論 文

# The Formation of Nitrogen Gas Pore During Solidification of 16Cr-3Ni Stainless Steels

Seong-Ho Yang[†], Do-Hyung Kim, Young-Hwan Park* and Zin-Hyoung Lee

## Abstract

질소 용해도가 낮은 δ상으로 응고가 시작되는 16Cr-3Ni 계 스테인리스강의 응고시 질소 기포 형성에 미치는 질소 함량과 냉각속도의 영향이 조사되었으며 이를 기반으로 질소 기포 결함이 발생하는 임계 질소 함량을 예측하는 방법을 제시하였다. 질소함량의 증가는 질소 기포 결함을 증가시켰으며, 냉각속도의 증가는 질소기포결함의 형성을 다소 억제할 수 있는 것으로 조사되었다. 실험적으로 구한 Fe-16Cr-3Ni-9Mn 합금의 임계 질소 함량은 0.19 wt%였으며, 임계 질소 압력은 평형응고로 가정한 경우 1.27 atm, Scheil 응고로 가정한 경우에는 1.23 atm으로 계산되었다. 질소 용해도를 증가시킬 수 있는 Mn 함량의 변화에 따른 임계 질소 함량의 변화를 예측하기 위하여 계산된 임계 질소 압력을 Fe-16Cr-3Ni-11Mn 합금에 적용하였으며 이를 통해 얻은 임계 질소 함량은 평형응고로 가정한 경우 0.25 wt%, Scheil 응고로 가정한 경우에는 0.24 wt% 로 예측되었다. 예측 결과의 타당성을 확인하기 위하여 Fe-16Cr-3Ni-11Mn 합금의 실험 결과와 비교하였으며, 일치하는 결과가 얻어졌다.

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**Key words:** Nitrogen, Solidification, Gas pores, Solubility, Stainless steels

## 1. Introduction

Nitrogen alloying has been recognized to have beneficial effects on mechanical and corrosion properties of stainless steels[1], and nitrogen that stabilizes austenite phase can substitute nickel.

However, segregated nitrogen in remaining melt can form gas pore during solidification of stainless steels especially solidifying primary δ-ferrite, because δ-ferrite has much lower solubility than liquid and austenite phase[2]. Rawers[3,4] and Satir-Kolorz et al.[5] reported the effect of nitrogen gas pressure and contents of alloying elements on the nitrogen solubility in Fe, Fe-Cr, Fe-Ni, Fe-Mn, Fe-Mo and Fe multi-component alloy systems.

Especially Satir-Kolorz et al. quantified the effect of alloying elements on the nitrogen solubility by obtaining the Cr equivalent factors defined as an interaction parameter of each alloy element divided by that of Chromium. Table 1 shows the interaction parameters and Cr equivalent factors of various alloying elements.

Table 1. Interaction parameters and Cr equivalent factors of various alloying elements at 1600°C[5]

| Element | Interaction parameter | Cr equivalent factor |
|---|---|---|
| Nb | -0.930 | 1.05 |
| Cr | -0.048 | 1.00 |
| Mn | -0.024 | 0.50 |
| Mo | -0.013 | 0.27 |
| Ni | 0.011 | -0.22 |
| Si | 0.043 | -0.90 |
| C | 0.118 | -2.46 |
| N | 0.130 | -2.70 |

In this research, the effect of nitrogen content and cooling rate on the formation of nitrogen gas pore was investigated. The segregation of nitrogen and all alloying elements was calculated with Thermo-Calc[6]. Comparison of the calculated and examined results led to estimate the formation of the nitrogen gas pore.

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## 2. Experimental procedures

To investigate the effect of nitrogen content and cooling rate on the formation of gas pores, a STS (stainless steel) and a water-cooled Cu mold (Fig. 1) were used. Also the critical nitrogen content was examined. The melt was prepared in an air induction furnace and the pouring temperature was about 1600°C. Gas pores in the castings were evaluated by radiography using γ-ray and density measurement.

Alloy composition was Fe-16Cr-3Ni stainless steels modified AISI 201. And the nitrogen content was in the range of 0.15 to 0.26 wt%. Table 2 shows chemical compositions of Fe-16Cr-3Ni-9Mn stainless steel castings. The segregation of nitrogen and alloying elements was calculated with ThermoCalc.

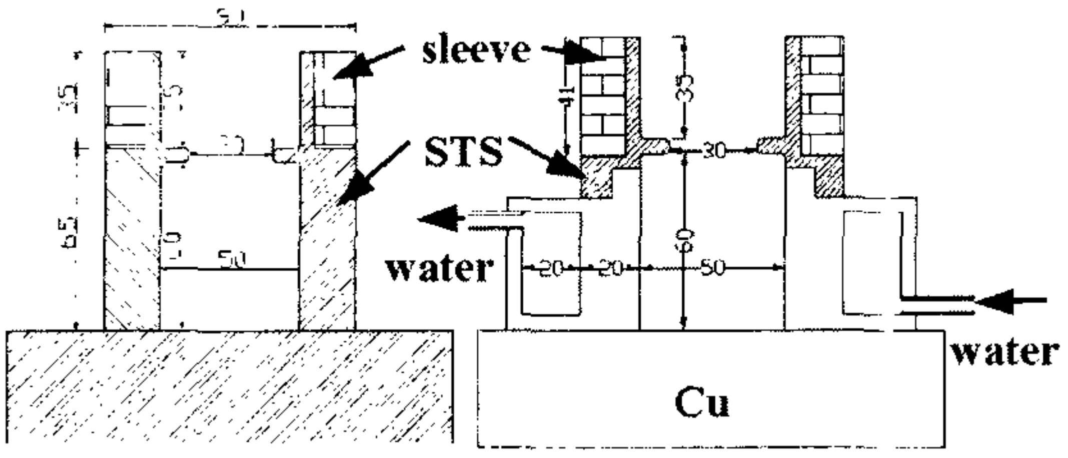


Fig. 1. Dimension of a STS and water-cooled Cu mold.

