研究速報

On Two Modifications of Nickel Oxide

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According to the literatures⁽¹⁾ which arrived recently in Japan, H.P. Rooksby found that nickel oxide (NiO) has a rhombohedral structure. This fact agrees with our experiment⁽²⁾ which was carried out without knowing his result. The cubic modification (rock-salt type), as was believed before, was also found to exist in some cases of our experiment.

For samples were used chiefly the nickel oxides formed by heating nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in the air, and occasionally the oxide films formed on metallic nickel by heating were used. In order to determine the crystal structure, X-ray diffraction cameras of two types, Debye-Scherrer (dia.=5cm) and focussing back reflection (dia.=8cm), were employed, iron, cobalt, nickel and copper radiations being used for the {400}, {420}, {422} and {511} {333} reflections, respectively.

The difference of the new crystal structure from the rocksalt type was observed as splitting of

Fig. 1 Microphotometer Curves of Diffraction Lines of the Oxide Obtained by Heating Nitrate at 1350°C for an Hour.

These values are consistent with Rooksby's results, $a=2.945\text{\AA}$, $\alpha=60^\circ 4.2'$ at 20°C.

Thus the deviation from the cubic structure is very slight. This fact indicates that both structures are not radically different, but that one of them may be formed from the other by a slight modification of the lattice probably originating from the lattice defects characteristic to the oxide.

In some cases, the lines were only diffused but not splitted, and the structure in these cases can be interpreted to be cubic. Which of the two modifications cubic or rhombohedral, is produced depends upon the condition of formation. In the case of nitrate, it was somewhat complicated and has not yet been determined. In the case of metallic nickel, it was comparatively simple. When the oxide film was very thin and the diffusion of nickel atoms from the substratum into the film was possible to take place, the structure of the oxide was cubic; but when the film became thick, its structure was different from the cubic, that is, a new separated line did appear. The thicker the oxide film, the stronger became the intensity of this separated line, and thus it was strongest when the diffusion was perfectly interrupted owing to splitting of the oxide film from the substratum during the

diffraction lines of the latter. The results of observation about the oxide obtained by heating nickel nitrate at 1350°C for an hour are given in Table 1 and Fig. 1, from which it is found that the structure is face-centered rhombohedral, the lattice constants being $a=4.16768 \pm 0.00004\text{\AA}$, $\alpha=90^\circ 3.8' \pm 0.3'$ at 9°C. This structure can also be regarded as simple rhombohedral, $a=2.9454 \pm 0.0002\text{\AA}$, $\alpha=60^\circ 4.4' \pm 0.4'$ at 9°C.

Fig. 2 Microphotometer Curves of {422} Lines of the Oxides Obtained by Heating Ni-Foils (0.01mm in Thickness) at 1300°C.

(1) *Chim. Abst.*, 38(1944), 2886; H. P. Rooksby, *Nature*, 160 (1947), July 5.

The present writers, unfortunately, have no opportunity to receive his detailed report: H. P. Rooksby, *Nature*, 152(1943), 304.

(2) A paper was read before the meeting of Nippon Kinzoku Gakkai (the Japan Institute of Metals) held at Tokyo in April, 1948. The outline is written in N. K. G. 12(1948), No.1, 12. The first report, "On the Lattice Defect in Nickel Oxide", was presented to SCAP on April 22, 1948.

oxidation or to the complete consumption of metallic nickel by the oxidation. In spite of such intensity change, the amount of the separation was not increased but was rather decreased (Table 2 and Fig. 2).

Table 1 Nickel Oxide from Nitrate

{hkl}	No. of Lines	Intensity Ratio	Spacing (Å)	Temperature (°C)	Separation by $K_{\alpha 1}$
{400}	1	—	1.04189 ± 4	7~12	—
{420}	2	1 : 1	0.9324 ± 2 0.9316 ± 2	21	10.0'
{422}	2	3 : 1	0.85088 ± 2 0.84993 ± 7	9	16.9'
{511}{333}	1	—	0.80224 ± 3	14	—

Table 2 {422} Lines of the Oxides Obtained by Heating

Nickel Foils (0.01 mm in Thickness) at 1300°C.

Heating Period (min)	Spacing (Å) for		Intensity Ratio	Sharpness	Degree of Consumption
	Low θ	High θ			
3	0.8514	0.8470	20 : 1	Very Diff.	Very Little
5	0.8513	0.8500	10 : 1	Diffuse	Little
10	0.8512	0.8502	5 : 1	Slightly Diff.	Partially
40	0.8511	0.8502	3 : 1	Sharp	Completely
60	0.8511	0.8502	3 : 1	Sharp	Completely

The details will be shortly published in the Memorial of the Institute of Scientific and Industrial Research of the Ôsaka University.

研 究

鐵-アルミニウム合金に於ける 規則格子の本性に關する一考察

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Hiroshi Sato : A Note on the Nature of the Superlattice Formation in Fe-Al Alloys. Many anomalous physical properties are experimentally observed during the superlattice formation in Fe-Al alloys. Such anomalies have not yet been completely explained in spite of extensive researches.

According to the author's investigation about the ferromagnetic superlattice, such anomalies must be due to the interrelations between the superlattice formation and the origination of the spontaneous magnetization. The origin of the singular properties of Fe-Al system can also be reduced to this fundamental idea.

With this general point of view, the phase diagram concerning superlattice formation in these binary alloys are reviewed.

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I. 緒 論

鐵-アルミニウム合金中の體心立方格子範圍に於て FeAl, Fe₃Al なる規則格子が存在することは、既に以前より認められて居り、そのX線的研究は特に Bradley, Jay⁽¹⁾ 及び

大澤, 村田⁽²⁾等の手に依つてなされ、又その比熱、磁氣等との關係については Sykes, Evans⁽³⁾等に依り研究され、比較的良く研究された規則格子の一つである。又 Fe₃Al 近傍の合金が種々磁性材料的に重要な性質を示すので更に増

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(1) A. J. Bradley, A. H. Jay, Proc. Roy. Soc. A., **136** (1932), 210; J. Iron and Steel Inst., **125** (1932), 339.

(2) 大澤, 村田, 本誌, **5** (1941), 259.

(3) C. Sykes, J. W. Bamfylde; J. Iron and Steel Inst., **130** (1934), 389.

C. Sykes, H. Evans; Proc. Roy. Soc. A., **145** (1934), 529; J. Iron and Steel Inst., **131** (1935), 225.