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Article

The Effects of Cr and Al Addition on Transformation and Properties in Low-Carbon Bainitic Steels

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Abstract: Three low-carbon bainitic steels were designed to investigate the effects of Cr and Al addition on bainitic transformation, microstructures, and properties by metallographic method and dilatometry. The results show that compared with the base steel without Cr and Al addition, only Cr addition is effective for improving the strength of low-carbon bainitic steel by increasing the amount of bainite. However, compared with the base steel, combined addition of Cr and Al has no significant effect on bainitic transformation and properties. In Cr-bearing steel, Al addition accelerates initial bainitic transformation, but meanwhile reduces the final amount of bainitic transformation due to the formation of a high-temperature transformation product such as ferrite. Consequently, the composite strengthening effect of Cr and Al addition is not effective compared with individual addition of Cr in low-carbon bainitic steels. Therefore, in contrast to high-carbon steels, bainitic transformation in Cr-bearing low-carbon bainitic steels can be finished in a short time, and Al should not be added because Al addition would result in lower mechanical properties.

Keywords: bainitic transformation; microstructure; property; Cr; Al

1. Introduction

Low-carbon bainitic steels are commonly designed with alloying elements added to achieve favorable properties [1–11]. It is well known that the mechanical properties of bainitic steel are significantly influenced by the volume fraction of bainite, the amount of retained austenite (RA), the precipitation of cementite, among other factors [2]. The main purpose of the addition of alloying elements is to promote bainitic transformation and control the microstructures. For example, the addition of manganese, copper, and nickel, among others, are strong austenite stabilizers and can result in high stability of austenite and higher amounts of RA [3–5]. Silicon is used to restrain the formation of cementite during bainitic transformation [6]. In addition, a higher strength can be achieved due to precipitation hardening and grain refinement effects by adding vanadium, titanium, molybdenum, or niobium [7–11].

Chromium (Cr) and aluminium (Al) are also very important alloying elements, which are commonly added to low-carbon bainitic steels. Some researchers have investigated the effect of Al addition on bainitic transformation [5,12–17]. For example, Jimenez-Melero et al. [5] and Zhao et al. [12] reported that the addition of Al significantly increases the chemical driving force for the formation of bainitic ferrite plates and shortens the austenite-to-bainite transformation time. Similar results were also obtained by Garcia-Mateo et al. [13] and Hu et al. [14,15]. They claimed that the addition of Co and Al accelerates the bainitic transformation by increasing the free energy change accompanying the austenite-to-bainite ferrite transformation. Moreover, Monsalve et al. [16] and Meyer et al. [17] proved that Al promotes the formation of ferrite.

As to Cr, You et al. [18] and Chance et al. [19] studied the effect of Cr on continuous cooling transformation (CCT) diagrams, indicating that a single C-curve is separated by a bay of austenite stability due to the presence of Cr. They claimed that the addition of Cr may delay the bainitic transformation. Kong et al. [20] and Zhang et al. [21] investigated the influence of Cr on the transformation kinetics, demonstrating that the addition of Cr enhances the hardenability of metastable austenite. Moreover, Zhou et al. [22] investigated the effect of Cr on transformation and microstructure, and showed that Cr appreciably restrains ferrite transformation.

In summary, some investigations have been conducted on the effects of individual Cr or Al addition on microstructure and properties of bainitic steels. Cr and Al, as important alloying elements, are often compositely added to many bainitic steels [12–15]. However, few studies have reported on the composite effects of the combined addition of Cr and Al on the transformation, microstructure, and properties in low-carbon bainitic steels. Therefore, three kinds of low-carbon bainitic steels were designed in the present study to investigate the effects of Cr and Al addition on bainitic transformation, microstructure, and properties. Heat treatment experiments were performed on ThermecMaster-Z hot thermal–mechanical simulator followed by microstructure and property analyses, as well as quantitative characterization of bainitic transformation with dilation data. The purpose of the present study is to clarify the effects of the combined addition of Cr and Al on the transformation, microstructure, and properties in low-carbon bainitic steels. The results are useful for optimizing the composition design of Cr–Al alloying low-carbon steels.

