BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 3349—3350 (1976)

Observation of the Scale Formed on Nickel in Nitrogen Oxide

Yoshio TAKASU, Shun-ichi MARU, and Yoshiharu MATSUDA

Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755

(Received May 4, 1976)

Synopsis. The state of the scale formed on nickel in nitrogen oxide was examined. Its characteristics are summarized as follows: (1) remarkable oxidation of the grain boundary, (2) the formation of a large amount of lattice defects, and (3) unequal oxidation behaviors for the various crystal planes.

Concerning reactions of metals with nitrogen oxide, some previous work has been reported.[1,2] Recently, the oxidation of nickel in nitrogen oxide has been found to obey the linear rate law with a faster reaction rate than that in oxygen.[3] In this study, the state of these scales was observed.

Measurements of oxidation rates or sample preparation were carried out with a high vacuum apparatus. Nitrogen oxide of a high purity in a glass cylinder from the *Takachiho Co.* was used without further purification. The oxygen was prepared by bulb-to-bulb distillation from a commercial cylinder at liquid nitrogen temperature. Test sample (99.98% Ni) were 1.0×1.0 cm^2 in area and have a thickness of 0.0050 cm. They were annealed *in vacuo* at 800 °C for 2 h, electropolished in a mixed acid (H_2SO_4–H_3PO_4–H_2O),[4] and rinsed in distilled water. The mean size of the grains was 20 μm.

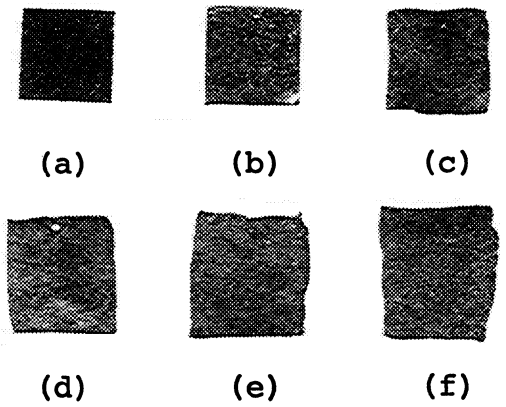

Fig. 1. Photographs of the specimens oxidized in nitrogen oxide,
where, (a): non-oxidized (electropolished), (b), (c), (d), (e), and (f): oxidized in 10 Torr of NO at 700 °C for 5, 10, 25, 40, and 90 min, respectively.

Figure 1 shows the size and shape of the specimens oxidized in nitrogen oxide, where (a) is a non-oxidized specimen and (b), (c), (d), (e), and (f) are specimens oxidized in 10 Torr of nitrogen oxide at 700 °C for 5, 10, 25, 40, and 90 min, respectively. As shown in this figure, the specimen increased in size and changed shape during the oxidation. The relation between the size of the specimen and the oxidation time was shown in Fig. 2. Since the specimens were curled or warped a little by the oxidation, the value r, the ratio of the mean length of each side of the specimen to that of a non-oxidized one, contained a noticeable error. Obviously, the r value increased rapidly during the oxidation. That is, the specimen oxidized in nitrogen oxide was very coarse and bulky. Moreover, even specimens oxidized to about 14 percent (P_{NO}=10 Torr, 700 °C, 10 min) at the early stage of the oxidation process were very brittle. These findings should suggest that preferential oxidation occured along grain boundary and the entire grain boundary was oxidized within less than 10 min. Then, all the scales oxidized in nitrogen oxide in this study were identified to be NiO using X-ray diffractometry. No nitrogen peak was found in the IMA (Ion-Micro-Analysis) spectra of these scales.[3] However, their color was grayish black, so that a large quantity of lattice defects, probably cation vacancies,[5] should be present in them. On the other hand, the scale formed in an oxygen atmosphere was greenish and dense. For example, even specimens oxidized at about 14 percent (P_{O_2}=10 Torr, 700 °C, 180 min) were not brittle and their size did not change in comparison with that prior to oxidation.

