Modelling of Effects of Cold Work on Sigma Phase Growth Rate in Super Duplex Stainless Steel

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By the modelling of the precipitation and growth behaviour of the sigma phase the quantitative effects of amounts of cold work was investigated in super duplex stainless steels. The cold work promotes sigma phase precipitation. The equation to describe the growth rate of sigma phase proposed formerly by the authors was employed. That is based on the classical nucleation theory and J-M-A-K formula.

The effects of cold work was incorporated in that equation as two parameters. Those parameters were determined using the experimental data. Experimental data was obtained by measuring the growth of sigma phase in the isothermally heated specimen at 1 173 and 1 223 K. The specimens consisting of 25mass%Cr-mass7%Ni-3mass%Mo-2mass%W-0.3mass%N super duplex stainless steel were prepared with various reduction levels of 3 to 10% in cold rolling process. As result the model to described quantitatively the effect of the amount of cold work on the acceleration of sigma phase was proposed. The validity of the model was confirmed by clarifying to have good fit to the experimental data referred from another work published.

KEY WORDS: duplex stainless steel; sigma phase; modelling; cold work; growth rate; kinetics.

1. Introduction

Duplex stainless steels are widely applied to the various structures because they exhibit high cost performance. These steels have the potential to obtain a high corrosion resistance, high strength and high toughness economically because they have lower nickel content in comparison with that in austenitic stainless steels. In later years, super duplex stainless steels improved in terms of corrosion resistance due to the increase in the amount of chromium, molybdenum, tungsten¹⁻⁴⁾ and nitrogen have been developed. The increase in the amount of these elements promotes the harmful intermetallic such as sigma phase. Therefore the prevention of this phase formation is an important subject in the welding, fabrication, and manufacturing process.

Many research works have focused on sigma phase precipitation in duplex stainless steel applicable to the heat treatment, hot work or welding process. In many research works focusing on the precipitation kinetics of the sigma phase, the growth properties were determined by using an experimental method and in steels of various chemistries.⁵⁻¹⁸⁾

It is well known that sigma phase precipitation is accelerated in cold worked steel duplex stainless steel.¹⁹⁾ Time-temperature-precipitation (TTP) curve of sigma phase

is shifted to the direction of shorter time in duplex stainless steels consisting of various chemical compositions. However it is not easy to extend those findings to any other duplex stainless steel in the different chemical composition. Regarding the solution treated steels the authors have proposed the model to describe the effect of alloying elements such as chromium or molybdenum on the growth of sigma phase in previous works.²⁰⁻²²⁾ In this paper as the first step to proposal of quantitative prediction way of the TTP curve of sigma phase precipitation in cold worked steels the modelling of effects of cold work on sigma phase growth rate and TTP curve in super duplex stainless steel was investigated using the model proposed in previous works.^{21,22)}

2. Experimental

Duplex stainless steel of UNS S39274 shown in **Table 1** were melt with a laboratory electric furnace. Those steels were fabricated to the 15 mm thick plates by hot forging and hot rolling followed by solution treatment. Solution treatment is performed at 1 323 K for 1 800 s and quenched by

Table 1. Chemical compositions of steels tested (mass%).

C	Si	Mn	P	S	Ni	Cr	Mo	W	N
0.02	0.16	0.50	0.019	0.001	7.13	25.34	3.05	2.03	0.316

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Fig. 1. Examples of sigma phase growth heated at 1 173 K in 10% cold worked steel and in as solution treated steel of 25mass%Cr-7mass%Ni-3mass%Mo-2mass%W-0.3mass%N.

water. The plates were cold worked with various reduction of 3%, 6%, 10% in thickness. Employing those plates the specimens were machined to be 11 mm thick, 11 mm wide and 60 mm long and heated at various constant temperatures at 1 173 K or 1 273 K during various time followed by quenching with helium gas. In addition the long term heating for 360 ks at each temperature same as the above tests in order to the equilibrium fraction of sigma phase. After the heat treatment the specimens were polished and electrochemically etched in 10% oxalic acid and 10 N KOH aqueous solution in cross section for microstructure observation. As an example **Fig. 1** shows the optical microstructure of cold worked 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel heated at 1 173 K for 1 000 s. Area fraction of sigma phase etched as black phase was measured with an image analyser. In this work all the % regarding chemical compositions mean mass%.

