Metastable order–disorder transition and sigma phase formation in Fe–V binary alloys

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The influence of binary and ternary alloying compositions and heating rate on the σ formation reaction are studied. Several ways are developed to supress the stable σ phase formation and to understand the metastable CsCl-type order–disorder transition in Fe–V alloys. The Fe–V ordered phase has a metastable critical transition temperature of between 850 and 880° C at equiatomic composition, and the so called "650° C anomaly" corresponds to the 550° C anomaly in Fe–Co alloys. The σ formation reaction does not commence most easily at equiatomic composition but at the iron-rich side of the 40 at. % V alloy. The Influence of ternary alloying additions on the σ formation in Fe–V alloys depends on the relative stabilities of the binary σ phase with iron or vanadium.

1. Introduction

The Fe–V system exhibits complete solubility of b c c phase at high temperatures with the σ phase occurring at low temperatures [1]. The b c c phase, which can be retained by rapid cooling from the homogeneity range, transforms to the CsCl-type ordered phase on holding below 600° C [1–3]. There is little known, however, about the order–disorder transition temperatures and the transformation kinetics, because of the formation of the stable σ phase in the composition range extending from 30 to 60 at. % V at temperatures below 1200° C. The present authors have investigated the CsCl-type order–disorder transition temperatures in the V–Mn–Fe, V–Mn–Cr and Fe–V–Cr ternary systems in order to obtain the interaction parameters of each binary system concerned, and have shown that a small amount of Mn or Cr addition reveals the order–disorder transition by suppressing the σ formation [4].

The present study was undertaken in order to confirm the metastable order–disorder transition temperatures in the Fe–V system by several methods to avoid the σ phase transformation. To find the temperatures the influences of binary and ternary alloying compositions and heating rate on the σ formation were studied. Then the composition dependence of the metastable order–disorder transition temperature in the Fe–V alloy system was determined.

2. Experimental procedures

Alloy samples weighing about 35 g were prepared by arc-melting pure metals of 99.7 to 99.9% purity under an argon atmosphere. The ingots were turned and remelted several times to achieve homogeneity. As the weight loss during melting was very little, the nominal compositions were accepted for the most of these alloys. All the ingots were homogenized at 1300° C for 2 h in a vacuum, quenched into iced brine to retain the b c c phase and then machined into specimens. If necessary, some of the specimens were heated at 550° C for 100 h to achieve the fully ordered state. Before the experiments, all the alloy specimens were confirmed to be of a single phase, the b c c or CsCl crystal structure, by X-ray examination.

Differential thermal analysis (DTA) was carried out using a Rigaku Denki Thermoflex with cylindrical specimens (7.8 mm ϕ × 16 mm) having a hole

at the centre of the bottom for a thermocouple. Heating rates of 1 to 20 deg min^{-1} were used. DTA for faster heating rates was performed in an infra-red image furnace with small specimens ($1.5\,\text{mm}\,\phi \times 4\,\text{mm}$), to which Alumel-Chromel thermocouples were spot-welded. An equiatomic V–Cr alloy was used as the inert reference standard for the DTA measurements.

X-ray analysis was carried out with V-filtered CrKα radiation using a Shimadzu VD–1A diffractometer. The lattice constants were determined mainly from the (2 1 1) diffraction line.

3. Results
3.1. Effect of alloy compositions

Some examples of DTA curves at a heating rate of 13 to 14 deg min^{-1} for Fe–V base ternary alloys are shown in Fig. 1. A broad exothermic peak at around 600° C for the quenched alloys should correspond to the ordering reaction of the disordered b c c matrix. This peak is missing for previously ordered specimens of the same alloys. The second, sharp exothermic peak occurs at different temperatures depending on alloy compositions, and corresponds to the σ phase formation. The highest temperature of the reaction, indicated as T_σ in Fig. 1, corresponds to the temperature where the reaction rate becomes a maximum under the continuous heating of 13 to 14 deg min^{-1}, while the σ formation commences 60 to 70° below this peak temperature. The effect of the ternary alloying additions on T_σ are summarized in Fig. 2.

The endothermic reaction, indicated as T_c in Fig. 1, is for the order–disorder for transformation characterized by the mode of λ-shaped endothermic troughs. Another broad endothermic trough observed at around 650° C on the alloys previously ordered, denoted as T_a in Fig. 1, will be discussed later in detail.

Although the order–disorder transition temperature T_c as well as the σ formation temperature T_σ should be affected by the additions of ternary alloying elements, the results of Fig. 1 suggest that one can expect in some cases the appearance of disordering without any sign of σ formation. Fig. 3, which illustrates examples of extrapolations from ternary regions, reveals that the CsCl-type order–disorder transition temperature in the equiatomic Fe–V alloy can be estimated to be between 850 and 880° C.

