HITACHI SCIENTIFIC INSTRUMENT
TECHNICAL DATA
TEM

SHEET NO. 109

SUBJECT: HIGH TEMPERATURE IN-SITU MICROSCOPY AND EELS SPECTROSCOPY OF A METAL PRECIPITATE

INSTRUMENT: THE HF-2000 FIELD EMISSION ANALYTICAL ELECTRON MICROSCOPE

CONTENTS

1. INTRODUCTION

The high temperature in-situ microscopy technique, which allows continuous observation of changes of fine structures during heating process inside the specimen chamber of a microscope, has been found useful for revealing a mechanism for changes of inner structures in R & D of advanced materials. Turbomolecular pumps have been employed for Hitachi's electron microscopes as they allow high temperature microscopy in a clean environment. A specially developed double-tilt bulk specimen holder (see Fig. 1) has also been used. We report here on high temperature in-situ microscopy and EELS analysis of the precipitation process of a metal oxide specimen.

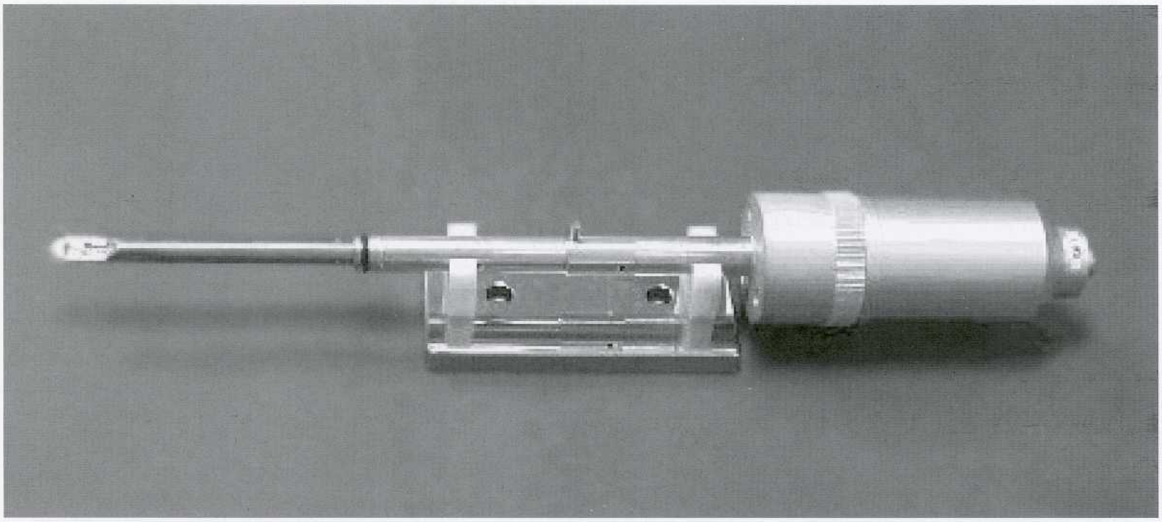


Fig. 1 A general view of a double-tilt bulk specimen heating holder developed by Hitachi, Ltd.

2. METHODS

2.1 Specimen preparation and microscopy techniques

A stainless steel specimen was heated from an ambient temperature to 700°C in a TEM specimen chamber. We observed a precipitation process in-situ, in which a metal oxide is precipitated on the specimen surface. We analyzed the precipitate at a high temperature using an EELS technique. EDX or Energy Dispersive X-ray spectroscopy is a common technique for TEMs. It is, however, difficult for high temperature specimens as they emit infrared rays which cause malfunction of EDX detectors. EELS technique is free of problems generated by light emission or infrared emission from high temperature materials. Table 1 shows microscopy and analysis conditions of the microscope.

