Research Article

Xiao Li* and Yinghui Wei

Effect of austenitising heat treatment on microstructure and properties of a nitrogen bearing martensitic stainless steel

https://doi.org/10.1515/phys-2019-0061
Received Apr 27, 2019; accepted Jun 03, 2019

Abstract: The effect of austenitising heat treatment on the microstructure, hardness and metal release of the nitrogen bearing, martensitic stainless steel 420U6 was investigated. The heat treatment was carried out at temperatures between 950 to 1,150°C with a holding time between 30 to 120min, followed by air cooling. The quenched microstructures observed by a scanning electron microscope indicated that by increasing the austenitising temperature and holding time, the number of carbides decreases while the grain size and the amount of retained austenite increases. For a given holding time, the hardness increases to a peak and then decreases continuously with the increase of temperature. The metal release test, according to the GB 4806.9-2016 standard, reveals that the metal release concentration is highly affected by the austenitising temperature. The parameters of the austenitising heat treatment, which can achieve the optimum combination of hardness and metal release, were obtained.

Keywords: nitrogen; martensitic stainless steel; heat treatment; microstructure; metal release; 420U6; GB 4806.9-2016

PACS: 61.82.Bg, 81.30.Kf , 81.40.Ef-, 81.65.Kn

1 Introduction

Martensitic stainless steels (MSSs) are widely used to make medical equipment, plastic moulds, bearings in the aerospace industry, and food-contact knives and scissors, etc., because this kind of stainless steel possesses high hardness, excellent wear and corrosion resistance [1, 2]. Carbon and chromium are the two basic alloying elements in MSSs. In general, the carbon content in MSSs is between 0.2 to 1.05 mass%, and the chromium content is between 12 to 18 mass%. Carbon can improve the hardness and wear resistance of MSSs by solution strengthening and precipitation strengthening which is realized by the formation of carbides during tempering. Chromium imparts good corrosion resistance through the formation of a thin layer of chromium oxide on the surface of MSSs [3].

However, due to the strong affinity between carbon and chromium, it is easy to form the coarse eutectic carbides such as M_7C_3 and $M_{23}C_6$ during the manufacturing process of MSSs. These carbides are harmful for the fatigue life and corrosion resistance of MSSs [4, 5]. The addition of the element of nitrogen into MSSs is an effective way to reduce the number and size of these large eutectic carbides [6], meanwhile, nitrogen can make these carbides distribute more evenly. Furthermore, nitrogen inhibits the austenite grain growth and the formation of δ-ferrite, strengthens MSSs by interstitial solid solution and precipitation of nitrides [7]. Therefore, nitrogen can improve the corrosion resistance, hardness and wear ability of MSSs [8–10].

In recent years, with the development of the new manufacturing techniques, (such as alloying with the elements which can increase the solubility of nitrogen in MSSs; induction melting through injecting nitrogen gas; pressure metallurgy; surface nitriding; etc., [11, 12]), the limitation of the low solubility of nitrogen in MSSs [3, 10] has been overcome, hence a series of nitrogen bearing MSSs have been developed [6]. 420U6 is a nitrogen bearing MSS which was independently developed by TISCO (Taiyuan Iron & Steel (Group) co., Ltd, China) and applied to replace the conventional MSS SUS420 J1 to make dinner knifes. Compared with SUS420 J1, 420U6 has a comparable hardness and a better corrosion resistance, and it especially possesses a lower metal release value which has

***Corresponding Author: Xiao Li:** College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan, China; State Key Laboratory of Advanced Stainless Steel Materials, Taiyuan, China; Email: lixiao_sgpv@163.com
Yinghui Wei: College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan, China

been stipulated in many regulations and standards such as GB 4806.9-2016.

The final performance of MSSs is greatly dependent on the austenization treatment [13]. The key parameters of the austenization process such as the heating temperature and holding time have a vital influence on the grain size of the high temperature austenite, the size and number of the undissolved carbides and the amount of the retained austenite, etc. [14]. The optimal combination of the different properties such as hardness, wear and corrosion resistance are determined by the quenched microstructure, so it is very important to precisely control the austenization process.