2. Experimental Procedure

Three low-carbon bainitic steels with different chemical compositions were designed and their compositions are given in Table 1. Silicon (Si), manganese (Mn), and molybdenum (Mo), as important alloying elements, are often added in bainitic steels. The addition of Si prevents the formation of carbide, as carbide is detrimental to mechanical properties. The addition of Mn and Mo can enhance the hardenability of metastable austenite, which increases the bainite amount. Therefore, some Si, Mn, and Mo were added to the three steels. In addition, only Cr addition to steel B was used to study the effects of Cr on transformation and properties in the low-carbon bainitic steel, while the combined addition of Cr and Al in steel C was used to investigate the effects of Al and the composite addition of Cr and Al. The three steels were refined using a laboratory-scale 50 kg vacuum furnace. Cast ingots were heated at 1280 °C for 2 h and then hot-rolled to 12 mm thick plates in seven passes. The start and finish rolling temperatures were 1180 °C and 915 °C, respectively. After rolling the plates, they were cooled to 550 °C at a cooling rate of 20 °C/s followed by final air-cooling to room temperature.

Table 1. The chemical compositions of steels (wt %).

Steels	C	Si	Mn	Cr	Mo	Al	N	P	S
A (base)	0.218	1.831	2.021	/	0.227	/	<0.003	<0.006	<0.003
B (Cr)	0.221	1.792	1.983	1.002	0.229	/	<0.003	<0.006	<0.003
C (Cr + Al)	0.219	1.824	2.041	1.021	0.230	0.502	<0.003	<0.006	<0.003

Samples for dilatometric tests were machined to a cylinder of 8 mm diameter and 12 mm height. The top and bottom surfaces of samples were polished conventionally to keep the measurement surface level. The experiments were conducted according to the procedure shown in Figure 1 on a ThermecMaster-Z hot thermal–mechanical simulator equipped with a light-emitting diode (LED) dilatometer to quantitatively analyze the bainitic transformation of the three steels. The specimens were heated to 1000 °C at a rate of 10 °C/s and held for 900 s to achieve a homogeneous austenitic microstructure, followed by cooling to 350 °C at a rate of 10 °C/s. The austenitizing temperature of 1000 °C is larger than Ac_3 (the temperature at which transformation of ferrite to austenite is completed during heating). The small grain size can be obtained at a lower heating temperature. In addition, there are few inclusions and precipitates in steels, so the holding time of 900 s was chosen. The cooling rate of 10 °C/s refers to the cooling ability in the central area of thick plates in industrial production. After isothermal holding for 3600 s at 350 °C for bainite precipitation, the samples were air-cooled to room temperature.

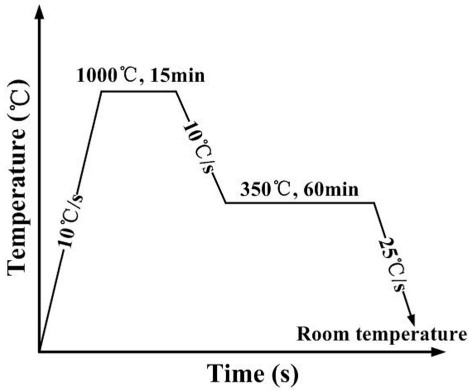

Figure 1. Experimental procedure.

According to the empirical Equations (1) in Ref. [23] and (2) in Ref. [24], the bainite starting temperature (B_S) and martensite starting temperature (M_S) of base steel are 471 °C and 336 °C, respectively. Therefore, the isothermal transformation temperature is designed to be 350 °C. It can be seen in Equation (2) that the Ms decreases by the addition of Cr, so the M_S temperature for steels B and C are smaller than 350 °C. It is known that finer bainite laths—and more of them—can be obtained at the lower phase transition temperature, which is beneficial for the mechanical properties of bainitic steel [11]. Moreover, martensite transformation will occur at the lower isothermal temperature (e.g., 300 °C). Bainite laths become coarse at the higher isothermal temperature (e.g., 400 °C), which is harmful to the mechanical properties of bainitic steel.

$$B_S\ (^\circ\mathrm{C}) = 630 - 45\mathrm{Mn} - 40\mathrm{V} - 35\mathrm{Si} - 30\mathrm{Cr} - 25\mathrm{Mo} - 20\mathrm{Ni} - 15\mathrm{W} \quad (1)$$

$$M_S\ (^\circ\mathrm{C}) = 498.9 - 333.3\mathrm{C} - 33.3\mathrm{Mn} - 27.8\mathrm{Cr} - 16.7\mathrm{Ni} - 11.1(\mathrm{Si} + \mathrm{Mo} + \mathrm{W}) \quad (2)$$

The time–temperature-transformation (TTT) curves of the three steels are plotted by MUCG83 software developed by Bhadeshia at Cambridge University (Figure 2). Chromium can enhance the stability and hardenability of austenite, so that the TTT curve moves to bottom-right with Cr addition, indicating that it is easy to obtain bainite at a certain cooling rate. In addition, higher temperature transformation may occur by Al addition, which is harmful to bainitic transformation.