Table 1 Microscopy and analysis conditions

Accelerating voltage	200 kV
Temperature range	Ambient ~ 700°C
Magnification	×50,000 ~ ×400,000
EELS analysis	3 seconds
EDX analysis	30 seconds
X-ray take-off angle	68°

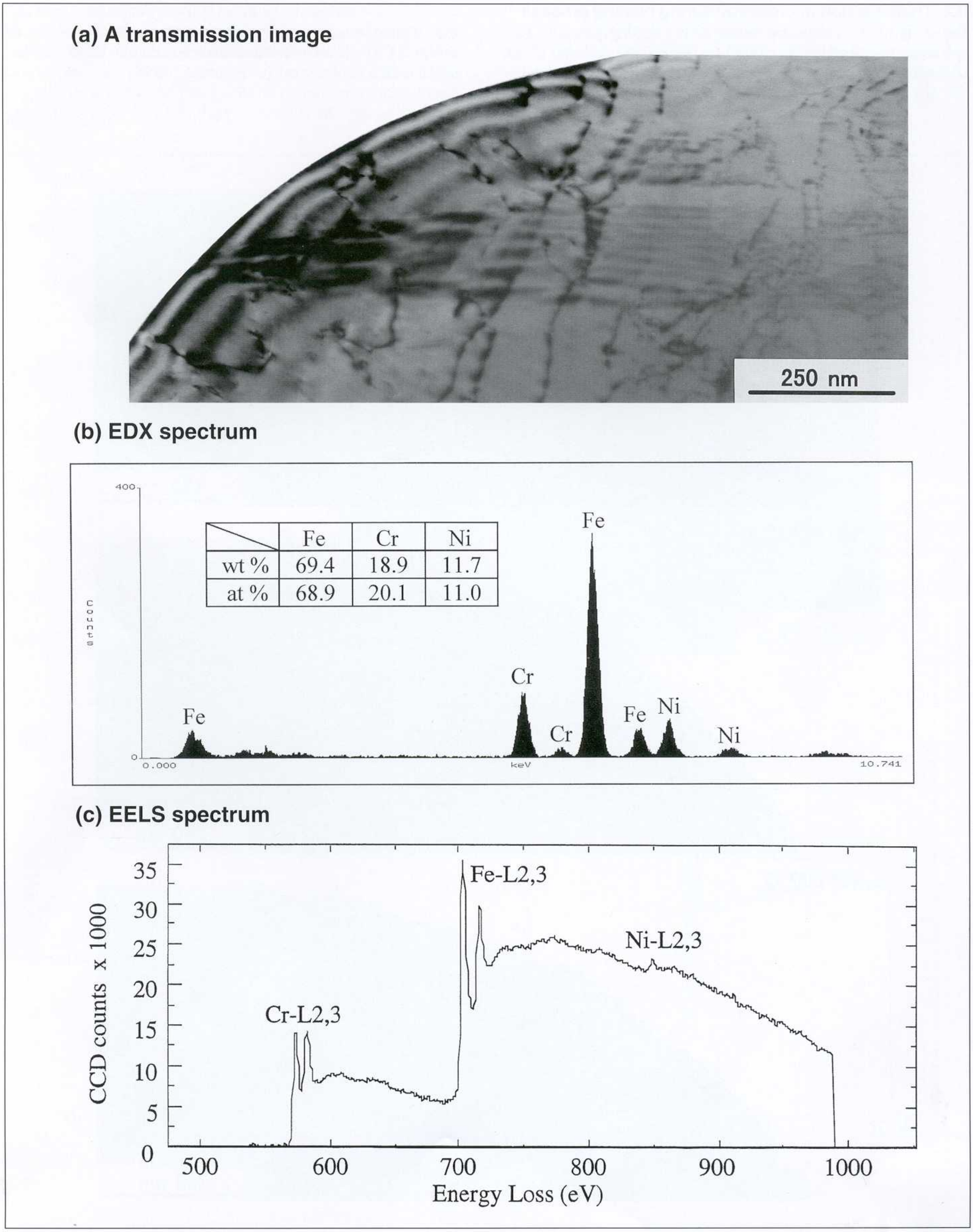
2.2 Instrumentation

For heating the specimen, we used a double tilt bulk specimen heating holder developed by Hitachi. This specimen holder allows accommodation of a bulky specimen up to 0.2 mm thick so that it allows direct microscopy of FIB prepared specimens. For microscopy and analysis, we used the HF-2000 field emission analytical TEM with Gatan's imaging filter and Noran's Voyager EDX system.