However, the research about the effect of austenization process on the microstructure and properties of the nitrogen bearing MSS 420U6 is rarely seen. In the present paper, the effect of austenization treatment on the microstructure, hardness and metal release of 420U6 was investigated, and the optimum parameters of austenization treatment are suggested.

2 Methodology

The experimental steel plate used in this study was provided by TISCO with a thickness of 7mm. The production route of the experimental steel was as follows: 180 tons (t) AOD (Argon Oxygen Decarbonization) → 180t LF (Ladle Furnace) → CC (Continuous Casting, the thickness of the slab is 200mm) → Slab Grinding → Reheating → Hot Continuous Rolling → Coiling → Bell-type Annealing (spheroidizing annealing at 850°C for 20h).

The chemical composition of the experimental steel is given in Table 1. The phase diagram of the steel calculated by Thermo-Calc software is shown in Figure 1, from which it can be seen that the A_3 point of the steel is 908°C. The optical micrograph of the as-received steel plate is shown in Figure 2, which indicates the globular carbides uniformly distributed in the ferritic matrix; the δ ferrite cannot be observed. Samples of suitable size were cut for the heat treatment experiments. These samples were austenitized at 950~1,150°C for 30, 60 and 120 mins, and then air cooled to room temperature. Samples used for microstructure observation were prepared by the conventional metallographic techniques and etched by the reagent composed of 1g ferric chloride, 5ml hydrochloric acid and 5ml ethanol.

These samples were observed by a scanning electron microscope (Nova Nano SEM430). The size and number of the carbides were analyzed by the Image-pro plus 6.0 software. Rockwell C scale hardness (HRC) of each sample was measured under the applied load of 1,471N. Finally, metal release tests were conducted according to the GB 4806.9-

Table 1: Chemical composition of the nitrogen bearing MSS 420U6 (wt. %)

