Recrystallization and diffusion mechanisms of segregation improvement in cast billets by high temperature reduction pretreatment

Hongqiang Liu¹, Zhicheng Cheng², Wei Yu²,∗ and Qingwu Cai¹

¹ Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Beijing 100083, People’s Republic of China
² Institute of Engineering Technology, University of Science and Technology Beijing, Beijing 100083, People’s Republic of China
∗ Author to whom any correspondence should be addressed.

E-mail: liuhongqiang@hbisco.com, czc_ustb@163.com, yuwei@nercar.ustb.edu.cn and caiqw@nercar.ustb.edu.cn

Keywords: 42CrMo, high temperature reduction pretreatment, continuous casting, recrystallization, segregation

Abstract

Controlling the segregation of alloying elements in steel can improve the uniformity of the structure and properties of the material. High Temperature Reduction Pretreatment (HTRP) is an effective technique to improve the internal quality of steel by generating plastic deformation in the core and providing the recrystallization energy. Comparative analysis was conducted to illustrate the effect of the HTRP on the internal quality of 42CrMo cast billets. To quantitatively analyze the recrystallization and diffusion mechanisms, the tested samples were measured using Scanning Electron Microscopy (SEM), Original Position Statistic Distribution Analysis (OPA) and Electron Probe Microanalysis (EPMA). The results show that the plastic deformation prompts the austenite to recrystallize. As the deformation of the HTRP sample increases, the recrystallized austenite grain size decreases significantly. It is also found that the statistical macro-segregation and micro-segregation ratios of substitutional elements Si, Mn, Cr and Mo decrease. The increase in austenite grain boundaries enables the increase in diffusion coefficient of the solid solution elements, which is the main reason for improving the segregation of the cast billet.

1. Introduction

42CrMo, as a medium carbon low alloy steel, is widely used in the manufacture of large forgings. The elements segregation deteriorates the casting quality of 42CrMo. Yang et al. [1] found that the uneven distribution of chemical elements led to the mechanical properties anisotropy. Some researches [2, 3] showed that segregation significantly reduced the grain boundary strength and weakened the cooperative deformation ability of the grains during hot working, and therefore causing the crack defects. Moreover, defects such as center segregation and porosity would be inherited to the rolled steel, thereby reducing the steel service performance.

Factors, such as temperature [4], local solute concentration [5, 6], time [7], the amount and rate of strain [8], the initial structure state, the phase composition of material, affect the recrystallization process. It is well documented that segregation affects recrystallization. For C-Mn steel, Slater et al. [9] found that compared with the original sample under the same initial conditions, the recrystallization time of the segregated sample was longer, and the recrystallized grain size was larger. The recrystallization process, in turn, also affects segregation. Torizuka and Murty [10] found that the grain boundary diffusion controlled the ferrite grain size by studying the deformation of the steel containing 0.15 wt.% C. Hotta et al. [11] revealed that the dynamic recrystallization of the austenite made the segregated elements much more homogenized in 9% Ni steel, compared to deformation at high strain rates.

The primary means of controlling the segregation of cast slab include hot metal pretreatment, electromagnetic stirring (EMS) [12, 13], and low superheat pouring, the soft reduction (SR) process [14].
thick plate and extra-thick plate, due to the requirements of rolling compression ratio, the deformation hardly affected the core based on the traditional process [15]. Recent research [16–18] showed that gradient temperature rolling (GTR) increased internal equivalent strain and improved the mechanical properties of steel. To further improve continuous casting quality, Li et al [19] proposed an alternative process, High Temperature Reduction Pretreatment (HTRP), which used the temperature gradient formed by the solidification of the cast slab to roll the billet in one pass after the solidification was completed. As an energy-saving process with minor changes to equipment, this process has been proven to reduce internal porosity with a small reduction [19, 20]. Compared with SR and EMS processes, it works after solidification and thereby avoids cracks in the subsequent solidification process. Based on HTRP process, this paper designed a set of comparative experiments with different reduction ratios to study the effect of recrystallization on the segregation of 42CrMo steel.
2. Experimental procedure

