Transition of rate mechanism from internal nitriding to rapid nitriding mechanism at 12.5 mol\%Cr in austenitic Fe-Cr-Ni alloy system

Kuniyasu GEMMA
Society of Advanced Science, 4-1-1 Kitakaname, Hiratsuka, Kanagawa, 259-1292, Japan
TEL: x81-463-50-5505 FAX: x81-463-50-5506 e-mail: sasinfo@sas-jas.gr.jp

Masashi SATO
Department of Applied Chemistry, School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa, 259-1292, Japan
TEL: x81-462-58-1211 FAX: x81-463-50-2426 e-mail: masashis@tokai-u.jp

Masae KANDA
Dept. of Astronautics and Aeronautics, Center of Applied Superconductivity and Sustainable Energy Research, Chubu University, 1200 Matsumoto-cho, Kasugai, Aichi, 487-8501, Japan
TEL: x81-568-51-9463 FAX: x81-568-51-1478 e-mail: kanda@isc.chubu.ac.jp

Ryota GEMMA
Department of Materials Science, School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa, 259-1292, Japan
TEL: x81-462-58-1211 FAX: x81-463-50-2426 e-mail: ryota.gemma@tokai.ac.jp

Kaoru HOSHINO
Parker S・N Kogyo Co., Ltd., 8-20-27 Fukayakami, Ayase-shi, Kanagawa, 252-1108, Japan
TEL: x81-467-78-6760 FAX: x81-467-78-6763 e-mail: psn-hoshino@pnk.co.jp

Jun-ichi KAWANO
Nippon Yakin Kogyo Co., Ltd. Kawasaki Plant, Technology Development Department Process Engineering, 4-2 Kojima-cho, Kawasaki-ku, Kanagawa, 210-8558, Japan
TEL: x81-44-271-3156 FAX: x81-44-271-3260 e-mail: junichi.kawano@nyk.jp
(Received 17 May, 2018 Accepted 22 July, 2020)

Transition from internal nitriding to rapid nitriding at 12.5 mol\% Cr in austenitic Fe-Cr-Ni alloy system is investigated from a Cr skeleton model based on atomic arrangement of Cr atoms in the alloys. The rapid nitriding is observed above the 12.5 mol\% Cr of alloys. Kinetics of the rapid nitriding is only performed at local space of 25.0 mol\% Cr in the alloys. The kinetics is discussed as a kind of lasering in thermodynamic system.

Keywords: Transition of nitriding mechanism, Inverted population, S phase

I. INTRODUCTION

Anomalous nitriding behaviour of austenitic stainless steels (for example marked rapid nitriding above approximate 700 K and a sudden decrease of the nitriding rate around 873 K) have been reported by many investigators. 1-10 Cause of these anomalies,
however, has not been revealed. Authors explained the
decrease of the rate from the viewpoint of a
termination of the rapid nitriding above the
temperature of 873 K. Therefore next issue was to
reveal the cause of the rapid nitriding. Recently we
discussed the rapid nitriding analogously with simple
lasering model based on a cyclic mechanism of
formation and reversion of a Cr-N type G.P. zone in a
meta-stable N supersaturated solid solution
(expressed as meta-γSN phase) formed just under the
nitrided surface of austenitic Fe-Cr-Ni alloys. Concentration of N in the
γSN phase formed in austenitic stainless steels at/near 673 K has been
reported as high as 38-45 mol% N. This N concentration is too high according to the
conventional idea of the austenitic stainless steels.
The phase is generally called as S phase in surface
engineering fields. In chemical affinities to form
nitride, Cr is the strongest among Fe, Cr and Ni
thermodynamically; Ni is rather repulsive to N. Therefore most of the N atoms in the γSN phase will
be attracted around Cr atoms.