C	Si	Mn	P	S	Cr	N	Fe
0.14	0.38	0.59	0.027	0.006	13.78	0.085	Balance

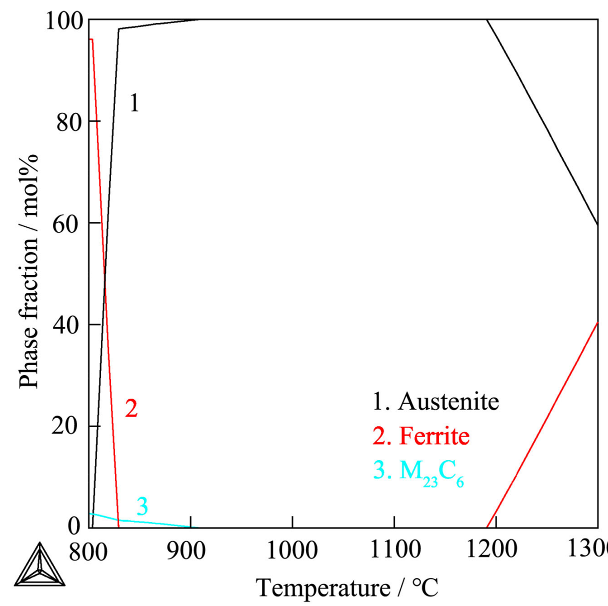

Figure 1: Phase diagram of 420U6 calculated by Thermo-Calc®

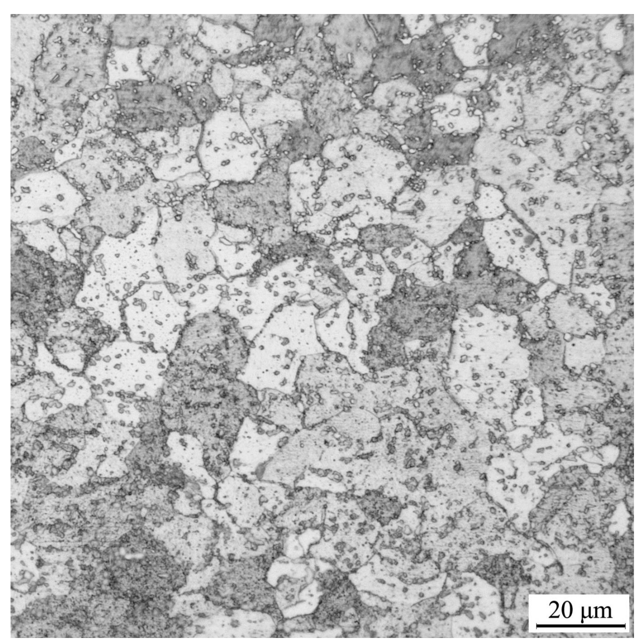

Figure 2: Optical Micrograph of the as-received steel plate

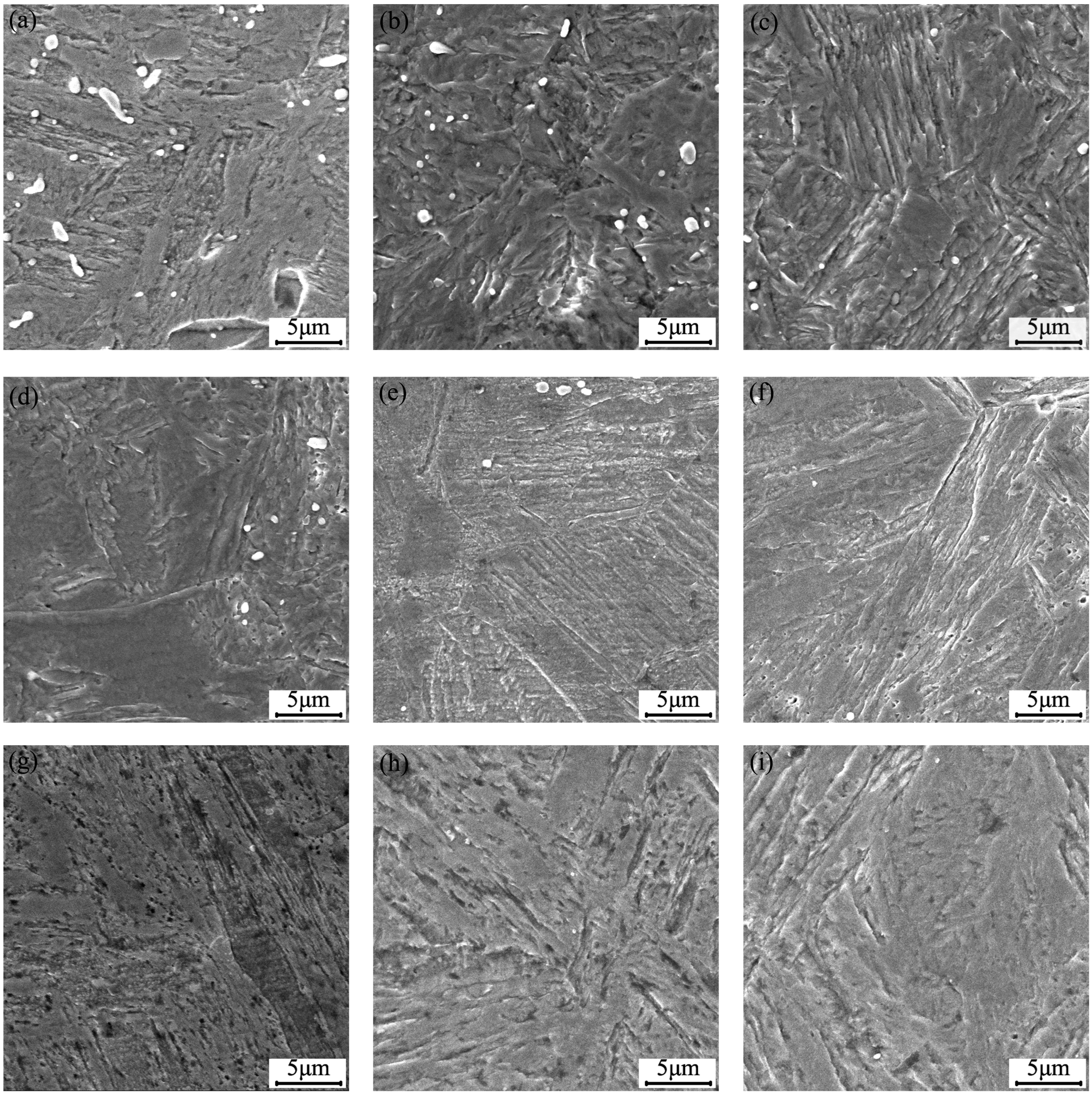

Figure 3: Typical SEM micrographs of 420U6 stainless steel heat treated at: (a) 950°C, 30min; (b) 950°C, 60min; (c) 950°C, 120min; (d) 1,000°C, 30min; (e) 1,000°C, 60min; (f) 1,000°C, 120min; (g) 1,150°C, 30min; (h) 1,150°C, 60min and (i) 1,150°C, 120min

2016 standard. The 4% acetic acid solution (volume fraction) was applied as the relevant solution. Some of the quenched specimens were immersed in the boiled solution for 30 min, then kept in room temperature for 24h, after which the solution was analyzed by the Inductively Coupled Plasma spectrometry (ICP) to determine the metal release values.

3 Results and discussion

3.1 Microstructure

The typical SEM micrographs of 420U6 stainless steel under different austenization conditions are shown in Figure 3. The microstructures mainly consist of lath martensite, undissolved carbides and retained austenite. The grain size of the martensite increases with the increase of solution temperature and holding time. Figure 4 shows the grain sizes at different heat treatment conditions. The fol-