3. Application of Kinetic Model to Cold Worked Steel

The incorporation of effect of cold work in growth model in the present theoretical model was investigated. It has been clarified in the previous work^{21,22)} that the growth of the sigma phase in the early stage in duplex stainless steels is according to the following equations based on the traditional nucleation theory.²³⁾ The parameter X , which is the ratio of the fraction of transformed phase to that in the equilibrium, is given as the following equation. In Eq. (1) t is heating time and m is the degree in the J-M-A-K law.²³⁾

$$X = 1 - \exp[-(k_p \cdot t)^m] \quad \text{..... (1)}$$

The growth rate constant k_p in Eq. (1) has been proposed as the following by the authors in the previous work.^{21,22)}

$$k_p = K_{00} (T_{eq} / \Delta T)^{4/5} D_{eff} \exp[-\phi (T_{eq} / \Delta T)^2 / RT] \quad \text{..... (2)}$$

$$\phi = \frac{32\pi}{15} V^2 N \sigma^3 / (C_p \Delta H)^2 \quad \text{..... (3)}$$

Here the parameter of K_{00} is expressed as the following form the previous work.²⁰⁾ R is gas constant and N is Avogadro's number.

$$K_{00} = \left[16\sqrt{2} \cdot \frac{\pi^2}{15} \cdot V C_0 N_x \omega_0^{1/2} \sigma^2 / (C_p \Delta H)^2 / r_a^4 \right]^{2/5} \quad \text{..... (4)}$$

The parameter of r_a is the lattice constant and ω_0 is super saturation defined as the same as the previous work²⁰⁾

$$= \left[\frac{\sqrt{2\pi}}{2} C_0 N_x \omega_0^{1/2} \phi / (V N \sigma r_a^4) \right]^{2/5} \quad \text{..... (5)}$$

Here the parameter of N_x is number of atoms to determine the growth rate, V is the molar volume, σ is the interface energy between sigma and ferrite phase, D_{eff} is the effective diffusion constant²⁰⁾ of the dominant atom, ΔH is the enthalpy of transformation of intermetallic, T_{eq} is the solvus temperature of the intermetallic phase, ΔT is the amount of undercooling ($=T_{eq} - T$), and C_p is the concentration of the dominant atom to determine the growth rate in the intermetallic phase and C_0 is concentration of the dominant atom to determine the growth rate in the steel.

In the cold worked duplex stainless steels the dislocation density can increase, so that the diffusion constant D_{eff} and the enthalpy of transformation of intermetallic ΔH can be influenced by cold work. Those two influence factors of cold work were incorporated in the growth rate constant k_p by applying the parameters of λ_1 and λ_2 as the function of

the amount of cold work.

$$k_{p,cw} = \lambda_1 K_{00} (T_{eq} / \Delta T)^{4/5} D_{eff} \exp[-\lambda_2 \phi (T_{eq} / \Delta T)^2 / RT] \quad (6)$$

, where the values of λ_1 and λ_2 equal to 1 in the solution treated steel without cold work.

Quantitative modelling of effects of cold work on sigma phase growth is achieved by determining of the parameters incorporated as the function of the amount of cold work. The growth rate constant k_p is the function of temperature and determined by the four parameters of D_{eff} , T_{eq} , ϕ and K_{00} . Two parameters D_{eff} and T_{eq} of four are given by the thermodynamics data base. So that by the following experiment the rests of two parameters ϕ and K_{00} were determined. The unknown parameters of λ_1 and λ_2 are determined by applying the experimental value of k_p at least at some two reference temperatures of T_{r1} and T_{r2} to the following equations.

$$k_{p,cw}(T_{r1}) = \lambda_1 K_{00} (T_{eq} / \Delta T_{r1})^{4/5} D_{eff} \exp[-\lambda_2 \phi (T_{eq} / \Delta T_{r1})^2 / RT_{r1}] \quad (7)$$

$$k_{p,cw}(T_{r2}) = \lambda_1 K_{00} (T_{eq} / \Delta T_{r2})^{4/5} D_{eff} \exp[-\lambda_2 \phi (T_{eq} / \Delta T_{r2})^2 / RT_{r2}] \quad (8)$$

4. Application of Model to Experimental Data

4.1. Sigma Phase Growth in Cold Worked Specimens

Figure 1 shows the examples of microstructure in cold worked specimens heated at 1 173 K for the durations of 100 s. In these micrographs the sigma phase is observed as black phase. The larger fraction of sigma phase was formed in the cold rolled specimen with 10% reduction. The black etched area fraction of sigma phase was measured with the image analyser²¹⁾ using the specimens heated at the constant temperature for the various durations.