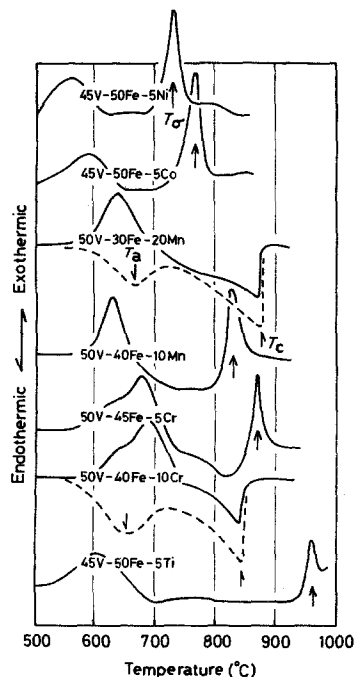DTA curves of Fe–V binary alloys are shown in Fig. 4, while the composition dependence of T_σ is

Figure 1 Differential thermal analysis curves of several Fe–V–X ternary alloys at a heating rate of 13 to 14 deg min^{-1}. Continuous lines represent the quenched state and dotted lines the previously ordered state.

summarized in Fig. 5. From these figures, in the Fe–V binary system the σ formation temperature T_σ is a minimum on the iron-rich side of the 40 at.%V alloy, showing that σ formation commences most easily here. It is interesting to note that the composition where the σ phase has the highest stability temperature does not coincide with the composition where T_σ is the lowest. This
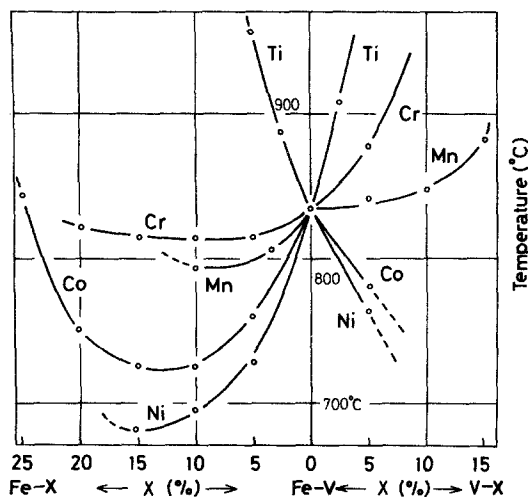

Figure 2 Effect of the ternary alloying additions on the σ formation temperature (T_σ) of Fe–V alloy.
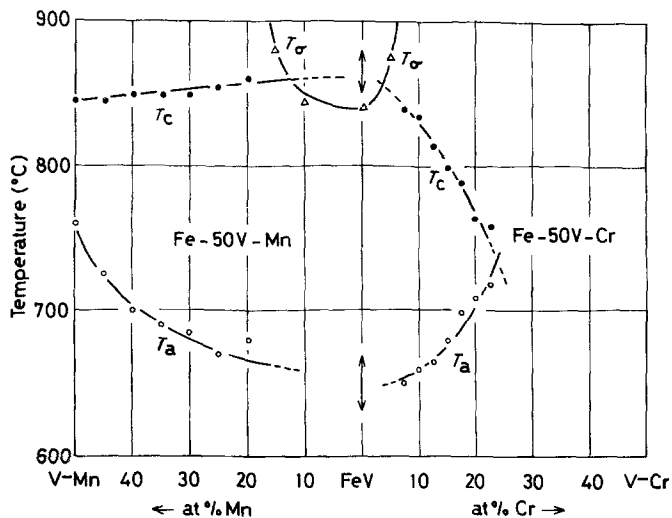
Figure 3 Determination of the CsCl-type order–disorder transition temperature (T_c) by extrapolation from ternary regions.

has enabled T_c to be measured to some extent even in the binary systems, as shown in Fig. 4, for vanadium-rich alloys with more than 60 at.% V and also for iron-rich alloys with less than 32.5 at.% V. In the case of 42.5 Fe–57.5 V alloy in Fig. 4, the endothermic trough at 820° C cannot be identified as corresponding to T_c, because it is known that the disordering reaction and σ formation are superimposed in this temperature range.

In Fig. 5 the composition dependence of the metastable order–disorder transition temperatures in the Fe–V system is surmised from the values extrapolated from ternary regions and from those obtained directly from the binary system.

3.2. Effect of heating rates

Fig. 6 shows the heating rate dependence of T_σ for 60 Fe–40 V and 50 Fe–50 V alloys, both quenched and also previously ordered. T_σ shifts to higher temperatures with increasing heating rates. On the other hand, it is confirmed that the order–disorder transition temperature is not essentially affected
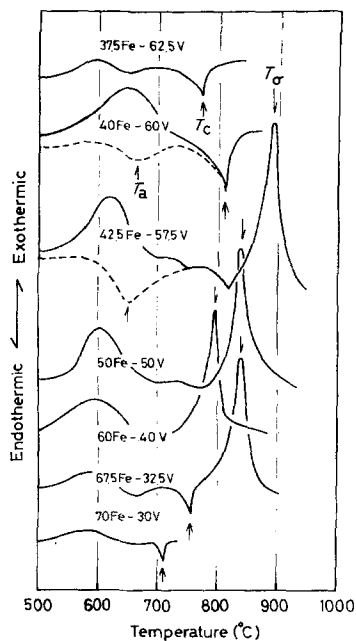