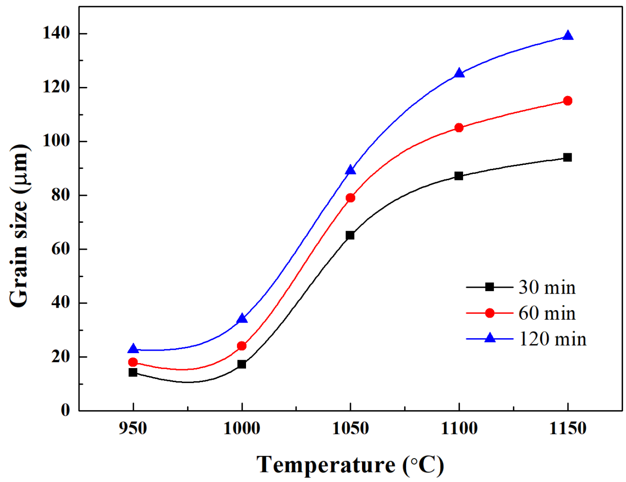

Figure 4: Grain size of quenched martensite at different heat treatment conditions

lowing equations are generally used to describe the kinetics of grain growth [15]:

$$d^2 - d_0^2 = kt \quad (1)$$

where

$$k = Aexp(\frac{-Q_{gg}}{RT}) \quad (2)$$

here, t is the annealing time, d is the average grain diameter at t, d_0 is the initial average grain diameter, k represents the dependence of grain growth on grain growth activation energy and absolute temperature, Q_{gg} is the activation energy of grain growth, T is the austenitising temperature, R is the gas constant, and A is a constant.

According to equation (1), the values of k at different temperatures can be calculated from the slopes of the regression straight lines between d^2 and t (as shown in Figure 5a). Taking the natural logarithm on both sides of equation (2) and substituting the value k and the respective temperature, then the Q_{gg} of 420U6 can be determined as 269.7 kJ mol^{-1} (Figure 5b). When austenitising temperature is 950°C, the number of undissolved carbides gradually deceases with the increase of the holding time from 30min to 120min (Figures 3a, b and c).