4.2. Determination of Parameters by Experiment

To clarify the applicability of Eq. (1) to the cold worked steels, the progress of transformation as the form of $\log(-\log(1-X))$ were plotted against the heating time as shown in **Figs. 2 and 3**. From the results it was found that the sigma phase grew according to the J-M-A-K²³⁾ Eq. (1) with the value of m as 2.5. The growth rate constants $k_{p,cw}$ obtained from those results. Using the values of $k_{p,cw}$ at the two reference temperatures of 1 173 K and 1 223 K the parameters of λ_1 and λ_2 were obtained as shown in **Table 2**. The experimental values of $k_{p,cw}$ were plotted against the temperature together with the calculated curves as shown **Fig. 4**. The calculated curves are produced applying the parameters to Eq. (6) based on the model proposed in the previous work.²¹⁾ The calculated curves sufficiently agreed with the experimental data. The relation between the parameters of λ_1 and λ_2 and the amount of cold work are shown in **Fig. 5**. Both parameters increased proportionally to the amount of cold work CW(%) and the following experimental formula for engineering use to estimate the influence of cold work were obtained.

$$\lambda_1 = 1 + 0.35CW(\%) \quad (9)$$

Fig. 2. Sigma phase growth during isothermal heating at 1 173 K in steels with various reduction level in cold rolling.

Fig. 3. Sigma phase growth during isothermal heating at 1 223 K in steels with various reduction level in cold rolling.

Table 2. Values of parameters λ_1 and λ_2 for precipitation model proposed in cold worked steels obtained by experiment.

CW (%)	T_{eq} (K)	ϕ	K_{00} (s ⁻¹)	λ_1	λ_2
0	1 339	200	2.8×10^{11}	1	1
3	1 339	200	2.8×10^{11}	1.9	1.1
6	1 339	200	2.8×10^{11}	3.5	1.3
10	1 339	200	2.8×10^{11}	4.3	1.4

$$\lambda_2 = 1 + 0.042CW(\%) \quad (10)$$

4.3. Extension to TTP-curve

TTP curve is understood to be a kind of contour line of the each progress of precipitation. The time t_c to each fraction ratio of precipitation X_0 is calculated by the Eq. (9) obtained from the above Eqs. (1) and (6).

Fig. 4. Effect of heating temperature on sigma phase growth rate constant in various cold worked steels.

Fig. 5. Coefficients λ_1 and λ_2 to apply parameters ϕ and K_{00} to cold worked steels.

$$t_c = (\lambda_1 K_{00})^{-1} [-\ln(1 - X_0)]^{0.4} (T_{eq} / \Delta T)^{-0.8} / D_{eff} \exp[\lambda_2 \phi (T_{eq} / \Delta T)^2 / RT] \quad \dots (11)$$

TTP curves for X_0 of 0.5% and 1.5% are drawn using this equation together with the experimental results with the volume fraction of 1% as the criteria as shown in Figs. 6 to 9. The curves obtained had approximately good fit to the experimental results shown as plotted data.

The temperature and the time at the nose of TTP curve are obtained as the solution when the value of $\partial t / \partial T$ of Eq. (9) equals to 0. The effect of the amount of cold work on the nose time of TTP curve predicted is shown in Fig. 10. The nose time with the criteria of 1% in sigma phase fraction in

Fig. 6. Comparison of C-curve calculated by physical model and experimental results in as solution treated without cold work steel.

Fig. 7. Comparison of C-curve calculated by physical model and experimental results in 3% cold worked steel.

Fig. 8. Comparison of C-curve calculated by physical model and experimental results in 6% cold worked steel.

Fig. 9. Comparison of C-curve calculated by physical model and experimental results in 10% cold worked steel.

Fig. 10. Effect of amount of cold work on nose time of 1% sigma phase fraction.

the 6% cold worked steel can be approximately half of that in as solution treated steel.

