

Grain boundary segregation of minor arsenic and nitrogen at elevated temperatures in a microalloyed steel

Yuan-zhi Zhu^{1,2)}, Zhe Zhu²⁾, and Jian-ping Xu¹⁾

1) The Key Laboratory of the Ministry of Education of China for Ferrous Metallurgy and Resources Utilization, Wuhan University of Science and Technology, Wuhan 430081, China

2) School of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

(Received: 5 July 2011; revised: 20 August 2011; accepted: 3 September 2011)

Abstract: Auger electron spectroscopy (AES) was used to investigate the grain boundary segregation of arsenic and nitrogen in a kind of microalloyed steel produced by a compact strip production (CSP) technology at 950 to 1100°C, which are similar to the hot working temperature of the steel on a CSP production line. It was discovered that arsenic segregated on grain boundaries when the steel was annealed at 950°C for 2 h. When the annealing temperature increased to 1100°C, arsenic was also found to have segregated on grain boundaries in the early annealing stage, for instance, within the first 5 min annealing time. However, if the holding time of the steel at this temperature increased to 2 h, arsenic diffused away from grain boundaries into the matrix again. Nitrogen was not found to have segregated on grain boundaries when the steel was annealed at a relatively low temperature, such as 950°C. But when the annealing temperature increased to 1100°C, nitrogen was detected to have segregated at grain boundaries in the steel.

Keywords: alloy steel; arsenic; nitrogen; segregation; grain boundaries

[This work was financially supported by the National Natural Science Foundation of China (No.50874083) and the Foundation of Hubei Educational Committee (No.Q20091110).]

1. Introduction

Arsenic is often found present in mineral ores used for iron making and steel making. This element is more difficult to be oxidized than ferrite in steels and is inclined to be preserved in final steel products [1-5]. Sometimes, even minor arsenic in steels would lead to deterioration in the mechanical properties of steels because the element tends to segregate on the grain boundaries of austenite at elevated temperatures. Occasionally, the content of arsenic at grain boundaries is even tens of times higher than that in the matrix of steels [6-7]. Because most of arsenic compounds have a low melting point, intergranular fracture may occur in the steels with an enrichment of arsenic on grain boundaries at elevated temperatures, which is called high-temperature brittleness of steels. Researches are available on the

segregation of arsenic on grain boundaries at temperatures ranging from 350 to 700°C. However, there are few reports on the grain boundary segregation of arsenic at temperatures ranging from 950 to 1100°C, which are similar to the hot working temperature of steels. For instance, in a compact strip production (CSP) process, the homogenization temperature of microalloyed steels is about 1100°C and the temperature of a steel workpiece just passing the last rolling mill is about 950°C. If arsenic segregates on austenite grain boundaries at this temperature range, cracks may occur in the hot working steel workpiece in the CSP process. Thus, it is of great importance to investigate the segregation behavior of arsenic on grain boundaries in steels at 950-1100°C.

Nitrogen is another element that would influence the mechanical properties of steels. Nitrogen is mainly present in two forms in microalloyed steels: solid solution in the fer-

Corresponding author: Yuan-zhi Zhu E-mail: tozyz1@163.com

© University of Science and Technology Beijing and Springer-Verlag Berlin Heidelberg 2012

rite matrix and forming carbonitrides with alloy elements, such as Nb, Ti, V, and Cr. The precipitation and dissolution of carbonitrides may have great effect on the microdistribution of minor nitrogen in microalloyed steels. Furthermore, the microdistribution of nitrogen would affect the mechanical properties of steels. Thus, the microdistribution of arsenic and nitrogen in a microalloyed steel at temperatures between 950 and 1100°C was studied by Auger electron spectroscopy (AES) in this paper.

