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Determination of Condition for Electrolytic Extractions of Nitrides in Steel by Means of Potentiostat*

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The polarizing characteristics of synthesized nitrides, Fe_3N , Fe_4N , Mn_3N_2 , Mo_2N , MoN , Cr_2N , CrN , VN , Si_3N_4 , AlN , TiN , ZrN and NbN , were studied by means of potentiostat in order to determine the condition for the electrolytic extractions of nitrides from iron and steel. From the results of polarization curves and natural electrode potentials of iron and nitrides, some useful informations were obtained as to the electrolyte and the electrolytic potential for the electrolytic extractions of nitrides contained in iron and steel; that is, if a suitable electrolytic potential is applied, both acidic and neutral solutions can be used as an electrolyte for the extractions except nitrides of Al, Fe and Mn. For the Fe-nitride, only neutral electrolyte is useful, while for the nitrides of Al and Mn, there seems to be no favorable electrolyte.

I. Introduction

Nitrogen has a quite strong affinity for many metallic elements and forms various kinds of nitride with them. In iron and steel, the nitrogen which is absorbed during melting or added intentionally, has favorable or unfavorable effects on properties of steel by forming a nitride with iron or with alloying element⁽¹⁾. However, many points regarding the nitrides, such as constitution of precipitate, precipitation behavior and its influence on properties of material, remain unexplained.

In the electrolytic extraction, the accuracy of experiment depends upon electrolyte, bath temperature, electrode potential and current density. Therefore, for the determination of a satisfactory electrolytic condition, details on electrochemical properties of each phase and the polarizing characteristic of each constituent in electrolytic solution are required. The potentiostat is a very effective instrument for this purpose. Recently, some interesting works⁽²⁾⁻⁽⁴⁾ have been reported in which the potentiostat was effectively used in the electrolytic extractions of carbides and intermetallic compounds. But the research on the

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electrolytic extraction of nitride is very few.^{(5),(6)} Such being the case, the present work was carried out to determine a satisfactory condition for the electrolytic extractions of nitrides from steel by means of the potentiostat, the nitrides which may be formed in steel being made by a synthetic method, and the polarizing characteristics of the nitrides in neutral and acidic solutions were studied.

II. Specimens and experimental method

The specimens were made by nitrogenizing pure metals Fe, Si, Al, Mn, Cr, V, Mo, Ti, Zr and Nb. The processes of manufacturing of these metals are shown in Table 1. For preparation of Fe-nitride the electrolytic iron was melted in

Table 1. Metals as received and specimens prepared.

Metals	Purity of metals as received	Preparation of specimens
Fe	99.8 %	Melted in vacuum, cast and rolled in plate
Al	99.99 %	Commercial plate as received
Mn	99.99 %	Arc-melted in argon gas and cut off in plate
Si	99.9 %	Zone-melted and cut off in plate
Cr	99.8 %	Arc-melted in argon gas and cut off in plate
Mo	99 %	Commercial plate as received
V	99.5 %	Arc-melted in argon gas and cut off in plate
Nb	99 %	Commercial plate as received
Zr	99 %	Commercial plate as received
Ti	99 %	Commercial plate as received

vacuum, cast, rolled in plate and nitrogenized after a trace of carbon was removed by wet hydrogen, while Cr, V, and Mn nitrides were made from commercial electrolytic high-purity materials by arc-melting in argon atmosphere. Other nitrides of Ti, Zr, Mo, Al and Nb were made from commercial plates. In nitrogenizing, plates of $20 \times 40 \text{ mm}^2$ with the thickness of about 1 mm were used.

Before nitrogenizing, these metallic plates were chemically polished, and purified N_2 or NH_3 gas was passed at various temperatures for different lengths of time to form a nitride layer, more than several tens of micron in thickness, on the surface of each plate. Using a saturated calomel electrode and a potentiostat of semiconductor type⁽⁷⁾, the polarization curves of various nitrides were determined in acidic or in neutral solutions as shown in Table 2, which are usually used for the electrolytic extractions of carbides, oxides, etc. Moreover, various kinds of nitride layer were identified by the spectrometer of GE-XR-D5 type. The specifications of the amplifier of potentiostat are as follows: the response time is $10^{-3} \sim 10^{-4}$ sec, the voltage accuracy about 0.1 mV, and the maximum current capacity

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Table 2. Electrolytes used.