The critical nitrogen partial pressure was determined by calculated results and critical nitrogen content. The critical nitrogen partial pressure was applied to Fe-16Cr-3Ni-11Mn stainless steels to estimate the critical nitrogen content. Fe-16Cr-3Ni-11Mn stainless steel castings were also cast to confirm validity of the estimated critical nitrogen content. Table 3 shows chemical compositions of Fe-16Cr-3Ni-11Mn stainless steel castings.

## 3. Results and discussions

### 3.1 The effect of nitrogen content and cooling rate

Fig. 2 and 3 show the radiographs of Fe-16Cr-3Ni-9Mn castings. Fig. 4 shows bulk density change with different nitrogen. A tendency to form nitrogen gas pore increased with increasing nitrogen content.

When the segregated nitrogen reaches the critical content in the residual melt between δ-ferrite dendrites,

Table 2. Chemical composition of Fe-16Cr-3Ni-9Mn stainless steel castings

| # | Mold | Cr | Ni | Mn | C | Si | N | Fe |
|---|---|---|---|---|---|---|---|---|
| 1) | STS | 16.30 | 3.05 | 8.59 | 0.021 | 0.38 | 0.15 | Bal. |
| | W.C Cu | 16.31 | 3.06 | 8.59 | 0.020 | 0.38 | 0.15 | Bal. |
| 2) | STS | 15.94 | 3.39 | 9.87 | 0.006 | 0.55 | 0.19 | Bal. |
| | W.C Cu | 15.93 | 3.38 | 9.87 | 0.006 | 0.54 | 0.19 | Bal. |
| 3) | STS | 16.13 | 2.90 | 9.15 | 0.021 | 0.52 | 0.20 | Bal. |
| | W.C Cu | 16.16 | 2.90 | 9.21 | 0.021 | 0.52 | 0.20 | Bal. |
| 4) | STS | 16.32 | 3.04 | 8.67 | 0.020 | 0.41 | 0.21 | Bal. |
| | W.C Cu | 16.31 | 3.06 | 8.59 | 0.020 | 0.38 | 0.21 | Bal. |
| 5) | STS | 16.05 | 3.03 | 9.03 | 0.021 | 0.48 | 0.23 | Bal. |
| | W.C Cu | 16.07 | 3.01 | 9.07 | 0.022 | 0.48 | 0.23 | Bal. |
| 6) | STS | 16.22 | 3.02 | 9.13 | 0.023 | 0.52 | 0.26 | Bal. |
| | W.C Cu | 16.21 | 2.99 | 9.07 | 0.021 | 0.52 | 0.26 | Bal. |

Table 3. Chemical composition of Fe-16Cr-3Ni-11Mn stainless steel castings

| # | Mold | Cr | Ni | Mn | C | Si | N | Fe |
|---|---|---|---|---|---|---|---|---|
| 1) | STS | 16.26 | 2.79 | 11.19 | 0.025 | 0.51 | 0.19 | Bal. |
| | W.C Cu | 16.29 | 2.75 | 11.02 | 0.023 | 0.50 | 0.19 | Bal. |
| 2) | STS | 16.33 | 2.78 | 11.09 | 0.022 | 0.49 | 0.25 | Bal. |
| | W.C Cu | 16.29 | 2.78 | 11.14 | 0.023 | 0.50 | 0.24 | Bal. |
| 3) | STS | 16.22 | 2.77 | 11.01 | 0.022 | 0.48 | 0.25 | Bal. |
| | W.C Cu | 16.20 | 2.78 | 11.07 | 0.023 | 0.48 | 0.25 | Bal. |

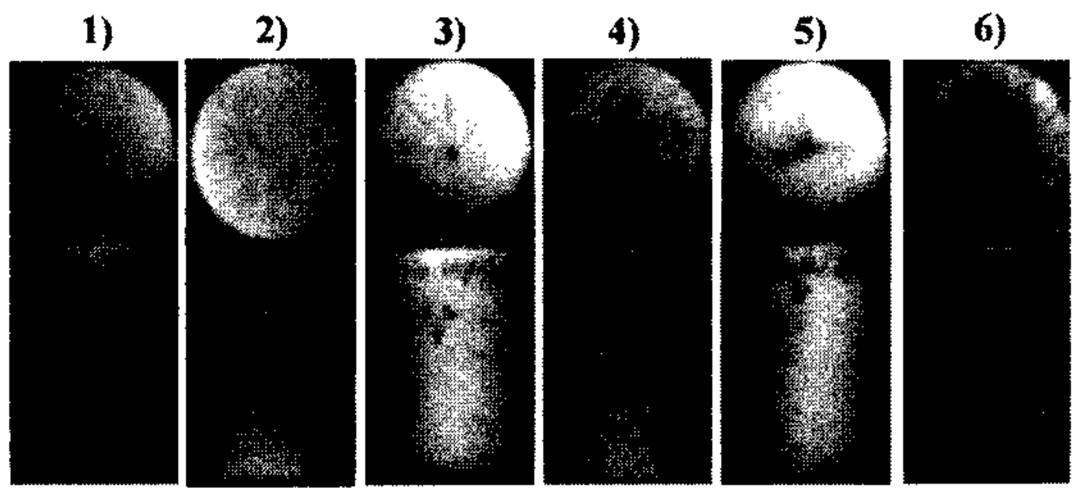


Fig. 2. Radiographs of Fe-16Cr-3Ni-9Mn stainless steel castings (STS mold); 1) 0.15, 2) 0.19, 3) 0.20, 4) 0.21, 5) 0.23, and 6) 0.26 wt%N.