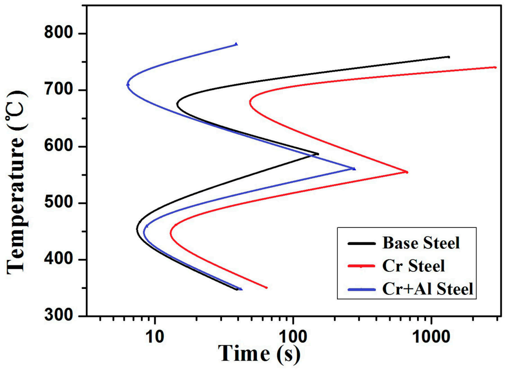

Figure 2. The time–temperature-transformation (TTT) curves of three steels.

Additionally, in order to investigate the properties of the tested steels, 140 × 20 × 10 mm blocks were cut from hot-rolled sheets and heat-treated using the same procedure shown in Figure 1. The specimens were mechanically polished and etched with a 4% nital solution for microstructure examination. Both bainite morphology and fracture surfaces were examined using a Nova 400 Nano field-emission scanning electron microscope (FE-SEM) operated at an accelerating voltage of 20 kV. The volume fraction of bainite in the three specimens was calculated by Image-Pro Plus software, and tensile tests were carried out on UTM-4503 electronic universal tensile tester at room temperature. Tensile specimens were prepared according to the ASTM standard and the beam displacement rate was 1 mm/min. Four tensile tests were conducted for each kind of tested steel and the corresponding average values were calculated in this work. In order to determine the volume fraction of RA, X-ray diffraction (XRD) experiments were conducted on BRUKER D8 ADVANCE diffractometer, using unfiltered Cu Kα radiation and operating at 40 kV and 40 mA.

3. Results

3.1. Microstructure

Figure 3 presents the microstructures of the three steels before heating treatment. It can be observed that the microstructures of the three steels mainly consist of lath-like bainite. The grain sizes of prior-austenite before heating treatment are measured by Image-Pro Plus software to be 34.6 ± 8.5 µm, 31.5 ± 8.5 µm, and 39.2 ± 8.5 µm for steels A, B, and C, respectively. In addition, few inclusions and precipitates are observed in the three steels due to very small amounts of N, P, and S (Table 1 and Figure 3). At the same time, the same processing routes are utilized for all three steels. Therefore, the influences of inclusions and precipitates in the three steels are small and similar.

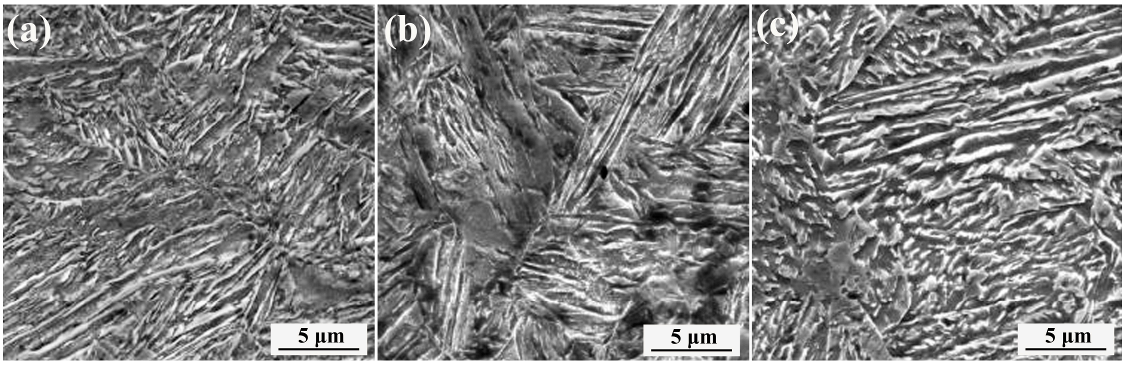

Figure 3. SEM micrographs of three low-carbon bainitic steels before heating treatment: (**a**) base, (**b**) Cr addition, and (**c**) Cr and Al addition.