	Composition of solutions
Neutral	10 % Na-Citrate + 1 % KBr + 0.1 % KI aqueous solution 10 % KBr aqueous solution
Acid	0.2 N HCl aqueous solution 0.5 N HCl aqueous solution 0.5 N HCl + 10 % Na-Citrate aqueous solution 2 % H ₃ PO ₄ aqueous solution

2A. The measurement was carried out at the rate of about 0.1 V/min.

III. Experimental results and considerations

1. Condition for formation of nitride

It was necessary to produce a uniform layer of pure single nitride, more than several tens of micron in thickness. The nature and the thickness of the nitride layers obtained were examined by X-ray diffraction and microscopic observation. Fig. 1 shows the relationship between nitrides and temperatures at which iron was

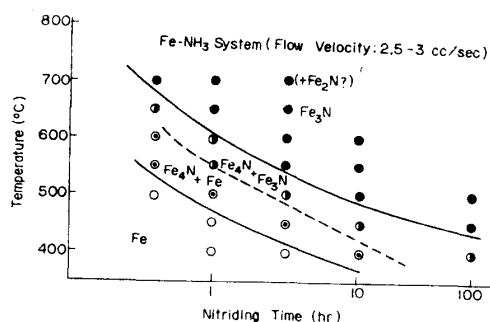


Fig. 1. Relation between the nitriding condition and nitride formed on surface of iron.

nitrogenized with NH₃ gas at the flow rate of 2.5~3 cc/sec. Fe₃N layer of a uniform thickness is easily formed by nitrogenization at high temperatures for a long time, but the uniform formation of Fe₄N alone was difficult, Fe₃N being mixed. By the same process, the synthesizing condition of forming a single nitride layer of a uniform thickness of more than 10 microns was determined from the relation of temperature and heating time. Table 3 shows the synthesizing conditions of respective nitrides. However, the single layer of nitrides, Fe₄N, Mn₃N₂, CrN, Cr₂N, MoN, Mo₂N and NbN, was hardly obtainable, a small quantities of other kinds of nitride being mixed. In addition, a trace of oxides was observed in AlN.

2. Polarizing characteristics of respective nitrides

Using the above-mentioned nitrogenized plates, the polarization curves in the acidic and the neutral solutions shown in Table 2 were obtained by means of

Table 3. Synthetic conditions for formation of simple nitrides.

Nitrides	Synthetic condition	Depth of nitrified layer (μ)
(Fe)	(Annealed at 1300°C × 5hr in wet H ₂)	
Fe ₃ N	Nitrified at 650°C × 10hr in NH ₃	more than 400
Fe ₄ N	" at 450°C × 10hr in NH ₃	5-10
AlN	" at 1100°C × 5hr in N ₂	more than 500
Mn ₃ N ₂	" at 800°C × 5hr in N ₂	10-20
Si ₃ N ₄	" at 1400°C × 5hr in N ₂	5-10
CrN	" at 850°C × 15hr in NH ₃	100
Cr ₂ N	" at 1200°C × 5hr in N ₂	100
MoN	" at 1000°C × 5hr in N ₂	5-10
Mo ₂ N	" at 800°C × 10hr in NH ₃	5-10
VN	" at 1400°C × 5hr in N ₂	50
NbN	" at 1400°C × 5hr in N ₂	20-30
ZrN	" at 1200°C × 5hr in N ₂	20-30
TiN	" at 1200°C × 5hr in N ₂	40

the potentiostat. Since it is concerned that the metal surface under the nitride layer might be exposed by dissolution of the nitrides with the electrolyte during measurement, these specimens were examined by X-ray diffraction after respective measurements. The results of measurement of polarization are shown in Figs. 2~7. Fig. 2 shows the result of pure metals and their nitrides measured in 0.5 N hydrochloric acid solution, in which dotted lines show the polarization curves of pure metals and solid lines those of nitrides. Iron begins to dissolve rapidly at about -0.4 V (S.C.E.) as Fe⁺⁺ ions. On the other hand, the natural electrode potentials of Mn₃N₂, AlN and Fe₃N are lower, being less noble, and the natural electrode potential ascends in order of VN, MoN, Mo₂N, CrN, Cr₂N, NbN and TiN. Si₃N₄ and ZrN are still stable at +1 V in electrode potential (S.C.E.). Stepped change in the polarization curve of Fe₃N will be attributed to the exposure of

