Migration of Co in Nickel Oxide/Hydroxide of a Nickel Electrode in a Ni/H_2 Cell

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OBJECTIVE OF STUDY

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BACKGROUND: COBALT REDISTRIBUTION IN NICKEL ACTIVE MATERIAL HAS BEEN REPORTED. THIS REDISTRIBUTION WAS SUSPECTED TO BE RELATED TO CAPACITY FADING.

- Zimmerman and Seaver in 1990
- Lim and Verzwyvelt in 1990

OBJECTIVE: TO ESTABLISH RELATIONSHIP BETWEEN COBALT REDISTRIBUTION AND CAPACITY FADING.

TECHNIQUES USED

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MICROSCOPIC COBALT DISTRIBUTION IN NICKEL ACTIVE MATERIAL STUDIED USING THREE EDX TECHNIQUES:

- LINE SCAN
- POINT-BY-POINT ANALYSIS
- DOT MAPS

Storage Test History of Nickel Electrodes in a Ni/H_2 Cell.

Electrode ID	Storage history, days				Initial Cell Cap.*, Ah	Final Cell Cap.*	
	Trickle	Ni-prech	Vac.	H2-prech.		Ah	% of init.
Co-10	New containing 10% Co						
Co-7	New containing 7% Co						
Co-4	New containing 4% Co						
W/Al	New containing 10% Co						
BP1(10Co;26%;H2)	0	0	0	565	5.08	4.78	94.1
BP3 (7Co;26%;H2)	0	0	0	565	5.47	4.91	89.8
BP5 (4Co;26%;H2)	0	0	0	565	5.80	5.29	91.2
BP2 (10Co;26%;Ni)	0	146	142	277	4.95	5.74	116.0
BP4 (7Co;26%;Ni)	0	146	142	277	5.48	5.59	102.0
BP6 (4Co;26%;Ni)	0	146	142	277	5.89	5.35	90.8
BP8 (D/Al;31%;H2)	0	0	0	*229	4.85	2.64	54.4
BP9 (D/Al;31%;0)	229	0	*134	0	4.93	3.82	77.5
BP3b(W/Al;26%;H2)	0	0	0	*268	3.41	1.76	51.6
BP4b (D/Al;26%;0)	0	0	*268	0	4.96	3.77	76.0
BP4c(D/Al;26%;H2)	0	0	0	*268	4.90	1.98	40.4

* Second measurement capacity by C/10 rate charge for 18 h followed by discharge at C/2 rate to 1.0 V.

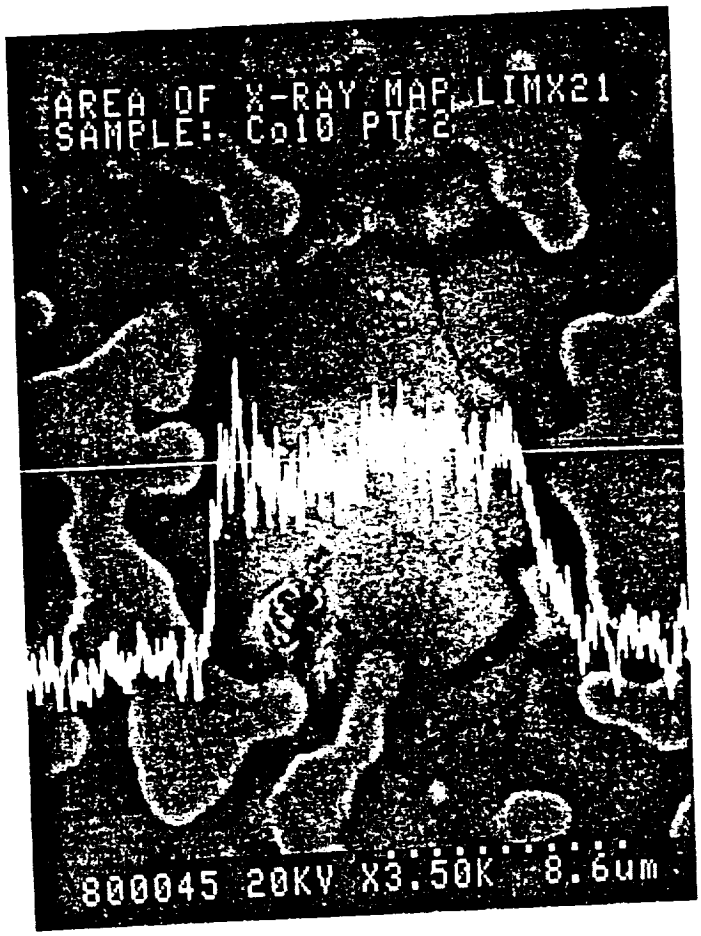

Fig. 1 SEM picture and EDX cobalt line scan result of metallographic sample of a new nickel electrode containing nominal 10% cobalt. Light colored islands in the picture are nickel metal particles and remaining grey area represent active material.

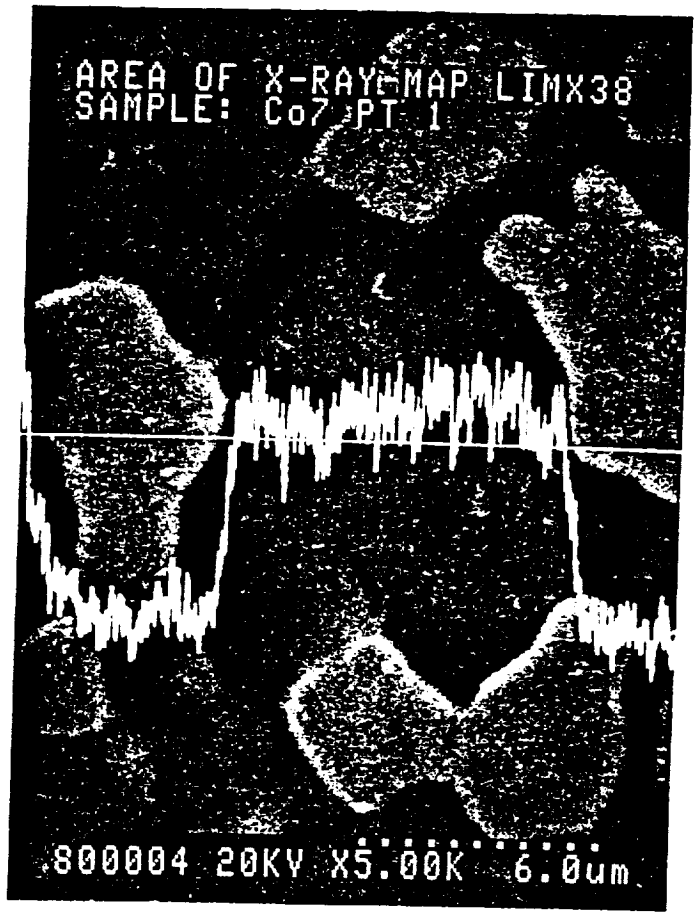

Fig. 2 SEM picture and EDX cobalt line scan result of metallographic sample of a new nickel electrode containing nominal 7% cobalt. Light colored islands in the picture are nickel metal particles and remaining grey area represent active material.