Figure 4 shows the typical SEM microstructures of the three steels after isothermal holding for 3600 s at 350 °C following austenization at 1000 °C for 900 s. The classification method proposed in Ref. [11,25] is used in the present work to identify the microstructure in low-carbon bainitic steels: the microstructure is classified as ferrite (F), bainite ferrite (BF), and martensite (M). It can be observed that the microstructures of the three specimens mainly consist of lath-like BF and martensite/austenite (M/A) islands as shown in Figure 4. Prior-austenite grain boundaries (AGB) are well defined, as shown by arrows in Figure 4b. The original austenite grain size of the three tested steels, which influences the bainite morphology [11], was calculated by Image-Pro Plus software (Table 2). The prior-austenite grain sizes of the three steels have no significant difference. In addition, some ferrite is observed in steel A (base steel) and steel C (Cr + Al steel), as marked by the arrow in Figure 4c, but there is no ferrite in steel B (Figure 4b). According to the micrographs, the volume fraction of bainite was calculated by Image-Pro Plus software using the method in Ref. [11,26]. Further, the volume fractions of RA were calculated based on XRD results using the method in Ref. [4,27]. The results are shown in Table 3.

It reveals that the sample with only Cr addition has the largest amount of bainite, while the base steel without Cr and Al addition has the smallest percentage of bainite. It is clear that, compared with base steel, Cr addition obviously increases the amount of bainite. However, the combined addition of Cr and Al decreases the bainite amount to the level of base steel, indicating that Al addition in Cr-bearing low-carbon bainitic steel obviously retards the bainitic transformation. It should be pointed out that the M_S of base steel is calculated to be 374 °C and 386 °C by empirical Equation (3) in Ref. [28] and (4) in Ref. [29], respectively. However, the microstructures of the three steels after isothermal transformation at 350 °C mainly consist of bainite rather than martensite (Figure 4). It indicates that the empirical Equations (3) and (4) for M_S are not suitable for the three tested steels in the present study. The calculated results of B_S and M_S with different equations are not the same. The M_S temperatures of the base steel calculated by some equations are higher than 350 °C and others are lower than 350 °C, indicating that the different equations were obtained with different steel grades and experimental conditions. Moreover, the B_S and M_S in these equations may be corresponding to equilibrium conditions. The B_S and M_S are also affected by cooling rate. Therefore, B_S and M_S calculated by theoretical equations can only be used as theoretical reference. The real B_S and M_S at a certain cooling rate for a steel grade should be measured by experiments.

$$M_S\ (^\circ\mathrm{C}) = 537.8 - 361.1\mathrm{C} - 38.9(\mathrm{Mn} + \mathrm{Cr}) - 19.4\mathrm{Ni} - 27.8\mathrm{Mo} \tag{3}$$

$$M_S\ (^\circ\mathrm{C}) = 561.1 - 473.9\mathrm{C} - 33\mathrm{Mn} - 16.7(\mathrm{Ni} + \mathrm{Cr}) - 21.1\mathrm{Mo} \tag{4}$$