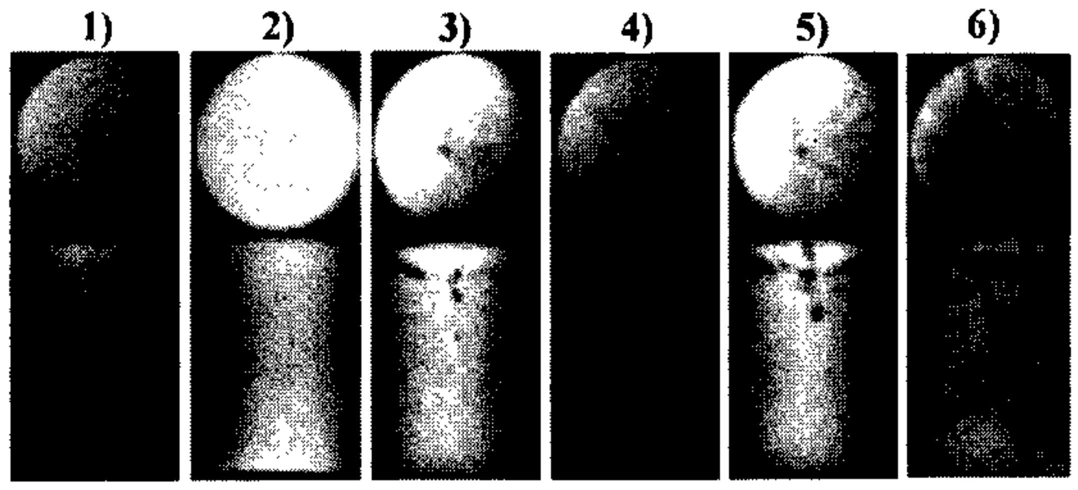


Fig. 3. Radiographs of Fe-16Cr-3Ni-9Mn stainless steel castings (water-cooled Cu mold); 1) 0.15, 2) 0.19, 3) 0.20, 4) 0.21, 5) 0.23, and 6) 0.26 wt%N.

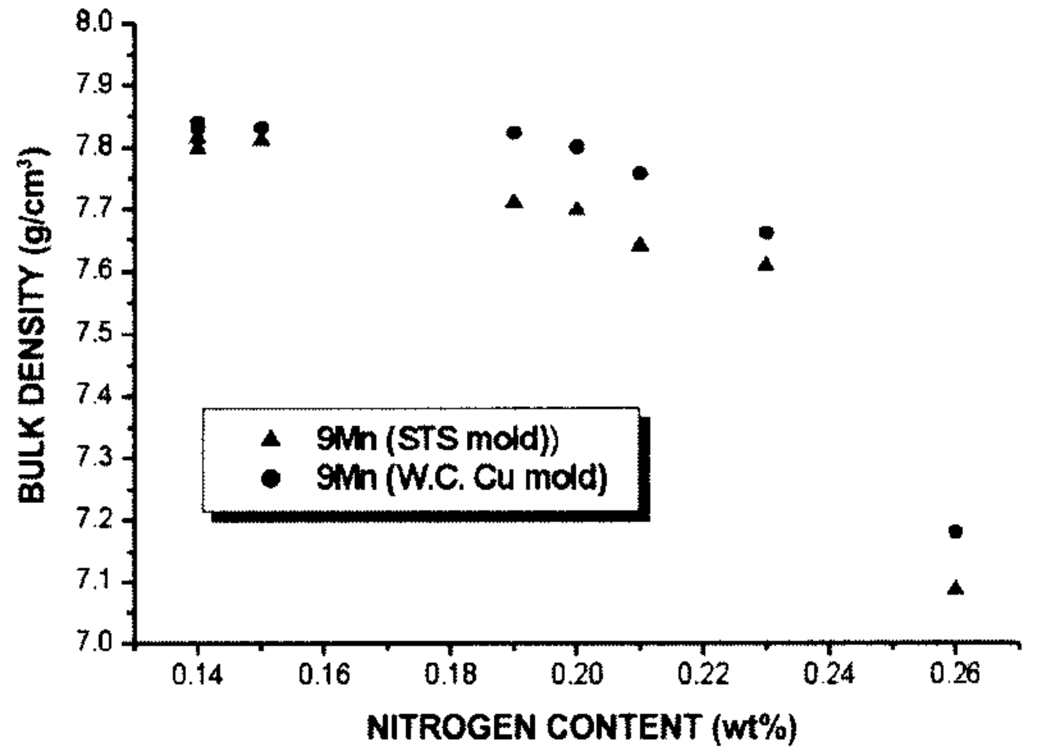
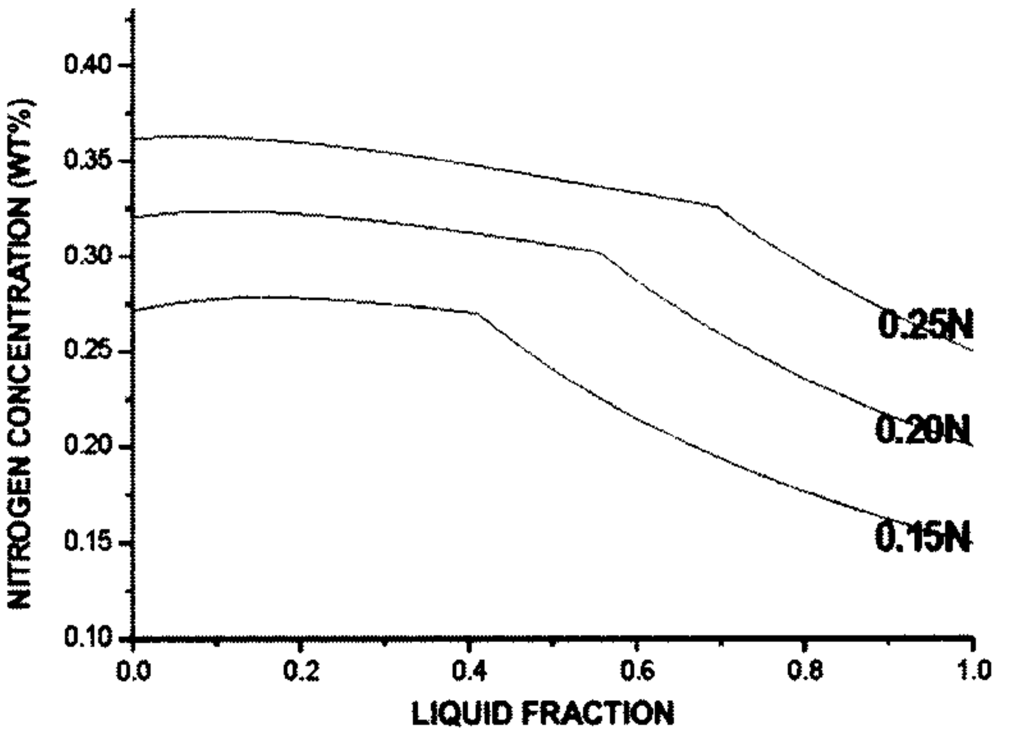
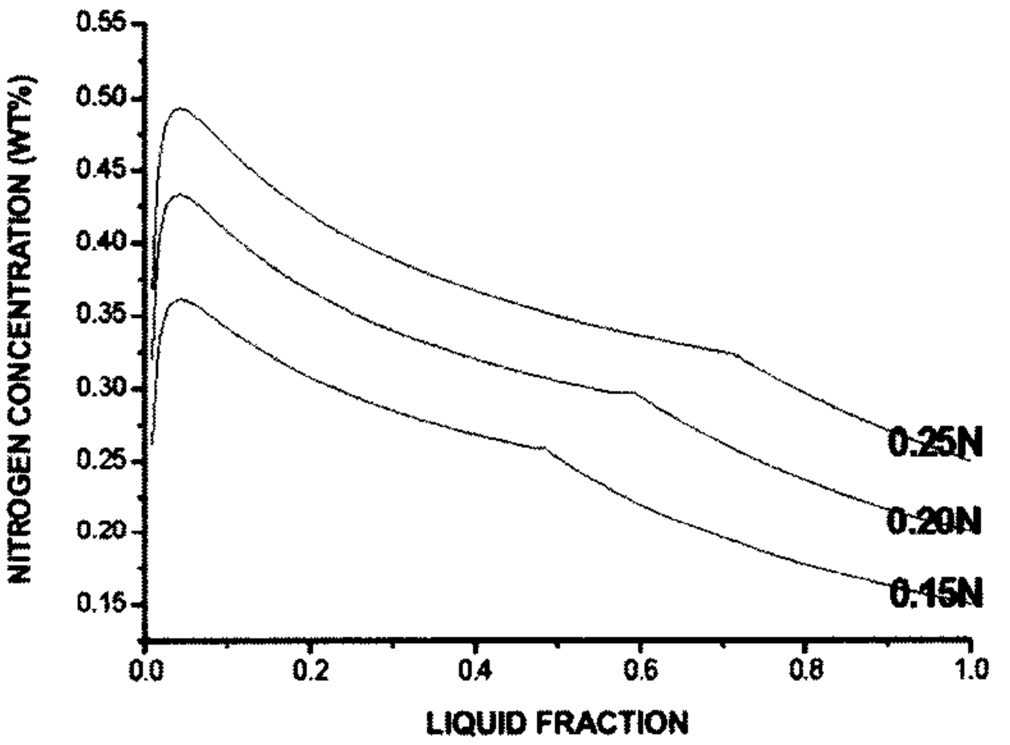