Now a concentration dependence of Cr for
nitriding mechanism in austenitic Fe-Cr-Ni alloys is
summarized as shown in Fig. 1 based on our previous
results. It is clear that the nitriding mechanism in the
alloy system transits from internal nitriding to rapid nitriding at concentrations ranging from 13 to 16
mass%Cr, although N concentration at the nitrided
surface increases with Cr mass% of alloys. According
to the theory of internal nitriding, the nitrided layer
growth is inversely proportional to Cr concentration because the diffusing N atoms are trapped by the Cr atoms regardless of ferritic or austenitic. From that viewpoint, the nitriding below 13 mass%Cr in Fig. 1 follows the theory well. Therefore, the marked increase of the nitrided layer thickness over 16
mass%Cr looks quite novel in contrast to the internal
nitriding mechanism. Obviously, the transition occurs
between 13 and 16 mass%Cr. However, the boundary
Cr-concentration of this transition is not yet known.
Theory of reaction resistance proposed by Tamman suggests that this boundary is near the concentration of 1/8 mol%Cr, that is 12.5 mol%Cr in the alloy system. The value of Cr% shown in Fig. 1 represents the as-weighed value before smelting. Therefore, the boundary concentration must be rechecked with using accurately analyzed new specimens. In this work the austenitic Fe-Cr-Ni alloys containing 11-15 mass%Cr were prepared and nitrided. The discussion on this transition focuses on a specific concentration of 12.5
mol%Cr.

Since coordination number of unit cell of fcc
lattice is 4, 12.5 mol%Cr in an austenitic alloy means
distribution of one Cr atom per two unit cells. When
displacement of this Cr atom is positioned at the interface of two fcc
cells, the unit cells can be illustrated as Fig. 2A. Regular brickworking of the pair of cells make space
lattices shown in Fig. 2B. In the space, the Cr atoms
are positioned at interplane of a set of shadowed and
unshadowed cells. This arrangement makes a regular
order of the Cr atoms in the alloy. Fig. 2C shows one
of (100) planes in the space lattice in Fig. 2B. Sites of the Cr atoms form a checker pattern on the plane. A kind of Cr network is developed with mesh of $\sqrt{2}a$
Fig. 3. An ordered arrangement of Cr atoms, “Cr skeleton”, in the lattice space shown in Fig. 2B. The Cr skeleton consists of two kinds of space enclosing Cr atoms; the space of Cr octahedrons and Cr tetrahedrons.

Fig. 4. Perspectives of the Cr octahedron and the Cr tetrahedron illustrating one pair of unit cells fully nitrided. The N atoms are positioned nearby Cr atoms in the lattice. (A) Cr octahedron (12.5 mol%Cr) in which 6 N atoms have positions inside the octahedral sites, evaluated as 42.85 mol%N. (B) Contrary to (A), Cr tetrahedron shows that N atoms cannot be within tetrahedral sites and of distance a between the networks; a is the lattice constant of the alloy. In three dimensional space, the networks constitute a kind of Cr skeleton including a body centred lattice as shown in Fig. 3. The figure also shows that the network consists of other skeletons which are part of octahedron and tetrahedron (expressed as Cr octahedron and Cr tetrahedron respectively). More detailed picture is illustrated in Fig. 4. The figure schematically demonstrates that possible sites for N in the Cr skeleton are octahedral sites, but not tetrahedral sites. The lattice parameters of the bct lattice are $a=\sqrt{2}a$ and $c=2a$. In this arrangement, the Cr atoms are positioned at the furthest distance each other in the lattice of the alloy, and also shows one of ideal mixing condition of the alloy in general sense.

II EXPERIMENTAL PROCEDURE

II-A Specimen preparation

Five kinds of mixtures of Fe, Ni and Cr were weighed ranging from 11 to 15 mass%Cr in austenitic range of Fe-Ni-Cr system. About 1.0 kg of each mixture was melted by means of high frequency induction smelting and casted into a metal mold. Sample ingots of 120 mm long and 26-34 mm φ in size were obtained. Chemical analysis of the samples (denoted as Cr11-Cr15) are shown in Table 1. Nitriding specimens were cut off from the slabs in the size of 8 mm x 15 mm x 30 mm, and the surface was polished by emery of #800. These were nitried after degreasing in a supersonic cleaning bath with fresh acetone.

II-B. Nitriding

Five specimens were simultaneously nitried under practical two step nitriding process in an industrial furnace at 823 K for 28.8 ks. The first step was of the NH$_3$ dissociation ratio held with 38-44 % for 21.6 ks period. Following this, the second step was carried out at the ratio of 60-65 % for 7.2 ks continuously in the same furnace. After the nitriding, the microstructures and thickness of the nitrided layers formed on the surface were observed by optical microscopy; marble reagent diluted by ethanol was used as etchant. Migration of N in these specimens was estimated from EPMA profiles.