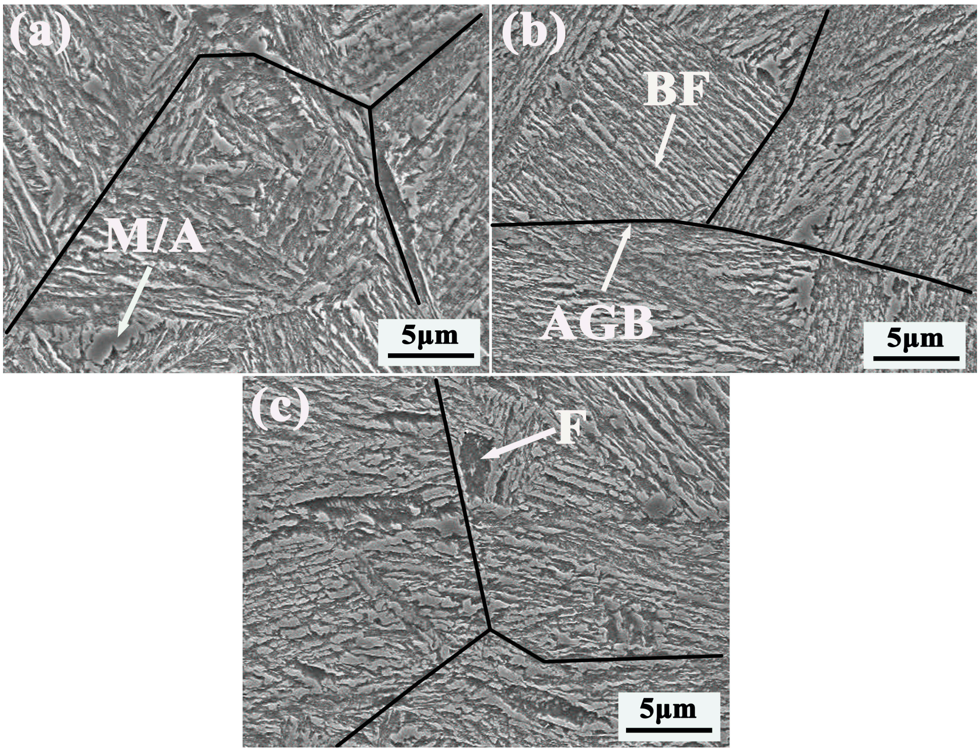

Figure 4. SEM micrographs of three low-carbon bainitic steels after isothermal holding at 350 °C for 3600 s: (**a**) base, (**b**) Cr addition, and (**c**) Cr and Al addition.

Table 2. Prior-austenite grain sizes of three steels (μm).

	Base	Cr	Cr + Al
Prior-austenite grain size	30.8 ± 9.4	29.4 ± 9.1	32.6 ± 8.5

Table 3. The volume fractions of bainite ferrite (BF) and retained austenite (RA) in three steels.

Steels	$V_{(BF)}$ (%)	$V_{(RA)}$ (%)
A (base)	45.6	3.5
B (Cr)	68.4	11.5
C (Cr + Al)	48.6	10.7

3.2. Mechanical Properties

The engineering strain–stress curves of the three tested steels are presented in Figure 5, and the corresponding mechanical properties are given in Table 4. Both the strength and the elongation are improved by only Cr addition, while the combined addition of Cr and Al has no significant effect on strength and elongation. Compared with steel A (base steel), the ultimate tensile strength (UTS) of Cr addition steel (steel B) increases by 135 MPa, while the UTS and yield strength (YS) increments of Cr and Al additional steel (steel C) are only 21 MPa and 12 MPa, respectively. Additionally, the strength and total elongation (TE) of steel C (Cr + Al) is unexpectedly smaller than that of steel B (only Cr), suggesting that no further improvement of mechanical properties occurs by Al addition in Cr-bearing bainitic steel.

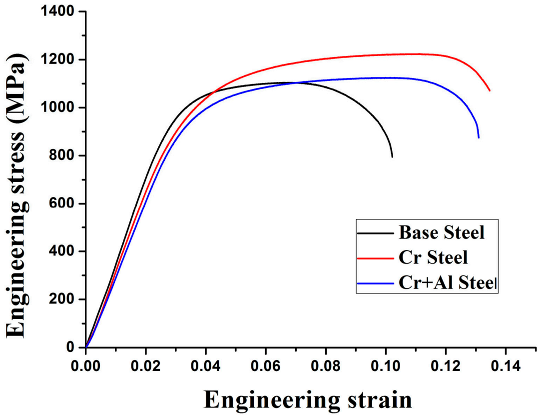

Figure 5. Engineering strain–stress curves of three tested steels with different compositions.

Table 4. Mechanical Properties of steels with different compositions.

Steels	UTS (MPa)	YS (MPa)	TE (%)	UTS × TE (GPa%)
A (base)	1103 ± 18	867 ± 22	10.2 ± 0.4	11.25 ± 0.007
B (Cr)	1238 ± 21	889 ± 18	13.1 ± 0.8	16.22 ± 0.017
C (Cr + Al)	1124 ± 15	873 ± 16	12.8 ± 0.5	14.39 ± 0.008

UTS: ultimate tensile strength; YS: yield strength; TE: total elongation.

Figure 6 displays the tensile fracture morphologies of the three steels. The mix of quasi-cleavage and dimples is exhibited in steel A (base steel), as shown by arrows in Figure 6a. A small number of quasi-cleavage fractures with a river pattern are observed in steel A, without Cr and Al addition (Figure 6a), indicating a portion of brittle fracture [19]. Nevertheless, this kind of brittle fracture microstructure rarely appears in steels B (only Cr) and C (Cr + Al). Additionally, it is observed that the diameters of dimples in the fracture of the steels with only Cr addition and combined addition of Cr and Al are larger than that of steel A without Cr and Al addition. This means that the toughness of steel is improved by Cr addition. The result is consistent with the mechanical properties of steels listed in Table 4.

