Kinetics of Austenite Formation in Dual Phase Steels

Mohsen ASADI ASADABAD, Massoud GOODARZI and Shahram KHEIRANDISH

Department of Materials and Metallurgical Engineering, Iran University of Science and Technology, Tehran, I. R. Iran.

(Received on December 10, 2007; accepted on June 11, 2008)

In this research study a low carbon steel with composition of C=0.11 %; Mn=1.30 %; Cr=0.45 %; Si=0.20 %; Al=0.03 % and Fe=bal. was cast and used in hot rolled condition. After intercritical annealing at different temperatures for different times, dual phase structures with various volume fraction of martensite were produced. Then the volume fraction of martensite for different samples were measured.

Study of the relationship between temperature and time of intercritical annealing and martensite volume fraction showed that a new equation as $f_{\gamma}/f_e = 1 - \exp(-kt^n)$ can be used to give variation of martensite volume fraction with temperature and time of annealing. Also it is found that k coefficient changes exponentially with annealing temperature.

KEY WORDS: dual phase steels; kinetics of austenite formation; intercritical annealing; kinetics model.

1. Introduction

The microstructure of dual phase steels contains ferrite and martensite phases.^{1–3)} This microstructure increases the strength of sheet steels significantly while their ductility and formability remain intact.^{2–5)} By intercritical annealing of low carbon steels, a two-phase structure of ferrite–austenite forms, in which the austenite phase transforms to martensite through quenching the steel from intercritical annealing temperature in water. In other words, during intercritical annealing transformation of ferrite to austenite is not completed, and some of ferrite remains next to the newly formed austenite. This means that increasing time at annealing temperature increases the volume fraction of austenite to final volume fraction in equilibrium with ferrite at any given temperature.

Because of the role of martensite phase in mechanical properties of dual phase steels, the kinetics of austenite formation during intercritical annealing is most critical and is studied by many researchers.^{7–15)} It was shown that formation austenite in dual phase steels is a diffusion-controlled growth^{8,9)} and some of researchers proposed that^{16–18)} the empirical equation of Johnson–Mehl–Avrami (JMA) with Kolmogorov modification (JMAK) can be used for austenite transformation during intercritical annealing. The modified version of JMA model is as follows^{19,20)}:

$$f_{\gamma} = 1 - \exp(-kt^n) \dots\dots\dots (1)$$

where f_{γ} is austenite volume fraction, t is annealing time, n is Avrami's exponent and k is the rate constant. Avrami's exponent is constant while the rate constant is a function of temperature.

It was shown that k is a temperature dependent parameter related to growth rate, nucleation frequency and a shape factor, and n depends on nature of nucleation and growth processes²¹⁾ and was shown that, in addition to morphology,

the rate of nucleation has a significant effect on the value of n . In addition, dependency of k to growth rate and n to nucleation rate more observed.²²⁾ According to different kinetics models, in Johnson–Mehl equation, exponent n vary from 0.5 to 4.²³⁾ The kinetics of austenitization of ferritic nodular cast iron described by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model²⁴⁾ showed that the values of parameter n changes in a relatively wide range from 0.6 to 1.3. For austenite formation in maraging steel studied by using equation of Johnson–Mehl–Avrami,²⁵⁾ the Avrami's exponent was determined as $n=0.97$.

Kirkaldy^{26,27)} analyzed the effect of chemical composition on the isothermal transformation time and found that C, Mn, Si, Cr, Ni and Mo can prolong the incubation time. The effects of C and Cr increase the diffusion resistance and therefore decrease driving force. The effects of Mn are related to the decrease of driving force only because it does not strongly partition.

For the cooling transformation of austenite, the only important structural parameter is the austenite grain size, and its effect is restricted to the nucleation rate. In the austenite formation, the type of carbide particles, its shape and state of dispersion are capable of making a considerable influence, not only on the nucleation rate but also on the growth rate.²²⁾

In the present investigation, the validity of JMAK model is criticized, by measuring the martensite volume fraction produced by quenching of annealed samples in different times and temperatures and a new kinetic equation for austenite transformation during intercritical annealing is presented.