3. MICROSCOPY AND ANALYSIS

3.1 Transmission microscopy and analysis at a room temperature

Fig. 2 shows a transmission image of a stainless steel (a), an EDX quantitative analysis result (b), and an EELS qualitative analysis result (c).



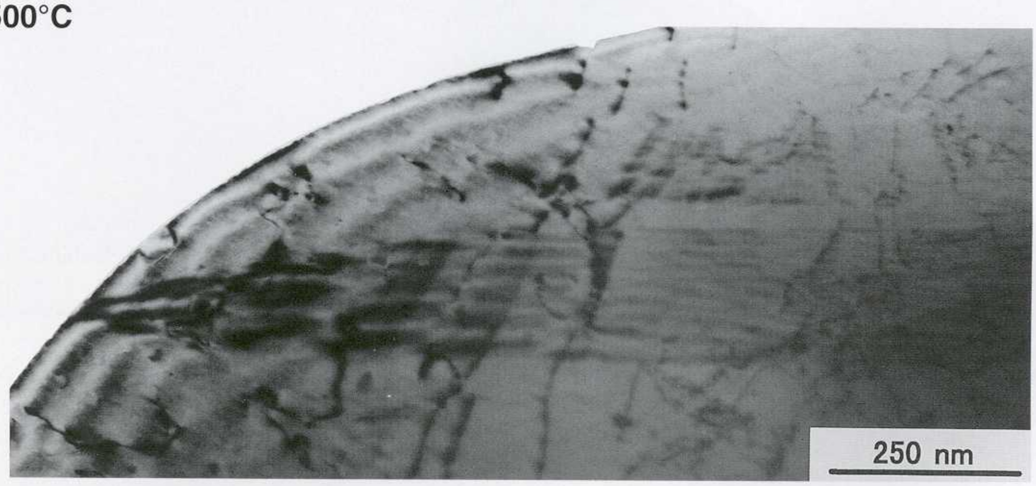
	Fe	Cr	Ni
wt %	69.4	18.9	11.7
at %	68.9	20.1	11.0

Fig. 2 A transmission image (a), EDX spectrum (b) and EELS spectrum (c) taken from a stainless steel specimen at a room temperature
Accelerating voltage: 200 kV Magnification: ×50,000

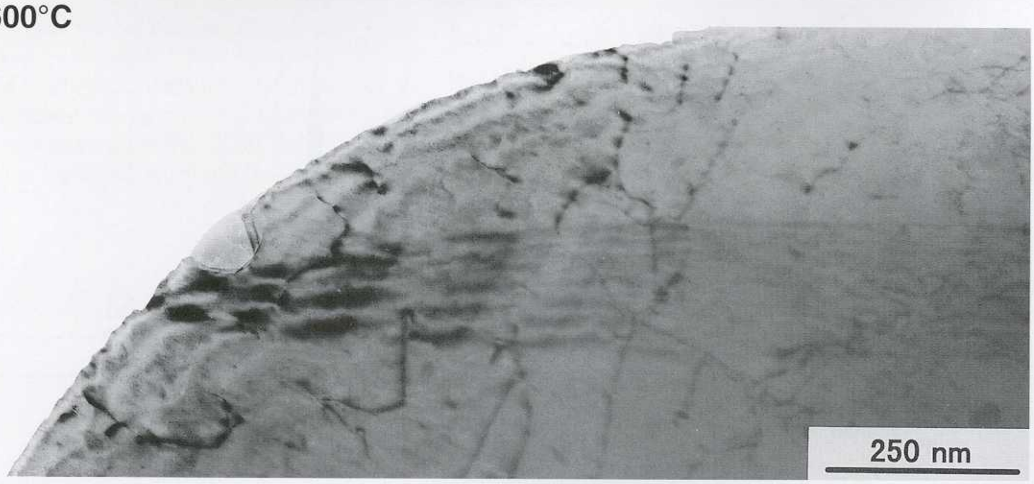
3.2 Transmission microscopy during heating process

Fig. 3 shows a transmission image during heating process. The specimen temperatures are 500°C (a), 600°C (b), and 700°C (c) respectively. At 500°C, you may recognize the surface undulation. Precipitates of particles having a few nm diameter can be seen at 600°C. These precipitates have grown into large particles, each having a diameter of 20 ~ 30 nm at 700°C.

