STEM study of "ferritchromit" from the Heng-Chun chromitite

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Abstract

Electron-diffraction studies indicate that the deviation from spinel stoichiometry in "ferritchromit" from the podiform chromitite deposit at Heng-Chun in southern Taiwan can be reasonably explained by the topotaxial intergrowth of an RO phase (rock-salt structure) in an R_3O_4 spinel, where R = Fe, Cr, Mg, and Al. The absence of creep-induced defect microstructures in "ferritchromit" and its deviation from spinel stoichiometry indicate that it was formed by metasomatism subsequent to the deformation of the Cr-rich spinel core. The topotaxial oxides $RO + R_3O_4$ were later oxidized to $RO + R_3O_4 + R_2O_3$ (corundum structure). The depletion of Al and Mg accompanied by enrichment of Cr and Fe in "ferritchromit" is related to the formation of interleaved layers of trioctahedral chlorite and serpentine in the matrix.

Introduction

Podiform chromite deposits containing mainly Cr-rich spinel occur generally within the tectonic peridotite unit of ophiolite complexes (Duke, 1983). Serpentinization, chloritization, or later metasomatism commonly produces "ferritchromit" at borders or along cracks of Cr-rich spinel grains, and the normal "ferritchromits" differ significantly in their compositional variation, high reflectivity, and low hardness from their Cr-rich spinel cores (Weiser, 1967; Kern, 1968; Mihalik and Saager, 1968; Beeson and Jackson, 1969; Onyeagocha, 1974; Hamlyn, 1975; Ahmed and Hall, 1982). In general, solid-state alteration and/or overgrowth from solution are considered as possible mechanisms for the formation of "ferritchromit" (Beeson and Jackson, 1969; Ulmer, 1974).

It is known that natural magnetites may be partially oxidized to form a protective surface layer of hematite (Colombo et al., 1964, 1965). The solubility of hematite in magnetite (or vice versa) was described by Basta (1959), and the solubility of ternary mixtures of Al_2O_3, Cr_2O_3, and Fe_2O_3 in spinel was studied by Dewendra et al. (1983). In addition, the intergrowth of compounds having the rock-salt and spinel structures has been observed in iron oxides (Bernal et al., 1959; Rau, 1985) and in other systems (Comer et al., 1966; Chen et al., 1982; Graef et al., 1985; Tsai and Shen, 1986). It is not clear whether inhomogeneity of the mineral composition at borders of the Cr-rich spinel grains is due to intergrowths of oxides other than those having the spinel structure or to solid solution of different spinels.

Although transmission electron microscopy (TEM) studies of Cr-rich spinel in podiform chromitite deposits have been reported (Doukhan et al., 1979, 1984), the authors are aware of no TEM study of "ferritchromit." The present TEM study is intended to characterize the microstructures of "ferritchromit" in a podiform chromitite deposit recently found at Heng-Chun, southern Taiwan (Chu et al., in prep.). Evidence of metasomatism among Cr-rich spinel, "ferritchromit," and phyllosilicates has also been investigated by scanning transmission-electron microscopy (STEM) coupled with energy-dispersive X-ray (EDX) analysis.

Materials and methods

The sample studied was recovered from the Heng-Chun chromitite deposit, which was found recently in a metasomatized serpentinite block containing aggregates of Cr-rich spinel in the Kenting mélange, southern Taiwan (Chu et al., in prep.). Most of the Cr-rich spinel in this deposit is strongly fractured and transected by a network of serpentine- and chlorite-filled shears (Fig. 1a). Petrographic and electron-microprobe analysis (Chu et al., in prep.) indicate that the Cr-rich spinel is ophiolitic in origin, and defect microstructures characteristic of plastic deformation have been found in the spinel cores by TEM (Hwang et al., in prep.). The chemical compositions of the Cr-rich spinel cores, "ferritchromit," and the surrounding phyllosilicates (serpentine and chlorite) were compiled from Chu et al. (in prep.) and are listed in Table 1. Within "ferritchromit," depletion in Mg and Al and enrichment in Cr and Fe relative to the spinel core result in higher reflectivity in its backscattered-electron (BEI) image (Fig. 1b).

