composition of the alloys. Sabatini et al.[5] have succeeded in determining the atomic ratio of Si to C in SiC using this method. While the spectrum from Al films is a sharp single peak centred at 15eV, Ni film shows rather complicated shape. It comes from the fact that the energy loss of the incident electron due to the interband trasition of free electrons occurs in this energy range in the case of Ni and superimposes on the plasmon loss spectrum. The assignments of these peaks centred at 14, 21 and 27 eV have been tried by Missel et al.[6] but remains undetermined. On the other hand, the energy loss spectra from the Raney nickel which was prepared by development in aqueous solution of 5% or 20% NaOH shows a single peak as shown in Fig. 8 (A, B). The peak values slightly vary around 22 eV for each catalyst particle. This change in plasmon loss energy shows the difference in the content of residual aluminum depending on the degree of development. At the same time it should be poined out that plasmon energy of the Raney nickel is lower than that of the pure
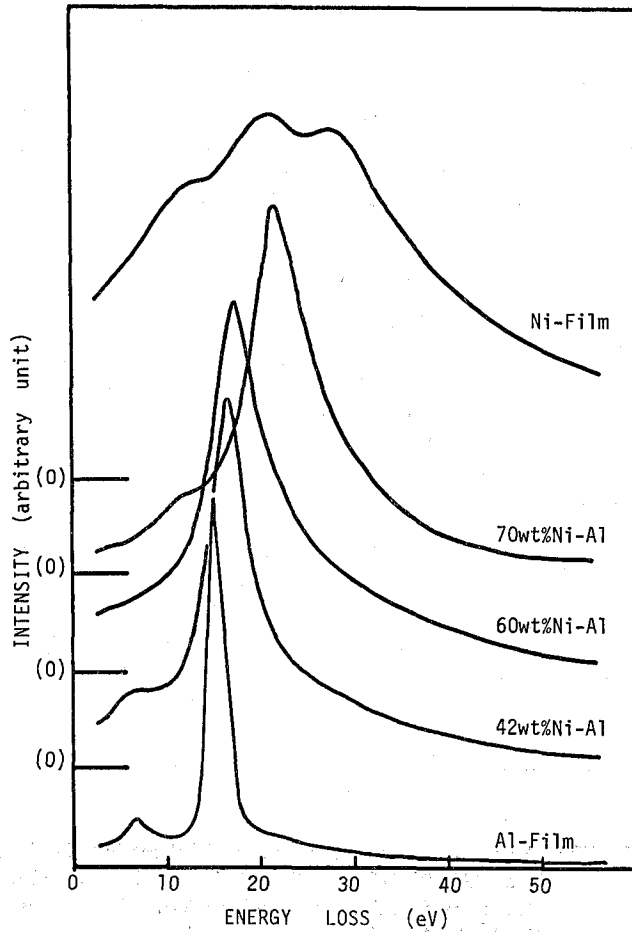
Fig. 7. The electron energy loss spectrum from Ni-Al alloys with different compositions and vacuum evaporated thin film of Ni and Al. The dependence of plasmon loss energy and FWHM on the contents of Ni is clear.

Table 1. The observed plasmon peak energies and FWHM in eV for Ni-Al alloys and Raney nickels with different contents of Ni. The data for Ni and Al films are also included for comparison.

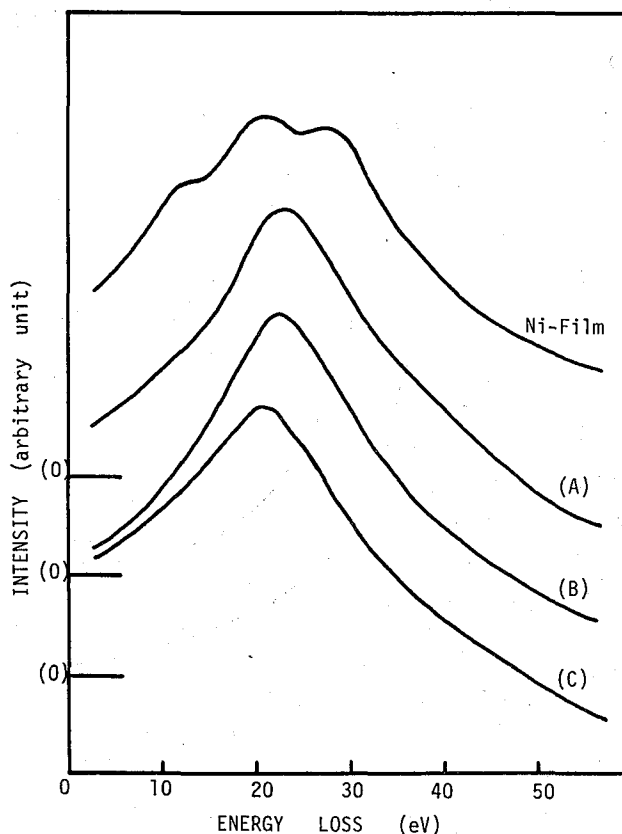| Sample	ΔE	$\Delta E_{1/2}$ (FWHM)
Al	15.2 eV	2.4 eV
42%NiAl	16.8	6.0
60%NiAl	17.6	8.3
70%NiAl	21.8	9.1
Ni	20.5, 26.4	—
Raney Ni(a)	21.2	26.6
Raney Ni(b)	23.1	30.6
Raney Ni(c)	20.6	30.0

Fig. 8. The plasmon loss spectrum of Raney nickel catalyst developed
in 5%(A), 20%(B) NaOH solutions and in glycol acid
after treated in 5% NaOH solution(C). The spectra of
Ni-film is also exhibited for comparison.

nickel. In other words the electron density in the catalyst is lower than that in the pure
nickel. The existence of a small amount of residual aluminum contributes to this pheno-
mena. If the aluminum precipitates as a crystalline particle among the Raney nickel, two
kinds of peak, one from Al at about 15 eV and the other at 20-27 eV from Ni, can be
observed at the same time as a superimposed spectrum[7]. The shapes and the plasmon
peak energies for the Raney nickel catalyst shown in Fig. 8 clearly prove the fact that the
residual aluminum in Raney nickel rather exists in the catalyst as random substitutions
or interstitials in nickel crystal lattices.