2. Experimental

Steel samples of 10 mm×10 mm×5 mm in size were directly cut down from a hot-rolled steel strip produced by the CSP technology in Lianyuan Iron & Steel Co. Ltd., China. The chemical composition of the steel is given in Table 1. The steel samples were divided into two groups that were reheated to 950 and 1100°C, respectively. At the temperatures, the steel samples were annealed for different times. Then, the steel was rapidly quenched into water and cooled to room temperature to ensure that arsenic and nitrogen would not diffuse away from their previous locations in this cooling process.

Table 1. Chemical composition of the studied steel wt%

C	Ti	Nb	Cr	Mn	P	S	As	N
0.085	0.11	0.013	0.36	1.8	≤0.025	≤0.020	0.03-0.050	0.001

The heat-treated samples were then ground and polished and were etched in a solution of 5wt% picric acid. Grain boundaries can be observed clearly in this way. An AES system was used to investigate the microdistribution of arsenic in the steel studied. Before AES investigations, argon plasma was used for 30 min to remove the dust on the sample surfaces that had been formerly polished. Then, the clear surfaces were used for further AES analysis. To make sure of the accuracy of the detected results of AES spectra, at least five points of the compositions of arsenic and nitrogen both at grain boundaries and in the matrix of the steel were detected by AES. Typical results were used for discussion in this paper. The relative content of arsenic or nitrogen in the steel described in this paper was based on the intensity of AES peaks of the corresponding elements.

3. Results

The as-received steel strip was produced by the CSP technology. The CSP process was introduced in Ref. [8-10].

The distribution of arsenic and nitrogen in the as-received steel is shown in Fig. 1. The AES peaks show that the intensity of arsenic both on grain boundaries (point 1) and in the matrix was very low, which means that there was no obvious segregation of arsenic on grain boundaries in the steel during this CSP process. It is necessary to analyze the processing parameters of the steel to explain this phenomenon. The CSP hot-rolled steel has undergone temperatures as high as 1100°C. At such a high temperature, carbides should be in a solid solution state or semi-solid solution state [11]. The semi-solid solution carbides were deformed in hot rolling, which produced enough defects, such as voids to saturate arsenic atoms in the matrix of the steel. The systematic free energy could be lowered in this way rather than the segregation of arsenic atoms at grain boundaries. However, the intensity of the AES peak of nitrogen in the matrix is much stronger than that at grain boundaries, which may be attributed to nitrogen escape from grain boundaries in the grinding process of steel samples, while the solid solution of nitrogen in the matrix is still present.

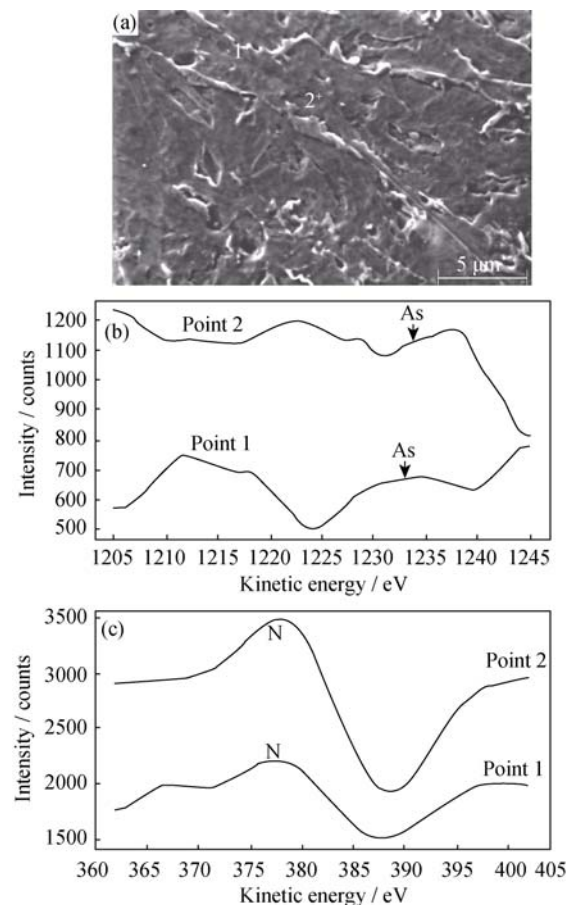


Fig. 1. Micrograph (a) and typical arsenic (b) and nitrogen (c) AES peaks of the as-received CSP hot-rolled steel strip.