The rims of Cr-rich spinel that contain "ferritchromit" and the surrounding phyllosilicates were selected from thin sections and ion-milled to electron transparency. A TEM study with a JEOL 200CX electron microscope operated at 200 kV was used to obtain selected-area diffraction (SAD) patterns and electron micrographs. The thinned TEM samples were also qualitatively analyzed by the STEM-EDX technique at 40 kV in the JEOL 200CX.
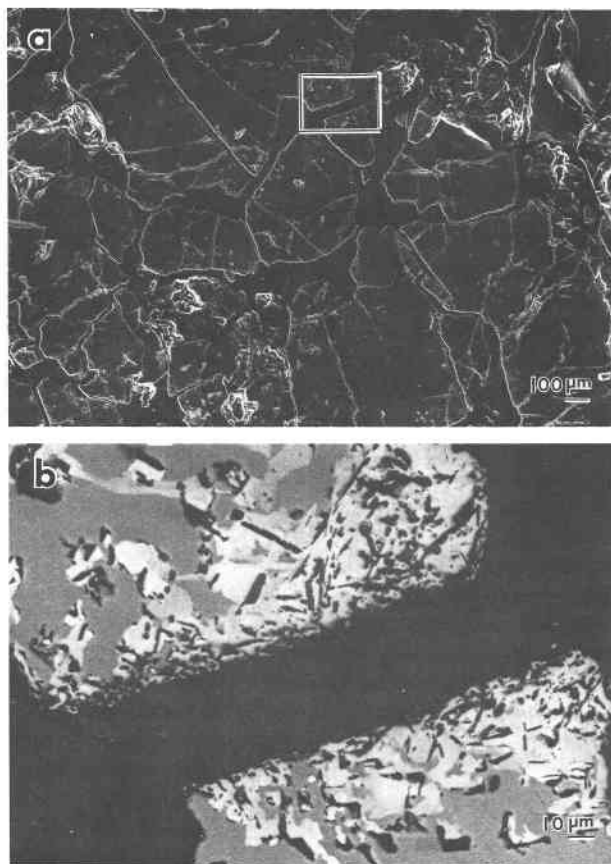
Fig. 1. (a) Secondary electron image showing the brecciated texture of Cr-rich spinel from the Heng-Chun chromitite. (b) Backscattered-electron image enlarged from the rectangular area in (a) showing the Cr-rich spinel core (gray), "ferritchromit" rim (bright), and surrounding phyllosilicates (dark).

TABLE 1. Composition of Cr-rich spinel, "ferritchromit," chlorite, and serpentine in Heng-Chun chromitite

	Cr-rich spinel	"Ferritchromit"	Chlorite	Serpentine
	(11)*	(7)*	(3)*	(3)*
Cr_2O_3	35.89(37)	45.15(66)	0.30(14)	0.25(7)
Al_2O_3	31.62(55)	16.73(138)	20.15(94)	1.88(65)
MgO	16.73(77)	14.33(53)	35.05(67)	39.61(188)
FeO_{tot}†	14.04(35)	22.59(213)	1.20(27)	1.98(31)
TiO_2	0.23(3)	0.27(5)	0.01(1)	0.04(3)
MnO	0.05(2)	0.13(4)	0.02(2)	0.04(1)
CaO	—	=	0.08(2)	0.10(2)
Na_2O	—	—	0.01(1)	0.02(2)
SiO_2	—	—	31.81(81)	40.13(50)
Total	98.57 wt%	99.19 wt%	88.64 wt%	84.07 wt%
	(32)**	(32)**	(14)**	(7)**
Cr	6.700(70)	9.222(154)	0.021(10)	0.009(3)
^{IV}Al			1.089(58)	0.060(37)
Al	8.799(157)	5.089(355)		
^{VI}Al			1.085(67)	0.046(34)
Mg	5.885(259)	5.516(140)	4.782(110)	2.853(81)
Fe_{tot}†	2.773(68)	4.884(525)	0.092(21)	0.080(14)
Ti	0.041(5)	0.052(9)	0.001(1)	0.001(1)
Mn	0.011(4)	0.029(10)	0.002(2)	0.001(1)
Ca	—	=	0.008(2)	0.005(1)
Na	—	=	0.002(2)	0.001(1)
Si	—	—	2.911(58)	1.940(37)
Fe^{3+}‡	0.558(267)	2.114(352)		
Fe^{2+}	2.215(225)	2.770(179)		
R^{3+}	16.056(66)	16.425(78)		
R^{2+}	8.111(34)	8.316(50)		

* Number of EPMA analyses, after Chu et al. (in prep.).
** Number of oxygens used as a basis for recalculation (anhydrous basis).
† FeO_{tot} and Fe_{tot} include total Fe^{2+} + Fe^{3+}.
‡ Fe^{3+} = ⅔[Fe_{tot} + Mg + Mn − (2Ti + ½Al + ½Cr)] (Scribbins et al., 1984).