The material used in this research was 42CrMo steel, of which chemical compositions (in mass fraction, %) were obtained using a spark direct reading spectrometer (ARL4460), as shown in table 1. The experiment flow chart is shown in figure 1. Three square billets with section of 150 mm on side were casted by a vacuum induction melting furnace. The casting was conducted at about 1560 °C for 300 s, followed by a demoulding process. One billet was air cooled directly to room temperature and defined as original billet. The surface temperature of the other two were air cooled to 950 °C, at which the core temperature of the billet was estimated to be 1250 °C by ABAQUS software before rolled by one pass with reductions of 12 mm and 24 mm, respectively. These billets were defined as 8%-HTRP and 16%-HTRP billets, which were air cooled to room temperature after rolling. The dimensions of the roll were Φ750 mm × 550 mm and the rolling speed was 0.35 m s⁻¹.

The sample locations were extracted from the corresponding positions on the cast billet using the method shown in figure 2. The samples were soaked in a 1:1 hydrochloric acid aqueous solution at a temperature of 75 °C for 30 min for macrostructure observation. To study the prior austenite grain boundaries, the samples were eroded in a supersaturated picric acid solution for an optical microscope (OM) observation. To examine the element distribution, the cube samples with a side length of 10 mm at the corresponding positions of the cores were taken. Electron probe microanalysis (EPMA) was used to quantitatively analyze mapping results. Prior to EPMA, original position statistic distribution analysis (OPA) was performed to study the segregation status in the center of billets with a scanning region of 72 mm × 50 mm.

To explore the diffusion mechanism, the heat transfer module of the abaqus software was used for simulation and the unit system is SI (mm). Python software was used to randomly generate two-dimensional Voronoi diagrams with different grain boundary densities to simulate the effect of grain boundary densities on diffusion. They were named Original Billet and HTRP billet respectively. The conditions for calculating diffusion satisfied the following assumptions: (1) Regarding grain boundaries and dislocations as channels with a fixed width; (2) Disregarding the effect of the element diffusion concentration on the grain boundary diffusion coefficient D_GB and the bulk diffusion coefficient D₀ in the simulation process. Material size is 2 mm × 2 mm.

The specific heat capacity and density of the material are set to 1 respectively. According to the magnitude relationship between the grain boundary diffusion coefficient and bulk diffusion in the research [21], this study assumes that the diffusion coefficient of the element at the grain boundary is 1000 times higher than that of the element in the crystal. This simulation takes Cr as an example. The volume diffusion coefficient of Cr at 1250 °C is 1.06032 × 10⁻⁷ mm² s⁻¹.

At the initial moment, a gradient concentration field along the vertical direction was added to the surface to simulate the gradient concentration field formed by solidification shrinkage at the end of solidification. The Cr segregation concentration added to the upper side was 0.5% by mass. Its function was \( D = 2 \times 10^{-11} \times Y \) kg m⁻³ (Y was the distance from the bottom edge in the vertical direction).

3. Experimental results

3.1. Prior austenite grains

The macrostructures of the billets are presented in figure 3(a)–(c). The macrostructures all have obvious as-cast structures, with radial columnar crystal regions on the periphery and equiaxed crystal regions in the middle of the red square. As the reduction ratio increases, the area ratio of equiaxed crystal regions increases from 43% to...
54%, while the grain size decreases. In addition, the internal segregation defects in the original cast slab are clearly present. The interior of the HTRP samples, however, shows denser structures with finer porosities [22].

Figures 4(a)–(c) are the results of supersaturated picric acid erosion, which reveals that as the reduction ratio increases, the grain boundary density increases. The original austenite grains will form lath bundles with similar orientation after phase transformation [23]. The reconstruction method developed by Wang et al [24] was used to obtain the original austenite reconstruction results. The prior austenite reconstruction results (see figures 4(g)–(i)) corresponding to the EBSD results (see figures 4(d)–(f)), reveal the actual grain size and quantity of austenite at different reduction ratios. Since the complete grains cannot be photographed under a 50× optical microscope, the average grain size of the equiaxed crystals in the original casting slab is around 5000 μm according to the statistics macrostructures results (figure 3(a)), while the austenite grain size after 8% reduction pretreatment is ~500 μm (figure 4(b)), and it is reduced to ~350 μm (figure 4(c)) after 16% reduction pretreatment. Besides, the number of grains has increased significantly with the increase in reduction ratio.