However, when austenitising temperature is higher than 1,000°C, the number of the undissolved carbides reduces dramatically (Figure 3d, e, f, g, h and i). This indicates that the effect of temperature on the dissolution of carbides is a greater factor than the holding time. The variations of the number and the average diameter of carbides with austenitising temperature when holding time is 30min are shown in Figure 6. It can be seen that the average diameter of carbides also decreases with the increase of temperature. The dissolution of carbides at higher temperatures and longer holding times reduces the pinning effect on the grain growth; therefore, the austenite grains grow bigger and faster with an increase of temperature and holding time (Figure 4).

In addition, the dissolution of the carbides leads to more alloying elements such as carbon, chromium, etc. dissolving into the austenite matrix, which enhances the stability of the austenite and supresses the transformation from austenite to martensite during quenching. Thus, with the increase of temperature and holding time, more retained austenite will be found in the quenched microstructure.

3.2 Hardness and metal release

The hardness of the quenched samples under different austenitising conditions is shown in Figure 7. It is evident that, for a given holding time, the hardness increases to a peak when austenitising temperature reaches 1,000°C, after which it decreases considerably with the increase of temperature. Compared with 950°C, more carbides are dissolved in the austenite matrix when the temperature goes to 1,000°C, which results in the carbon super saturation and the distortion of the lattice, thus improves the hardness.

However, when the temperature is higher than 1,000°C, although the austenite matrix dissolves more carbides, the austenite becomes more stable and more retained austenite is formed in the quenched microstructure. Moreover, with the increase of temperature, the number of carbides decreases which weakens the pinning effect of these particles, thus coarser grains and larger martensitic packets are obtained in the final microstructures (Figure 3 and 4). Therefore, when the temperature exceeds 1,000°C, the combination of these factors reduces the hardness of 420U6 stainless steel. In this study, the quenched hardness reaches its highest value of 50.3HRC when the austenitising temperature is 1,000°C and the holding time is 30min.

The metal release of chromium and nickel under different austenitising temperatures at a given holding time of 30min is shown in Table 2. All the released concentrations of Cr and Ni under different austenization conditions comply with the requirements of the GB 4806.9-2016 standard.

Furthermore, the released concentration of Cr is highly affected by the austenitising temperature, and it increases according to the following order of temperature: 1,050°C < 1,000°C < 1,100°C < 950°C < 1,150°C. The release of Ni shows a similar tendency but with a much lower released concentration compared with that of Cr. At the lower temperature of 950°C, more carbide is presented in the marten-

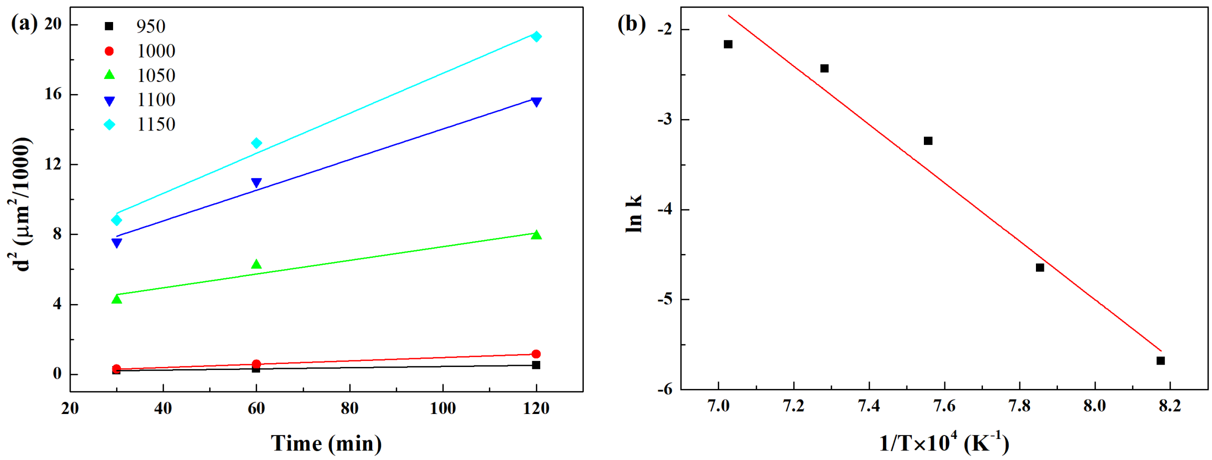

Figure 5: Linear relationships between (a) d^2 and time and (b) ln k and $1/T\times10^4$