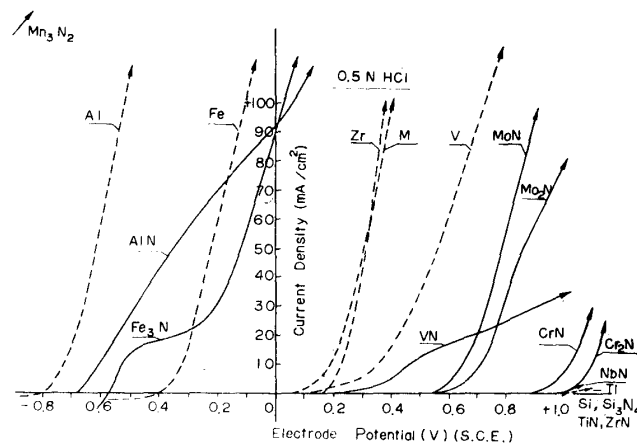


Fig. 2. Polarization curves of pure metals and nitrides in 0.5N hydrochloric acid solution.

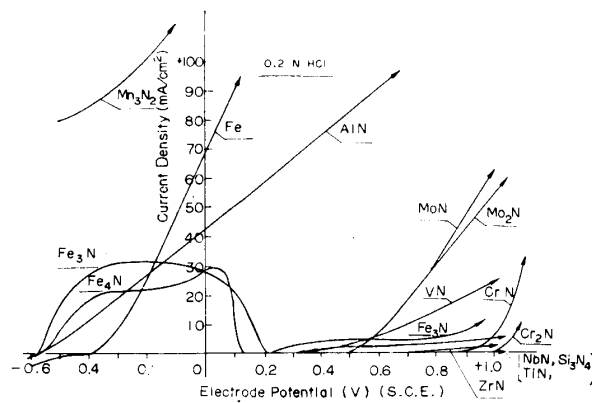


Fig. 3. Polarization curves of iron and nitrides in 0.2 N hydrochloric acid solution.

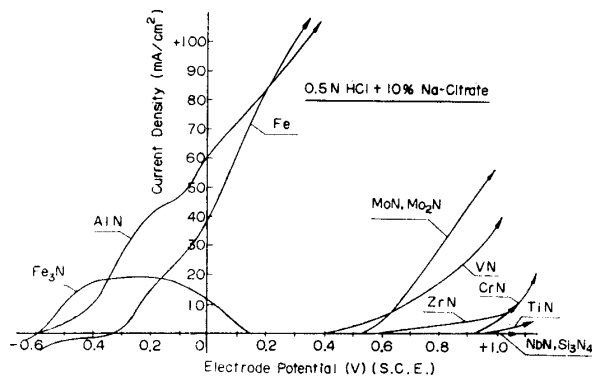


Fig. 4. Polarization curves of iron and nitrides in 0.5 N hydrochloric acid-10% sodium citrate solution.

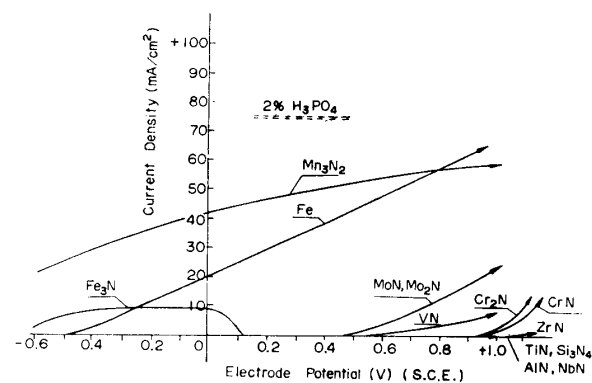


Fig. 5. Polarization curves of iron and nitrides in 2% phosphoric acid solution.

iron metal by dissolution of Fe_3N on the surface.