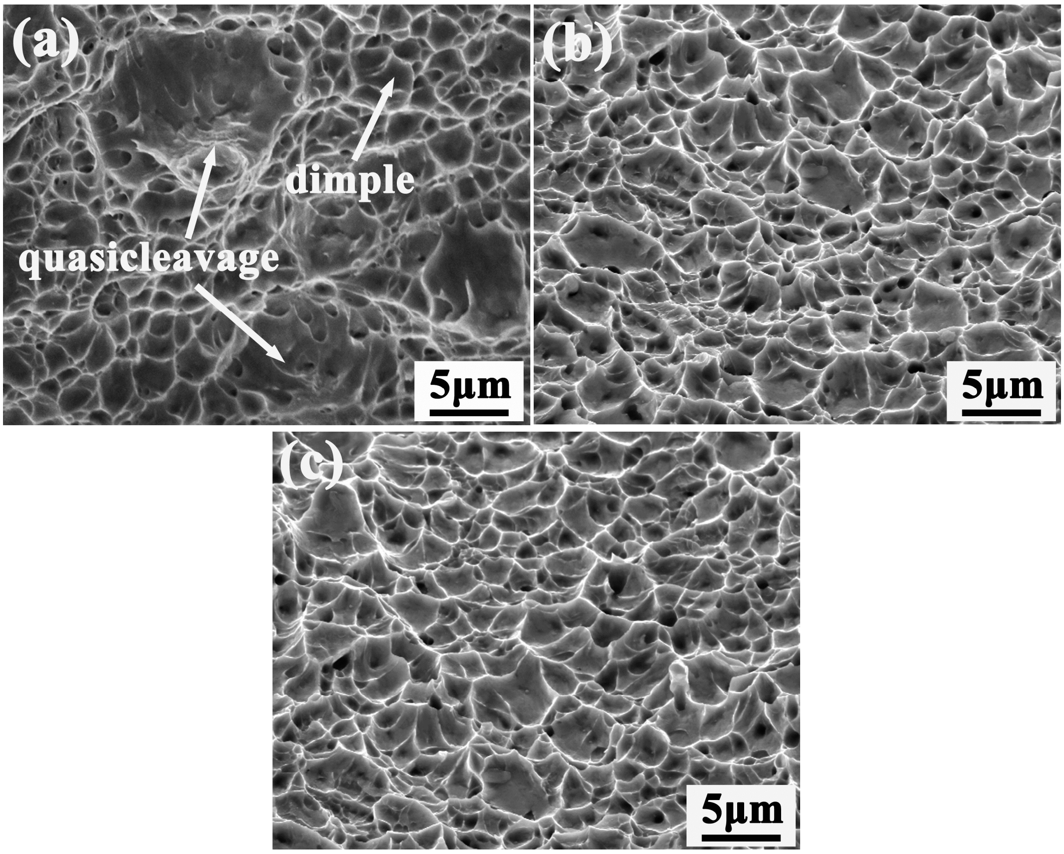

Figure 6. Fractographs of three tested steels with different compositions: (**a**) base, (**b**) Cr addition, and (**c**) Cr and Al addition.

3.3. Thermal Dilatometry

In order to quantitatively and accurately investigate the influence of combined Cr and Al addition on bainite transformation, dilatometric experiments were conducted on the thermo–mechanical simulator. According to the recorded dilatometric data, dilatation curves of the three steels are plotted. Figure 7 shows the recorded dilatation curves and transformation rates of the three steels during isothermal holding at 350 °C. Figure 7a shows dilatations as a function of holding time during isothermal holding at 350 °C, where the beginning of isothermal holding was selected as the zero point of abscissa and ordinate axes. The transformation temperature was constant and no extra force was applied on the sample during isothermal holding, thus the dilatation in Figure 7a represents the real bainite transformation amount. It can be observed that compared with the base steel, the final amount of bainite obviously increases with the addition of Cr, but it merely slightly rises with the combined addition of Cr and Al. Moreover, the amount of bainite transformation of steel C (Cr + Al steel) is obviously smaller than that of steel B (Cr steel), indicating that the addition of Al in Cr-bearing bainitic steel has a negative effect on the amount of bainite.