Fig. 4. Bulk density change of castings with different nitrogen content

nitrogen gas pores can nucleate. The gas pore shows the shape grown first along the solidification direction. And the gas pores, which can rise, were observed at the upper part of the casting.



**(a) EQUILIBRIUM SOLIDIFICATION**



**(b) SCHEIL SOLIDIFICATION**

Fig. 5. The segregation of nitrogen during solidification of Fe-16Cr-3Ni-9Mn with different nitrogen content.

## 3.2 Determination of critical nitrogen partial pressure

The software for the calculation was ThermoCalc and database was TCFE 2000. If nitrogen gas phase considered in the calculation, nitrogen can segregate only up to the equilibrium concentration with gas phase. So it is reasonable that gas phase was excluded to make nitrogen supersaturate until nucleation of gas pore during solidification. Calculation was done for equilibrium and Scheil solidification, because real solidification is somewhere in between equilibrium and Scheil solidification.

Fig. 5 shows the nitrogen concentration in the residual melt during solidification of Fe-16Cr-3Ni-9Mn stainless steels with different nitrogen content for equilibrium and Scheil solidification. As solidification proceeds, the nitrogen concentration in the residual melt increases. An inflection point means the formation of austenite phase.

The nitrogen partial pressure in the residual melt can be determined by the segregation of nitrogen and all other alloying elements during solidification.

Satir-Kolorz[5] et al. measured the effect of nitrogen partial pressure and the contents of alloying elements on the solubility of nitrogen in steel melt and reported an empirical formula as follows

$$e_N^{Cr}\cdot(\ \%Cr_{eq}) + r_N^{Cr}\cdot(\ \%Cr_{eq})^2$$
$$= \log K + 0.5\log P_{N_2} - \log[\ \%N] - e_N^{N}\cdot[\ \%N]$$

where $e_N^{Cr}$ and $r_N^{Cr}$ mean the 1st and 2nd order interaction parameter of chromium. The logarithm of the equilibrium constant K at 1600°C of pure iron melt is 1.354. The Cr equivalent concentration ($\%Cr_{eq}$) can be defined by $\Sigma C_N^{Xi}\cdot(\%X_i)$ and $C_N^{Xi}$ is the Cr equivalent factors of alloying elements at 1600°C in Table 1.