2. Experimental Procedure

The steel with composition of Fe–0.11%C–0.14%Si–1.30%Mn–0.45%Cr–0.03%Al has been cast in sand mold

Fig. 1. The ferritic–martensitic microstructure of dual phase steel after intercritical annealing for 120 s and quenching in water. (a) $f_m=0.16$, $T=730^\circ\text{C}$. (b) $f_m=0.31$, $T=760^\circ\text{C}$.

in vertical position. The $200\times 40\times 16$ mm slabs have been hot rolled at 1200°C to thickness 1.8 mm, homogenized at 950°C for 1 h and normalized at 900°C for 15 min.

To study the effect of time and temperature of intercritical annealing on the rate of formation of austenite, the normalized samples were heat treated at different temperatures and for different times. For intercritical annealing an electric resistant furnace in constant temperatures was used. Heating rate of samples was about 300°C/s . To select the proper temperature for annealing, Ac_1 and Ac_3 temperatures for the steel were calculated using Eqs. (2) and (3),²⁸⁾

$$Ac_1 = 723 - 10.7\text{Mn} - 16.9\text{Ni} + 29.1\text{Si} + 16.9\text{Cr} + 290\text{As} + 6.38\text{W} \dots\dots\dots(2)$$

$$Ac_3 = 910 - 203C^{0.5} - 15.2\text{Ni} + 44.7\text{Si} + 31.5\text{Mo} + 104\text{V} + 13.1\text{W} \dots\dots\dots(3)$$

and it is found that $Ac_1=721^\circ\text{C}$ and $Ac_3=849^\circ\text{C}$. Then five different temperatures were selected in between Ac_1 and Ac_3 , i.e. 730°C , 760°C , 790°C , 820°C and 850°C . The holding times were selected to be between 5 and 1800 s according to literatures,^{9,10)} and the samples were finally quenched in water. The microstructures of samples were studied by optical and scanning electron microscopy. Martensite volume fraction measured by point counting method based on ASTM E562-83 standard.

3. Results

Quantitative measurements showed that pearlite percent in this steel in as cast and normalized samples is about 16% and average grain size of ferrite is about $18\mu\text{m}$. Microstructural observation showed that intercritical annealing and quenching create a ferritic–martensitic structure. Micrographs of two dual phase structures that form at two different temperatures are shown in **Figs. 1(a)** and **1(b)**. Figure 1(a) is related to annealed sample at 730°C for 120 s and then quenched in water, while Fig. 1(b) shows the microstructure of annealed sample at 760°C for 120 s and then quenched in water. Quantitative measurements showed that annealing at 730°C for 120 s resulted in formation of 16% martensite, while the martensite content of annealed sample at 760°C for the same time was 31%.

Figure 2 shows SEM micrograph of the steel after intercritical annealing at 730°C for only 30 s. In addition to ferrite phase, some amount of martensite and not transformed pearlite can be seen in this micrograph.

Figure 3 shows variation of dual phase structure of

Fig. 2. The SEM microstructure of steel, containing martensite, ferrite and pearlite. Annealing temperature= 730°C , $t=30$ s and quenched in water.

Fig. 3. The microstructure of dual phase steel after annealing at $T=790^\circ\text{C}$ for different times. (a) $t=60$ s, ($f_m=0.48$); (b) $t=120$ s, ($f_m=0.54$); (c) $t=300$ s, ($f_m=0.63$).

quenched samples after intercritical annealing at 790°C for different times. Figure 3(a) shows the microstructure of quenched sample after annealing for 60 s. This microstructure contains 48% martensite. The microstructure related to annealed sample at 790°C for 120 s is shown in Fig. 3(b). The volume fraction of martensite in this case is 54%. The last picture (Fig. 3(c)) is for annealing time of 300 s, and shows that the volume fraction of martensite is increased to 63%. For annealing time more than 300 s, at 790°C it was seen no increase in the volume fraction of martensite. **Figure 4** shows fully martensitic structure that produced after quenching from 850°C. The holding time in this temperature was 60 s.