In Fig. 3, some characteristic features are seen in the polarization curves of Fe_3N and Fe_4N in 0.2 N hydrochloric acid solution. The active range is localized between about -0.6 and $+0.1$ V (S.C.E.), beyond which these nitrides become

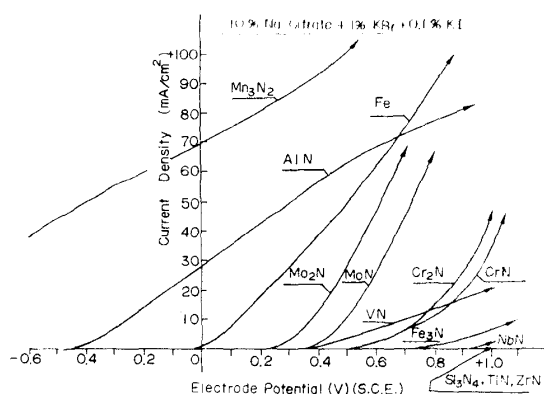


Fig. 6. Polarization curves of iron and nitrides in 10% sodium citrate-1% potassium-bromide-0.1% potassium-iodide solution.

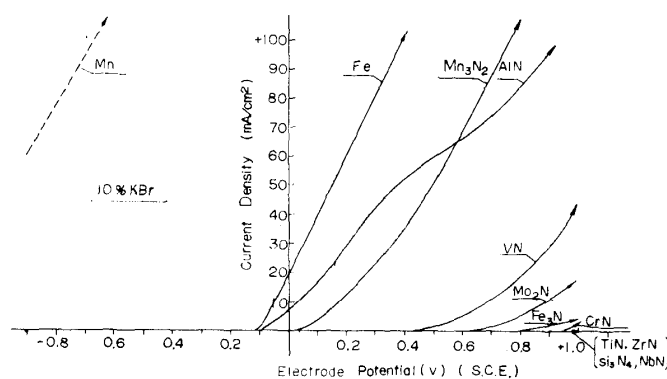


Fig. 7. Polarization curves of iron, manganese and nitrides in 10% potassium-bromide solution.

inactive. The surface of the specimen was examined by X-ray diffraction after being held for 2 hours at 0.5 V (S.C.E.) within the inactive range. The cause of inactivation will be attributed to the formation of an unknown passive substance. Behaviors of other nitrides are analogous to those in 0.5 N hydrochloric acid solution.

Fig. 4 shows the polarization curves of iron and various nitrides in 0.5 N hydrochloric acid solution to which was added 10 per cent sodium citrate to prevent the deposit of hydrates. In this case the current densities were low as compared with those shown in Fig. 2, but no marked difference was seen in the polarizing characteristics of the respective nitrides. On the other hand, as shown in Fig. 5, when 2 per cent phosphoric acid solution was used, Fe_3N became inactive at more than about +0.12 V (S.C.E.), similar as in hydrochloric acid solution. Nitride AlN showed a characteristic polarization curve in this solution, being hardly dissolved even at +1.0 V (S.C.E.). This may be attributed to the passivity of some unknown film formed on the surface of AlN. Other nitrides showed no large difference in their characteristics except that the degree of activation was somewhat smaller than that in hydrochloric acid solution,

The polarizing characteristics of respective nitrides showed some different behaviors in the neutral solutions from those in the acidic solutions. Fig. 6 shows the polarization curves of iron and nitrides in 10 per cent sodium citrate solution containing 1 per cent potassium bromide and 0.1 per cent potassium iodide, while Fig. 7 shows those in 10 per cent potassium bromide solution. The polarizing behavior of Fe_3N in the neutral solution is noticeable, being more stable than MoN , Mo_2N , VN , Cr_2N and CrN (Fig. 6). In general, nitrides of Mo, V and Cr in the neutral solutions, especially in sodium citrate solution, were somewhat more soluble than in the acidic solutions. It is noteworthy that the activating potentials of Mn_3N_2 and AlN in potassium bromide solution are higher than those in acidic solutions as shown in Fig. 7. Si_3N_4 , ZrN , TiN and NbN are fairly stable in the neutral solution as in the acidic solution.

From the above-mentioned results, it will be possible to determine the electrochemical characteristics of the nitrides in various solution. As an example, in Table 4 current densities of nitrides measured at $+0.5\text{ V}$ are tabulated.