Table 2: Metal release of chromium and nickel under different austenitising conditions

Austenitising temperature (°C)	Holding time (min)	Cr (mg/kg)	Ni (mg/kg)
950	30	0.33	0.06
1,000	30	0.17	0.03
1,050	30	0.16	0.01
1,100	30	0.24	0.04
1,150	30	0.35	0.21
Upper limit value required in GB 4806.9-2016		2.0	0.5

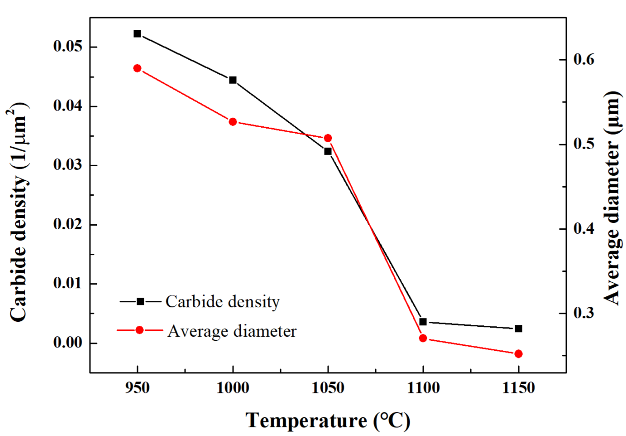

Figure 6: The density and average diameter of carbide at different austenitising temperature when holding time is 30min

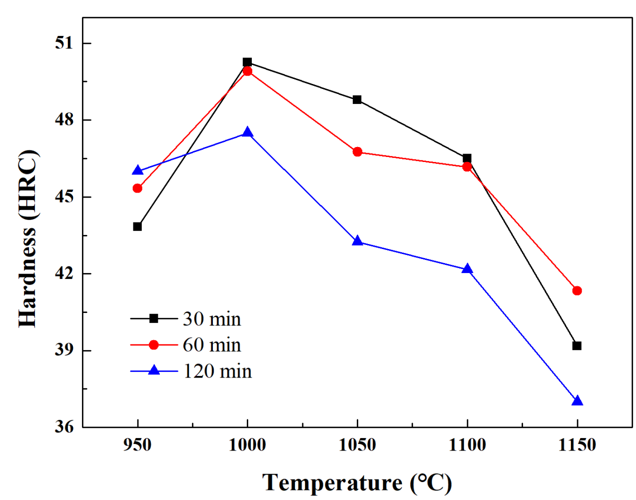

Figure 7: The variation of hardness with austenitising temperature and holding time

site matrix, and more Cr depleted zones form around the carbide. These Cr depleted zones deteriorate the corrosion resistance of the steel thus more metal is released. The higher released concentrations of Cr and Ni at the temperature of 1,150°C may be related to the higher content of retained austenite.

4 Conclusion

We investigated the effect of austenitising heat treatment on the microstructure, hardness and metal release of the nitrogen bearing, martensitic stainless steel 420U6. Our conclusions are:

(1) With an increase of austenitising temperature and holding time, the grain size of the quenched martensite increases, and the activation energy of grain growth (Q_{gg}) for this steel is calculated to be 269.7 kJ mol^{-1}. The number of the undissolved carbides decreases with the increase of temperature and holding time. The decrease of the number of the carbides improves the stability of the high temperature austenite and thus increases the amount of the retained austenite in the quenched martensite.
(2) For any holding time, with the increase of temperature the hardness of the quenched specimen increases to a peak at 1,000°C, after which it decreases considerably. Under the experimental conditions of this study, all the metal release contents of the quenched specimens meet the requirement of the GB 4806.9-2016 standard.
(3) To obtain the optimum combination of hardness and metal release, the parameters of the austenitising heat treatment is suggested as 1,000°C for 30min.