| Elements | C | Si | Mn | P | S | Ni | Cr | N (ppm) | O | Fe |
|----------|---|----|----|---|---|----|----|---------|---|----|
| Cr11     | 0.032 | 0.40 | 0.53 | 0.004 | 0.0014 | 15.46 | 10.86 | 0.002 | 174 | Bal | 10.97 |
| Cr12     | 0.034 | 0.40 | 0.54 | 0.004 | 0.0016 | 14.94 | 11.92 | 0.002 | 165 | Bal | 11.93 |
| Cr13     | 0.032 | 0.45 | 0.53 | 0.006 | 0.0018 | 13.85 | 12.85 | 0.002 | 172 | Bal | 12.87 |
| Cr14     | 0.038 | 0.45 | 0.54 | 0.006 | 0.0019 | 12.83 | 13.89 | 0.002 | 167 | Bal | 13.84 |
| Cr15     | 0.034 | 0.43 | 0.54 | 0.006 | 0.0020 | 11.87 | 14.98 | 0.002 | 191 | Bal | 15.11 |

Table 1. Chemical analysis of alloys used (mass%) with converted mol%Cr.
III. EXPERIMENTAL RESULTS

Typical nitrided layer and structures formed in the Cr11, Cr13 and Cr15 specimens are shown in Fig. 5. When examining the relationship between the morphology of nitrided layer and Cr concentration, the tendency is similar with the previously reported one \(^{12}\), that is, the lower Cr layer is characterized by a coarse double pattern shown in Fig. 5A. The double disappear in alloys with rich Cr such as layer of the Cr15 alloy. If we focus on the nitrided layer growth in these specimens, it is clearly seen that the layer formed in the Cr13 is the minimum in thickness. The Cr13 specimen is analyzed to be 12.85 mass%Cr as shown in Table 1. In the Cr15 specimen, not only the nitrided layer grows thicker than that in the Cr13, but also a thin white layer is formed at the nitriding front as shown in Fig. 5C. This thin layer is known as common feature of the rapid nitrided layer formed in austenitic stainless steels. \(^{5,15}\)

Fig. 5. Optical microphotographs of nitrided layers formed in various specimens nitrided at 823 K for 28.8 ks. (A) Cr11, (B) Cr13, (C) Cr15. Thin white layer observed in the Cr15 specimen is a well-known feature of rapid nitriding.

EPMA profiles obtained from the nitrided specimens are presented in Fig. 6. The specimens were plated by Ni before EPMA scanning.

![EPMA profiles](image)

Fig. 6. Line scanning profiles of EPMA obtained from nitride layers formed in 11Cr-15Cr specimens nitrided at 823 K for 28.8ks.

IV. DISCUSSION

We have clearly seen that the nitriding mechanism transits near 12.87 mol%Cr in austenitic Fe-Cr-Ni alloy. Below that Cr%, the nitriding follows internal nitriding mechanism; the nitrided layer growth is inversely proportional to the Cr concentration. According to the conventional theory, diffusing N atoms are trapped by the Cr atoms and the trapping serves to slow down the growth of the nitrided layer. This mechanism has been reported in various steels. \(^{16-18}\) In high Cr austenitic Fe-Cr-Ni alloy system, however, the theory applies only below the range of approximately 13 mass%Cr as shown in Fig. 1 and Fig. 7. This limit accords very well by

![Cr concentrations vs. thickness of nitrided layer](image)
considering that the 12.5 mol%Cr concentration as boundary concentration for the marked change of nitriding mechanisms. Thus, based on Cr skeleton model, the internal nitriding is considered to take place until the Cr skeleton is fully developed. Now, by substituting one Cr atom for the centred atom in the Cr octahedron, one new octahedron is produced in the Cr skeleton, and that is illustrated as Cr² octahedron in Fig. 8. The alloy including the Cr² octahedron is, therefore, richer in Cr% than the 12.5 mol%Cr. The N atoms held in the Cr² octahedron are less diffusible than that in the Cr octahedron because these N atoms are placed between two Cr atoms in such a chain as - Cr-N-Cr - arrangement. Let us note here this order is orientated and developed to [100] direction in the fcc space lattice of the alloy. In other words, it is easy to form a G.P. zone such as (Cr · N)x . Thus, the slowdown in the nitrided layer growth must be observed in the alloys above 12.5 mol%Cr on standpoint of internal nitriding theory. On the contrary to the theory, the experimental result shows the rapid nitriding.

