

Electron Diffraction Study on Nickel Surfaces Tarnished in the Course of Heat-Treatment in Hydrogen

著者	OGAWA Shiro, WATANABE Denjiro
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	4
page range	41-47
year	1952
URL	http://hdl.handle.net/10097/26484

Electron Diffraction Study on Nickel Surfaces Tarnished in the Course of Heat-Treatment in Hydrogen*

Shiro OGAWA and Denjiro WATANABE

The Research Institute for Iron, Steel and Other Metals

(Received November 20, 1951)

Synopsis

When nickel plates for vacuum tubes are annealed in hydrogen gas at 900~1000°C in the process of production, their surfaces often tarnish and show milk-white appearance, which considerably lowers their commercial value. In order to infer the cause of this tarnishing, six kinds of plates were selected and their surfaces were examined by electron diffraction after heat-treatment. Milk-white surfaces generally gave diffuse rings which were entirely different from the nickel pattern. Three specimens did not alter their appearances after the treatment. One of them gave a few diffuse rings and elongated spots, while the other two, one of which was made in U. S. A., yielded many comparatively sharp rings. According to our analyses, the rings obtained from the two milk-white surfaces were due to (Mg, Ca) SiO₃ and NiO, and those from the two lustrous surfaces belonged to nickel and Mg₂SiO₄ in one case and to nickel, MnO, MnS and NiO or to nickel, Mg₂SiO₄, MnO and NiO in the other case. From the fact that a greater part of diffraction rings of the milk-white surfaces could be explained as being due to (Mg, Ca) SiO₃, it was concluded that the tarnishing was due to silicates of light metals. Silicates like (Mg, Ca) SiO₃ and Mg₂SiO₄ must be removed during melting, and if a small quantity of them remains and even though disperses over the whole material, it may gradually aggregate in grain boundaries at the heat-treatment, which finally causes the tarnishing of surfaces.

I. Introduction

When nickel plates for vacuum tubes are annealed in hydrogen gas at 900~1000°C, after they have been rolled, the surfaces of some of the plates tarnish and show milk-white appearance. This is often the case with the plates produced after the war and lowers their commercial value. Though, in manufacturing factories, some measures have, therefore, been taken with a certain success, it remains absolutely necessary for its fundamental prevention to clarify the nature of the tarnishing. The present work was carried out to offer an aid to prevent them from tarnishing by finding out its cause by the use of electron diffraction.

II. Experimental method

Six different kinds of nickel plates, about 0.1 mm in thickness, were used. The results of the examination of tarnishing and the chemically analyzed compositions are shown in Table 1. The plates were heat-treated at 900°C for from 20 minutes to one hour in hydrogen current dehydrated by H₂SO₄ and CaCl₂. In the meantime, a comparison was made between the results after heating of the rolled plates and of those etched previously by concentrated hydrochloric acid. The electron diffraction

* The 662nd report of the Research Institute for Iron, Steel and Other Metals.

Table 1.

Specimen	Deoxidizer	Appearance	Fe	Mn	Si	C	S	Ca	Mg
A 1999 (ingot)	—	—	0.05	0.09	0.04	0.01	—	—	—
(plate)	—	very tarnished	—	0.11	0.12	0.01	0.011	0.005	0.077
No. 1 (plate)	Mn 0.5	tarnished	0.12	—	0.042	—	0.0:0	—	0.27
No. 7 (plate)	Mn 0.5 Mg 0.4	lustrous	0.14	0.38	0.035	—	0.022	—	0.009
No. 8 (plate)	Si 0.5 Mg 0.1	tarnished	0.20	—	0.38	—	0.022	—	0.045
No. A (plate)	(made in U. S. A.)	lustrous	—	0.12	0.011	—	—	—	—
A 2017 (plate)	—	lustrous	0.21	0.25	0.05	0.01	—	—	—

tion camera⁽¹⁾ was of hot cathode type and the accelerating voltage was about 40 KV. and camera length 505 mm.