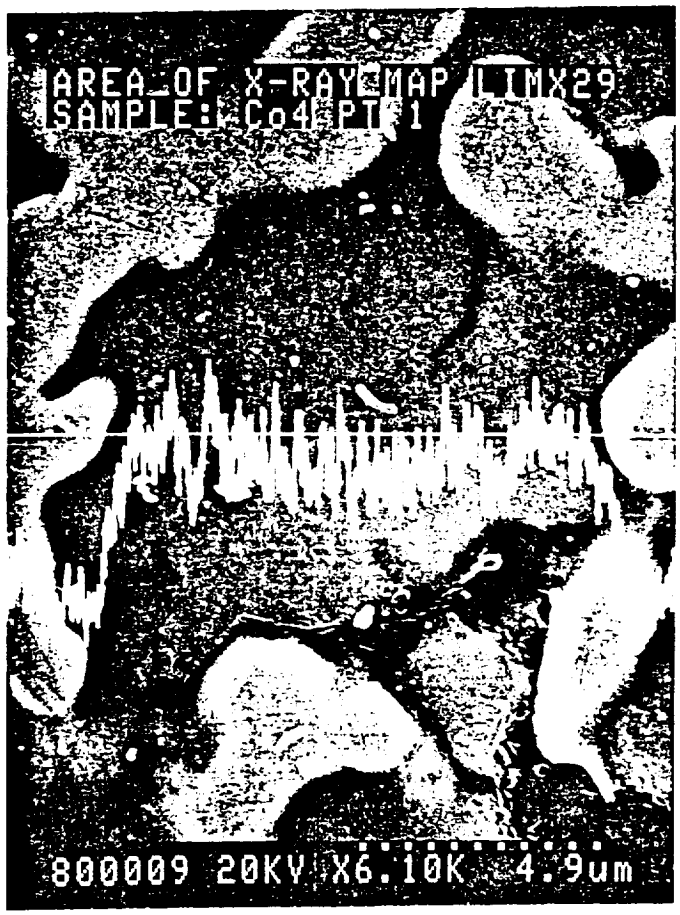

Fig. 3 SEM picture and EDX cobalt line scan result of metallographic sample of a new nickel electrode containing nominal 4% cobalt. Light colored islands in the picture are nickel metal particles and remaining grey area represent active material.

Fig. 4 SEM picture and EDX cobalt line scan result of metallographic sample of a nickel electrode from BP 8. Light colored islands in the picture are nickel metal particles and remaining grey area represent active material.

Fig. 5 SEM picture and EDX cobalt line scan result of metallographic sample of a nickel electrode from BP2. Light colored islands in the picture are nickel metal particles and remaining grey area represent active material.

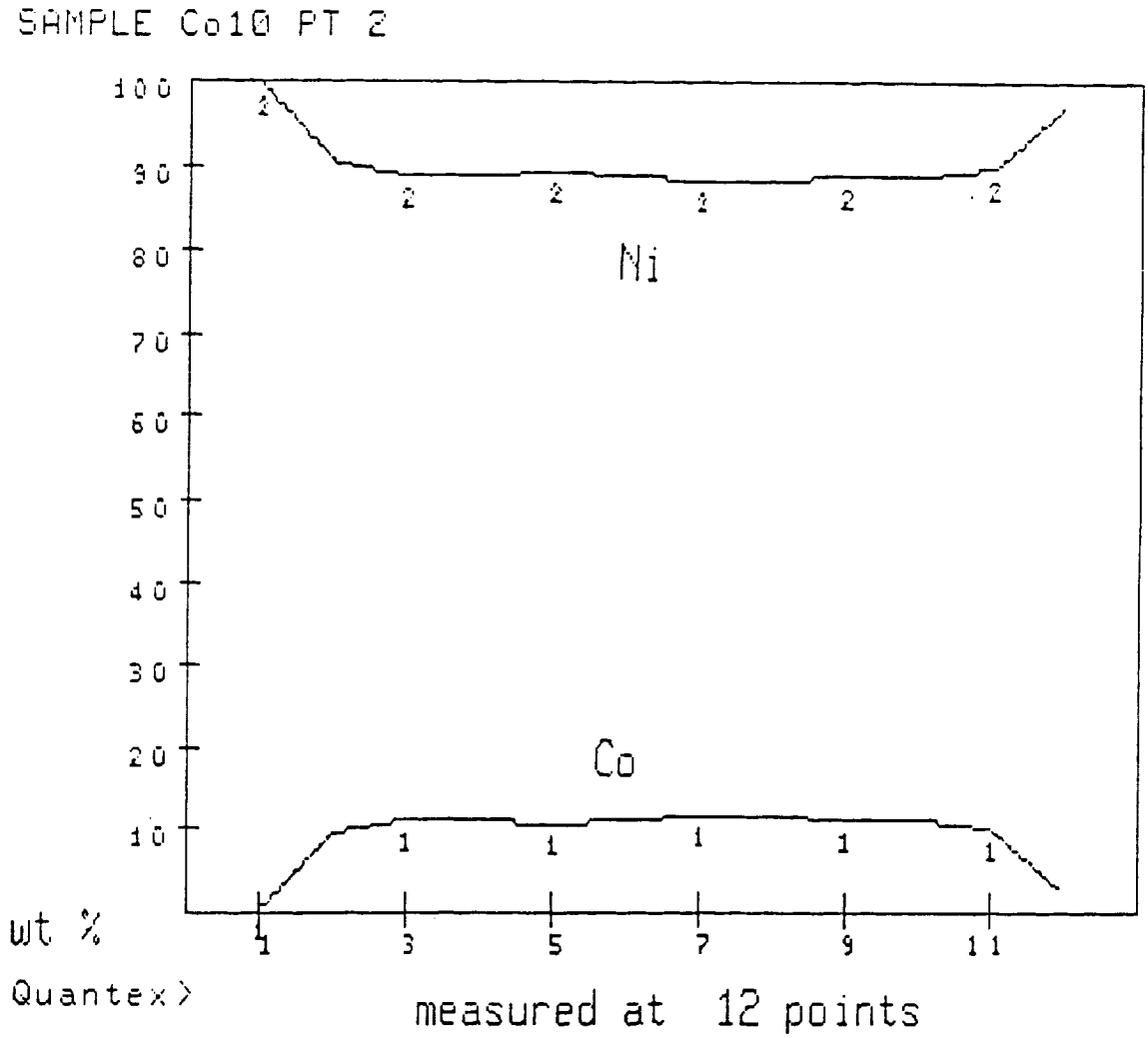

Fig. 6 Point-by-point analysis results of cobalt and nickel in the same sample and in the similar region as the EDX line scan in Fig. 1.