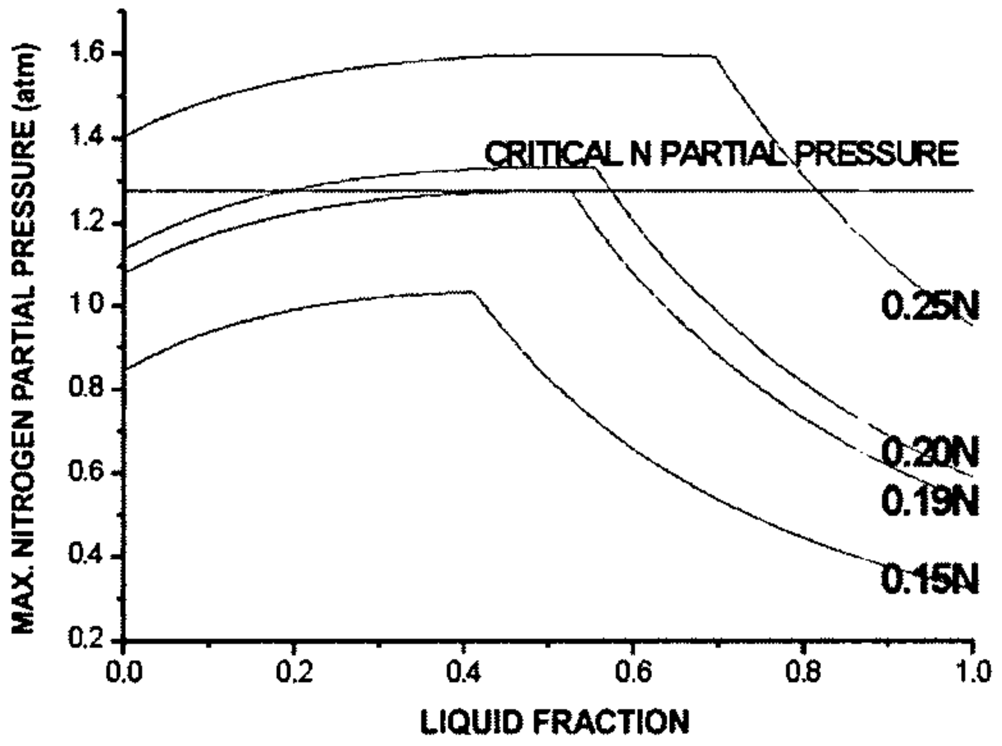
In this approach, the effect of temperature on the equilibrium between nitrogen gas and steel melt was ignored and the nitrogen partial pressure during solidification of Fe-16Cr-3Ni-9Mn stainless steels was calculated as shown in Fig. 6. The critical nitrogen partial pressure was 1.27 and 1.23 atm for equilibrium and Scheil solidification respectively, reflecting the experimental result of critical nitrogen content (0.19 wt%).

## 3.3 Estimation of the critical nitrogen content of Fe-16Cr-3Ni-11Mn stainless steels

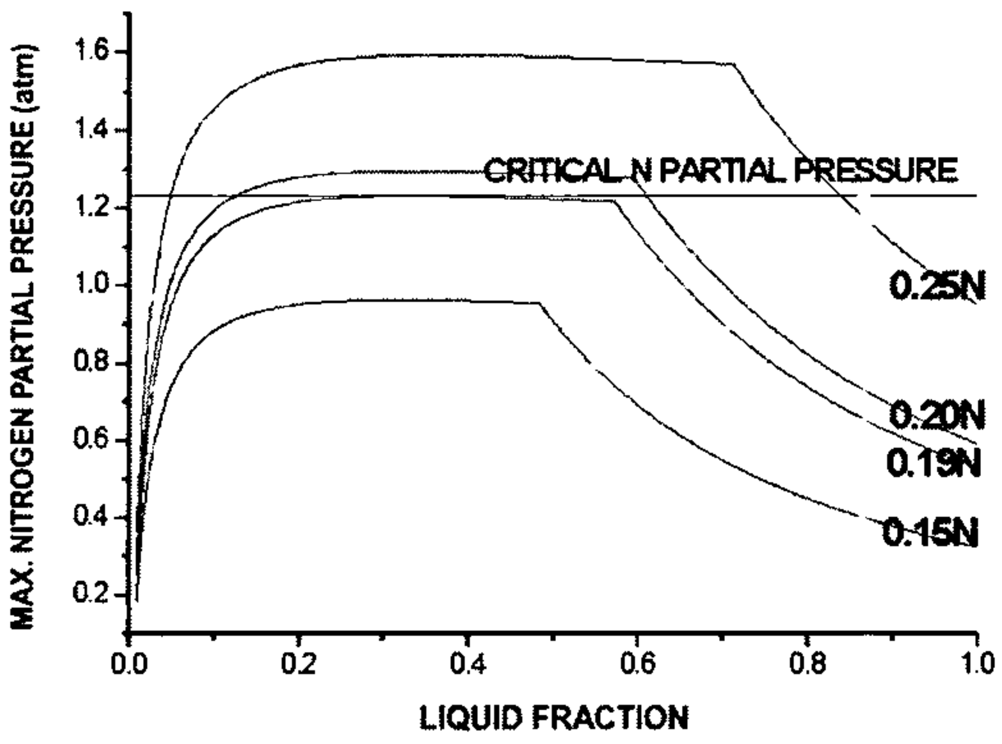
Manganese is an element that stabilizes austenite phase and increases nitrogen solubility at the same time since nitrogen has much greater solubility in austenite than ferrite phase. So it can be expected that an increase in Mn content can suppress the formation of nitrogen gas pores.

Fig. 7 shows the nitrogen partial pressure during solidification of Fe-16Cr-3Ni-11Mn stainless steels.