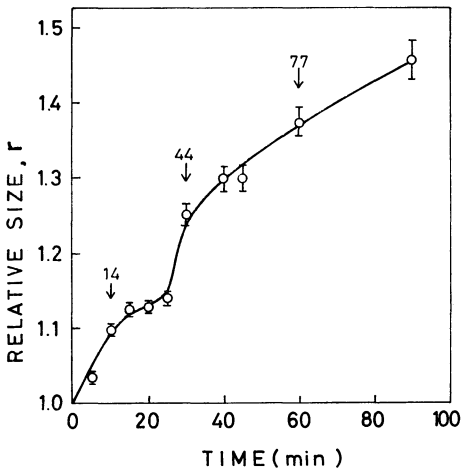

Fig. 2. Relation between the size of specimen and oxidation time.
The numerical values shown in this figure signify the percent of nickel oxidized.

Figure 3 represents the optical metallographs of scales formed in nitrogen oxide and oxygen, where (a) is a non-oxidized specimen, (b) is a specimen oxidized in 10 Torr of oxygen at 700 °C for 180 min, and (c), (d), and (e) are specimens oxidized in 10 Toor of nitrogen oxide at 700 °C for 5, 10, and 40 min, respectively. The surface oxidized in oxygen, (b), was relatively uniform in this photograph, while those in nitrogen oxide (c, d, and e) were not uniform. Namely, in the latter case, the grain boundaries were extremely swollen

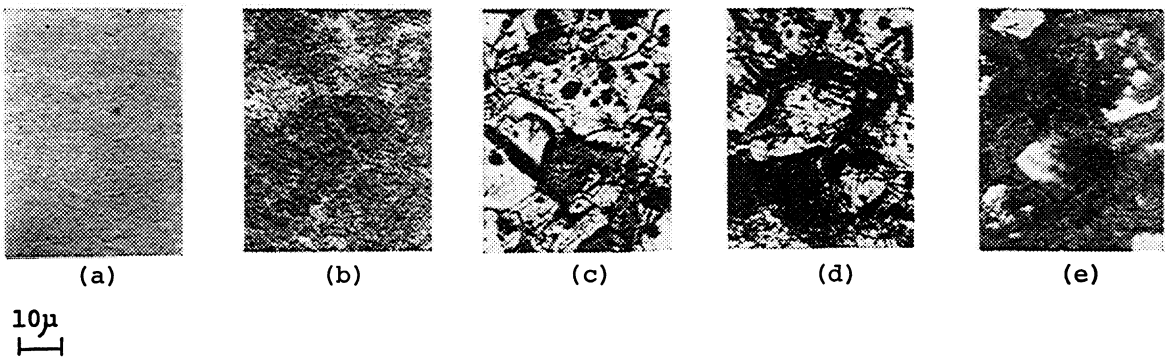

Fig. 3. Optical metallographs of the specimen oxidized in nitrogen oxide or oxygen, where, (a): non-oxidized (electropolished),
(b): oxidized in 10 Torr of O_2 at 700 °C for 180 min,
(c), (d), (e), and (f): oxidized in 10 Torr of NO at 700 °C for 5, 10, and 40 min, respectively.

during the oxidation. Moreover, the state of a few grains became very coarse (black in the photograph), while others did not. As described above, the main characteristics of the state of the scale formed on nickel in nitrogen oxide can be summarized as follows: (1) remarkable oxidation of the grain boundary, which caused the specimen to become coarse, bulky, and brittle, (2) the formation of a large amount of lattice defects, and (3) unequal oxidation behavior among the various crystal planes.

These findings appeared in the rapid diffusion rate of nickel ions through the bulky oxide layer with a large amount of lattice defects and, at the same time, agree with previous results and estimations[3] that the oxidation of nickel in nitrogen oxide was governed by a surface reaction in spite of its rapid oxidation obeying the linear rate law.

References

1) E. Schröder and G. Tamman, *Z. Anorg. Allg. Chem.*, **28**, 179 (1923).
2) M. Faber, A. J. Darnell, and D. M. Ehrenberg, *J. Electrochem. Soc.*, **102**, 446 (1955).
3) Y. Takasu, Y. Matsuda, S. Maru, and N. Hayashi, *Nature (London)*, **255**, 544 (1975).
4) Y. Takasu, H. Shimizu, S. Maru, M. Tomori, and Y. Matsuda, *Corros. Sci.*, **16**, 159 (1976).
5) R. Newman and R. M. Chrenko, *Phys. Rev.*, **144**, 1507 (1959).