5. Discussion

The physical meaning of effect of cold work on the parameters of λ_1 , λ_2 is investigated. Dislocation density is increased by cold working. As results the number of nucleation sites and vacancy density are increased. The parameter of λ_1 is considered as consisting of the product of the parameters of λ_{1a} and λ_{1b} . The parameter λ_{1a} regards the increase of number of nucleation sites N_x resulting in $\lambda_{1a}N_x$ in Eq. (4) and the parameter λ_{1b} regards the increase of vacancy to accelerate the diffusion of atoms. The diffusion of dominant atom of alloying elements such as chromium is driven by exchanging positions in the lattice between the atoms and the vacancies. Therefore the increase of vacancy by cold working accelerates the diffusion of atoms due to the increase of diffusion path. As results It is understood the parameter of λ_1 means the proportional coefficient which reflects the increase of dislocation with the increase of the amount of cold work. However the effect of acceleration of diffusion by dislocation can be reduced in the higher temperature. The parameter of λ_2 is considered to play the role to reduce the excessive acceleration effect with the elevation

Fig. 11. Comparison calculated curve of 5% sigma phase fraction by this work's model and measured data in other work in 25 mass%Cr-7 mass%Ni-3 mass%Mo-0.2mass%N steel.

of temperature as described in the following.

While the driving force for nucleation of intermetallic phase ΔG corresponds to $C_p \Delta H \Delta T / T_{eq}^{23}$ the growth rate constant in the cold worked steel is written as the following in the basis of Eqs. (3) and (6).

$$k_{p,cw} = \lambda_1 K_{00} (T_{eq} / \Delta T)^{4/5} D_{eff} \exp \left[-\lambda_2 \frac{32\pi}{15} V^2 N \sigma^3 / (\Delta G)^2 / RT \right] \quad \text{..... (12)}$$

When the driving force is as ΔG_{cw} in the cold worked steel,

$$k_{p,cw} = \lambda_1 K_{00} (T_{eq} / \Delta T)^{4/5} D_{eff} \exp \left[-\frac{32\pi}{15} V^2 N \sigma^3 / (\Delta G_{cw})^2 / RT \right] \quad \text{..... (13)}$$

$$\Delta G_{cw} = \Delta G / \sqrt{\lambda_2} \quad \text{..... (14)}$$

From the above equation the parameter of λ_2 has the effect to reduce the driving force of nucleation. As results that contributes to reducing the excessive acceleration by the increase of dislocation in the higher temperature range. Because the effect of the term of

$$\exp \left[-\frac{32\pi}{15} V^2 N \sigma^3 / (\Delta G_{cw})^2 / RT \right]$$

on the value of $k_{p,cw}$ is the less in the higher temperature range.

To clarifying validity and extendability of this model proposed, the applicability to the data obtained in another work¹⁹⁾ was investigated. The data were extracted from the Maeharas' work¹⁹⁾ published in TETSU-to-HAGANE. That work has shown the experimental data regarding the growth properties of sigma phase in cold worked steels with the reduction of 12.5% by cold rolling. Those have been obtained using the steel corresponding to SUS329J4L and by measuring fractions of sigma phase after heated at 1 073 K for various duration. For the reference the time to the fraction of 5% of sigma phase were extracted from the experimental data.¹⁹⁾ The TTP curves of 5% sigma phase fraction of SUS329J4L

steel as solution treated was calculated applying the value of parameters of T_{eq} , K_{00} and ϕ of 25Cr-7Ni-3Mo-0.3N steel shown in previous work²¹⁾ to Eq. (11). The TTP curves of 5% sigma phase fraction in cold worked steel was calculated using Eq. (11) after calculating the parameter of λ_1 and λ_2 by applying the value of CW of 12.5% to Eqs. (9) and (10). The results are shown in **Fig. 11**, where the referred experimental data were plotted together. The experimental data plotted from in another work had good fit to the calculated TTP curve at 1 073 K. From the results the validity and extendability of this model proposed to another duplex stainless steel consisting of different chemical composition was confirmed.

6. Conclusion

The following conclusions were obtained from the investigation regarding the sigma phase precipitation in cold worked duplex stainless steels.

(1) The sigma phase precipitation is accelerated by the increase in the amount of cold work.

(2) It was confirmed the sigma phase in the cold worked steel in the early stage of precipitation grows according to the kinetic model based on the classical nucleation theory proposed.

(3) The physical model was proposed to describe quantitatively the acceleration effect of cold working on the sigma phase precipitation as a function of the amount of cold work.

(4) The validity of the model proposed was confirmed by good fit to the experimental data of the duplex stainless steel consisting of different chemical composition referred from another work published.