Table 4. Current densities (mA/cm^2) of various nitrides at 0.5 V (S.C.E.) of electrode potential. ($A_{0.5}^{MN}$)

0.5N HCl	0.2N HCl	2% H_3PO_4	0.5NHCl+10% Na-Citrate	10% Na-Citrate +1% KBr+0.1 KI	10% KBr
$\text{Mn}_3\text{N}_2 >400$ (Fe_3N) (400)	Fe 179	Mn_3N_2 53.0	Mn_3N_2 200	Mn_3N_2 106	Fe 115
Fe 390	Mn_3N_2 94.0	Fe 34.2	Fe 130	Fe 62.0	AlN 60.0
AlN 150	AlN 84.0	VN 1.64	AlN 122	AlN 38.0	Mn_3N_2 50.0
VN 20.0	Fe_4N^* 4.00	Mo_2N 1.00	VN 3.00	Mo_2N 24.0	VN 2.10
MoN 0.20	VN 2.48	Fe_3N^* 0.50	Fe_3N^* 0.20	MoN 11.0	Mo_2N 0.20
Mo_2N 0.06	Fe_3N^* 2.00	TiN 0.10	Mo_2N 0.12	VN 5.53	Fe_3N 0.06
Cr_2N 0.03	Mo_2N 0.42	AlN 0.04	CrN 0.02	Cr_2N 1.60	CrN 0.00 ₅
CrN 0.01	CrN 0.02	Si_3N_4 0.00 ₅	TiN 0.01	CrN 0.84	TiN 0.00 ₅
Si_3N_4 0.00 ₅	Cr_2N 0.01	NbN 0.00 ₃	ZrN 0.01	Fe_3N 0.32	Si_3N_4 0.00 ₀
NbN 0.00 ₅	Si_3N_4 0.00 ₀	ZrN 0.00 ₀	Si_3N_4 0.01 ₁	Si_3N_4 0.19	ZrN 0.00 ₀
TiN 0.00 ₀	NbN 0.00 ₀	Cr_2N 0.00 ₀	NbN 0.00 ₀	TiN 0.03	NbN 0.00 ₀
ZrN 0.00 ₀	TiN 0.00 ₀			ZrN 0.01	
	ZrN 0.00 ₀			NbN 0.00 ₀	

* Passive state

The natural electrode potentials of nitrides which are important as a polarizing characteristic, were measured after being held in solution for about 20 minutes, the values of which are shown in Table 5.

The stabilities of nitrides in respective solutions can be presumed from these tables, namely, ZrN , Si_3N_4 , NbN and TiN are fairly stable in both neutral and acidic solutions, and VN , MoN , Mo_2N , Cr_2N and CrN are rather stable in both solutions. On the other hand, Mn_3N_2 and AlN are unstable as a whole, but Fe_3N (Fe_4N) is unstable only in the acid solution.

Table 5. Natural electrode potentials (S.C.E.) of iron and various synthesized nitrides (E_0^{Fe} and E_0^{MN}).

0.5N HCl	0.2N HCl	2% H ₃ PO ₄	0.5NHCl+10% Na-Citrate	10% Na-Citrate +1% KBr +0.1%KI	10% KBr
Mn ₃ N ₂ -1.30V	Mn ₃ N ₂ -1.30V	Mn ₃ N ₂ -1.0 V	Mn ₃ N ₂ -1.0 V	Mn ₃ N ₂ -1.0 V	Fe -0.42V
AlN -0.66	AlN -0.62	Fe ₃ N -0.63	AlN -0.66	Fe -0.70	Mn ₃ N ₂ -0.40
Fe ₃ N -0.56	Fe ₃ N -0.58	Fe -0.55	Fe ₃ N -0.60	AlN -0.36	AlN -0.35
Fe -0.53	(Fe ₄ N)-0.57	AlN -0.43	Fe -0.40	NbN -0.20	NbN -0.14
NbN +0.03	Fe -0.52	Si ₃ N ₄ -0.16	NbN -0.19	VN -0.15	VN -0.10
VN +0.04	VN +0.06	NbN +0.02	Si ₃ N ₄ -0.06	ZrN -0.06	Fe ₃ N +0.02
ZrN +0.08	ZrN +0.11	VN +0.08	ZrN -0.04	Si ₃ N ₄ -0.05	Si ₃ N ₄ +0.03
Si ₃ N ₄ +0.22	Si ₃ N ₄ +0.30	Mo ₂ N +0.26	VN -0.02	Fe ₃ N -0.03	ZrN +0.03
Mo ₂ N +0.32	NbN +0.32	TiN +0.28	Mo ₂ N +0.20	Cr ₂ N +0.02	Mo ₂ N +0.14
Cr ₂ N +0.38	Mo ₂ N +0.34	ZrN +0.33	TiN +0.23	Mo ₂ N +0.05	Cr ₂ N +0.14
TiN +0.51	Cr ₂ N +0.37	Cr ₂ N +0.43	Cr ₂ N +0.30	CrN +0.17	CrN +0.24
CrN +0.56	CrN +0.52	CrN +0.46	CrN +0.35	TiN +0.28	TiN +0.44
	TiN +1.00				