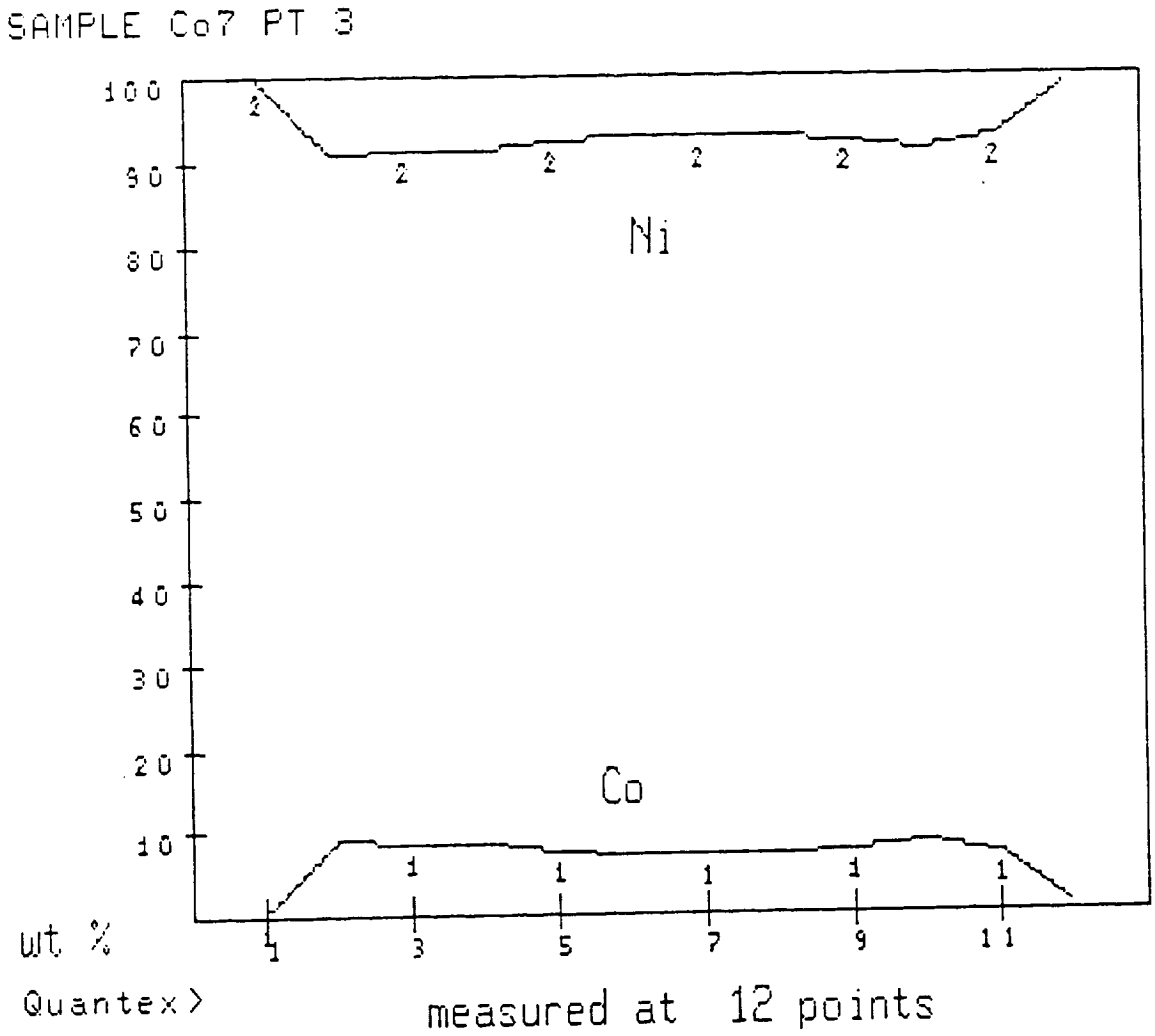

Fig. 4.7 Point-by-point analysis results of cobalt and nickel in the same sample and in the similar region as the EDX line scan in Fig. 2.