3.2. Segregation status

The two-dimensional macroscopic OPA mapping results of Cr, Mn, Mo and Si elements are shown in figure 5. Among them, Mn element has the highest decrease of the statistical segregation degree, which is reduced by 25% from 0.0727 to 0.0545, while Mo element has the lowest decrease of the statistical segregation degree, which is reduced by 19.55% from 0.1156 to 0.093. The definition of the statistical segregation degree S is the confidence extension ratio of median value at 95% of confidence limit of weight ratio, which can be expressed as [25]:

$$S = \frac{Z}{C_0}$$  \hspace{1cm} (1)

where \((C_1, C_2)\) is the 95% confidence interval after analyzing the statistical distribution of the weight ratio of each element; \(Z = \frac{C_2 - C_1}{2}\) which represents the permissive content range and \(C_0 = \frac{C_1 + C_2}{2}\) is median.

EPMA results of a typical region are shown in figure 6, indicating the white region on the matrix along with some pore defects is the element-rich region. With the increase of the HTRP process reduction ratio, the grid size...
of the white segregation region is reduced. In the results of 16%-HTRP, except for the Mn and Mo element mapping scan results (figures 6(i) and (l)), the grid-like element-rich region are basically invisible.

According to the EPMA mapping results, 15 points (figures 6(a)–(c)) were taken at equal distances on the three fragments respectively, and the micro-segregation ratio $K$, which can reflect the degree of element segregation in micro-zones, was calculated as shown in figure 7. The micro-segregation ratio $K$ of the solute defined as the ratio between the solute content at the interdendrite region and that at the dendrite center [26]. The micro-segregation ratios of Si, Mn, Cr, Mo in the original billet are 1.63, 1.58, 1.52, 2.55, respectively. And the micro-segregation ratios of Si, Mn, Cr, Mo in the 16%-HTRP billet are 1.32, 1.36, 1.30, 1.99, respectively. Among them, Mo element has the highest decrease of the micro-segregation ratios, which is reduced by 22%, while Mo element has the lowest decrease of the micro-segregation ratios, which is reduced by 14%. The micro-segregation ratios of Si, Mn, Cr, Mo decreases with increasing HTRP reduction ratio. The micro-segregation states of Mn, Mo are almost same as that of macro-segregation.

4. Discussion

4.1. Recrystallization analysis
As the reduction ratio increases, the proportion of central columnar crystal regions gradually decreases, and the equiaxed crystal grains become denser (see figures 3 and 4). That is when the dislocations inside the material accumulate to a certain critical density through plugging and multiplication, and then reach the critical strain, recrystallization will be triggered. Based on the static recrystallization kinetic equation of 42CrMo steel established by Lin et al [27], as shown in equation (2), the internal static recrystallization percentage of the testing steel with a reduction ratio of 8% is 62.9% at 1 s after rolling. Static recrystallization mainly occurs in this research, which is consistent with the experimental results.
Figure 6. Two-dimensional electron probe microanalysis (EPMA) mapping results diagram of microstructure (a)–(c); Cr (d)–(f); Mn (g)–(i); Mo (j)–(l); Si (m)–(o).
where $X_{\text{srex}}$ is the volume fraction of static recrystallization, and $t_{0.5}$ is the time required for 50% static recrystallization to occur.

4.2. Macro-defects improvement

Comparing figures 3(a) and (b), the internal defects of 8%-HTRP billet are small and dispersed, while those of original billet are large and clearly present. Based on the research of Xin et al, the reason is that thermal compressive stress makes the pore interface close and squeeze to each other, turning large defects into several micro-porosity [28]. As the reduction ratio increases, the internal defects of 16%-HTRP billet (figure 3(c)) are similar to those of original billet (figure 3(a)). It’s because the excessive three-dimensional compressive stress will induce micro-porosity coalescence to form large-size micro-porosity [22].