References

[1] Lu S., Yao K., Chen Y., Wang M., Chen N., Ge X., Effect of quenching and partitioning on the microstructure evolution and electrochemical properties of a martensitic stainless steel, Corrosion Sci., 2016, 103, 95-104.
[2] Bonagani S. K., Bathula V., Kain V., Influence of tempering treatment on microstructure and pitting corrosion of 13 wt.% Cr martensitic stainless steel, Corrosion Sci., 2018, 131, 340-354.
[3] Krishna S. C., Gangwar N. K., Jha A. K., Pant B., George K. M., Effect of Heat Treatment on the Microstructure and Hardness of 17Cr-0.17N-0.43C-1.7 Mo Martensitic Stainless Steel, J. Mater. Eng. Perform., 2015, 24, 1656-1662.
[4] Ghosh R., Krishna S. C., Venugopal A., Narayanan P. R., Jha A.K., Ramkumar P., et al., Corrosion and nanomechanical behaviors of 16.3Cr-0.22N-0.43C-1.73Mo martensitic stainless steel, Corros. Sci. Technol., 2016, 15, 281-289.
[5] Krishna S.C., Tharian K.T., Chakravarthi K.V.A., Jha A.K., Pant B., Heat treatment and thermo-mechanical treatment to modify carbide banding in AISI 440C steel: a case study, Metallogr. Microstruct. Anal., 2016, 5, 108-115.
[6] Feng H., Jiang Z. H., Li H. B., Jiao W. C., Li X. X., Zhu H. C., et al., Hot Deformation Behavior and Microstructural Evolution of High Nitrogen Martensitic Stainless Steel 30Cr15Mo1N, Steel Res. Int., 2017, 87, 9999.
[7] Li H. B., Jiao W. C., Feng H., Jiang Z. H., Ren C. D., Influence of Austenitizing Temperature on the Microstructure and Corrosion Resistance of 55Cr18Mo1VN High-Nitrogen Plastic Mould Steel, Acta Metall. Sin. (Engl. Lett.), 2016, 29, 1148-1160.
[8] Zhu H. C., Jiang Z. H., Li H. B., Zhang S. C., Feng H., Liu F. B., Effect of pressurization technology on steel-making and solidification of high-grade special steels, Ironmak. Steelmak., 2015, 50, 37-44.
[9] Schneider R., Perko J., Reithofer G., Heat Treatment of Corrosion Resistant Tool Steels for Plastic Moulding, Mater. Manuf. Process., 2009, 24, 903-908.
[10] Seifert M., Siebert S., Huth S., Theisen W., Berns H., New Developments in Martensitic Stainless Steels Containing C + N, Steel Res. Int., 2015, 86, 1508-1516.
[11] Sun L., Li J., Zhang L., Yang S., Chen Y., Production of nitrogen-bearing stainless steel by injecting nitrogen gas, J. Iron. Steel Res. Int., 2011, 18, 7-11.
[12] Krishna S. C., Karthick N. K., Jha A. K., Pant B., Venkitakrishnan P. V., Microstructure and Properties of Nitrogen-Alloyed Martensitic Stainless Steel, Metallogr. Microstruct. Anal., 2017, 6, 425-432.
[13] Ma H. Y., He Y. S., Lee K. Y., Shin K., Effect of Heat Treatment on Microstructural Evolution of 13Cr Martensitic Stainless Steel, Key Engineering Materials, 2017, 727, 29-35.
[14] Zhu Q. T., Li J., Shi C. B., Yu W. T., Effect of Quenching Process on the Microstructure and Hardness of High-Carbon Martensitic Stainless Steel, J. Mater. Eng. Perform., 2015, 24, 4313-4321.
[15] Shenton P. A., Sellars C. M., Grain growth during the thermomechanical processing of austenitic stainless steels, Ironmak. Steelmak., 1995, 22, 78-80.