3. Electrolytic condition for extraction of nitrides from steel

When nitrides are dispersed in iron matrix, the condition for their extractions by the electrolytic method can be determined from the polarizing characteristics of iron and respective nitrides. When the polarization curves of iron and dispersed nitride (MN) are known as shown in Fig. 8, in which E_0^{Fe} and E_0^{MN} are natural

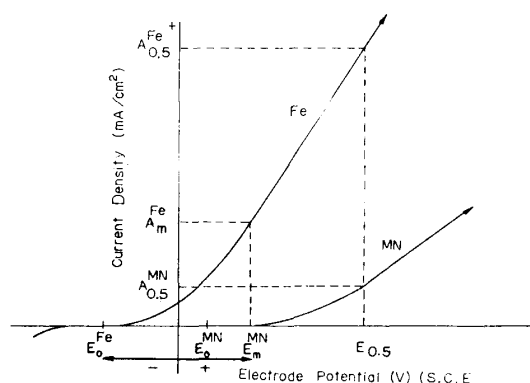


Fig. 8. Explanatory diagram of electrolytic potential for electrolytic isolation of nitride (MN) from iron (Fe).

- E_0^{Fe} and E_0^{MN} : Natural electrode potential of iron and nitride.
 E_m^{MN} : Electrode potential of nitride at $+0.01\text{A}/\text{cm}^2$ of current density.
 A_m^{Fe} : Current density of iron at E_m^{MN} .

electrode potentials of iron and nitride MN respectively, the potential range between E_0^{Fe} and E_0^{MN} , being $E_0^{Fe} < E_0^{MN}$, will be a suitable condition for the extraction of nitrides from iron as the anodic residue. On the other hand, the electrolytic

extraction of nitrides will be impossible, when $E_0^{Fe} < E_0^{MN}$. Since the natural electrode potential of nitrides shown following Fe in Table 4 is higher than that of iron, these nitrides may be extracted from iron. However, as the ordinary electrolytic current density for electrolytic extraction from iron is about $10 \sim 50 \text{ mA/cm}^2$, it was assumed that the highest potential for possible electrolytic extraction, E_m^{MN} , is the voltage at the current density of 0.01 mA/cm^2 . Table 6 shows the potential, E_m^{MN} ,

Table 6. Presumed maximum electrode potentials (S.C.E.) for electrolytic isolation of nitrides in iron (E_m^{MN} at $+0.01 \text{ mA/cm}^2$).

Electrolytes	0.5 NHCl	0.2 NHCl	2% H ₃ PO ₄	0.5 NHCl+10% Na-Citrate	10% Na-Citrate +1% KBr +0.1% KI	10% KBr
Nitrides						
Mn ₃ N ₂	—	—	—	—	—	(-0.1 V)
Fe ₃ N	—	—	—	—	+0.2 V	+0.2
AlN	—	—	+0.1 V	—	—	(-0.2)
VN	+0.1 V	+0.1 V	+0.1	+0.1 V	+0.2	+0.2
MoN, Mo ₂ N	+0.3	+0.4	+0.4	+0.2	+0.1	+0.2
CrN, Cr ₂ N	+0.5	+0.5	+0.8	+0.5	+0.2	+0.6
NbN	+1.0	+1.0	+1.0	+1.0	+1.0	+1.0
TiN	+0.9	+0.9	+0.5	+0.9	+0.6	+0.6
ZrN	+1.0	+1.0	+0.8	+0.5	+0.7	+0.7
Si ₃ N ₄	+1.0	+1.0	+1.0	+1.0	+0.5	+0.8