III. Result of experiment

The results of the analyses of the electron diffraction patterns obtained from the above specimens are shown in the left half of Table II. From these results, it will be seen that no considerable difference is observable between the plates heat-treated directly and those etched before the treatment. Many of the specimens showed polycrystalline diffraction rings, the lattice spacings of which are shown in Table 2. The column A1999 indicates the averaged results of eight samples with the strongest tarnish. Their diffraction rings were almost all diffused, in which no ring caused by nickel was observable, whereas the rings of large intensity were seen at small diffraction angles. The column No. 1 shows that the specimens with milk-white tarnish showed no ring at small diffraction angles, whereas the other rings were almost similar to those of A1999 in intensity and spacing. The column No 7 indicates that those without tarnish showed a few diffuse rings and spots remarkably elongated towards the shadow edge (the intersection between the elongation of the specimen surface and the photographic plate). From this fact it seems that flat and comparatively large crystals existed on the surfaces of these specimens. The spots and rings, however, were too few in number to analyze the surface products satisfactorily. In column No. 8 are arranged those specimens with tarnish which showed scarcely any ring and spot in the diffraction photographs except only one halo, or surface conditions of which apparently seemed to be unfit for the electron diffraction study, in other words, on the surfaces of which the roughness seemed so considerable that the transmission of electron due only to elastic scattering was checked. No. A (made in U. S. A.), together with A2017, was among the non-tarnishing ones and showed considerably lustrous surface even after the heat-treatment. When these specimens were examined by electron diffraction, the patterns showed many rings comparatively sharp, in which were seen strong rings of nickel and of other different materials. In other words, though the condition of the surfaces apparently

(1) S. Ogawa and D. Watanabe: Sci. Rep. RITU, A 2 (1950), 462.