When the catalyst particles suffer further development by treating with glycol acid,
the plasmon peak value (Fig. 8(C)) decreases to 20.6 eV contrary to our expectation,
indicating that the content of aluminum increases by the development. This may be
resulted by the fact that some parts of nickel crystallities in the Raney nickel is also
dissolved into the glycol acid by the heavy treatment in it. The increase in the ratio
of Al content to Ni is caused by the decrease of nickel content. In such a case, the
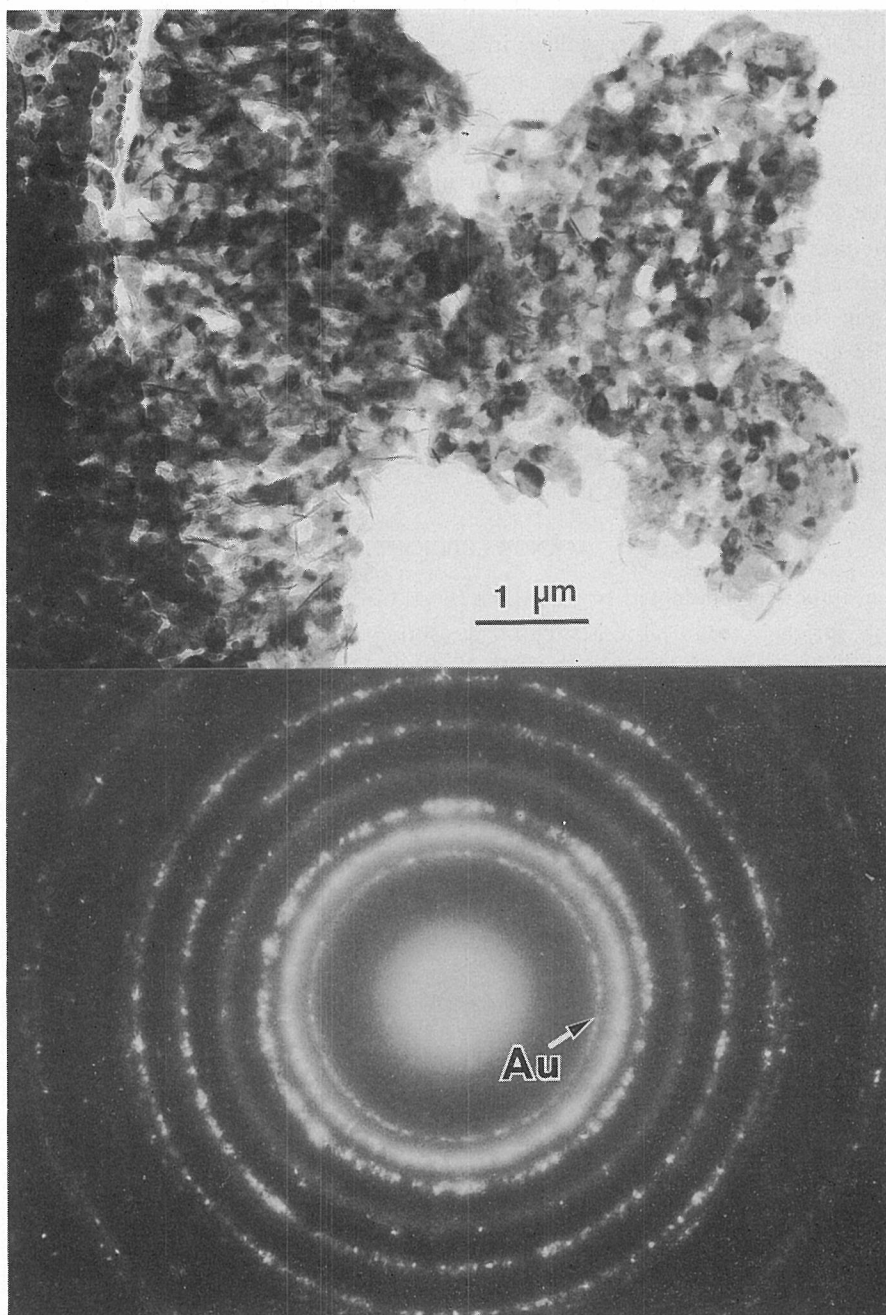crystal growth of Raney nickel or the rearrangement of atoms took place. Fig. 9 shows

Fig. 9. Electron micrograph and its selected area diffraction pattern of Raney nickel particle developed by successive treatment in 55% NaOH solution and glycol acid. The topotactic relationship between before and after the development has been destroyed.

an electron micrograph of heavily developed Raney nickel. The SAED from the particle shows that the orientation of crystallites in a grain become random and the sizes become larger.

The conclusion reached are summarized as follows;

(1) The formation of the Raney nickel catalyst from the Ni–Al alloy is topotactic even when the reaction occurs under violent condition.

(2) The Raney nickel particles contain many lattice defects and especially the unstable structures can be observed on the edge of the particles.

(3) It has been proved that a small amount of residual aluminum disperses at random among the Raney nickel crystal lattices.

(4) The electron density of the Raney nickel is lower than that of the pure nickel. These facts (2), (3) and (4) ought to be the causes of the high activity of Raney nickel as an catalyst.

(5) The plasmon energy can be used to measure the extent of the development of Raney nickel catalyst.

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