Here, we now have to introduce an idea of synergetics to explain the experimental results. We have discussed previously the rapid nitriding as a new cooperated phenomenon (synergetics ¹³) with a mechanism as follows; a formation and resolution (reversion) of a G.P. zone in meta-γSN phase formed under the surface of austenitic stainless steels under giant N fugacity (fN) of NH₃. ⁹ The fN of 90%NH₃ - 10%H₂ mixture is calculated as approximate 10⁶[atm]⁻¹ at 723 K ²¹ ; subscripted [atm] is dimension of the fugacity related to equilibrium constant. Each reaction steps described above are summarized as follows in brief. At the initial step, the meta-γSN phase is formed on the austenitic steel denoted [Fe-Cr-Ni]AUS as reaction (1).

\[
\text{[Fe-Cr-Ni]AUS + NH}_3 \rightarrow \text{meta-γSN + 3/2H}_2, \text{Δ}h_1 \quad (1)
\]

Since the meta-γSN is approximately of 40 mol%N, ¹², ¹³ a G.P. zone such as [Cr·N]GP is easily formed with precipitation of x number of N atoms (xN⁺) in the meta-γSN phase as reaction (2),

\[
\text{meta-γSN} \rightarrow [\text{Cr·N}]_{\text{GP}} + x\text{N}^+, \text{Δ}h_2 \quad (2)
\]

Since enthalpy of the Δh₂ is exothermic, a part of the thermal energy will contribute to the increase of the frequency of thermal vibration of the N⁺ in the lattice. The high frequency of the N⁺ allows to diffuse itself rapidly. At the same time, another part of the Δh₂ will be dissipated to raise the temperature of neighbor [Cr·N]GP formed previously under the giant fN of NH₃. Thus, in the course of the reaction above, the [Cr·N]GP is reversed into new meta-γSN as reaction (3),

\[
[\text{Cr·N}]_{\text{GP}} + \text{N} \rightarrow \text{meta-γSN}, \text{Δ}h_3 \quad (3)
\]

Thanks to the giant heat described above, the cycle between reactions (2) and (3) yields the rapid nitriding continuously. The meta-γSN is not formed at inner matrix far from the surface of the alloy because there is free from the giant fN of gaseous NH₃ there. As a result, CrN is formed there as reaction (4),

\[
\text{[Fe-Cr-Ni]AUS + xN}^+ \rightarrow x\text{CrN} + y\gamma'\text{-Fe}_4\text{N}, \text{Δ}h_4 \quad (4)
\]

Thus, the rapid nitriding results by the N⁺ atoms activated into a higher diffusivity compared with common interstitial diffusion in lattice. The phenomenon is regarded as an amplification of diffusion of N atom. The [Cr·N]GP will be formed easily in the Cr² octahedron and hardly in the Cr octahedron as discussed previously. The Cr² octahedron shown in Fig. 8 coordinates eight metal atoms involving two Cr atoms with six N atoms. Therefore, when one [Cr·N]GP is associated like an embryo in the octahedron, four N⁺ are precipitated there. The 12.5 mol%Cr alloy consists of only Cr octahedrons and tetrahedrons, and no Cr² octahedron theoretically as shown in Fig. 3. Therefore, the mechanism of rapid nitriding should be considered only in the Cr² octahedron. Since the number of Cr²
octahedrons increases with Cr%, clustering Cr\(^2\) octahedrons are considered over the 12.5 mol%Cr in these alloys. Considering the cycle between reactions (2) and (3) being taking place in the clusters, the rapid nitriding will be distinct as shown in Figs. 1 and 7. The ratios between the number of Cr and Cr\(^2\) octahedrons above 12.5 mol%Cr in austenitic alloys are calculated as Table 2. When the Cr skeleton fully consists of Cr\(^2\) octahedrons, the Cr concentration is 25.0 mol%Cr (for example AISI310 steel).