(a) 500°C



(b) 600°C



(c) 700°C

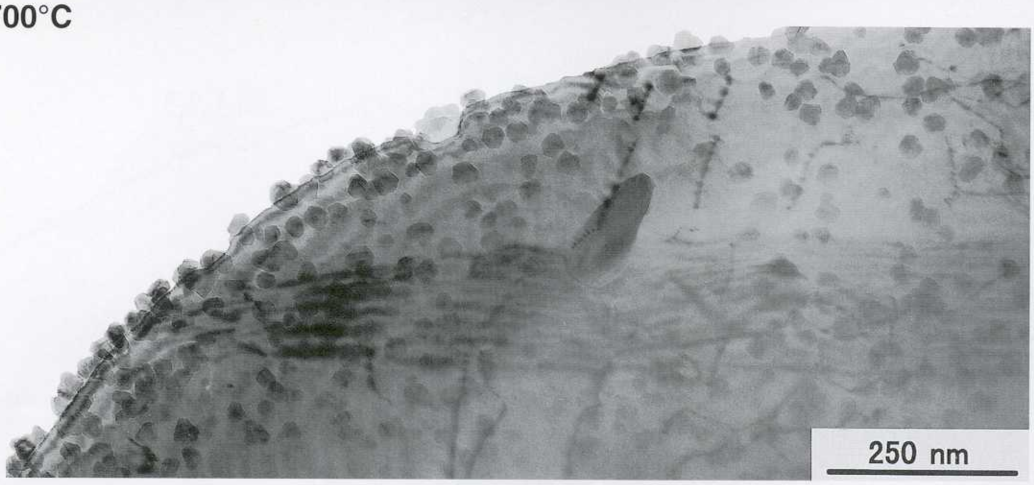


Fig. 3 A transmission image of a stainless steel during heating process (a) : 500°C, (b): 600°C, (c): 700°C
Accelerating voltage: 200 kV Magnification: ×50,000

3.3 EELS analysis during heating process

Fig. 4 shows a transmission image of a precipitate at 700°C (a), and EELS analysis taken at a precipitate (analysis point 1) and at a matrix (analysis point 2) (b) and (c) respectively. The EELS analysis shows that the precipitate is chromium oxide. Fig. 5 shows EELS spectra taken from a matrix at an ambient temperature (a) and 700°C (b). The spectrum (b) taken at 700°C shows Cr-$L_{2,3}$ lower with respect to Fe-$L_{2,3}$ when compared with the spectrum (a) taken at an ambient temperature. This is probably due to precipitation which lowered the concentration of Cr in the matrix.