In addition, dilatation rates versus holding time during isothermal holding at 350 °C are given in Figure 7b. It shows that bainite transformation in steel C with combined Cr + Al addition and steel A without Cr and Al is completed prior to steel B with individual Cr addition. Although the maximum amount of bainite appears in steel B (Cr steel), the fastest transformation rate shows up in steel C (Cr + Al steel). It indicates that the addition of Al accelerates initial bainitic transformation, while the addition of Cr delays bainitic transformation. Besides, it is noticed that there is no distinguishable difference in the transformation processes between steel A (base steel) and steel C (Cr + Al steel). The time consumed to complete bainitic transformation is basically equal for the two steels, indicating that the combined Cr and Al addition has an ignorable effect on bainitic transformation rate compared with the base steel. Moreover, bainitic transformation completes quickly in the three low-carbon steels in the present study. This is contrast to high-carbon steels in which several hours or days are needed to finish bainitic transformation [13,15].

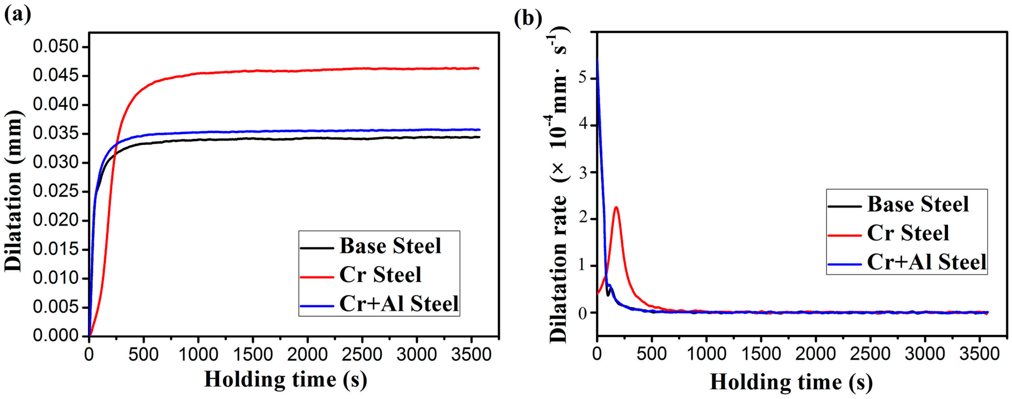

Figure 7. (**a**) Dilation curves and (**b**) transformation rates of three steels recorded by dilatometer on thermal simulator during bainitic transformation at 350 °C.

4. Discussions

4.1. Influence of Cr Addition

SEM micrographs (Figure 4) show that steel A mainly consists of bainite sheaves, a small amount of ferrite, and M/A, while no ferrite exists in steel B. As reported by some researches [30–32], bainitic transformation is characterized by incomplete reaction, thus some untransformed austenite after isothermal holding could transform into martensite. The results of dilatometric test (Figure 7) and microstructural determination (Table 3) both indicate that the bainite amount obviously increases with about 1% Cr addition. For bainitic steels, more bainite amount and RA fractions can improve mechanical properties [3,33,34]. In the present work, compared with steel A, the volume fractions of bainite and RA in steel B increase by 22.8% and 8%, respectively, resulting in an increment of 135 MPa in UTS and about 3% in TE. It can also be explained from the viewpoint of wetting of grain boundaries. It can be observed that the M/A particles with lath morphology clearly wet the austenite grain boundary (AGB) as shown in the bottom-right in Figure 4b, while they wet few AGBs in Figure 4a,c. It was reported by Straumal et al. [35] that the transition from incomplete to complete surface wetting is a phase transformation. It indicates that more M/A particles distribute in steel B (Cr steel) than steel A (base steel) and steel C (Cr + Al steel). The increased surface area contact of martensite particles with ferrite facilitates stress transfer from ductile to hard phase, which contributes to its high strength [36]. It demonstrates that a small amount of Cr addition in low-carbon bainitic steel improves strength of steel with a better total elongation. The existence of ferrite in steel A indicates that high-temperature phase transition happens during the cooling process before bainite transformation. However, with the Cr addition, the ferrite transformation is avoided, resulting in an increased bainite fraction. It is reported that Cr causes a separation of the bainite C-curve and extends the bainite formation field [18,19]. Similar results can be obtained from Equations (1) and (2). The addition of Cr decreases the B_S and M_S, which contributes to the greater amount of bainite. Moreover, Cr addition enhances the hardenability of metastable austenite [22] and increases the stability of austenite to ferrite [37]. Therefore, more undercooled austenite can transform into lath-like BF in the Cr addition steel, which leads to the improvement of the mechanical properties of steel B.