In precipitation of NaCl type carbides (such as TaC, VC) in austenitic steels, preferred orientations for the lattice are known as [100\(_{MC}\)///100\(_{AUS}\), [010\(_{MC}\)///010\(_{AUS}\), and [001\(_{MC}\)///001\(_{AUS}\) subscripted MC and AUS mean NaCl type carbide and austenite, respectively. Lattice structure of CrN is of almost the same as that of VC phase in space lattice and their parameters. The relationship suggests that the \([Cr\cdot N]_{GP}\) is formed easily in a cluster of the Cr\(^2\) octahedrons, that is, the reaction (2) proceeds easily. In nitrided 18Cr-8Ni steel, the ratio of Cr/ Cr\(^2\) octahedron is estimated as 0.44. The N concentration in both of the octahedrons in the meta-\(\gamma\)\(_{SN}\) phase of the steel is expected to be the same as 42.85 mol%N approximately. Under a giant \(f_N\), reversion of \([Cr\cdot N]_{GP}\) formed in the Cr\(^2\) octahedron will not be so hard isothermally, when the G.P. zone is formed as embryo-like. Furthermore, the reversion is assisted thermally, by the G.P. zone formation in the Cr\(^2\) octahedrons, too. It should be stressed here that the reversion is an inverted population process from low chemical potential of \([Cr\cdot N]_{GP}\) to higher meta-\(\gamma\)\(_{SN}\) phase assisted by the giant \(f_N\) and a part of \(\Delta h_2\). The \(f_N\) plays a role of pumping of chemical potential of N (N potential), analogous to pumping in lasering, although the kinds of pumped energies are different. The atom of N* diffuses at a higher diffusible level elevated by \(\Delta h_2\) than that at spontaneous diffusion under thermal equilibrium. In this viewpoint, the precipitation and diffusion of the N* is compared to stimulated emission in lasering analogously while jump diffusion mechanism of N atom in lattice is comparable with spontaneous emission in that.

Table 2. Number and ratio of the Cr and Cr\(^2\) octahedrons and their ratio in austenitic Fe-Cr-Ni alloys with the concentration ranging from 25.0 mol%Cr.

| Cr concentrations [mol%Cr] | Number of Cr and Cr\(^2\) octahedrons, N [x10\(^{10}\)] | Ratio of N, Cr\(^2\)OCTA |
|---------------------------|-------------------------------------------------|--------------------------|
| 12.5                      | 0.125                                           | 0                        |
| 13.0                      | 0.120                                           | 0.005                    |
| 13.5                      | 0.115                                           | 0.010                    |
| 14.0                      | 0.110                                           | 0.015                    |
| 14.5                      | 0.105                                           | 0.020                    |
| 15.0                      | 0.100                                           | 0.025                    |
| 16.0                      | 0.090                                           | 0.035                    |
| 17.0                      | 0.080                                           | 0.045                    |
| 18.0                      | 0.070                                           | 0.055                    |
| 19.0                      | 0.060                                           | 0.065                    |
| 20.0                      | 0.050                                           | 0.042                    |
| 22.0*                     | 0.030                                           | 0.095                    |
| 25.0*                     | 0                                           | 0.125                    |

Fig. 9. Duplex structures of lattices (I) and (II) in austenitic Fe-Cr-Ni alloy. (A) and (B) converted from the Cr octahedron (12.50 mol%Cr) and Cr\(^2\) octahedron (25.0 mol%Cr) fully nitrided into 42.85 mol%N respectively. The lattices (I) and (II) shows only the corner atoms in convenience; ●:Cr, ○:Fe or Ni coordinated in the (I) and (II). Mixture of (A) and (B) will constitute the surface of S phase.
For convenience, duplex structures of fcc converted from the full nitrided Cr and Cr\(^2\) octahedrons are shown in Fig. 9. As shown in Fig. 9B, \(\gamma_{SN}\)-phase of 25.0 mol\%Cr steel, such as AISI 310 steel are fully nitrided to maximum concentration of 42.85 mol\%N. Clearly, bonding between Cr and N takes place easier in the lattice of shown in Fig. 9B than that of Fig. 9A.

V. CONCLUSION

Presumed 12.5 mol\%Cr as boundary concentration of the transition in nitriding mechanism of austenitic Fe-Cr-Ni alloys is confirmed experimentally. Experimental results are summarized as follows;

1. In 12.87 mol\%Cr specimen, the nitrided layer growth was minimum. In specimens ranging from 10.91 to 12.87 mol\%Cr, the layer growth decreased slightly with the Cr% to follow the theory of internal nitriding mechanism.

2. Over the 12.87 mol\%Cr, the layer growth increased reversely with increasing the Cr%. Rapid nitriding takes in the 13.87 mol\%Cr specimen, and became remarkable in the 15.11 mol\%Cr specimen.

Thus, the presumption made before the experiment was confirmed. The experimental results proved that the nitriding mechanism in austenitic Fe-Cr-Ni alloys transits from internal nitriding to rapid nitriding at 12.5 mol\%Cr. This border concentration is well explained by the experimental results and thus prove the Cr skeleton model, supporting that the concentration of 12.5 mol\%Cr is the key. According to the Cr skeleton model, kinetics of the rapid nitriding occurs only in case the Cr\(^2\) octahedron are fully nitrided.