Natural electrode potential of Fe	-0.53	-0.52	-0.55	-0.40	-0.70	-0.42

of each nitride. The natural electrode potential of iron written in the bottom of this table represents the lowest potential for the possible electrolytic extraction. It can be seen from this table that all nitrides except those of Mn, Fe and Al may be extracted in hydrochloric acid solution at potentials between E_m^{MN} and E_0^{Fe} shown in the table. Similarly, all nitrides tested may be extracted from iron except those of Mn and Fe in phosphoric acid solution, and those of Mn and Al in sodium citrate solution. In potassium bromide solution, all the nitrides may be extracted, but potentials, E_m^{MN} , of nitrides, Mn₃N₂ and AlN, are -0.1 V and -0.2 V (S.C.E.) respectively, for which the current density of iron is extremely low and hence a long time will be required for electrolytic extraction of these nitrides. The above consideration is applied not only to the electrolysis of iron alloy containing one kind of nitride, but also to alloys containing many kinds of nitride. For example, in an iron alloy containing Fe- and Cr-nitrides, the former may be isolated in neutral sodium citrate solution at about $-0.2 \sim +0.6 \text{ V}$ (S.C.E.) and the latter in 0.5 N hydrochloric acid solution at about $-0.4 \sim +0.2 \text{ V}$ (S.C.E.).

The foregoing electrolytic condition for the extractions of nitrides in steel has been determined from the polarizing characteristics of synthesized nitrides. In

industrial steels, however, it is risky to determine the electrolytic condition only from the experimental results on synthesized nitrides, because the nitrides in steel are not pure compounds and in many cases distributed finely. Nevertheless, Ilschner-Gensch⁽²⁾ has succeeded in isolating various phases in Ni-base heat-resisting alloys under the condition determined by the same method as the above-described, and hence it is possible to determine a suitable condition for the electrolytic extractions of nitrides in industrial steel.

According to previous work on various nitrides, NbN^{(8),(10)}, SiN⁽⁹⁾, TiN⁽⁸⁾, ZrN^{(8),(11),(12)}, VN^{(8),(9)}, CrN and Cr₂N^{(8),(13)} are insoluble in water, acidic (such as nitric acid, hydrochloric acid and sulfuric acid) and alkaline solutions. On the other hand, nitrides of Al, Mn and Fe are unstable; AlN⁽¹⁴⁾ decomposes in water and in acidic and alkaline solutions, while nitride of Mn is gradually dissolved even in cold water and readily in dilute acid or in alkaline solution⁽¹⁵⁾. Fe-nitrides are known to be insoluble in water but easily dissolved in acidic solutions such as hydrochloric acid and sulphuric acid.^{(8),(13)}

From these chemical properties it is easily understood that the extraction of Fe-, Al- and Mn- nitrides in steel is extremely difficult. That is, it is considered that the electrolytic extraction of these nitrides is impossible in acidic solution, and that the complete extraction of Al- and Mn-nitrides is not expected in the neutral solution since they are unstable in solution containing OH⁻ ion, while Fe-nitride may be extracted in the neutral solution. Pawlek et al.⁽⁶⁾ extracted AlN, Si₃N₄ and TiN together with oxides by electrolysis of electric iron sheet containing 3~4.5 per cent silicon, in 5 per cent sodium citrate-1.2 per cent potassium bromide solution at a constant current density of 50 mA/cm². Koch et al.⁽⁵⁾ also extracted Mo₂N, CrN, Fe₂N and AlN by electrolyzing aluminium-treated steel in 5 per cent sodium citrate—1.2 per cent potassium bromide—0.6 per cent potassium iodide solution at about 10 mA/cm². From the polarization curve in Fig. 6, it is clearly seen that Si₃N₄, TiN, Mo₂N, CrN, Fe₂N and Fe₄N can be satisfactorily extracted at the current density of 10~50 mA/cm², though only AlN is out of expectation in the present experiment. It is necessary to carry out further studies on the electrolytic isolation of Mn- and Al-nitrides.

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Summary

The electrolytic condition for the extractions of nitrides in steel has been investigated by determining the polarizing characteristics of synthesized nitrides by means of potentiostat. In the present experiment, synthesized nitrides, Fe_3N , (Fe_4N) , Mn_3N_2 , MoN , Cr_2N , CrN , VN , Si_3N_4 , AlN , TiN , ZrN and NbN , were used. A useful information on the extractions of nitrides from steel was obtained from the polarization curves and the natural electrode potentials of these nitrides and iron; that is, nitrides except Al-, Fe- and Mn-nitrides can be extracted either in neutral or in acidic solution provided a suitable electrolytic potential is adopted. Moreover, it was considered that Fe-nitrides could be extracted in the neutral solution, but Al- and Mn-nitrides could not by the electrolytic method.