The critical nitrogen pressures were applied to Fe-16Cr-3Ni-11Mn stainless steels. The nitrogen partial

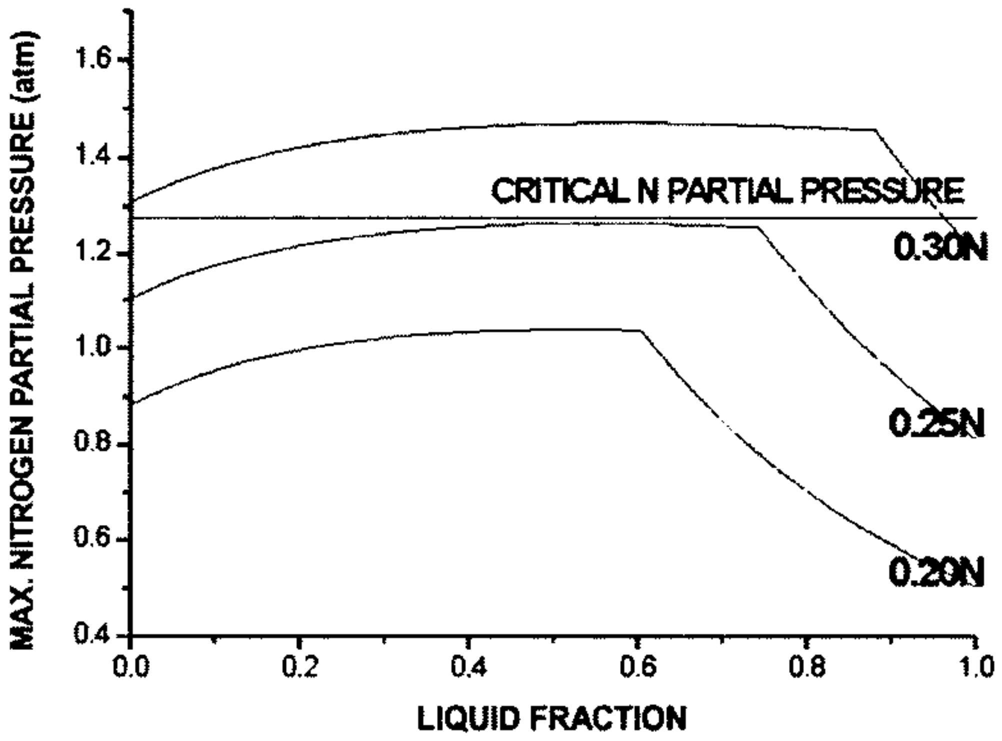


(a) EQUILIBRIUM SOLIDIFICATION

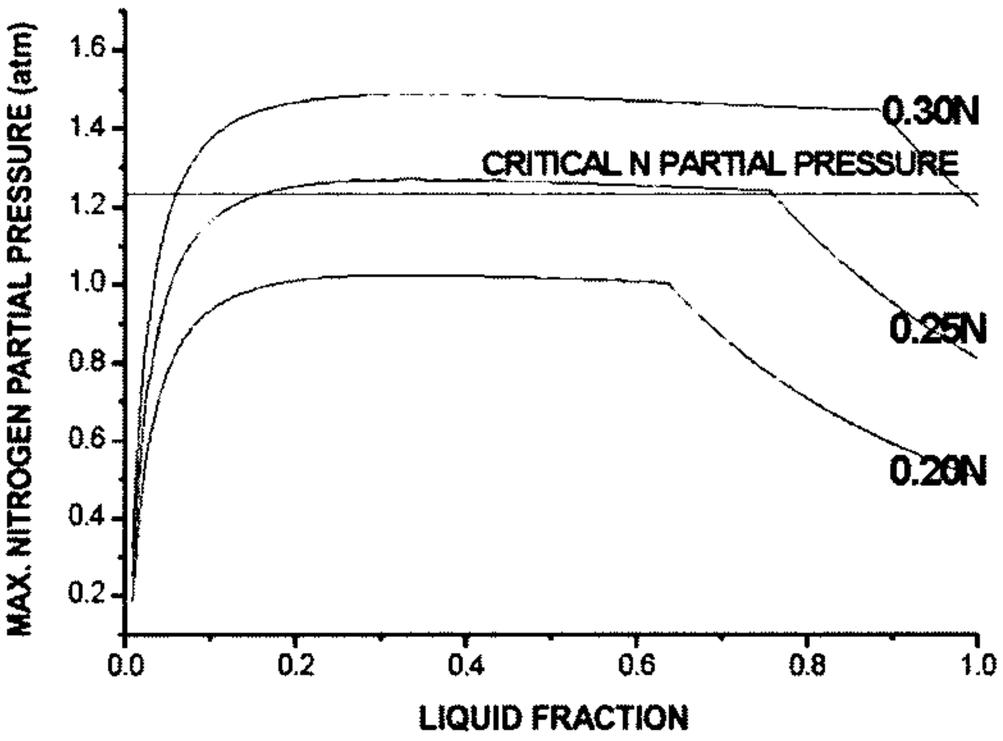


(b) SCHEIL SOLIDIFICATION

Fig. 6. The nitrogen partial pressure during solidification of Fe-16Cr-3Ni-9Mn with different nitrogen content.