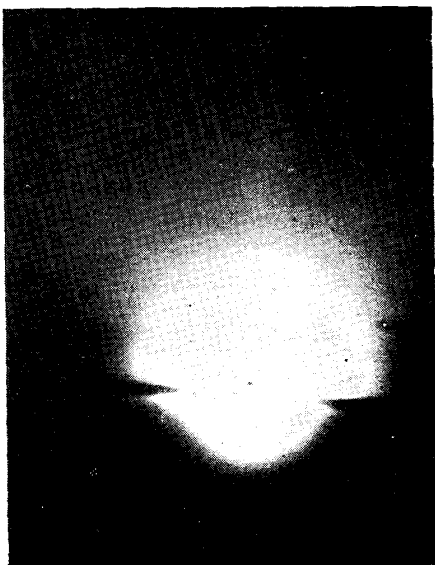


Fig. 1. A 1999
Heat-treated at 900°C
for 1 hr.
Milk-white appearance

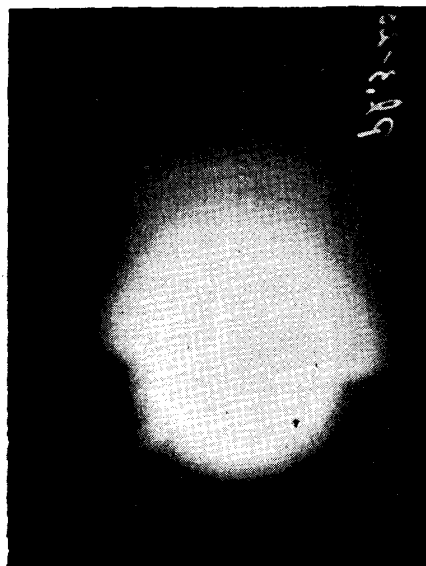


Fig. 2. No. 1
Heat-treated at 900°C
for 1 hr.
A little milk-white appearance

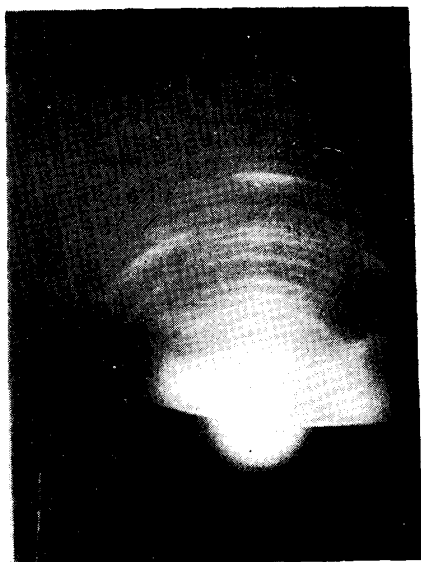


Fig. 3. No. A
Heat-treated at 900°C
for 1 hr.
Lustrous.



Fig. 4. A 2017
Heat-treated at 900°C
for 1 hr.
Lustrous.

Table 2.

Observed lattice spacings						Lattice spacings of reference substances measured by X-ray.							
A 1999 milk-white	No. 1 a little milk-white	No. 7 lustrous	No. 8 milk-white	No. A lustrous	A 2017 lustrous	A 2017 lustrous	(Mg, Ca) SiO ₃	Mg ₃ SiO ₄	(Mg, Fe) ₂ SiO ₄	Ni	NiO	MnO	MnS MgS
2.99 m		2.99 m		2.99 m			3.24 mw	3.49 vw	3.64 s				3.01 s
2.88 w	elongated		only one				2.99 vs	3.00 w	2.90 w				
2.55 s	2.56 w	2.77 m	diffuse	2.58 vw	2.80 w		2.90 vw	2.78 s	2.54 s			2.56 s	2.61 vs
2.36 w	and	2.50 vs	ring	2.40 w	2.47 vs		2.53 s	2.50 vs					
2.31 s	2.31 w	2.25 s		2.23 vw	2.23 m		2.44 vw	2.35 vw			2.37 w		
2.19 v.w		2.04 vs		2.01 vw	2.04 vs		2.31 w	2.27 s	2.17 w			2.22 vs	
2.04 v.w	2.04 vw	2.04 vs		1.88 vw	1.99 w		2.21 vw	2.17 m		2.03 s	2.05 s		
1.78 m	1.77 m	1.87 w		1.80 m	1.77 m		2.14 m	2.05 vvw	1.79 vvw				1.84 s
		1.87 vw		1.70 vw	1.70 w		1.84 w	1.95 vvw		1.76 m			
1.64 m	1.65 w	1.64 vw		1.63 w	1.67 m		1.75 mw	1.88 vvw					
1.61 w	1.57 w	1.58 m		1.57 vw	1.57 vs		1.67 vw	1.80 vvw	1.56 vw			1.57 s	1.57 m
1.50 vs	1.50 s	1.50 m		1.50 vs			1.59 vvw	1.57 vw	1.54 vw				1.50 m
	1.42 vw	1.45 m		1.44 vs	1.44 vs		1.56 vvw	1.54 mw	1.54 vw				
1.39 w	1.39 w	1.37 vw		1.39 w	1.38 w		1.52 w	1.51 m	1.48 vw				
							1.50 w	1.48 m					
							1.44 vvw	1.44 vvw	1.45 ms				
							1.42 m	1.40 hr.w					
							1.41 w						