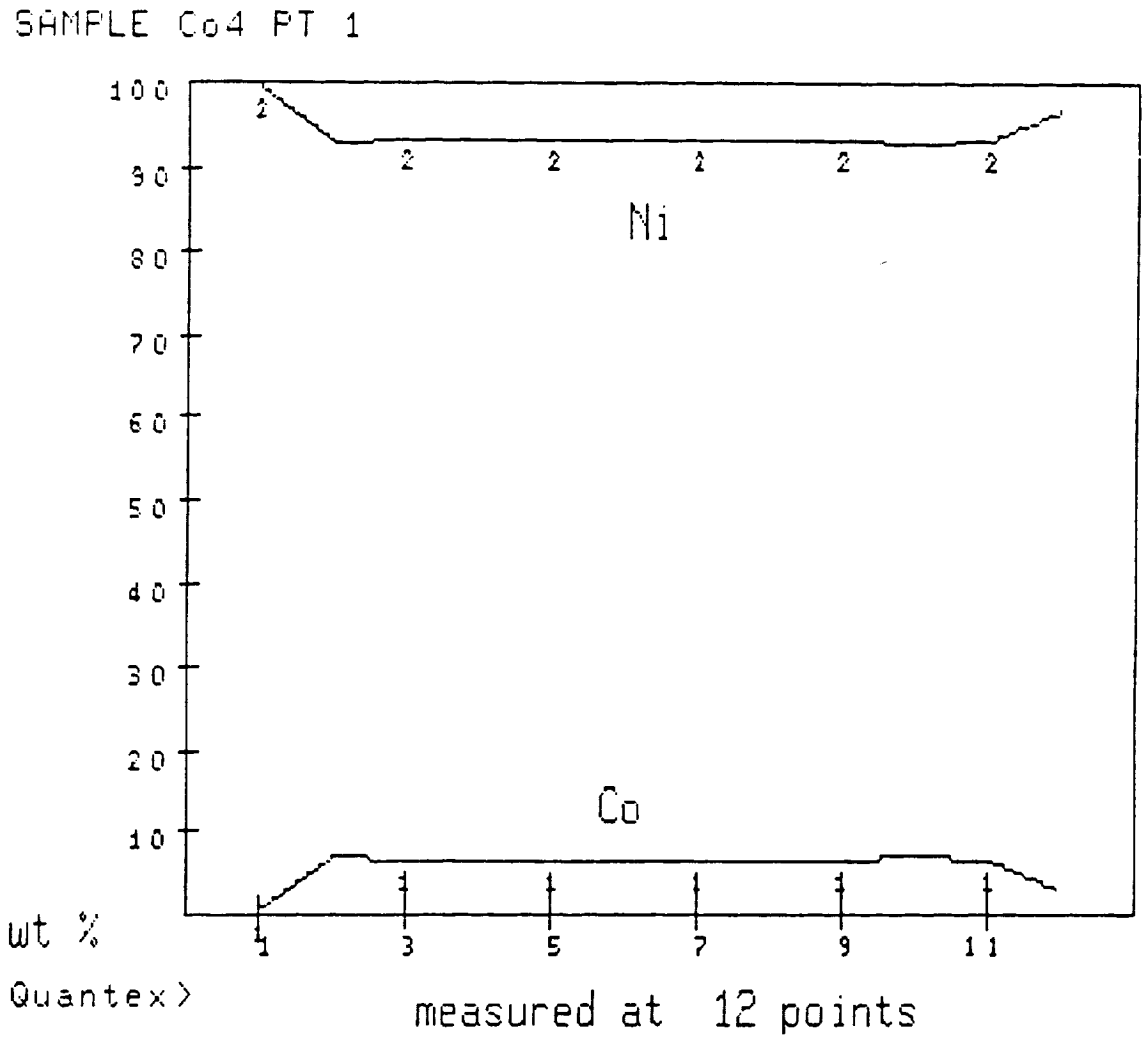

Fig. 4.8 Point-by-point analysis results of cobalt and nickel in the same sample and in the similar region as the EDX line scan in Fig. 3.

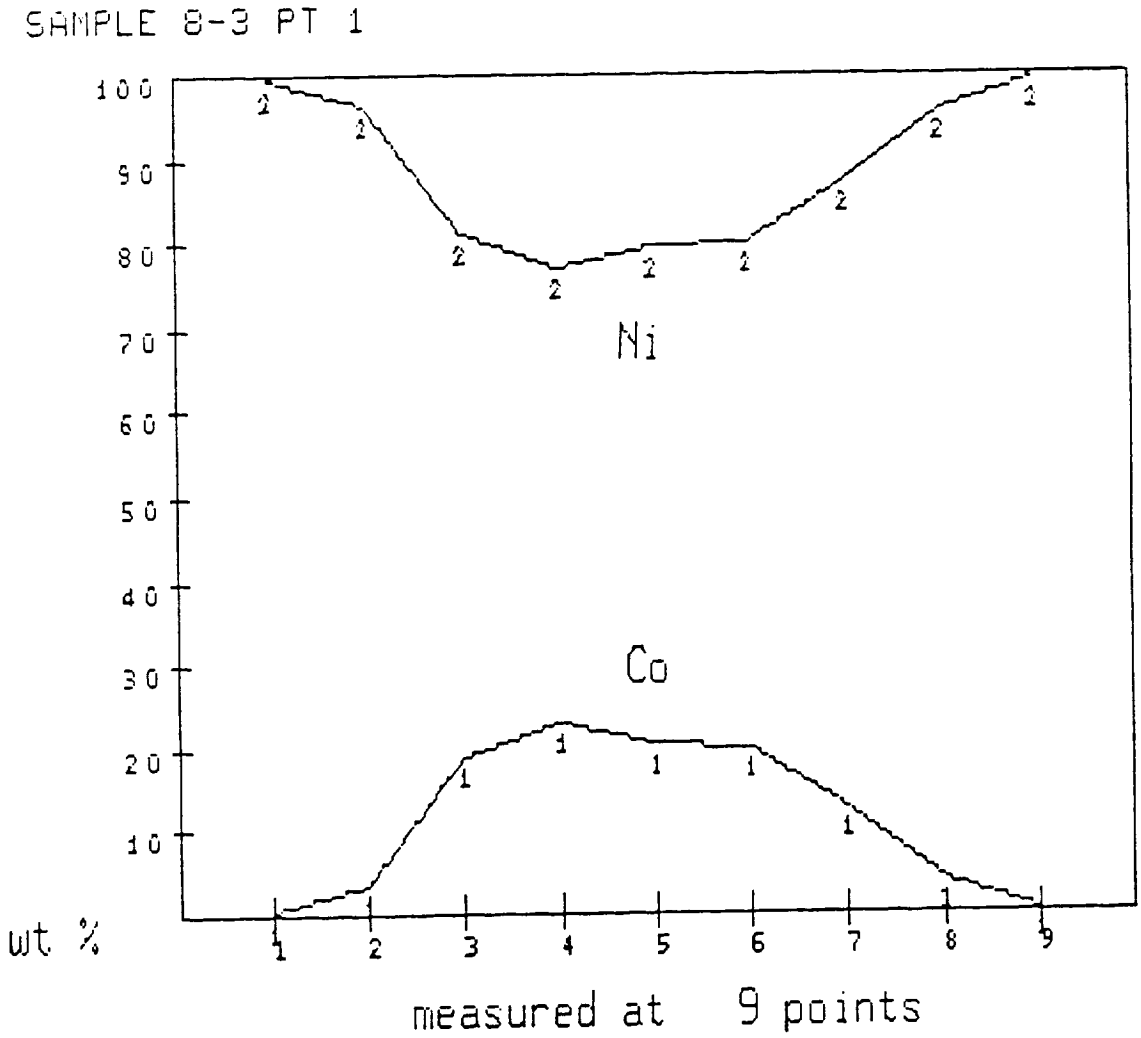

Fig. 9 Point-by-point analysis results of cobalt and nickel in the same sample and in the similar region as the EDX line scan in Fig. 4.