The microstructure of the steel annealed at 950°C for 2 h is illustrated in Fig. 2. It shows that the intensity of arsenic AES peaks in the matrix of the steel annealed is as similarly strong as that in the as-received steels. However, the intensity of arsenic AES peaks on grain boundaries in the steel annealed is much stronger than that in the as-received steels. This phenomenon indicates that arsenic segregated on grain boundaries from the matrix in the reheating process.

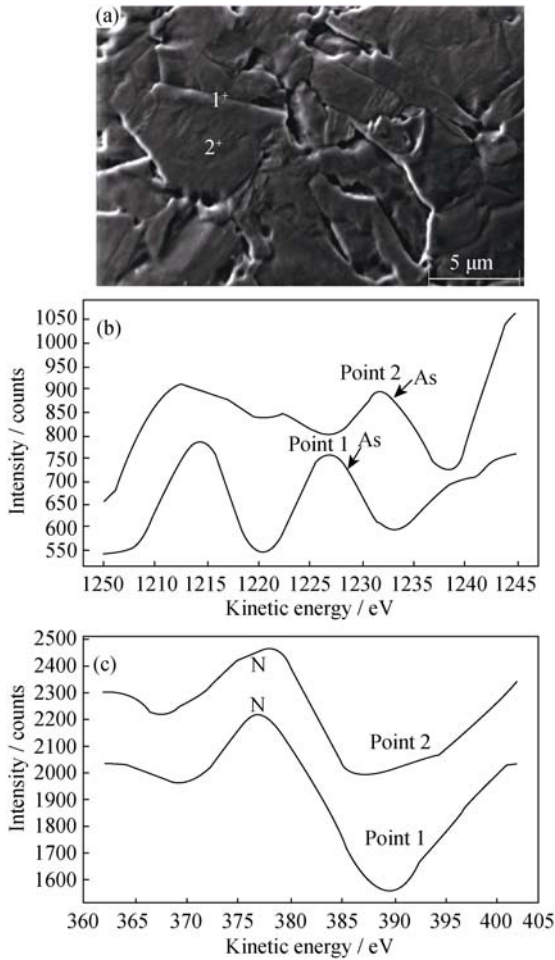


Fig. 2. Micrograph (a) and arsenic (b) and nitrogen (c) AES peaks of the CSP hot-rolled steel strip annealed at 950°C for 2 h.

Other steels were annealed at 1100°C for 5 min. The microdistribution of arsenic and nitrogen is given in Fig. 3. It shows that the content of arsenic in the matrix in this annealed steel is similar to that in the as-received steel, but the arsenic content on grain boundaries in the annealed steel is obviously higher than that on grain boundaries in the as-received steel, which means that arsenic is enriched at grain boundaries in the 5-min annealing process. However, the intensity of nitrogen AES peaks on grain boundaries in the steel annealed for 5 min is just a little stronger than that

in the as-received steel. The intensity of nitrogen peaks in the matrix of the steel is almost the same strong as that in the as-received steels.