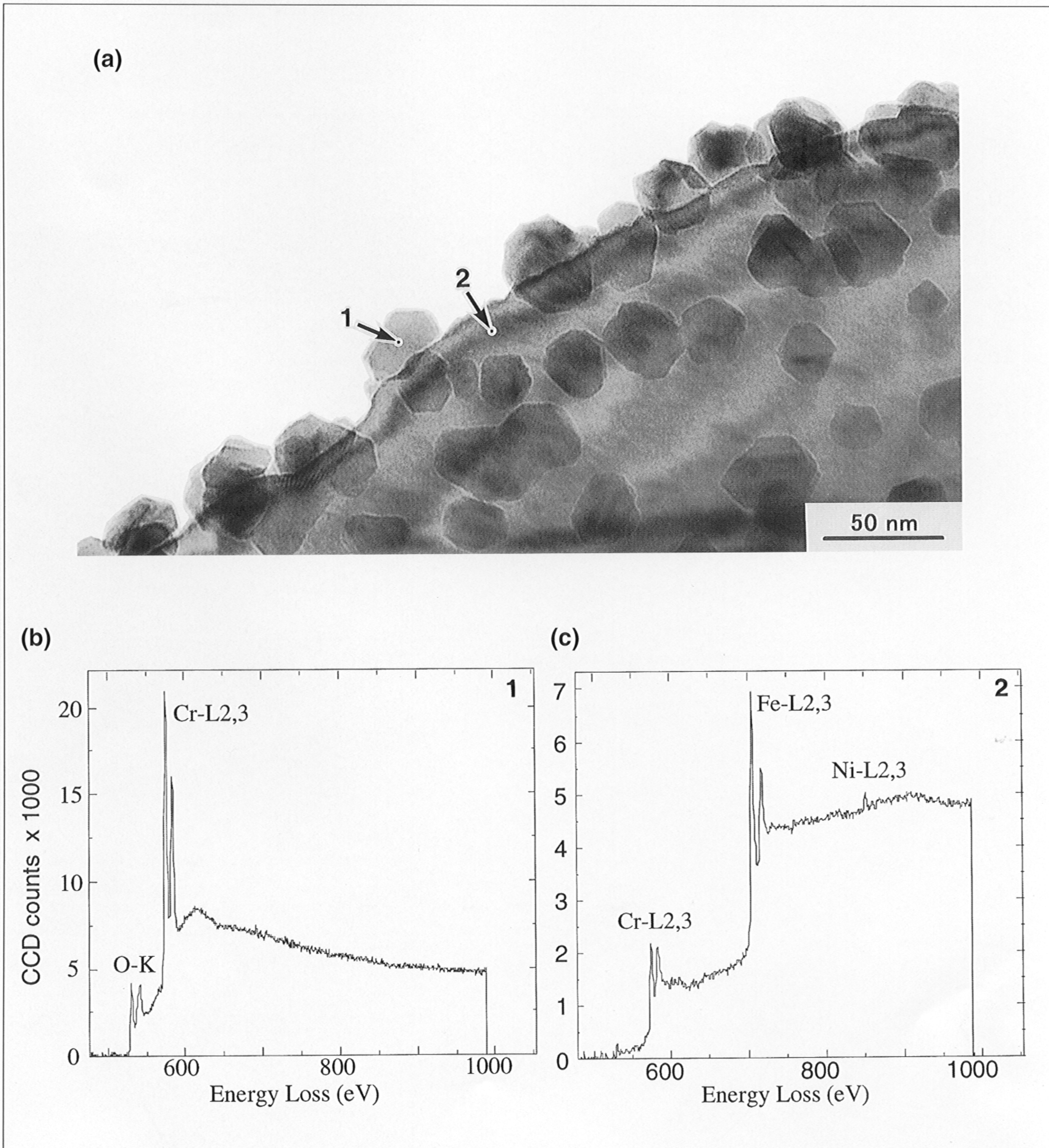


Fig. 4 A transmission image (a) and EELS spectra (b) and (c) at 700°C (b): Precipitate, (c): Matrix
Accelerating voltage: 200 kV Magnification: ×50,000