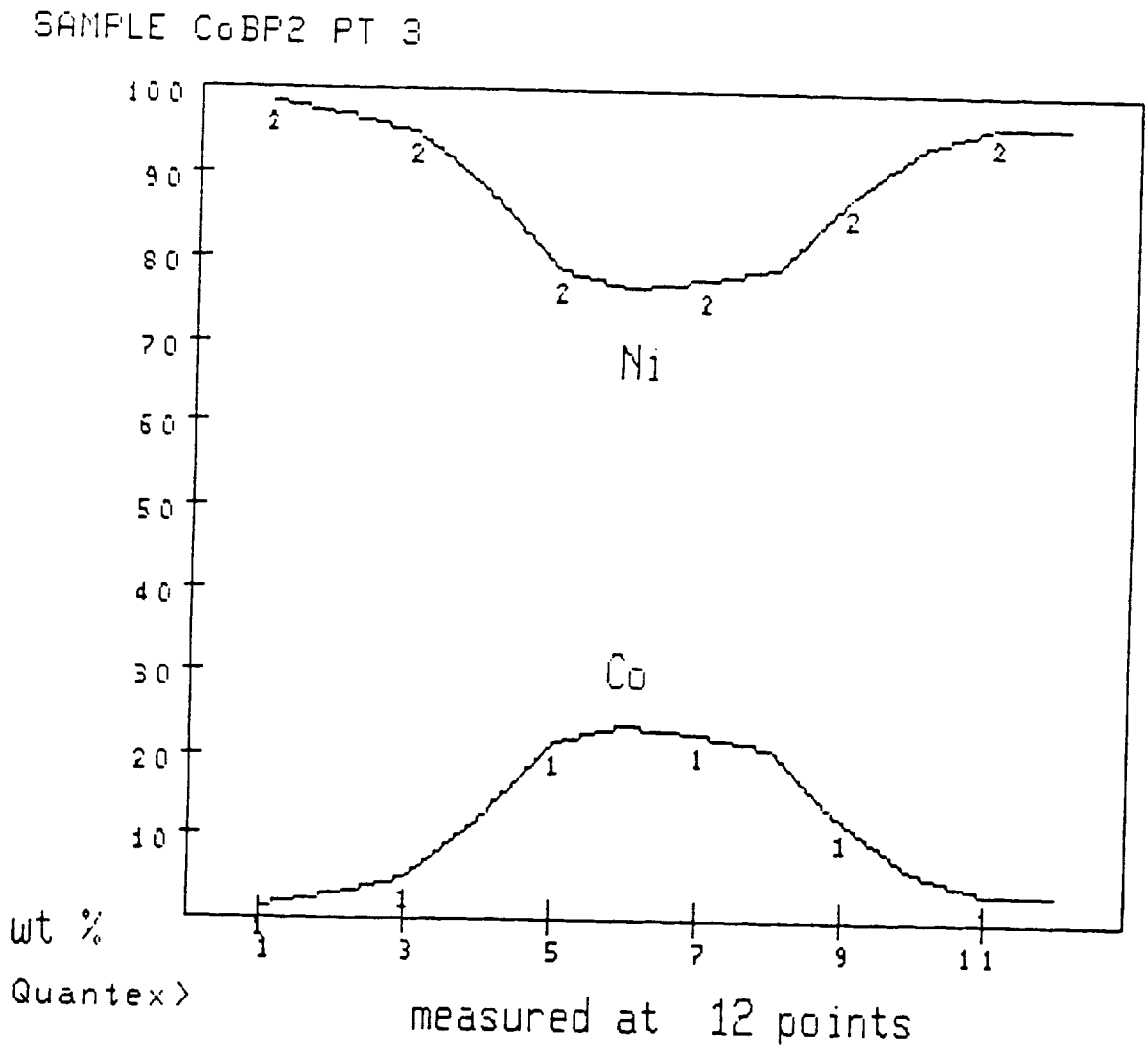

Fig. 10 Point-by-point analysis results of cobalt and nickel in the same sample and in the similar region as the EDX line scan in Fig. 5.

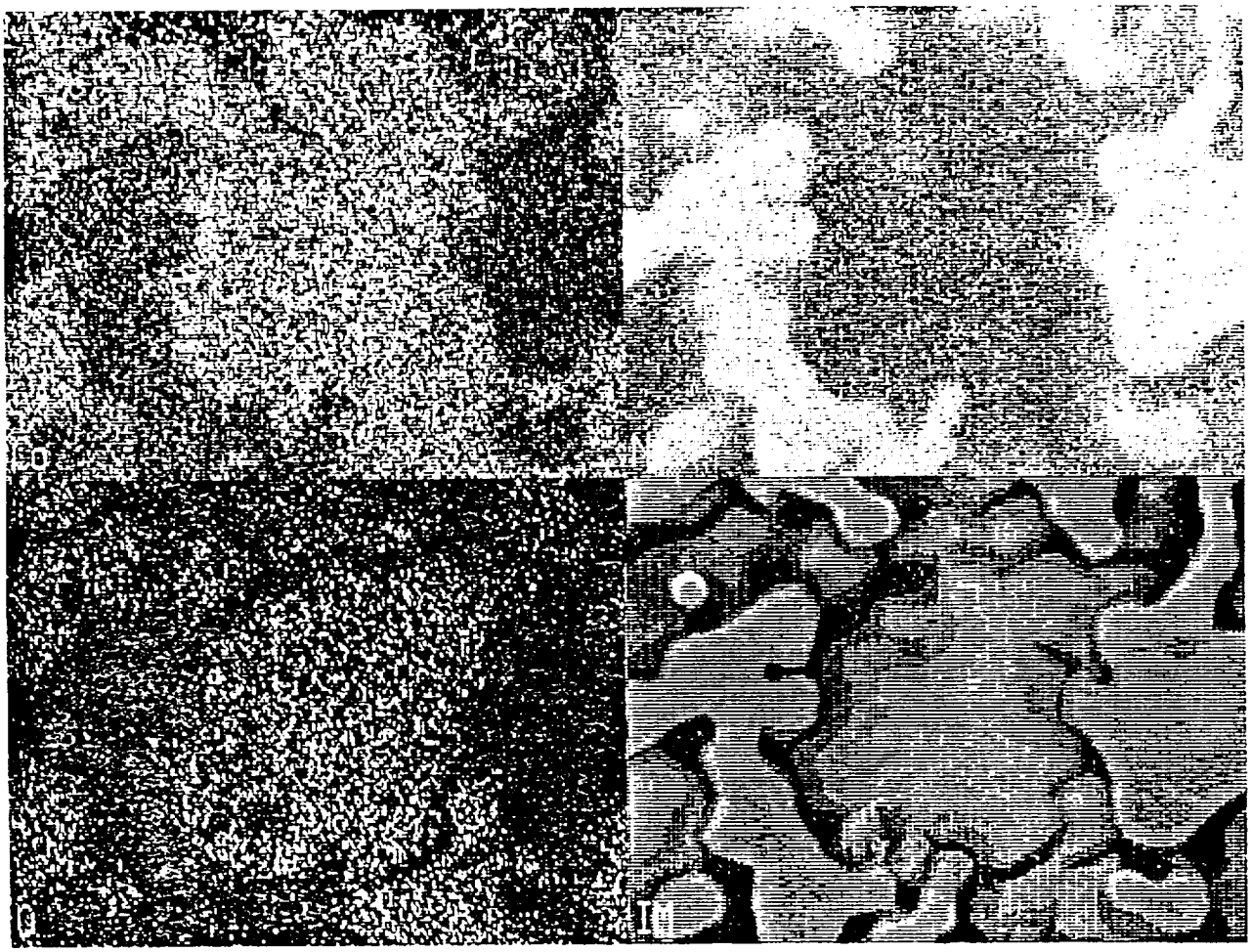

Fig. 11 EDX maps of Ni, Co and O in the same sample and in the similar region as in Fig. 1. Brightness of area represent the concentration of the corresponding elements.