If it is considered that all austenite can transform to martensite, by quenching annealed samples in water, then it can be assumed that martensite volume fraction (f_m) equals to austenite volume fraction (f_γ). Then it is possible to use micrographs to obtain volume fraction of austenite formed at annealing temperatures at different times. The results of measuring the volume fraction of martensite (or austenite) as a function of annealing temperature and time are shown in **Fig. 5**. It can be seen that by increasing annealing temperature and time, the volume fraction of austenite increases. Variation of volume fraction of austenite with time for all temperatures follows the same pattern. Also it can be seen that the volume fraction of austenite at all temperatures reaches to a constant value after a certain time, which this time decreases with increasing temperature.

4. Discussion

During intercritical annealing, austenite forms in two steps. The first step is transformation of pearlite to austenite

Fig. 4. Fully martensitic microstructure of the study steel after annealing at $T=850^\circ\text{C}$ for $t=60$ s.

Fig. 5. Variation of measured martensite volume fraction (f_m) after annealing at different temperatures and for different times.

and then the second step is dissolution of ferrite in the newly formed austenite.⁸⁾ After annealing at 730°C for 120 s amount of austenite was 16% (Fig. 1(a)), which is result of pearlite transformation. On the other hand, increasing temperature by amount of 30°C for the same annealing time (120 s) causes increasing martensite content by 15% (Fig. 1(b)). It means that increasing temperature causes some amount of dissolution of ferrite in the austenite takes place (step two). Although transformation of pearlite occurs rapidly,⁸⁾ but SEM micrograph (Fig. 2) showed that 30 s at 730°C is not sufficient for complete dissolution of pearlite. Therefore, more time or higher temperature is needed for first step to be completed.

The microstructure of annealed samples at 850°C for times less than 60 s consists of martensite and ferrite. Thus at this temperature after 60 s, the second step of austenite formation, which is austenite growth within ferrite can be completed. By comparing resulted microstructures after annealing at 790°C and at 850°C for different times, it can be concluded that the rate of second step of austenite formation depends highly on temperature. By advancing dissolution of ferrite in the austenite, carbon content of austenite decreases and this can affect both martensite start temperature and martensite hardness.¹⁾

Some investigators¹⁶⁻¹⁸⁾ use the modified version of JMA model (Eq. (1)) to calculate volume fraction of austenite at different times. But the problem with this model is that by going time to the infinity volume fraction of austenite becomes one, while by annealing dual phase steels at intercritical temperature, the austenite volume percent never reaches 100 in the microstructure, as it is shown in Fig. 5. If the volume fraction of austenite is substituted by the ratio of volume fraction of austenite, at a certain time, over equilibrium volume fraction of austenite at that temperature, in the modified JMA model, this problem disappears. Then the new modified equation can be proposed as follows:

$$\frac{f_\gamma}{f_e} = 1 - \exp(-kt^n) \quad \text{.....(4)}$$

where f_e is equilibrium volume fraction of austenite.

This new model is valid if double logarithm of $f_e/(f_e - f_\gamma)$ is a linear function *versus* $\ln t$. This can be shown as follows:

$$\ln \ln \frac{f_e}{f_e - f_\gamma} = \ln k + n \ln t \quad \text{.....(5)}$$

In **Fig. 6** $\ln \ln (f_e/(f_e - f_\gamma))$ *versus* $\ln t$ for different annealing temperature is indicated. In all cases $\ln \ln f_e/(f_e - f_\gamma) - \ln t$ relationship can be represented by straight lines which are interpolated by using least square regression. The slopes of these lines are Avrami's exponent (n) and their intercept with $\ln \ln (f_e/(f_e - f_\gamma))$ axis are $\ln k$. The measured values of f_e and calculated values of Avrami's exponent and rate constant for different annealing temperatures are given in **Table 1**. Equilibrium volume fraction of austenite (f_e) as a function of annealing temperature is shown in **Fig. 7**. It can be seen that f_e is linearly increased with annealing temperature. Using measured values of f_e and calculated values of n and k , f_γ can be obtained at every annealing temperature and time through new model (Eq. (4)). The results are shown in **Fig. 8**, which are in a very good agreement with