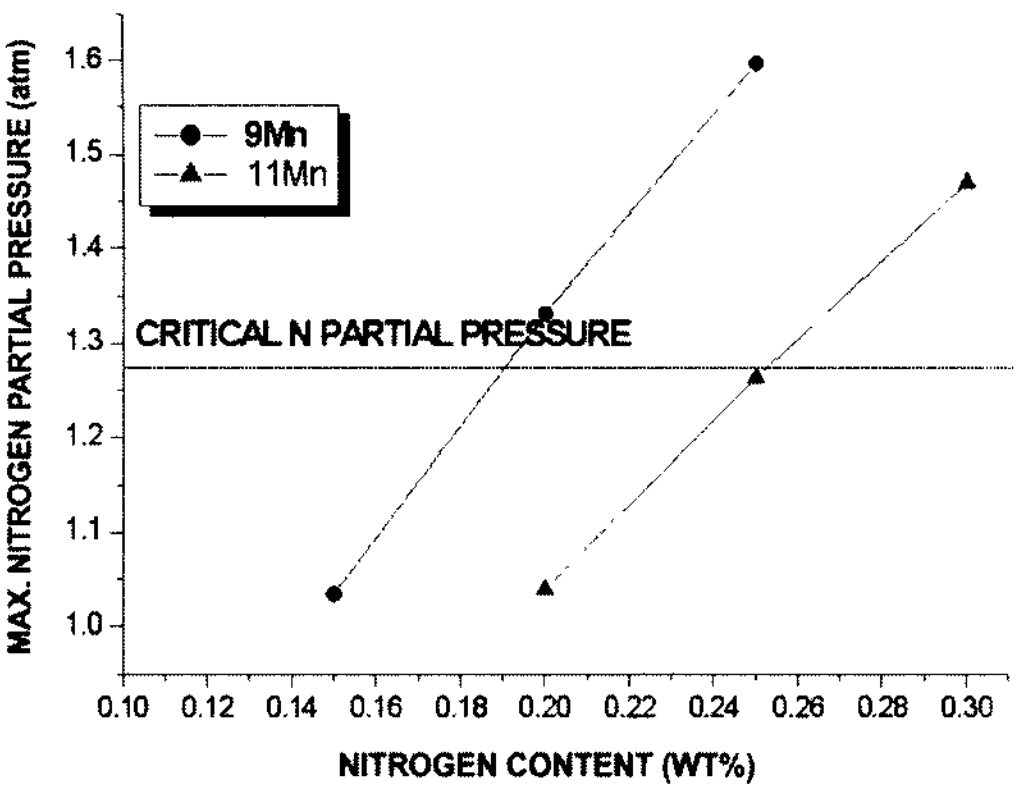


(a) EQUILIBRIUM SOLIDIFICATION

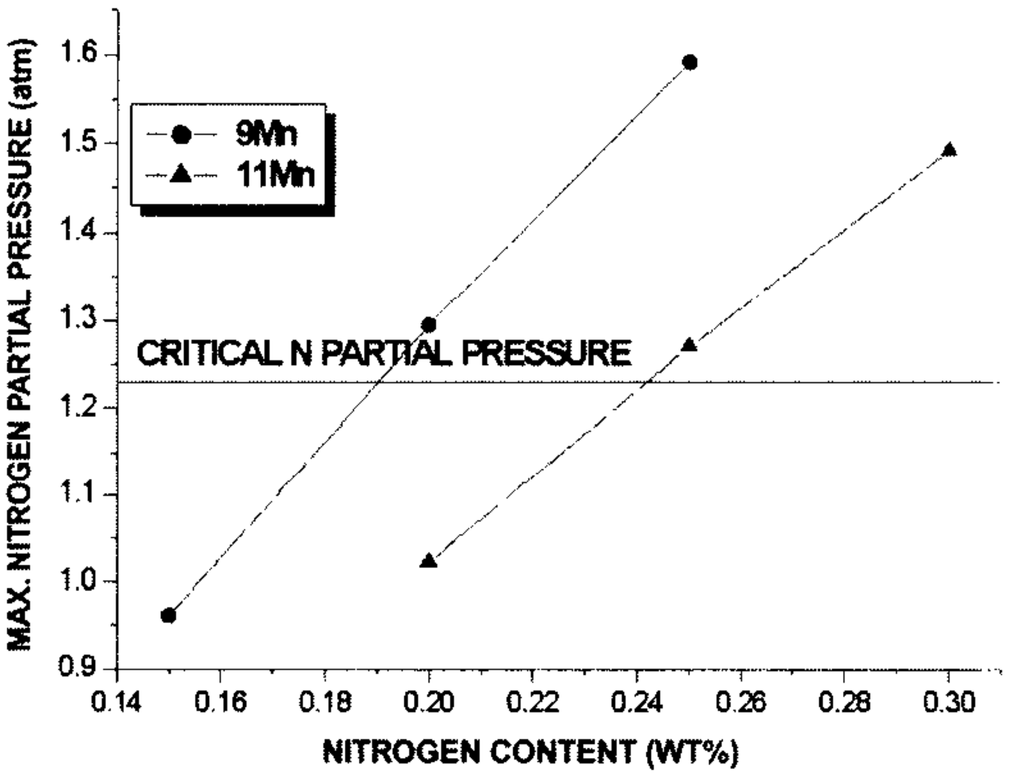


(b) SCHEIL SOLIDIFICATION

Fig. 7. The nitrogen partial pressure during solidification of Fe-16Cr-3Ni-11Mn with different nitrogen content.



(a) EQUILIBRIUM SOLIDIFICATION



(b) SCHEIL SOLIDIFICATION

Fig. 8. Maximum nitrogen partial pressures in the residual melt during solidification of Fe-16Cr-3Ni-xMn (x = 9 and 11) with different nitrogen content.

pressure reaches to the critical nitrogen pressure at about 0.25wt%N.

Fig. 8 shows maximum nitrogen pressure in the residual melt during solidification of Fe-16Cr-3Ni stainless steel containing 9 and 11wt% Mn. Therefore, the estimated critical nitrogen contents of Fe-16Cr-3Ni-9Mn are 0.25 and 0.24wt% for equilibrium and Scheil solidification respectively.

### 3.4 Experimental verification

An increase in Mn content suppressed the formation of nitrogen gas pore as expected. Fig. 9 and Fig. 10 show radiographs of Fe-16Cr-3Ni-11Mn stainless steel castings. A small amount of nitrogen gas pore was observed at the upper part of the casting containing 0.25 wt%N (Fig. 9 (2)).