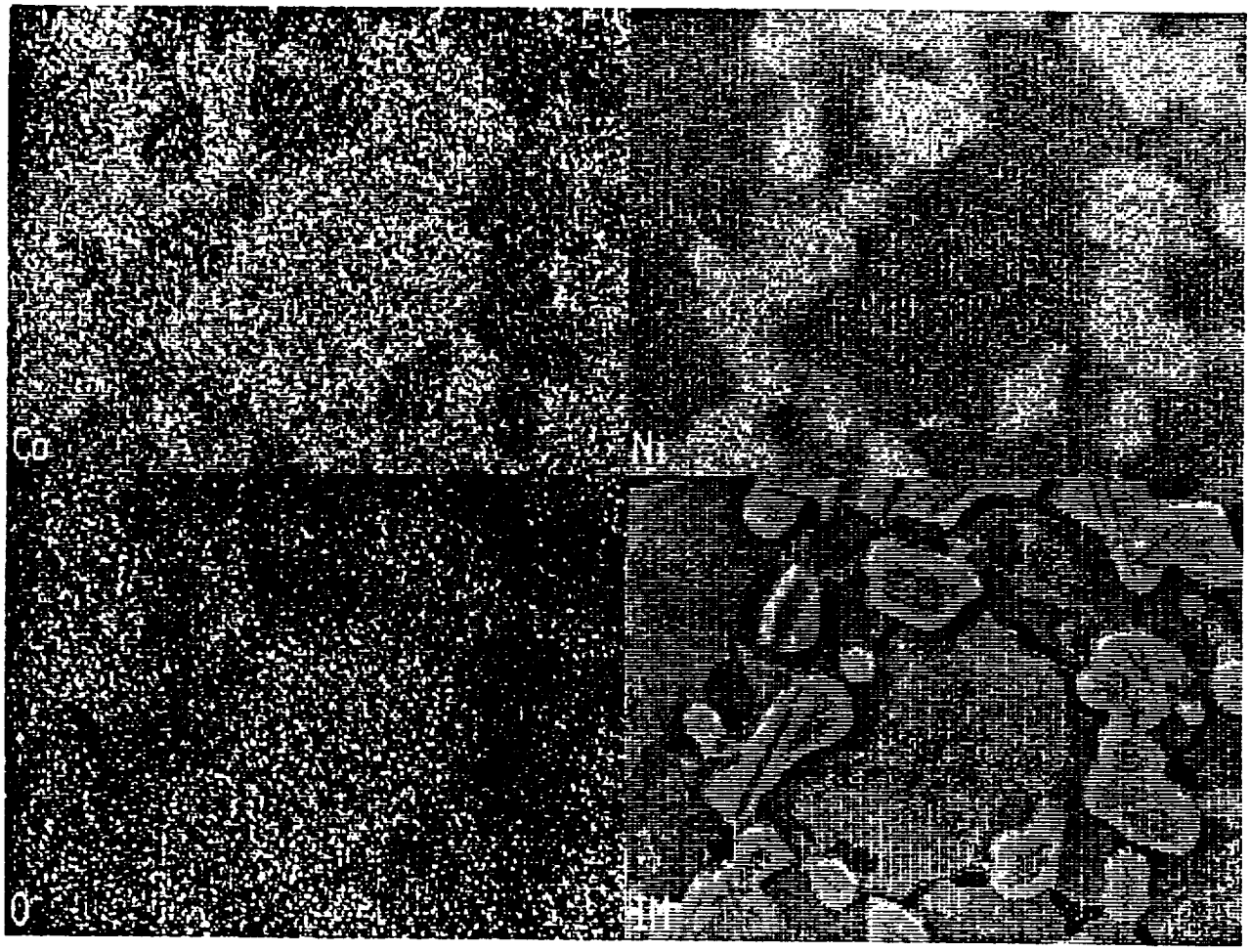

Fig. 12 EDX maps of Ni, Co and O in the same sample and in the similar region as in Fig. 4.2. Brightness of area represent the concentration of the corresponding elements.