RESULTS

Electron-diffraction (Fig. 2a) and dark-field image analyses (Figs. 2b, 2c) indicate that oxides having the rock-salt (RO, where R = cations) and spinel (R_3O_4) structures can be identified in "ferritchromit" for the following reasons. First, the diffraction spots A and B in Figure 2a are not necessarily diffracted from the same areas, as shown by the dark-field images of Figures 2b and 2c, respectively, and the extra diffracted areas in Figure 2c, compared to Figure 2b, indicate that spot B can be reasonably interpreted as the 200 reflection of an RO phase superimposed on the 400 spot of an R_3O_4 phase. Second, the cations in "ferritchromit" (Table 1) in excess of those in stoichiometric spinel also support the co-existence of an RO phase with a spinel oxide. Using Figure 2a, the orientational relationship between the cubic oxides was determined to be

$$\{001\}_{RO} \| \{001\}_{R_3O_4},$$

which is the most efficient way for nucleating topotaxial oxides (Bonev, 1972), as observed in other systems (Ber-

nal et al., 1959; Comer et al., 1966; Chen et al., 1982; Rau, 1985; Graef et al., 1985; Tsai and Shen, 1986). Since the oxide mixture RO + R_3O_4 has a composition different from that of spinel (Table 1) and was found only at rims of spinel crystals, it follows that the RO phase was formed by oriented transformation in an open system with a partial alteration in chemical composition of the primary R_3O_4 crystal. According to the terminology of Bonev (1972), RO + R_3O_4 are therefore considered to be topotaxial phases. Further study using high-resolution electron microscopy is required to characterize the coherency and interwoven structure of topotaxic oxides in "ferritchromit," as Graef et al. (1985) have done for the system NiO-TiO_2.

In our specimens, the topotaxic oxides are a few tens to a few hundreds of ångströms in size, as shown by the representative dark-field images (Figs. 2b, 2c). Besides the topotaxial oxides, a ring-SAD pattern of oxides was found locally at rims of "ferritchromit" (Fig. 3); this pattern was identified as being due to the oxides RO + R_3O_4 + R_2O_3 (corundum structure). These phases have a larger grain size (about several hundreds of ångströms in size) than RO + R_3O_4, as shown by the corresponding electron micrograph in Figure 3. The tangled dislocations, dipoles, and subgrain boundaries that were found in Cr-rich spinel cores (Hwang et al., in prep.) were not observed in "ferritchromit."
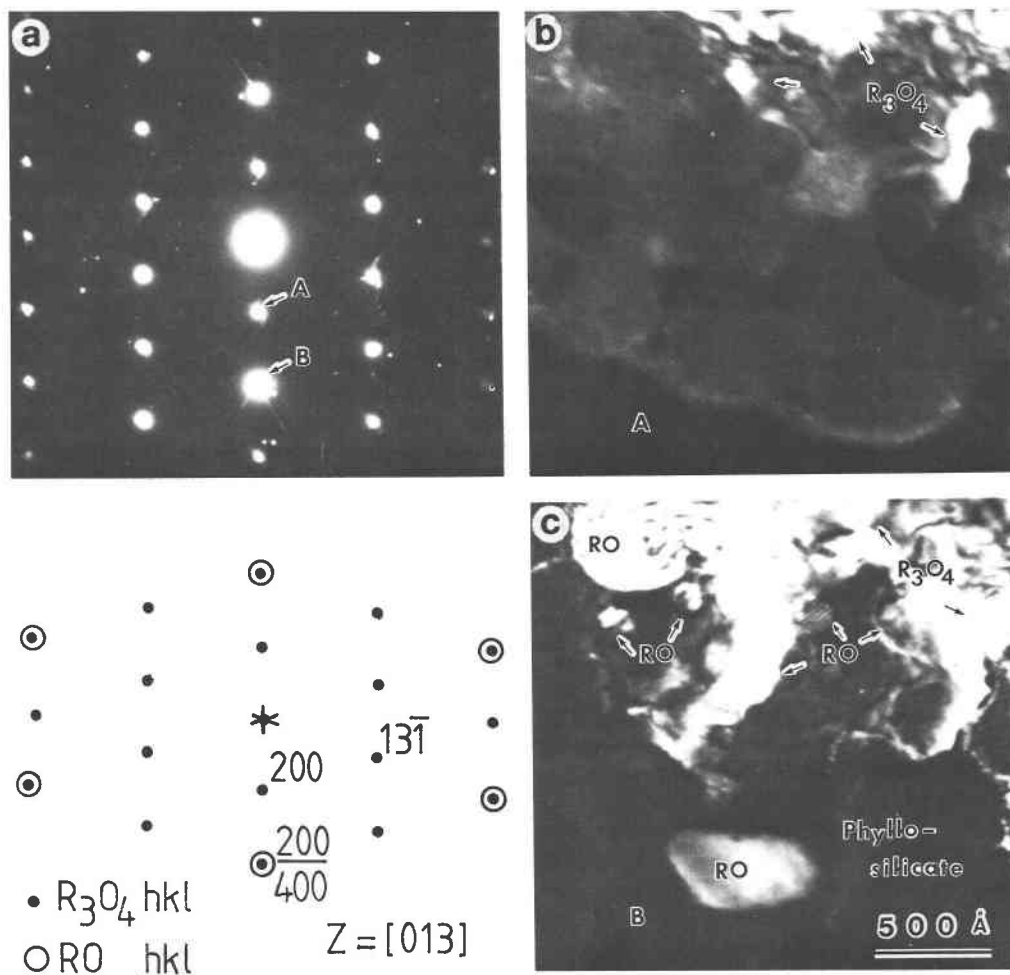
Fig. 2. (a) SAD pattern (electron beam parallel to the zone axis [013]) and schematic indexing of "ferritchromit" showing the topotaxial RO (rock-salt structure) phase in R_3O_4 spinel. (b) Dark-field image obtained from diffracted beam A in Fig. 2a, which is interpreted as 200 of R_3O_4. (c) Same area as (b) but imaged from B, which is interpreted as 200 of RO superimposed on (400) of R_3O_4, showing R_3O_4 as well as RO regions. Note that the individual RO phase is tens to hundreds of ångströms in size and is distinct from the R_3O_4 phase, as shown by comparison of (b) and (c).