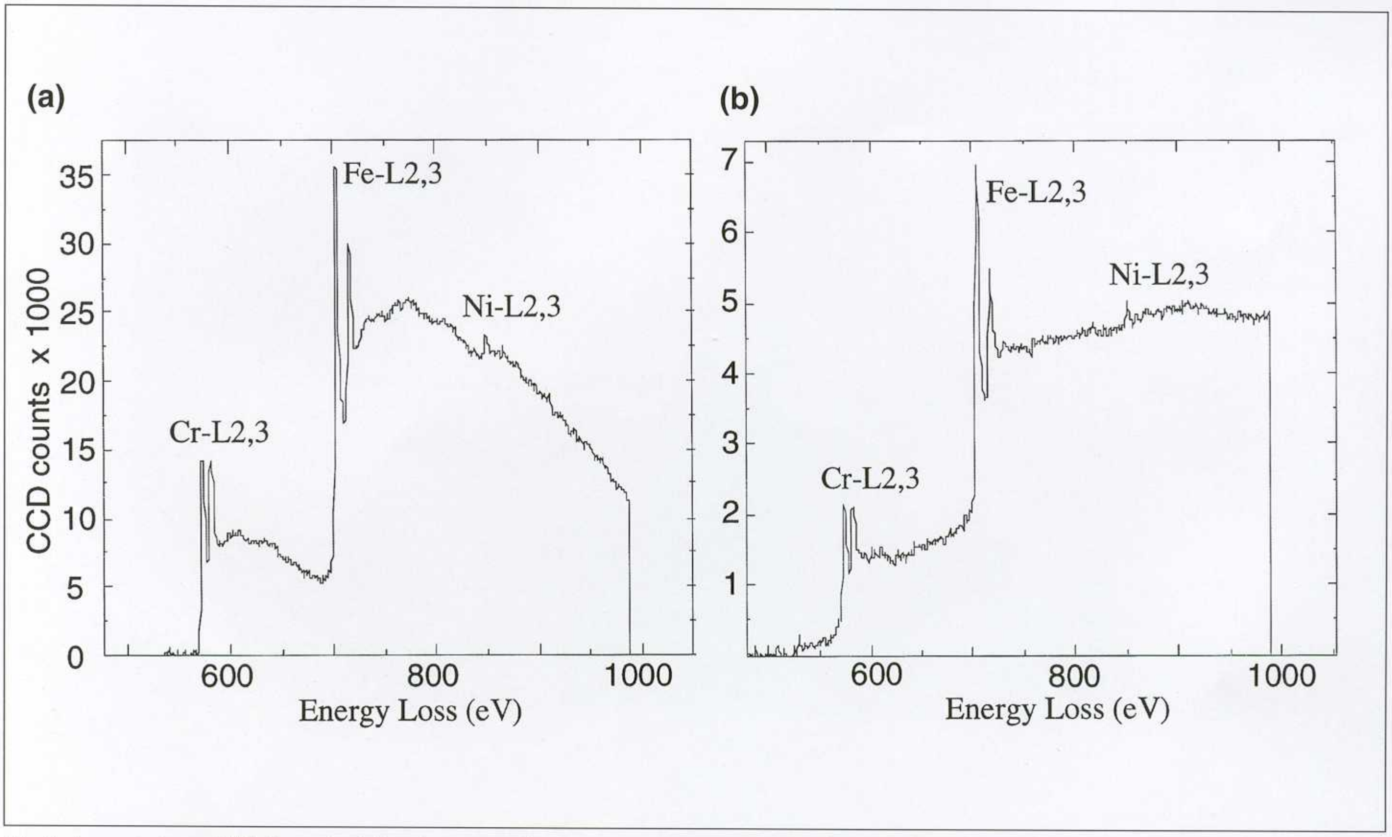


Fig. 5 A comparison of EELS spectra taken from a matrix at a room temperature (a) and 700°C (b).

3.4 High resolution transmission image during high temperature heating process

Fig. 6 shows an entire view of a precipitate at 700°C (a) and a high resolution image of the same (b). The high resolution image (b) shows a crystal lattice spacing of 0.267 nm which is in good agreement with a lattice spacing of Cr_2O_3 (104) plane.