4.2. Influence of Al Addition

Figure 7 shows that bainite transformation is accelerated by Al addition, which is consistent with the results by Hu et al. [14,15], Caballero et al. [37] and others. SEM micrographs (Figure 4) indicate that steel B (Cr steel) mainly consists of bainite sheaves without ferrite, while a small amount of ferrite presents in steel C (Cr +Al steel), showing that Al addition promotes the formation of ferrite. According to the dilation diagram (Figure 7), the total dilatation of steel C (Cr + Al steel) is only 0.0368 mm, reduced by 19.5% compared to steel B (Cr steel, 0.0457 mm), which is consistent with the result listed in Table 3. It indicates that 0.5% Al addition in Cr-bearing steel obviously reduces the final bainite amount. In addition, the product of tensile strength and total elongation for steel C (Cr + Al steel) slightly decreases from 16.22 GPa% for steel B (Cr steel) to 14.39 GPa%. Fonstein et al. [38] and Meyer et al. [17] reported that Al addition can promote the formation of a high-temperature transformation product such as ferrite. Therefore, the amount of bainite transformation decreases because of less supercooled austenite. On the other hand, the results by Caballero and Bhadeshia [37] indicate that Al addition has no significant effect on final bainite amount. This depends on whether the ferrite transformation occurs. There is no ferrite transformation in their study, while ferrite appears in the present study, which leads to the decrease of bainite amount. Therefore, the mechanical properties of steel C (Cr + Al steel) are slightly smaller compared to steel B (Cr steel).

4.3. Influence of Composited Addition of Cr and Al

It can be observed from Table 3 that the volume fractions of bainite in steels A and C are 45.6% and 48.6%, respectively. Also, from the dilation curves, the dilatation of steel C (Cr and Al) is 0.0368 mm, increased by 0.0022 mm compared to the 0.0346 mm expansion of base steel, demonstrating that the effect of combined addition of Cr and Al on bainite transformation is very small. In addition, the UTS of steel C (Cr and Al) increases by only 21 MPa compared with base steel, indicating that the strengthening effect of combined Cr and Al addition has no significant improvement over that of steel A (base steel). As mentioned previously, although the only Cr addition increases the final bainite transformation amount, Al addition in Cr-bearing low-carbon steel reduces the amount of bainite transformation because of the formation of high-temperature transformation product (F). This means that the addition of Al weakens the promotion function of Cr on bainite transformation. Therefore, the composite strengthening effect of Cr and Al addition has no significant improvement over that of base steel. Al addition is very effective at shortening the bainitic transformation time in high-carbon bainitic steel [13,37]. However, for the low-carbon bainitic steels, bainitic transformation can finish in a short time even without Al addition (Figure 7), and Al should not be added in Cr-bearing low-carbon bainitic steels because Al addition would result in lower mechanical properties.

5. Conclusions

Three low-carbon bainitic steels were designed in the present work. Metallographic method and dilatometry were used to investigate the effects of Cr and Al addition on bainitic transformation, microstructures, and properties. The results show that the individual addition of Cr is effective for improving the strength of low-carbon bainite steel by increasing the amount of bainite transformation. In addition, in Cr-bearing low-carbon steel, Al addition leads to lower mechanical properties due to decreased amount of bainite transformation, although the addition of Al accelerates the initial bainitic transformation and shortens the austenite-to-bainite transformation time. Moreover, the addition of Al can effectively shorten the bainitic transformation time in high-carbon bainitic steels. However, bainitic transformation in Cr-bearing low-carbon bainitic steels can finish in a short time. Therefore, it is not necessary to add Al for the acceleration of bainitic transformation because Al addition would result in lower mechanical properties.

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Author Contributions: Guang Xu, supervisor, conceived and designed the experiments; Junyu Tian conducted experiments, analyzed the data and wrote the paper; Mingxing Zhou, conducted experiments; Haijiang Hu conducted experiments; Xiangliang Wan, conducted experiments. All authors participated in the discussion of experimental results.

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