Fig. 6. Variation of $\ln \ln(1/(1-f_t/f_e))$ with $\ln t$ at different temperatures.

Table 1. Measured equilibrium volume fraction of austenite and calculated values of n and k for Eq. (4).

Annealing Temperature (°C)	Equilibrium Volume Fraction of Austenite, f_e	Avrami's Exponent, (n)	Rate Constant, (k)
730	0.27	0.712	0.033
760	0.44	0.714	0.041
790	0.63	0.709	0.070
820	0.80	0.755	0.077
850	1.00	0.873	0.091

Fig. 7. Variation of equilibrium volume fraction of austenite (martensite), f_e with annealing temperature.

experimental data (distinct points).

To show the validity of the proposed model, the results of the model are compared with three sets of experimental data.^{8,29,30} This comparison is shown in Fig. 9, and it can be seen that the results of this model at 740°C, in spite of different compositions and history processing, are very close to the experimental data. Also this comparison shows the validity of values of n and k in Eq. (4) to predict the results in other conditions rather than the present study ones. The austenite transformation behavior affected by grain size of steel,³¹ therefore in both Souza's³⁰ and the present work were done in a finer grained material which gave rise to faster transformation than Speich's⁸ and Estay's²⁹ experiments that the mean ferritic diameter is about 20 μm .

In this study, values of n at different temperatures are between 0.7–0.9, which can be concluded that the value of n , at least for the current process, is not function of temperature. J. Lis and A. Lis³² studied the kinetics of austenite formation during intercritical annealing of 0.047C–3.97Mn–0.17Ni steel with $A_{c1}=647^\circ\text{C}$ and $A_{c3}=850^\circ\text{C}$. The kinetics of $\alpha \rightarrow \gamma$ phase transformation were described

Fig. 8. Variation of measured and calculated martensite volume fraction (f_m) after annealing at different temperatures and for different times.

Fig. 9. Comparison of volume fraction data from various sources and present model in 740°C.

by Johnson–Mehl–Avrami equation and with $n=1$. At 700°C, the value of k , were determined as 12×10^{-4} .

Values of n in kinetic law $f=1-\exp(-kt^n)$ in diffusion-controlled growth are between 0.5–2.5.³³ If nucleation rate decrease, the value of n decrease about 1. In intercritical annealing, there is a diffusion-controlled growth,^{8,9} and nucleation rate decreases. There are two independent effects leading to a decrease in nucleation rate as the austenitizing time is increased. One of these is the increase in austenite grain size and the other is the removal of carbide particles.²² Therefore, it is expected that values of n decrease below 1. Also in dual phase steels, austenite nucleate and grow at grain boundaries of ferrite and as was shown²² nucleation grain boundary decreases value of n . Therefore, kinetics behavior in formation austenite is completely different from austenite transformation to ferrite and pearlite, where value of n changes between 2³⁴ and 3.³⁵

It can also be extracted extra information from rate constant. It is well accepted that the rate constant, k , changes exponentially with temperature (Arrhenius equation). In other words, it can be written:

$$k = A \exp\left(\frac{-Q}{RT}\right) \dots \dots \dots (6)$$

where A is a constant depends on the system, Q is activation energy, R is the gas constant and T is annealing temperature (in Kelvin). The Eq. (6) can be written in logarithmic form as follows:

$$\ln k = \ln A - \frac{Q}{RT} \dots \dots \dots (7)$$

Variation of $\ln k$ with $1/T$ along with superimposed regres-

Fig. 10. Linear variation of $\ln k$ with $1/T$.

sion line is shown in Fig. 10. Again it can be seen a very good agreement between experimental and calculated values. The slope of the shown line is $-Q/R$, which gives activation energy as 83 086 J, and intercept of the line with $\ln k$ axis when $1/T$ approaches zero is the A constant, which can be obtained as 713.55.