The rapid nitriding mechanism presented previously \(^{12}\) is perceived more effectively by this work. Under inverted population condition in quantum and electromagnetic systems, laser and maser are well known examples. Since condition of a super saturated solid solution such a \(\gamma_{SN}\)-phase in an inverted population in thermodynamic system, the mechanism of the rapid nitriding is regarded as a lasering in thermodynamic system.

ACKNOWLEDGEMENTS

Authors would like to thank Mr. Y. Miyamoto for his support in EPMA profiling. Professor K. Nagata, Prof. T. Matsuo, Prof. T. Sato, Prof. M. Takeyama and Prof. H. Fukuyama at Tokyo Institute of Technology are gratefully acknowledged for their wide discussion and suggestion to the work. Authors also would like to thank Ms. T. Mori, Ms. K. Watanabe, Ms. N. Suzuki and Ms. N. Arayashiki, Society of Advanced Science office members, for helping to correct the manuscript and the figures.

REFERENCES

1. J. P. Lebrun, H. Michel, M. Gantois, Memb. Sci. Metall. 69, 727 (1972).
2. B. Edendoher, Harte – Tech. Mitt. 30, 204 (1975).
3. S. Kiyooka, T. Homma, NETSU-SHORI 14, 33 (1974).
4. B. Billon, A. Hendry, Surface Eng. 1, 114 (1985).
5. K. Gemma, M. Kawakami, J. Jpn. Inst. Metals 52, 701 (1988).
6. K. Gemma, M. Kawakami, High Temp. Mat. Proc. 8, 205 (1989).
7. K. Gemma, H. Ueda, C. Mihara, M. Kawakami, J. Mater. Sci. 27, 3461 (1992).
8. K. Gemma, Y. Satoh, I. Ushioku, M. Kawakami, Surface Eng. 11, 240 (1995).
9. K. Gemma, T. Ohtsuka, T. Fujiiwara, M. Kawakami, J. Mater. Sci. 36, 5231 (2001).
10. K. Gemma, T. Tahara, M. Kawakami, J. Mater. Sci. 31, 2885 (1996).
11. H. Haken, Synergetics: An introduction: nonequilibrium phase transition and self-organization in physics, chemistry and biology, Springer-Verlag, Berlin, p. 159 (1983).
12. S.-P. Hannula, P. Nononen, J. Molaris, In: Focit, J., Hendry, A. (eds), Proceedings of the international conference on high nitrogen steel, The institute of metals and société française de métallurgie, Lille, p. 266 (1989).
13. D. Williamson, P. J. Wilburf, F. F. Fickeit, S. Parascandola, In: Bell, T., Akamatsu, K. (eds), Proceedings of an international current status seminar on thermochemical surface engineering of stainless steels, Osaka, p. 333 (2001).
14. K. Ichii, K. Fujiwara, T. Takase, NETSU-SHORI 25, 151 (185).
15. Y. Sun, T. Bell, Z. Kolosvary, J. Flis, Heat Treatment Met. 26, 9 (1999).
16. P. M. Hekker, H. C. Rozendaal, E. J. Mittemeijer, J. Mater. Sci. 20, 718 (1985).
17. I. E. Kindlmann, G. S. Ansell, Metall. Trans. 1, 163 (1970).
18. H.-J. Spies, D. Berfner, Harte. Tech. Mitt. 47, 346 (1992).
19. G. Tammann, Nachr. Kgl. Ges. Wiss. Göttingen, p. 373 (1917).
20. G. Tammann, Nachr. Kgl. Ges. Wiss. Göttingen, p. 161 (1917).
21. E. Lehrer, Z. Electrochem. 36, 382 (1930).
22. F. H. Froes, B. W. K. Honeycombe, D. H. Warrington, Acta Met. 15, 157 (1967).
23 J. S. T. van Aswegen, R. W. K. Honeycombe, D. H. Warrington, Acta Met. 12, 1 (1964).
24 T. N. Younger, D. M. Daddrill, T. G. Becker, J. Iron Steel Inst. 200, 693 (1961).
25 J. J. Irani, R. T. Weiner, J. Iron Steel Inst. 203, 398 (1965).
26 E. T. Turkdogan, J. Ignatowice, J. Iron Steel Inst. 188, 242 (1958). (JCPDS CARD No.11-65).
27 JCPDS CARD No. 1-1159.
28 P. Duwez, F. Odel, J. Electrochem. Soc. 97, 299 (1950).