The phyllosilicates adjacent to "ferritchromit" consist of chlorite (clinochlore) and serpentine, which are interleaved at the scale of individual layers and which are locally discontinuous, as shown by the lattice fringes of the (00*l*) planes (Fig. 4a) of chlorite (14 Å) and serpentine (7 Å). Commonly the phyllosilicates have been decomposed to a polycrystalline RO phase about 100 Å in size and a poorly crystallized silica matrix (Fig. 4b). In contrast to the topotaxial RO in "ferritchromit," this RO phase has a ring-SAD pattern and was probably formed by calcination during retrograde metamorphism or by the ion thinning and electron irradiation (Shen et al., in prep.).

The STEM-EDX spectra of Cr-rich spinel and "ferritchromit" indicate that the depletion of Al and Mg, along with enrichment of Fe and Cr, always occurred in "ferritchromit" relative to the spinel core. Since the RO phase is found intimately intergrown with the R_3O_4 phase in

"ferritchromit," it was not possible to identify the RO phase by means of STEM-EDX. However, the depletion of Al and Mg, the enrichment of Fe and Cr, and the higher Fe/Cr ratio in "ferritchromit" than in the spinel core indicate that the RO phase in "ferritchromit" is Fe-rich. The RO grains in decomposed phyllosilicate are probably Mg-rich (Shen et al., in prep.) because of the high content of Mg in the parent phyllosilicates (Table 1), although they are too small to analyze by the STEM-EDX technique.