Value of k in kinetic law is dependent on nucleation rate and more on growth rate of reaction. The number of nuclei formed per unit volume apparently decreases with temperature, although the growth rate and driving force is increasing.²²⁾ As temperature increases, the value of k increases and therefore reaction rate increases.

The kinetics of the $\alpha \rightarrow \gamma$ phase transformation during heating of the 1045 steel weld, modeled using Johnson–Mehl–Avrami analysis.³⁶⁾ The results yielded kinetic parameters for the JMA prediction of the transformation as $n=0.82$, which is very close to value obtained in the present study, and $\ln A=12.3$, with an activation energy of $Q=117.1$ kJ/mol. However, it should be noted that austenite kinetics is affected by different parameters and extracted values are empirical.

5. Conclusion

In this investigation, relationship between heat treatment parameters and kinetics of austenite formation in dual phase steel was studied, and following conclusions were obtained:

(1) It was observed that increasing time at a certain intercritical annealing temperature increases austenite volume fraction, until its equilibrium one, after which the volume fraction of austenite does not change with time.

(2) The equilibrium volume fraction of austenite increases with increasing intercritical annealing temperature. For the studied steel annealing at 850°C will result in 100% austenite after less than 100 s residing time.

(3) A new modified version of JMA model as $f_{\gamma}/f_c = 1 - \exp(-kt^n)$ was suggested which shows relationship between austenite (martensite) volume fraction and intercritical annealing time at different temperatures. After time reached to equilibrium one, austenite volume fraction, f_{γ} , is reached to its equilibrium value, f_c .

(4) Arrhenius equation of $k=713.55 \exp(-83\,086/RT)$ represents relationship between the rate constant, k , and temperature, where increasing temperatures increases k .