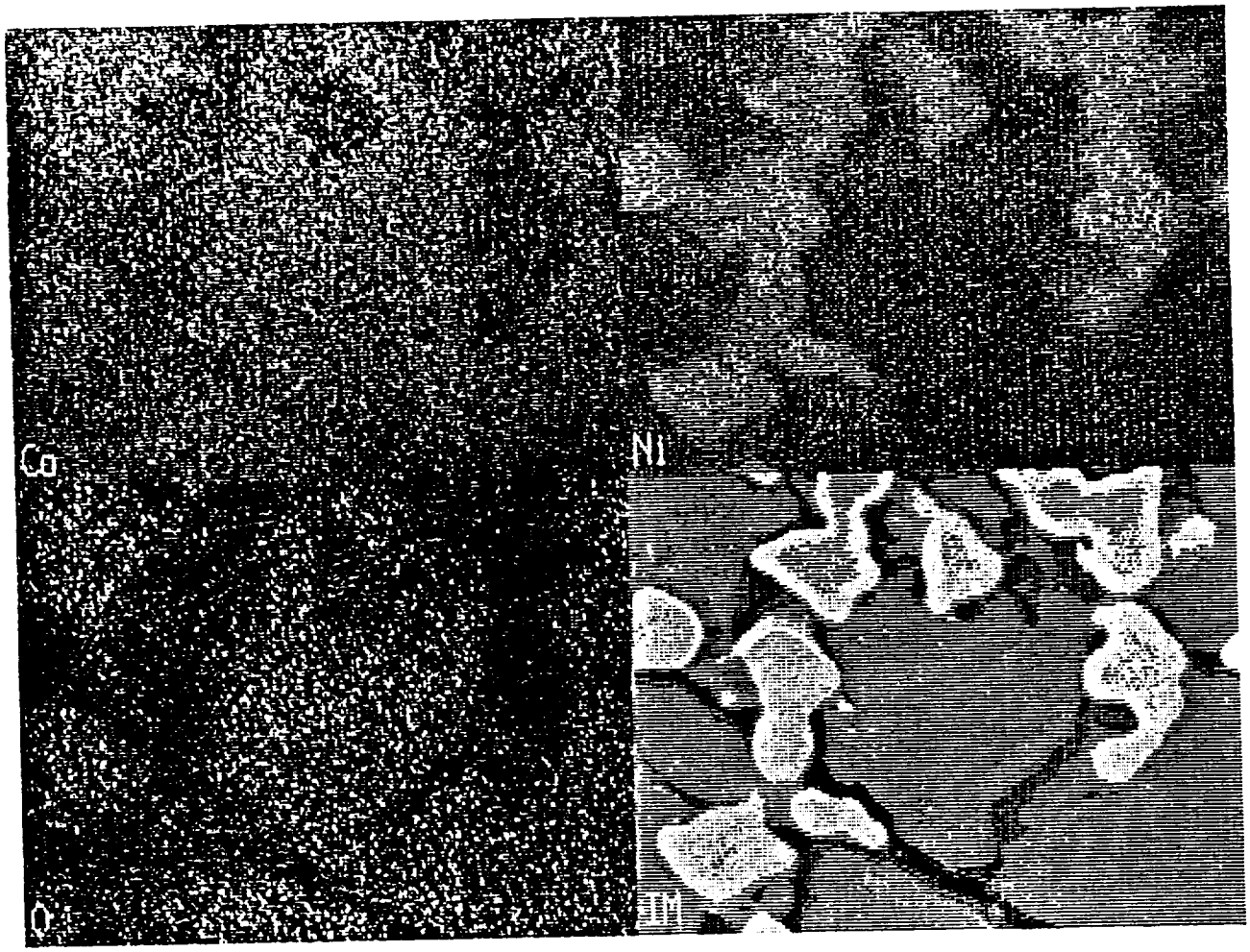

Fig. 13 EDX maps of Ni, Co and O in the same sample and in the similar region as in Fig. 4.3. Brightness of area represent the concentration of the corresponding elements.

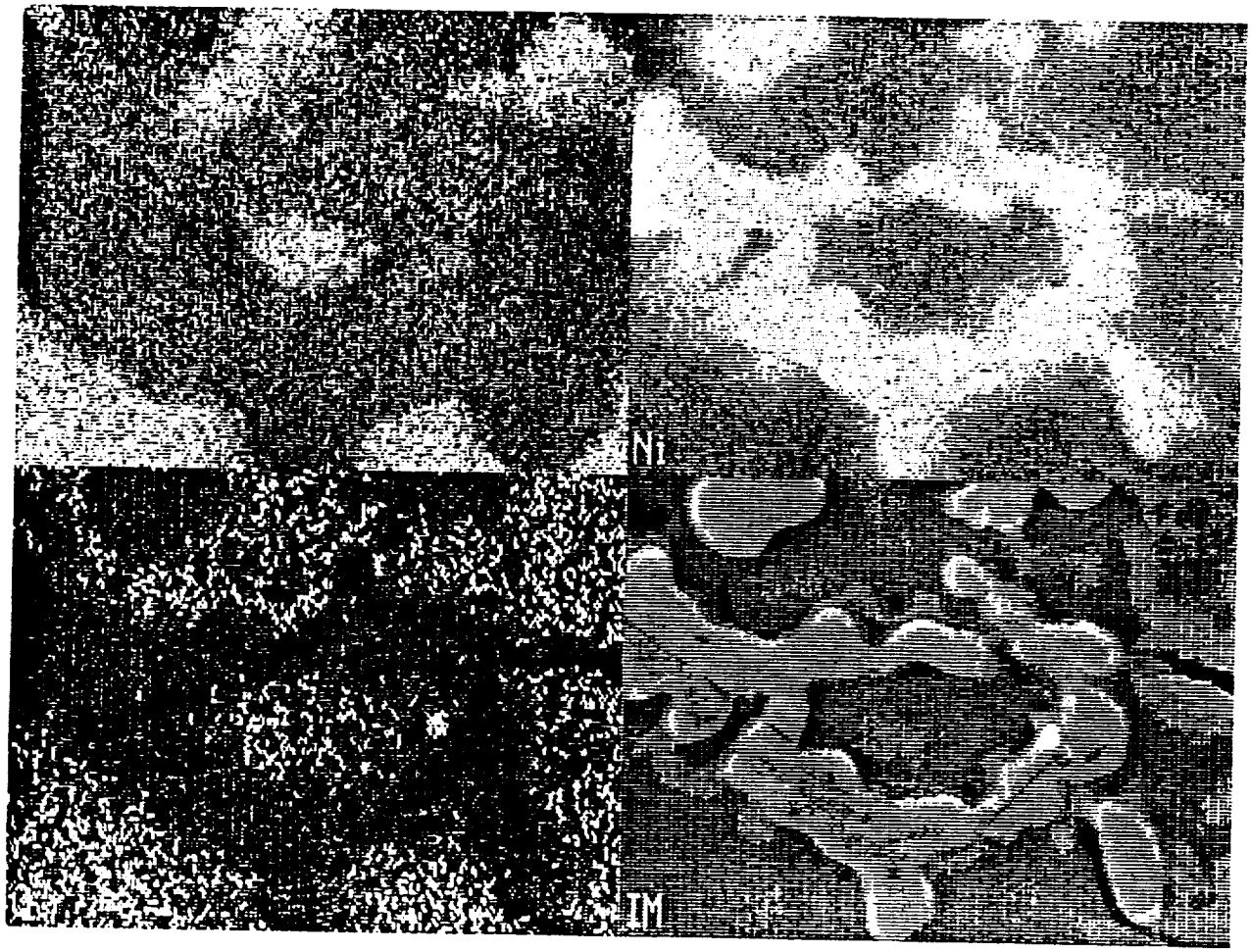

Fig. 14 EDX maps of Ni, Co and O in the same sample and in the similar region as in Fig. 4.4. Brightness of area represent the concentration of the corresponding elements.