DISCUSSION

The electron-microprobe data (Table 1) shows that "ferritchromit" has 24.7 cations, whereas Cr-rich spinel has approximately 24 cations calculated on the basis of 32 oxygens. The "excess cations" in "ferritchromit" can be reasonably explained by the intergrowth of cubic oxides having RO and R_3O_4 stoichiometries, both struc-
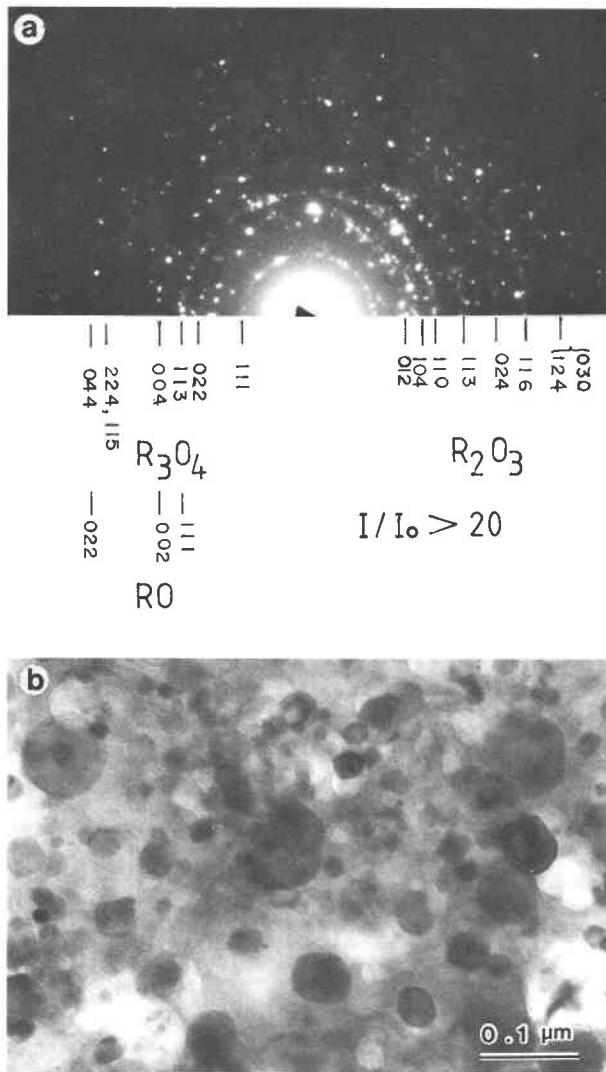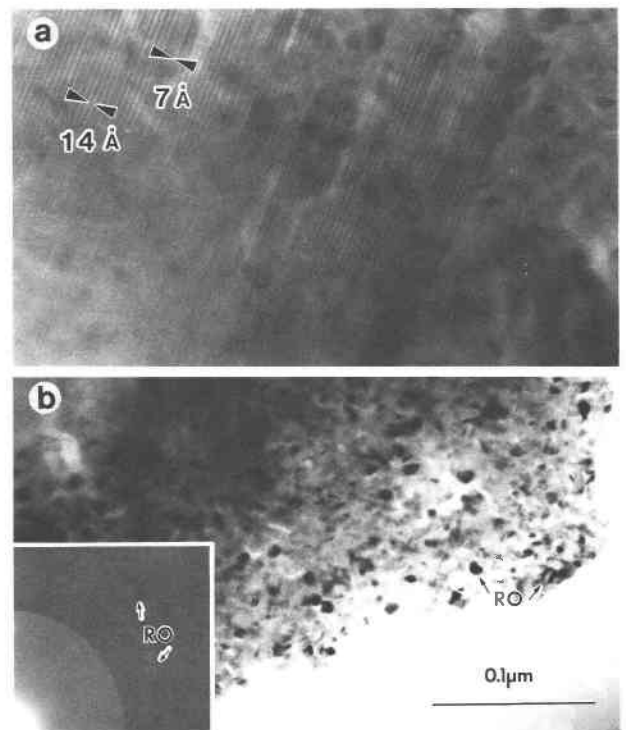
Fig. 4. (a) Lattice image showing an edge-on view of the interleaving and disturbance of basal layers of chlorite (14 Å) and serpentine (7 Å). (b) Electron micrograph showing polycrystalline MgO in decomposed phyllosilicates.

Fig. 3. (a) Ring-SAD pattern of the oxide mixture RO + R_3O_4 + R_2O_3 in a local area of "ferritchromit." (Only hkl values with intensities >20 are indexed.) (b) Bright-field image showing that the size of individual oxide grains is greater than several hundreds of ångströms.

tures being different only in the number and placement of the cations. However, the dissolution of ternary mixtures of Al_2O_3, Cr_2O_3, and Fe_2O_3 in periclase and spinel (Dewendra et al., 1983) and the present STEM-EDX analysis suggest that these sesquioxides also dissolve in the RO and R_3O_4 phases within "ferritchromit." It follows that both solid solution and mixtures of oxides rather than solid solution alone (Weiser, 1967; Ahmed and Hall, 1982) result in the compositional variation of "ferritchromit." Cation vacancies are probably also present in "ferritchromit" by analogy to wüstite, which has a nonstoichiometric rock-salt structure.