seemed to be the same as before the treatment, a trifle amount of unknown substances giving many strong rings actually existed on the surfaces. Since these unknown substances seemed to be similar to those which were considered to be the cause of tarnishing of milk-white appearance, A1999, No. A and A2017 were selected as the objects of analyses. Fig. 1, 2, 3 and 4 are the diffraction photographs of A1999, No. 1, No A and A2017, respectively. Although the microscopic observation seems to reveal the existence of the sulphides of manganese and magnesium on considerably tarnished surfaces, these sulphides crystallized in the rock-salt type all with almost identical lattice constant as shown in Table 2 and showed only a few diffraction rings, of which some of the larger spacings corresponded to those in our specimens. This fact, however, does not bring a satisfactory explanation for the existence of many diffraction rings in the pattern. Nor the oxides of nickel and manganese alone can be enough for a satisfactory explanation of these rings, and even if we assume the co-existence of these sulphides and oxides, a considerable number of diffraction rings still remains to be explained thoroughly. Moreover, it will be almost improbable to suppose that the milk-white tarnishes are attributed to so many materials. It will, however, be safe to presume that only one material may be the main cause of almost all the diffraction rings in A1999. The research into this unknown substance was very difficult because of few clues, but the result of our experiment suggested, at last, that the manganese content seemed to have little to do with this tarnish, as clearly seen in Table 1. On the other hand, it seemed to be probable that co-existence of a considerable amount of magnesium and silicon might cause tarnish and that no tarnish might be seen when the amount of one of them was not enough. Of course, this could not be said for certain because of the lack of the chemical analysis, but, if it is assumed that the co-existence of a considerable amount of magnesium and silicon causes intense tarnishing, then the existence of silicates of magnesium will be quite doubtful. To clarify this point, X-ray diffraction photographs were taken with powder specimens of $(\text{Mg, Ca})\text{SiO}_3$ (Olivine), Mg_2SiO_4 (Forsterite) and $(\text{Mg, Fe})_2\text{SiO}_4$. The lattice spacings calculated from these diffraction rings and their observed intensities are shown in the right half of Table 2. The crystal structures of these silicates all belong to the rhombic system and give a considerable number of diffraction rings. The greater part of the lattice spacings and intensities of the rings in our specimens of tarnishing quality have now come to be explained clearly by $(\text{Mg, Ca})\text{SiO}_3$ and Mg_2SiO_4 . From the data of each specimen, it will be seen that in A1999 most rings are caused by $(\text{Mg, Ca})\text{SiO}_3$ and the rest by NiO. This can also be applicable to No. 1. In No. A and A2017 the diffraction rings due to nickel were so intense that its substratum might be exposed on the greater part of the surface. It could be said, however, that in the case of No. A there also existed Mg_2SiO_4 and that in A2017 existed a trifle amount of MnO and MnS in some cases and of Mg_2SiO_4 , MnO and NiO in other cases. It will be right to assume that in these cases nickel oxide does not originally exist but is rather produced by oxidation of activated surface of nickel in the air after the hydrogen treatment. Although, in some results of the present

experiment, some inconsistencies with X-ray data on intensities of diffraction rings can be recognized, it must be taken into account that owing to the orientation of crystallite on the surfaces, the diffraction patterns of our specimens generally tend to show the variation in intensity along the rings and that the intensity does not always go together with the data of the X-ray examination. At any rate, from both facts that almost all the diffraction patterns of A1999 which were very difficult to analyze can successfully be explained by $(\text{Mg, Ca})\text{SiO}_4$ and that the existence of a trifle amount of Mg_2SiO_4 can be recognized on the surfaces of No. A and A2017 which showed no tarnish in their appearance, it can be concluded that the cause of milk-white tarnishing lies in the silicates of light metals. The existence of MnO and MnS as seen in A2017 seems to have been affected by comparatively more amount of manganese in the specimens. In short, silicates of magnesium which cause milk-white tarnishing ought to have been removed as slag during melting, and, when its removal is incomplete, the process of manufacturing and heat-treatment will give chances to a very trifle amount of the substance to diffuse in grain boundaries, making a considerable pile there.

Our sincere thanks are due to Dr. Omori, professor in the Institute of Mineralogy, petrology and Economic Geology, the Faculty of Science, Tohoku University, who was kind enough to share rock materials for our experiment in X-ray photographs. The present investigation has been supported partly by the fund of the Ministry of Education in Aid of Scientific Researches.