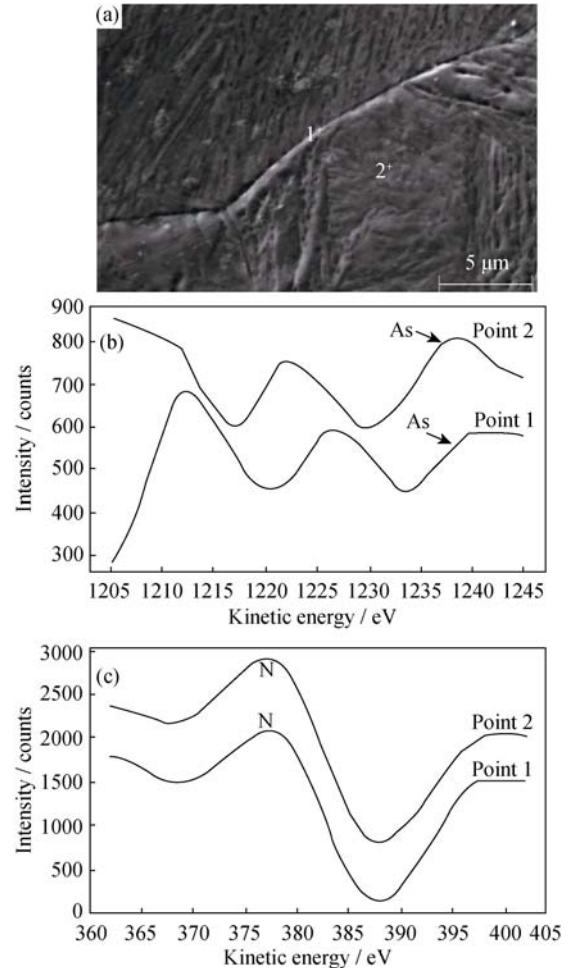


Fig. 3. Micrograph (a) and arsenic (b) and nitrogen (c) AES peaks of the CSP hot-rolled steel strip annealed at 1200°C for 5 min.

Some other as-received steels were annealed at 1100°C for 2 h. The microdistribution of arsenic and nitrogen in these steels is given in Fig. 4. It shows that the content of arsenic in the matrix of this annealed steel is similar to that in the as-received steel. The intensity of arsenic AES peaks on grain boundaries in the annealed steel is almost the same as that in the as-received steel. However, the intensity of arsenic AES peaks on grain boundaries in the steel annealed for 2 h is weaker than that in the steel annealed for 5 min, which means that arsenic is enriched at grain boundaries at first and then diffuses away from grain boundaries into the matrix of the steel. Thus, arsenic in the steel becomes homogeneous with a long enough annealing time. The intensity of nitrogen AES peaks in the matrix of the steel an-

nealed at 1100°C for 2 h becomes weaker than that in both the as-received steel and the steel annealed at 1100°C for 5 min.

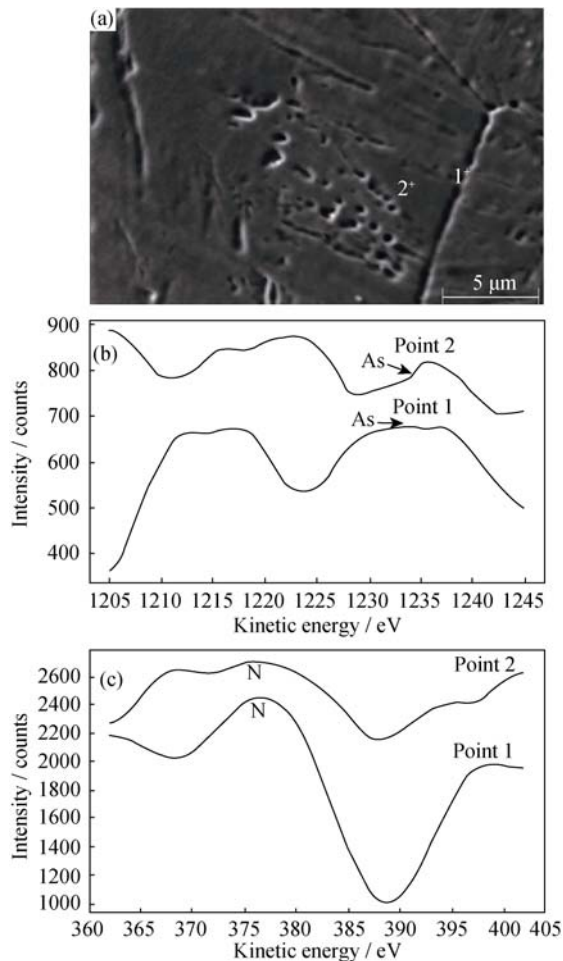


Fig. 4. Micrograph (a) and arsenic (b) and nitrogen (c) AES peaks of the CSP hot-rolled steel strip annealed at 1200°C for 2 h.