The absence of creep-induced dislocations and subgrain

boundaries in "ferritchromit" (Figs. 2b, 2c) along with the deviation from spinel stoichiometry indicate that the "ferritchromit" was formed by metasomatism subsequent to the deformation episodes of Cr-rich spinel. These episodes have been reconstructed by Hwang et al. (in prep.) on the basis of the defect microstructures observed in the spinel core. The texture of the Cr-rich spinel core surrounded by a "ferritchromit" rim (Fig. 1b) also suggest that the associated oxides in "ferritchromit" were formed by a "martitization" process rather than by exsolution. This interpretation is contingent upon the feasibility of solid-state diffusion in which Mg and Al ions diffuse out as Fe and Cr ions diffuse in (Beeson and Jackson, 1969). The interdiffusion of cations in sintered periclase-chromite refractories has been extensively studied (Kohn and Butler, 1985), and, in general, rapid diffusion of Mg and Al leaves (Fe,Cr)-rich rims on the chromite grains that are similar to those observed in "ferritchromit." Shelley et al. (1962) have shown that instead of going through grain boundaries, the diffusion of FeO and CoO in polycrystalline MgO takes advantage of the vacancies formed because of the nonstoichiometric character of FeO and CoO. The diffusion process in vacancy-bearing "ferritchromit" also appears to prefer bulk movement by means of vacancies as opposed to grain-boundary diffusion. Considering the occasional observations of rounded cor-

ners on Cr-rich spinel grains (Fig. 1a) and the sharp compositional transition into "ferritchromit," a precipitated secondary overgrowth on the original Cr-rich spinel, as suggested by Ulmer (1974), cannot be excluded.

The combined aspects of texture and progressive compositional variation from Cr-rich spinel core to "ferritchromit" to phyllosilicate (Table 1) indicate that the formation of "ferritchromit" is associated with chloritization and serpentinization. According to Table 1, the chlorite and serpentine have the formulae (on a hydrous basis) $(Ca_{0.01}Cr_{0.02}Al_{1.09}Fe_{0.09}Mg_{4.78})[(Si_{2.91}Al_{1.09})O_{10}](OH)_8$ and $(Ca_{0.01}Fe_{0.08}Cr_{0.01}Al_{0.05}Mg_{2.85})[(Si_{1.94}Al_{0.06})O_5](OH)_4$, respectively. It follows that more than 80% of the octahedral layers of chlorite and 95% of the octahedral layers of serpentine remain trioctahedral, which explains the interleaving of the chlorite and serpentine at the scale of individual layers. The depletion of Mg and Al in "ferritchromit" compared to the spinel core is presumably due to the outward diffusion of Mg and Al to the areas having a high activity of Si to form chlorite and serpentine.

Serpentinization may generate H_2 to form reduced assemblages (Eckstrand, 1975), and the nickeliferous opaque minerals accompanying "ferritchromit" are linked by Ahmed and Hall (1982) to serpentinization and/or chloritization. Ahmed and Hall (1982) further suggested that the reducing environment generated by the partial reaction

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$
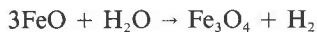
is more readily produced near the "ferritchromit" alteration sites than in ordinary serpentinization of olivine-rich rock. The possibility that H_2 at altered sites reduces R_3O_4 to an RO phase during serpentinization and/or chloritization is further supported by the significant counterdiffusion of cations through the oxygen framework at temperatures around 500 °C (Comer et al., 1966). Dehydration of phyllosilicates also gives an RO phase. In such reactions, however, a polycrystalline RO phase about 100 Å in size is formed as shown in Figure 4b. According to Ashley (1975), the oxygen fugacity fluctuated during various stages of serpentinization in the Coolac ultramafic belt. A fluctuation of oxygen fugacity probably occurred also during the formation of Heng-Chun chromitite, as indicated by the absence of "ferritchromit" at some borders and cracks of Cr-rich spinel grains (Fig. 1b). The oxide mixtures RO + R_3O_4 + R_2O_3 found locally at rims of "ferritchromit" (Fig. 3) were probably formed by oxidizing the topotaxial oxides RO + R_3O_4 (Fig. 2) after the emplacement of the podiform chromitite deposit in the Kenting mélange.

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