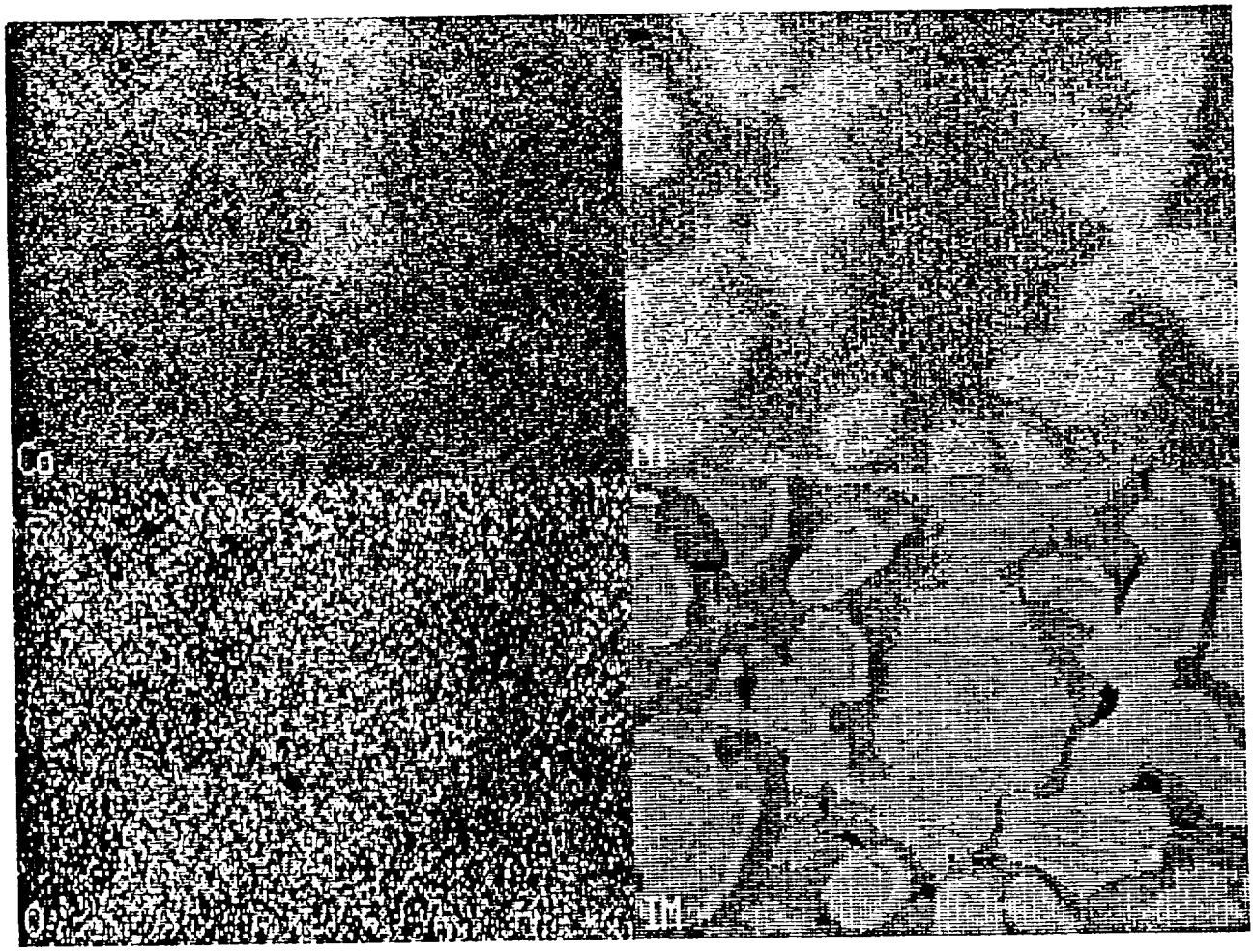

Fig. 15 EDX maps of Ni, Co and O in the same sample and in the similar region as in Fig. 4.5. Brightness of area represent the concentration of the corresponding elements.

SEM and EDX Observation Summary

Electrode ID	Dot-by-dot results Peak %Co	Dot-by-dot results Distribution	Line Scan Results	Dot mapping Results
Co-10	11~14	Flat	Flat	Match SEM
Co-7	7~11	Flat	Flat	Match SEM
Co-4	5~8	Flat	Flat	Match SEM
W/Al	10~14	Flat	Flat	Match SEM
BP1(10Co;26%;H2)	14~16	Flat	Flat	Co ≤ Ni ~ O
BP3 (7Co;26%;H2)	14~17	Sl. parabolic	Flat	Co ≤ Ni ~ O
BP5 (4Co;26%;H2)	8~14	Flat	Flat	Co ≤ Ni ~ O
BP2 (10Co;26%;Ni)	23~26	Parabolic	Parabolic	Co < Ni ~ O
BP4 (7Co;26%;Ni)	14~20	Sl. parabolic	Sl. parabolic	Co < Ni ~ O
BP6 (4Co;26%;Ni)	6~13	Sl. parabolic	Sl. parabolic	Co < Ni ~ O
BP8 (D/Al;31%;H2)	22~24	Parabolic	Parabolic	Co < Ni ~ O
BP9 (D/Al;31%;0)	14~19	Flat	Flat	Co < Ni ~ O
BP3b(W/Al;26%;H2)	22~26	Sl. parabolic	Sl. parabolic	Co < Ni ~ O
BP4b (D/Al;26%;0)	14~15	Flat	Flat	Co ≤ Ni ~ O
BP4c(D/Al;26%;H2)	20~21	Parabolic	Parabolic	Co < Ni ~ O

Comparison of Co Redistributions and Cell Storage History

Electrode ID	Capacity Fade % of init.	Peak Co, %	Severity of Co redistribution, 0~10*
BP1(10Co;26%;H2)	94.1	14~16	2
BP3 (7Co;26%;H2)	89.8	14~17	2
BP5 (4Co;26%;H2)	91.2	8~14	2
BP2 (10Co;26%;Ni)	116.0	23~26	10
BP4 (7Co;26%;Ni)	102.0	14~20	9
BP6 (4Co;26%;Ni)	90.8	6~13	8
BP8 (D/Al;31%;H2)	54.4	22~24	6
BP9 (D/Al;31%;0)	77.5	14~19	4
BP3b(W/Al;26%;H2)	51.6	22~26	4
BP4b (D/Al;26%;0)	76.0	14~15	2
BP4c(D/Al;26%;H2)	40.4	20~21	4

* Visual determination by the shrinkage of Co area from the dot maps.

CONCLUDING REMARKS

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- MIGRATION OF Co IN THE Ni ELECTRODE CONFIRMED
- THE DIRECTION OF MIGRATION IS FROM THE INTERFACE BETWEEN THE ACTIVE MATERIAL AND NICKEL METAL PARTICLES OF SINTERED PLAQUE INTO THE BULK OF ACTIVE MATERIAL.
- THERE WAS NO DIRECT CORRELATION BETWEEN CAPACITY FADING AND REDISTRIBUTION OF COBALT.
- PRACTICAL IMPLICATION: IT MIGHT BE A LITTLE EASIER TO DEVELOP A METHOD FOR CAPACITY RECOVERY THAN RECOVERING THE ORIGINAL DISTRIBUTION OF Co.