4. Discussion

4.1. Effect of annealing temperature and holding time on arsenic segregation at grain boundaries

It seems that the content of arsenic on grain boundaries increases when the steel was annealed at 950°C for 2 h, which means that arsenic tends to segregate at grain boundaries in this annealing process. However, if the annealing temperature increases from 950°C to 1100°C, the arsenic content on grain boundaries in the steel annealed for 2 h decreases to a similar level as that in the as-received steel. This result shows that arsenic is not inclined to segregate on grain boundaries when the steel was annealed for 2 h at a higher temperature, such as 1100°C, which is similar

to the homogenization temperature of the steel on the CSP line. Thus, it can be concluded that arsenic would not segregate on grain boundaries in this homogenization treatment process.

What is the reason for the above-stated behavior of arsenic in the steel? From the Fe-As phase diagram [12], it can be seen that arsenic atoms would stay at the interstitial space of bcc α -Fe at 950°C, while they would do at the interstitial space of fcc γ -Fe at 1100°C. The interstitial space of fcc γ -Fe is more symmetric than that of bcc α -Fe, which would lead to a smaller lattice distortion to saturate arsenic atoms with a relatively big atomic diameter. Thus, there is a lower strain energy for the solid solution of arsenic into the matrix of fcc γ -Fe than that of bcc α -Fe. It is chemically stable for arsenic to be dissolved into the matrix of γ -Fe at 1100°C. However, in the bcc α -Fe case, arsenic atoms tend to segregate on grain boundaries to lower the free energy of the whole system. Therefore, arsenic would segregate on grain boundaries when the steel was annealed at 950°C.

At 1100°C, the arsenic content at grain boundaries increased when the steel was annealed for 5 min. However, when the holding time at this temperature increased to 2 h, arsenic at grain boundaries decreased again. It shows that arsenic segregated at grain boundaries at first and then arsenic at grain boundaries diffused away from grain boundaries into the matrix again. In the as-received hot-rolled steel, a great deal of lattice distortion was present in the matrix for incomplete recrystallization in the hot-rolled steel. The solid solution of arsenic atoms in the interstitial space of fcc γ -Fe would cause an additional increase in the free energy of the whole system. If arsenic could diffuse away from the distorted lattice of the matrix in fcc γ -Fe into defect-enriched grain boundaries, the free energy would decrease. This is the reason for arsenic segregation at grain boundaries when the steel was annealed at 1100°C for 5 min. When the holding time increased to 2 h, the recrystallization process of the steel was completed. The interstitial space of fcc γ -Fe can saturate more arsenic atoms. Thus, arsenic diffused away from grain boundaries into the matrix of the steel again to lower the free energy of the whole system, which was a typical homogenization process.

4.2. Effect of annealing temperature and holding time on nitrogen segregation at grain boundaries

Nitrogen in the matrix increased slightly when the steel was annealed at 950°C for 2 h or at 1100°C for 5 min. This kind of slight increase may be attributed to the solid solution of some nitrides in the steel [13]. However, when the steel

was treated at 1100°C for 2 h, the content of nitrogen in the matrix decreased greatly. At this time, nitrides were dissolved completely. Usually, nitrogen tends to aggregate around such defects as dislocations [14]. However, most of dislocations disappeared in the annealing process at 1100°C. This kind of nitrogen would segregate at grain boundaries to obtain a lower systematic free energy. It was reported that nitrides did not form above ~300°C, but a film of nitrogen was present at grain boundaries [15]. In our study, after the steel was annealed at 1100°C for 2 h, it was possible to form a film of nitrogen on grain boundaries by additional nitrogen, which formerly segregated at dislocations in hot working.