REFERENCES

- 1) K. Ogawa, H. Okamoto, M. Ueda, M. Igarashi, T. Mori and T. Kobayashi: *Weld. Int.*, **10** (1996), 466.
- 2) K. Ogawa, H. Okamoto, M. Igarashi, M. Ueda, T. Mori and T. Kobayashi: *Weld. Int.*, **11** (1997), 14.
- 3) E. B. Haugan, M. Næss, C. T. Rodriguez, R. Johnsen and M. Iannuzzi: *Corrosion*, **73** (2017), 53.
- 4) H. Okamoto: Proc. Applications of Stainless Steel '92, (Stockholm), Stainless Steel World, Netherland, (1992), 360.
- 5) P. Ferro and F. Bonollo: *Metall. Mater. Trans. A*, **43** (2012), 1109.
- 6) H. Sieurin and R. Sandstrom: *Mater. Sci. Eng. A*, **444** (2007), 271.
- 7) A. P. Miodownik and N. Saunders: *Mater. Sci. Technol.*, **18** (2002), 861.
- 8) J. O. Nilsson, P. Kangas, A. Wilson and T. Karlsson: *Metall. Mater. Trans. A*, **31** (2000), 35.
- 9) J. W. Elmer, T. A. Palmer and E. D. Specht: *Metall. Mater. Trans. A*, **38** (2007), 464.
- 10) S. Wessman, L. Karlsson, R. Pettersson and A. Östberg: *Weld. World*, **56** (2012), No. 11–12, 79.
- 11) K. Nishimoto, K. Saida and O. Katsuyama: *Weld. World*, **50** (2006), No. 3–4, 13.
- 12) J. O. Nilsson, T. Huhtala, P. Jonsson, L. Karlsson and A. Wilson: *Metall. Mater. Trans. A*, **27** (1996), 2196.
- 13) S. Hertzman, T. Huhtala, L. Karlsson, J. O. Nilsson, M. Nilsson, R. Jargelius-Pettersson and A. Wilson: *Mater. Sci. Technol.*, **13** (1997), 604.
- 14) S. Hertzman, R. Pettersson, K. Frisk and T. Jerwin: Proc. 6th World Duplex Conf., (Venice), Associazione Italiana di Metallurgia, Milano, (2000), 347.
- 15) K. Kondo, M. Ueda, K. Ogawa, H. Okamoto and M. Igarashi: Proc. Innovation Stainless Steel, (Florence), Associazione Italiana di Metallurgia, Milano, (1993), 2191.
- 16) Y. H. Lee, K. T. Kim, Y. D. Lee and K. Y. Kim: *Mater. Sci. Technol.*, **14** (1998), 757.
- 17) Y. S. Ahn and J. P. Kang: *Mater. Sci. Technol.*, **16** (2000), 382.
- 18) Y. Machara, M. Koike, N. Fujino and T. Kunitake: *Trans. Iron Steel Inst. Jpn.*, **23** (1983), 240.
- 19) Y. Machara, N. Fujino and T. Kunitake: *Tetsu-to-Hagane*, **68** (1982), 673 (in Japanese).
- 20) K. Ogawa and T. Osuki: *Q. J. Jpn. Weld. Soc.*, **33** (2015), 55 (in Japanese).
- 21) K. Ogawa and T. Osuki: *ISIJ Int.*, **59** (2019), 122.
- 22) K. Ogawa and T. Osuki: *ISIJ Int.*, **59** (2019), 129.
- 23) T. Nishizawa: Thermodynamics of Microstructures, ASM International, Materials Park, OH, (2008), 91.
- 24) Y. Shimada, M. Hatakeyama, J. Hirabayashi, Y. Yamamoto, K. Sato and S. Sunada: *Mater. Trans.*, **60** (2019), No. 11, 2378.
- 25) I. F. Machao and A. F. Padilha: *ISIJ Int.*, **40** (2000), 719.
- 26) Y. Shimode, J. Cui, C.-Y. Kang and K. Miyahara: *ISIJ Int.*, **39** (1999), 191.
- 27) W. Reick, M. I. Pohl and A. F. Padilha: *ISIJ Int.*, **38** (1998), 567.
- 28) S.-C. Kim, Z. Zhang, Y. Furuya, C.-Y. Kang, J.-H. Sung, Q.-Q. Ni, Y. Watanabe and I.-S. Kim: *Mater. Trans.*, **46** (2005), 1656.
- 29) S.-H. Jeon, I.-J. Park, H.-J. Kim, S.-T. Kim, Y.-K. Lee and Y.-S. Park: *Mater. Trans.*, **55** (2014), 971.
- 30) K. Ogawa and T. Osuki: *ISIJ Int.*, **60** (2020), 1016.
- 31) S.-H. Jeon, S.-T. Kim, S.-Y. Kim, M.-S. Choi and Y.-S. Park: *Mater. Trans.*, **54** (2013), 1473.