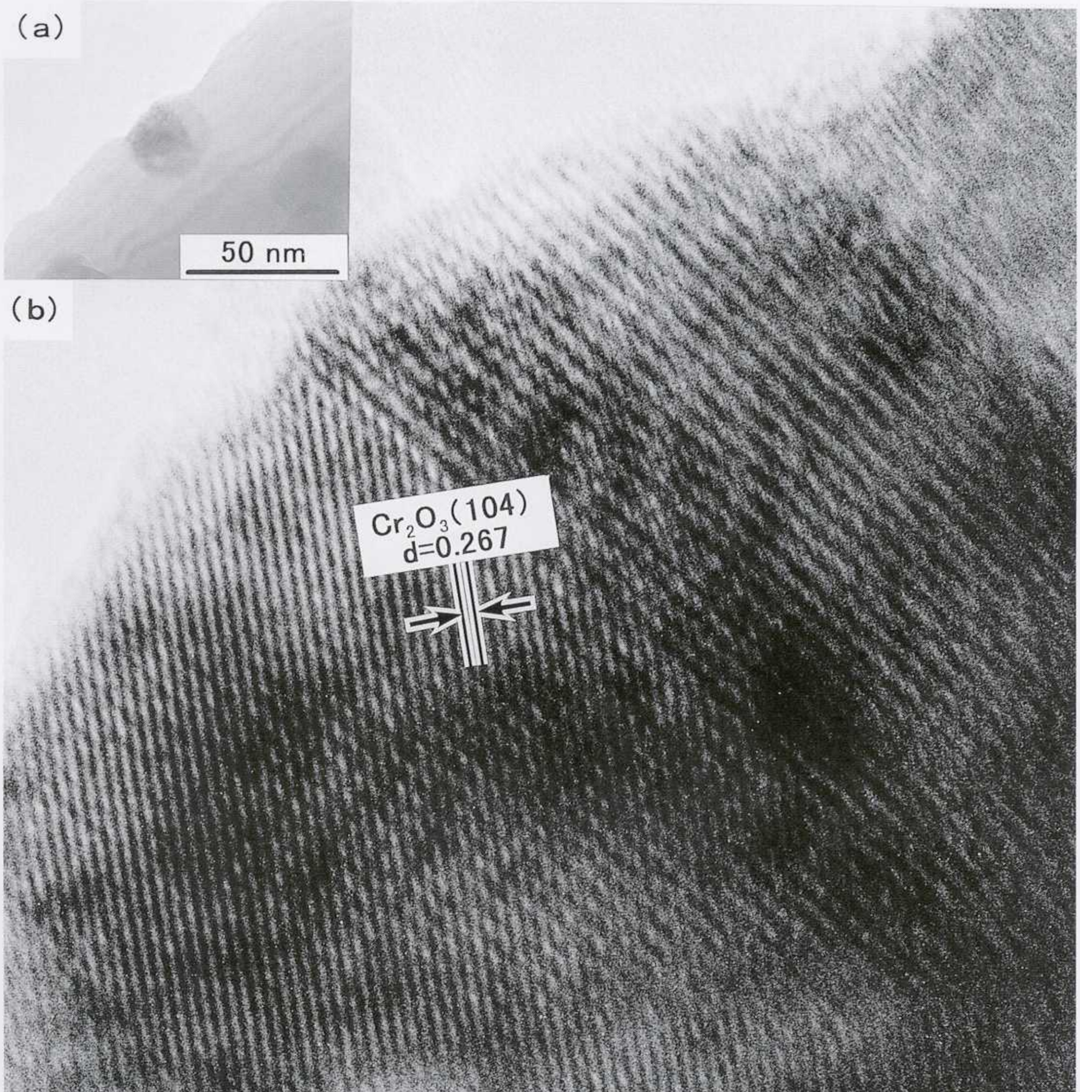


Fig. 6 A low magnification image (a) and a high resolution image (b) of a chromium oxide particle (Cr_2O_3) precipitated by heating.
Accelerating voltage: 200 kV Magnification: ×400,000

4. CLOSING REMARKS

We have introduced microscopy and EELS analysis of chromium oxide (Cr_2O_3) on a stainless steel specimen as one example of high temperature in-situ microscopy of a precipitation process from a metal specimen using a double-tilt bulk specimen heating holder. This technique is useful for various material studies as it allows real-time analysis of changes of structures and compositions at high temperatures. We trust that it will be found useful not only for metals and ceramics but also other advanced materials including semiconductors.

Printed in Japan (H) **EX-E850-10** 2000.3