REFERENCES

- 1) G. R. Speich: Fundamentals of Dual Phase Steels, ed. by R. A. Kot and B. L. Bramfitt, TMS-AIME, Warrendale, PA, (1981), 3.
- 2) T. Tanaka, M. Nishida, K. Hashiguchi and T. Kato: Structure and Properties of Dual Phase Steel, ed. by R. A. Kot and J. W. Morris, TMS-AIME, Warrendale, PA, (1979), 221.
- 3) P. R. Mould and C. C. Skena: Formable HSLA and Dual-Phase Steels, ed. by A. T. Davenport, AIME, New York, (1979), 183.
- 4) M. T. Shehata and A. F. Crawley: *Can. Metall. Q.*, **22** (1983), 181.
- 5) H.-J. Klaar, I. A. El-Sesy and A.-H. A. Hussein: *Steel Res.*, **61** (1990), 85.
- 6) G. R. Speich and R. L. Miller: Solid–Solid Phase Transformations, TMS-AIME, Warrendale, PA, (1981), 843.
- 7) M. M. Souza, J. R. C. Guimaraes and K. K. Chawla: *Metall. Trans. A*, **13A** (1982), 575.
- 8) G. R. Speich, V. A. Demarest and R. L. Miller: *Metall. Trans. A*, **12A** (1981), 1419.
- 9) J. J. Yi, I. S. Kim and H. S. Choi: *Metall. Trans. A*, **16A** (1985), 1237.
- 10) H. K. Khaira, A. K. Jena and M. C. Chaturvedi: *Mater. Sci. Eng. A*, **161A** (1993), 267.
- 11) Y. J. Park and G. T. Eldis: Metallurgy of Continuous-Annealed Sheet Steel, ed. by B. L. Bramfitt and P. L. Mangonon, TMS-AIME, Warrendale, PA, (1982), 321.
- 12) G. I. Garcia and A. J. Deardo: Solid–Solid Phase Transformations, TMS-AIME, Warrendale, PA, (1981), 855.
- 13) J. S. Gau and G. Thomas: Metallurgy of Continuous-Annealed Sheet Steel, ed. by B. L. Bramfitt and P. L. Mangonon, TMS-AIME, Warrendale, PA, (1982), 333.
- 14) W. C. Jeong and C. H. Kim: *Scr. Metall.*, **19** (1985), 37.
- 15) G. I. Garcia and A. J. Deardo: *Metall. Trans. A*, **12A** (1981), 521.
- 16) S. K. Nath, S. Ray, V. N. S. Mathur and M. L. Kapoor: *ISIJ Int.*, **34** (1994) 191.
- 17) J. Mahieu, D. Van Dooren, L. Barbe and B. C. De Cooman: *Steel Res.*, **73** (2002), 267.
- 18) J. Mahieu, J. Maki, B. C. De Cooman and S. Claessens: *Metall. Mater. Trans. A*, **33A** (2002), 2573.
- 19) A. K. Sinha: Physical Metallurgy Handbook, McGraw-Hill, New York, (2003), 245.
- 20) T. Waterschoot, K. Verbeken and B. C. De Cooman: *ISIJ Int.*, **46** (2006), 138.
- 21) R. C. Sharma: Phase Transformation in Materials, CBS, India, (2002), 146.
- 22) J. W. Christian: The Theory of Transformations in Metals and Alloys (Part I+II), Pergamon, Oxford, (2002), 529, 797.
- 23) J. Burke: Kinetics of Phase Transformations in Metals, Pergamon, London, (1965), 145.
- 24) J. Kohout: *J. Mater. Sci.*, **43** (2008), 1334.
- 25) Z. Guo, W. Sha and D. Li: *Mater. Sci. Eng. A*, **373A** (2004), 10.
- 26) J. S. Kirkaldy, B. A. Thomson and E. Barganis: Hardenability Concepts with Applications to Steel, ed. by D. V. Doane and J. S. Kirkaldy, TMS-AIME, Warrendale, PA, (1978), 126.
- 27) J. S. Kirkaldy and D. Venugopalan: Phase Transformations in Ferrous Alloys, ed. by A. R. Marker and J. I. Goldstein, TMS-AIME, Warrendale, PA, (1984), 125.
- 28) L. E. Samuels: Optical Microscopy of Carbon Steels, ASM, Metals Park, Ohio, (1980), 53.
- 29) S. Estay, L. Chengji and G. R. Purdy: *Can. Metall. Q.*, **23** (1984), 121.
- 30) M. M. Souza, J. R. C. Guimaraes and K. K. Chawla: *Metall. Trans. A*, **13A** (1982), 575.
- 31) M. Militzer, R. Pandi, E. B. Hawbolt and T. R. Meadowcroft: Proc. Materials Solution '97 on Accelerated Cooling/Direct Quenching Steels, ASM, Materials Park, OH, (1997), 151.
- 32) J. Lis and A. Lis: *J. Achieve. Mater. Manufact. Eng.*, **26** (2008), 195.
- 33) E. S. Machlin: An Introduction to Aspects of Thermodynamics and Kinetics Relevant to Materials Science, Elsevier, Amsterdam, (2007), 284.
- 34) M. Gómez, S. F. Medina and G. Caruana: *ISIJ Int.*, **43** (2003), 1228.
- 35) S. E. Offerman, L. J. G. W. van Wilderen, N. H. van Dijk, J. Sietsma, M. Th. Rekveldt and S. van der Zwaag: *Acta Mater.*, **51** (2003), 3927.
- 36) J. W. Elmer, T. A. Palmer, S. S. Babu, W. Zhang and T. Debroy: *Weld. J.*, **83** (2004), 244.