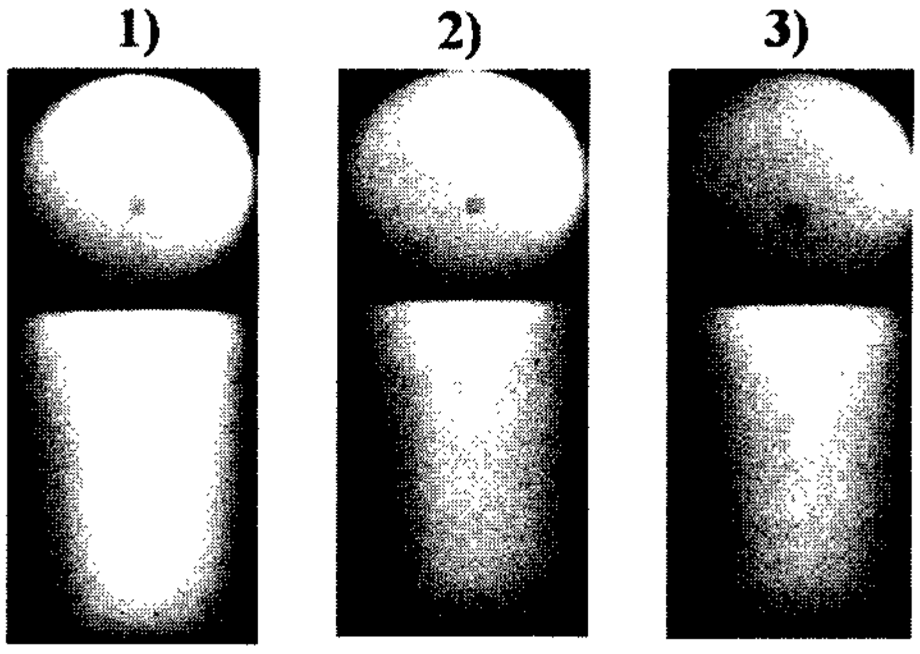


Fig. 9. Radiographs of Fe-16Cr-3Ni-11Mn stainless steel castings (STS mold); 1) 0.19, 2) 0.25, and 3) 0.25 wt%N.

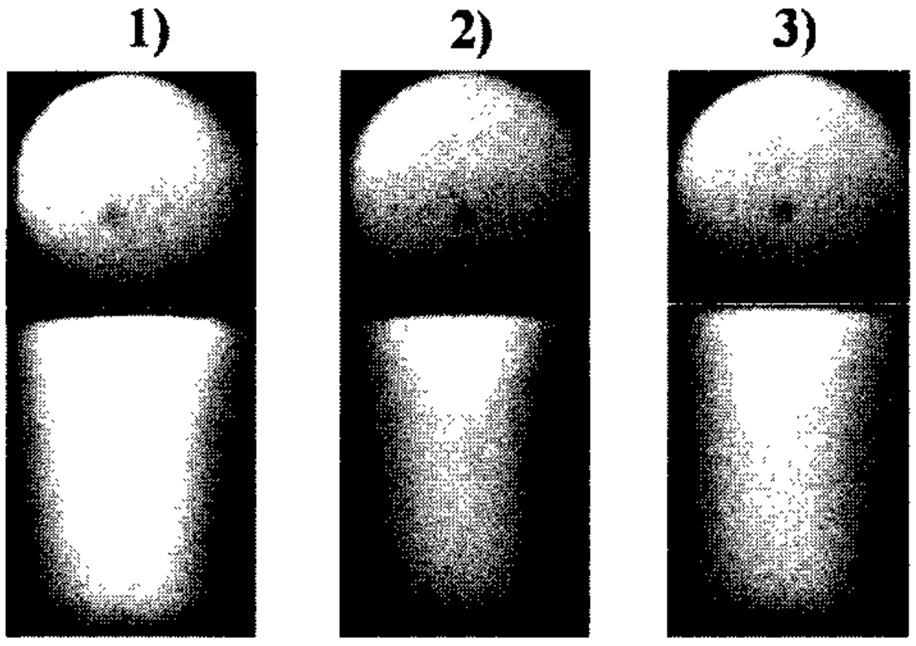


Fig. 10. Radiographs of Fe-16Cr-3Ni-11Mn stainless steel castings (water-cooled Cu mold); 1) 0.19, 2) 0.24, and 3) 0.25 wt%N.

All castings except one casting (Fig. 9 (2)) has no gas pores. So it can be said that the critical nitrogen content of Fe-16Cr-3Ni-11Mn stainless steel was about 0.25wt%N. This value shows good agreement with estimated value.

## 4. Conclusions

The effect of nitrogen content and cooling rate on the formation of gas pores in Fe-16Cr-3Ni-9Mn stainless steels was investigated. The critical nitrogen content for the formation of gas pores was 0.19 wt%, and the amount of nitrogen gas pores increased with initial nitrogen content of casting. Increasing cooling rate reduced the amount of the nitrogen gas pores slightly.

The segregation of nitrogen and alloying elements were calculated with ThermoCalc.

The calculated data and the experimental results were compared to calculate the critical nitrogen pressure. The critical nitrogen partial pressure was 1.27 atm and 1.23 atm for equilibrium and Scheil solidification respectively.

The critical nitrogen pressure was applied to Fe-16Cr-3Ni-11Mn stainless steels and the estimated critical nitrogen content was 0.25 and 0.24 wt% for equilibrium and Scheil solidification respectively.

The critical nitrogen content of Fe-16Cr-3Ni-11Mn stainless steels experimentally investigated was about 0.25 wt% that was coincident with estimated critical nitrogen contents.

## Acknowledgements

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## References

[1] V. G. Gavriljuk: ISIJ int., "Nitrogen in iron and steel", 36(7)(1996), 738-745.

[2] H. K. Feichtinger and G. Stein : Mater. Sci. Forum, "Melting of high nitrogen steels", 318-3(1999), 261-270.

[3] J.S. Dunning, J.W. Simmons and J.C. Rawers : JOM-J. Min. Met. Mat. S., "Advanced processing technology for high-nitrogen steels", 46(3)(1994), 40-42.

[4] J.C. Rawers, G. Asai, R. Doan and J. Dunning, J. Mater. Res., "Mechanical and microstructural properties of nitrogen-high pressure melted Fe-Cr-Ni alloys", 7(5) (1992), 1083-1092.

[5] A. H. Satir-Kolorz and H. K. Feichtinger : "On the solubility of nitrogen in liquid iron and steel alloys using elevated pressure", Z Metallkd, 82 (9)(1991), 689-697.

[6] J.O. Andersson *et al.* : CALPHAD, "THERMO-CALC & DICTRA, computational tools for materials science", 26(2002) 273-312