As the proceeding of solidification process, solute elements are enriched in the unsolidified molten steel, thus segregation is formed (figure 10(a)). This kind of segregation is particularly serious near the solidification shrinkage region which seriously deteriorates the macroscopic element distribution, as shown in figure 5. So, the healing of the macroscopic shrinkage defects also decreases the macro-segregation region. In contrast with original billet, there are few porosities on the longitudinal section of HTRP, indicating that the HTRP temperature filed could cause considerable plastic strain to improve macro-defects (figure 8).
In general, defect healing is divided into three types (figure 8): the first type is that external compression makes interfaces of micro-porosity fit. And then the fit interfaces are healed subsequently by recrystallization and atomic diffusion. The second type is that large pores are segmented into smaller pores by the compression effect. Since the subsequent strain is not enough to make it pressed together, it exists in the cast slab in the form of micro-porosity. The third type is an evolution of the second. When the large pores are compressed, they are segmented into several micro-porosity. And as the compression continues, the micro-porosity gathers to form micro-porosity clusters (figure 3 (c)).

4.3. Micro-defects improvement

Elements segregation status, as shown in figures 5 and 6, proves that the HTRP can promote uniform elements redistribution. As reported, some experiments [29–31] have shown that compared with the equilibrium grain boundaries, the discrete diffusion coefficient of grain boundaries in non-equilibrium boundaries can be increased by 2–4 orders of magnitude, and the activation energy of grain boundary diffusion can be reduced by 1.5–2 times. By using ABAQUS software, the calculated result of diffusion is presented in figure 9. HTRP provides strain storage energy for grain recrystallization, resulting in the multiplication of prior austenite grain boundaries (PAGBs), as shown in figure 4, which act as diffusion channels intensify the diffusion of solute atoms.

On the effect of the temperature field of the HTRP process, central strains in HTRP billets are confirmed to be higher than that in original billet [22], causing the deformation of existing dendrites, which shorten the distance (figures 10(b) and (c); $d_2 < d_1$) between element-rich area and element-poor area (i.e., reduction of the distance required for element homogenization).

The element-rich region provides the concentration required for recrystallization, the HTRP process provides the energy required for recrystallization, and the original coarse-equiaxed grain boundaries provide...
nucleation sites. Thus, composition fluctuation, energy fluctuation and structure fluctuation conditions required for recrystallization and nucleation are provided. Due to the large amount of strain and lattice distortion energy in the segregation area, the high energy increases the thermal vibration of the solute elements, which causes the element atom to move away from the original element-rich position (figure 10(b)) through grain boundaries, thereby forming the migration and redistribution of the solute elements to the vicinity of the element-poor region (figure 10(c)).

5. Conclusions

The following conclusions can be drawn from this study:

1. The area ratio of equiaxed crystal regions increases and the grain size decreases with the increase of the reduction ratio. Under the experimental conditions, the static recrystallization mainly occurs in 42CrMo under HTRP process.

2. Defect healing is divided into three types: external compression made interfaces of micro-porosity fit; large pores are segmented into smaller pores; the micro-porosity gathers to form micro-porosity clusters.

3. The segregation degree of Si, Mn, Cr and Mo have decreased after HTRP. Recrystallization occurs in the core of the HTRP process slab, and it therefore increases the austenite grain boundary density, improves the diffusion coefficient of elements, and as a result, promotes the diffusion of elements at the grain boundary.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Zhicheng Cheng https://orcid.org/0000-0001-5771-1872
Wei Yu https://orcid.org/0000-0002-3492-9462