5. Conclusions

(1) Arsenic segregated at grain boundaries when the steel was annealed both at 950°C for 2 h and at 1100°C for 5 min. However, when the holding time of the steel at 1100°C increased to 2 h, arsenic diffused away from grain boundaries into the matrix.

(2) Nitrogen did not segregate at grain boundaries when the steel was annealed at a relatively low temperature, such as 950°C. However, when the annealing temperature increased to 1100°C, nitrogen was found to have segregated at grain boundaries in the steel.

References

- [1] R.F. Tylecote, The composition of metal artifacts: a guide to provenance, *Antiquity*, 44(1970), p.19.
- [2] M.A. Islam, J.F. Knott, and P. Bowen, Critical level of intergranular fracture to affect the toughness of embrittled 2.25Cr-1Mo steels, *J. Mater. Eng. Perform.*, 13(2004), p.600.
- [3] Y.H. Ju, J.L. Zhang, and H. Guo, Research on arsenic removal in sintering process in Nansteel, *Sintering Pelletizing*, 34(2009), p.53.
- [4] N. Balasubramanian, T. Kojima, and C. Srinivasakannan, Arsenic removal through electrocoagulation: kinetic and statistical modeling, *Chem. Eng. J.*, 155(2009), p.76.
- [5] Z.L. Yi, H.H. Sun, X.Q. Wei, and C. Li, Iron ore tailings used for the preparation of cementitious material by compound thermal activation, *Int. J. Miner., Metall. Mater.*, 16(2009), p.355.
- [6] R.F. Tylecote and R. Thomsen, The segregation and surface enrichment of arsenic and phosphorus in early iron artifacts, *Archaeometry*, 15(1973), p.193.
- [7] C.L. Briant and S.K. Banerji, Intergranular failure in steel: the role of grain-boundary composition, *Int. Met. Rev.*, 23(1978), p.164.
- [8] Y.Z. Zhu, X.J. Cheng, Z.D. Xiang, and Z. Zhu, Scale accretion on homogenization furnace rollers in compact strip production mills and its densification mechanism, *ISIJ Int.*, 48(2008), p.598.
- [9] C.P. Reip, S. Shanmugam, and R.D.K. Misra, High strength microalloyed CMn(V-Nb-Ti) and CMn(V-Nb) pipeline steels processed through CSP thin-slab technology: microstructure, precipitation and mechanical properties, *Mater. Sci. Eng. A*, 424(2006), p.307.
- [10] Y.Z. Zhu, J. Rao, Z. Zhu, Z.D. Xiang, and Z.F. Wu, Surface inclusions and their evolution on strip rolled on CSP line and in following cold rolling process, *Ironmaking Steelmaking*, 36(2009), p.548.
- [11] Y.Z. Zhu, Z. Zhu, Z.M. Yin, and Z.D. Xiang, Evolution of carbides and carbon content in matrix of an ultra-high carbon sintered steel during heat treatment process, *Int. J. Miner. Metall. Mater.*, 16(2009), p.299.
- [12] V. Raghavanm, *Phase Diagrams of Ternary Iron Alloys*, India Institute of Metals Calcutta Press, Delhi, 1988, p.11.
- [13] S.Q. Yuan and G.L. Liang, Dissolving behavior of second phase particles in Nb-Ti microalloyed steel, *Mater. Lett.*, 63(2009), p.2324.
- [14] E.D. Hondros, Interfacial segregation of nitrogen in iron, *Met. Sci.*, 1(1967), p.36.
- [15] V.G. Gavriljuk, H. Berns, C. Escher, N.I. Glavatskaya, A. Sozinov, and Y.N. Petrov, Grain boundary strengthening in austenitic nitrogen steels, *Mater. Sci. Eng. A*, 271(1999), p.14.