References

[1] Yang W et al 2010 Heredity of Solidification Structure and Segregation of Spring Steel Billet Rolled IRON & STEEL. 45 32–3
[2] Feng R et al 2015 Microstructural characterization and formation mechanism of abnormal segregation band of hot rolled ferrite/pearlite steel J. Alloys Compd. 646 787–93
[3] Krauss G 2003 Solidification, segregation, and banding in carbon and alloy steels Metall. Mater. Trans. B 34 781–92
[4] Huang Y et al 2019 Flow behaviour constitutive model of Cu–Cr–Zr alloy and 35CrMo steel based on dynamic recrystallization softening effect under elevated temperature J. Cent. South Univ. 26 1530–62
[5] Shah V et al 2020 Effect of silicon, manganese and heating rate on the ferrite recrystallization kinetics ISIJ Int. 60 1312–23
[6] Cram D G et al 2012 The effect of solute on discontinuous dynamic recrystallization Acta Mater. 60 6390–404
[7] Zhou L et al 2020 Recrystallization law of micro–carbon low alloy deep drawing dual phase steel T. Metal. Heat Treat. 45 45–50
[8] Zhang Z et al 2020 Study on hot deformation behavior and dynamic recrystallization of new bainite bearing steel J. Plast. Eng. 27 158–167z
[9] Slater C, Mandal A and Davis C 2019 The influence of segregation of mn on the recrystallization behavior of C–Mn steels Metall. Mater. Trans. B 50 1627–36
[10] Torizuka S and Murty S V S N 2007 Relationship between grain boundary diffusion and ferrite grain size formed through dynamic recrystallization during large strain deformation Mater. Sci. Forum 558–595 595–600
[11] Hotta S et al 2006 Effects of dynamic recrystallization on γ′ grain refinement and improvement of micro segregation of as cast austenite in 9% ni steel ISIJ Int. 45 538–46
[12] Liu Y and Wang X 2007 The effect of electromagnetic stirring in the secondary cooling zone on the center segregation of continuous casting slab J. Univ. Sci. Technol. B. 29 582–5
[13] Li W et al 2014 Effect of final electromagnetic stirring to solidification structure of bloom Foundry Technol. 35 2329–31
[14] Siveson P, Raihle C M and Konttinen I 1993 Thermal soft reduction in continuously cast slabs Mat. Sci. Eng. A. 173 299–304
[15] Jang Y C et al 2008 Temperature dependent fracture model and its application to ultra heavy thick steel plate used for shipbuilding Int. J. Mod. Phys. B 22 5438–8
[16] Xie B et al 2016 Development of high strength ultra-heavy plate processed with gradient temperature rolling, intercritical quenching and tempering Mat. Sci. Eng. A. 680 454–68
[17] Cai Q et al 2015 Finite element simulation and investigation on ultra-heavy plate rolling with temperature gradient Henan Metall 23
[18] Li G et al 2017 Effect of gradient temperature rolling (GTR) and cooling on microstructure and properties of E40–grade heavy plate Arch. Civ. Mech. Eng. 17 121–31
[19] Li G, Yu W and Cai Q 2016 Investigation of reduction pretreatment process for continuous casting J. Mater. Process. Tech. 227 41–8
[20] Wang Y et al 2017 Effects of reduction pretreatment on the internal quality of casting billets Steel Res. Int. 88 1600337
[21] Xu Y et al 2017 Determination of Fe–Si alloy grain boundary diffusivity of silicon based on voronoi grain microstructure J. East China Univ. Sci. Tech. 43 436–42
[22] Ning Z et al 2020 Effect of reduction pretreatment process on evolution of micro-porosity in 42CrMo billet J. Iron. Steel Res. Int. 28 413–23
[23] Morito S, Adachi Y and Ohba T 2009 Morphology and crystallography of sub-blocks in ultra-low carbon lath martensite steel Mater. Trans. 50 1919–23
[24] Wang Z et al 2018 Prior austenite orientation reconstruction of coherently transformed products and its application on austenite twinning Chinese J. Eng. 040 945–53
[25] Wang H 2004 Original position statistic distribution analysis—new analytical method in quality evaluation of process metallurgy and metal materials Sci China. 14 98–105
[26] Cui J et al 2020 Evolution of the microstructure and microsegregation in subrapidly solidified Mg–6Al–4Zn–1.25Sn magnesium alloy Adv. Eng. Mater. 23 2000583
[27] Lin Y, Chen M and Zhong J 2009 Static recrystallization grain size model of 42Crmo steel J Cent. South Univ.: Sci Tech. 02 411–6
[28] Xin R, Ma Q and Li W 2016 Microstructure and mechanical properties of internal crack healing in a low carbon steel Mat. Sci. Eng. A. 662 65–71
[29] Kolobov Y R et al 2002 Grain boundary diffusion and mechanisms of creep of nanostructured metals Interf. Sci. 10 31–6
[30] Grabovetskaya G P et al 2008 Grain-boundary diffusion of nickel in submicrometalline molybdenum processed by severe plastic deformation Tech. Phys. Lett. 34 1356–8
[31] Divinski S V et al 2011 Ultra-fast diffusion channels in pure ni severely deformed by equal-channel angular pressing Acta Mater. 59 1974–85