Figure 4 Differential thermal analysis curves of binary Fe–V alloys at a heating rate of 13 to 14 deg min⁻¹. Continuous lines represent the quenched state and dotted lines the previously ordered state.
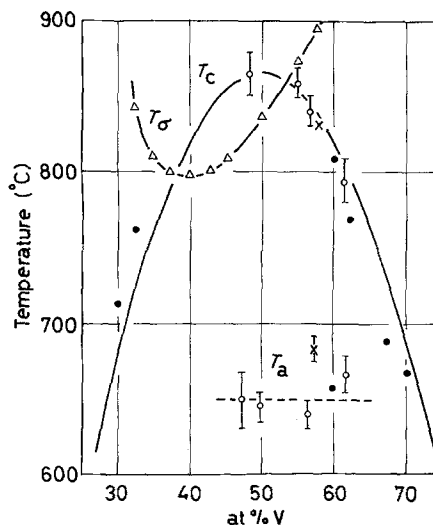

Figure 5 The composition dependence of the σ formation temperature (T_σ) and the CsCl-type order–disorder transition temperature (T_c). The open circles are the values extrapolated from ternary regions, the solid circles are the values measured for binary Fe–V alloys, and the cross is the value measured at the faster heating rate of 60 deg min⁻¹.
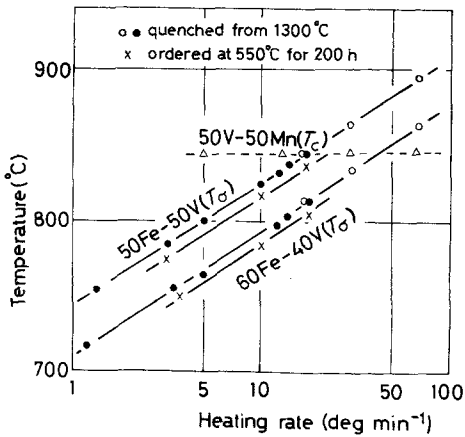
Figure 6 The effect of heating rate on the σ formation temperature (T_σ) for 50 Fe–50 V and 60 Fe–40 V alloys.

by heating rate, as shown in Fig. 6 by the results for a V–Mn alloy using the same equipment. Thus T_c of the 42.5 Fe–57.5V alloy can be measured by DTA at faster heating rates, and the result shown in Fig. 5 is in good agreement with those obtained by previous methods.

3.3. Lattice constant and hardness in the quenched and ordered states
Fig. 7 shows the composition dependence of the lattice constant with those previously reported [5, 6] for the quenched and ordered Fe–V alloys. The lattice constant of the ordered state is smaller than that of the quenched state and the difference in lattice constant between the quenched and the ordered states is most marked at around the equiatomic composition. Fig. 7 clearly shows that the lattice constant of the disordered b c c phase in

the Fe–V system has a marked negative deviation from Vegard's law.

Fig. 8 shows the composition dependence of hardness for the quenched and ordered alloys. As shown in Fig. 8, the solution hardening of vanadium by iron and of iron by vanadium is prominent and the maximum hardness is not observed in the middle of the system but at the composition around 70 at.% V. The ordered state is less hard than the quenched state, as in other systems having an order–disorder transition [7, 8].

4. Discussion
In the present work, the $\alpha \rightarrow \sigma$ transformation kinetics have been examined for convenience by the dynamical method of continuous heating, rather than by isothermal reaction experiments as has been done by others [9]. The influence of ternary alloying additions on the σ formation should be considered from the viewpoint of the phase stability of ternary σ phases. Fig. 9 illustrates the homogeneity ranges of σ phase in Fe–V–X ternary systems [10, 11], where X refers to Ti, Cr, Mn, Co or Ni, with lines drawn in to show the equivalent electron vacancy concentration, $N_v = 3.42$. This figure can be used to predict the occurrence of stable ternary σ phase fields. The equation reported by Greenfield and Beck is used to estimate the stable ternary σ phase [12].

As shown in Fig. 2, the σ formation temperature T_σ shifts to lower temperatures with the substitutions of Co and Ni for V, which are unfavourable for the formation of stable ternary σ phases. This can be understood by the fact that the most stable
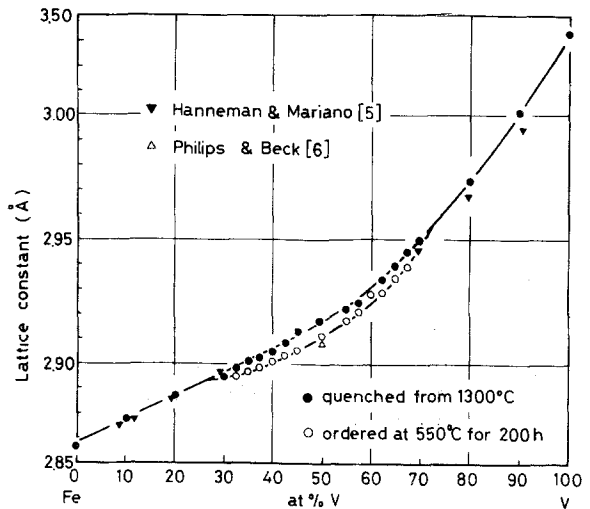

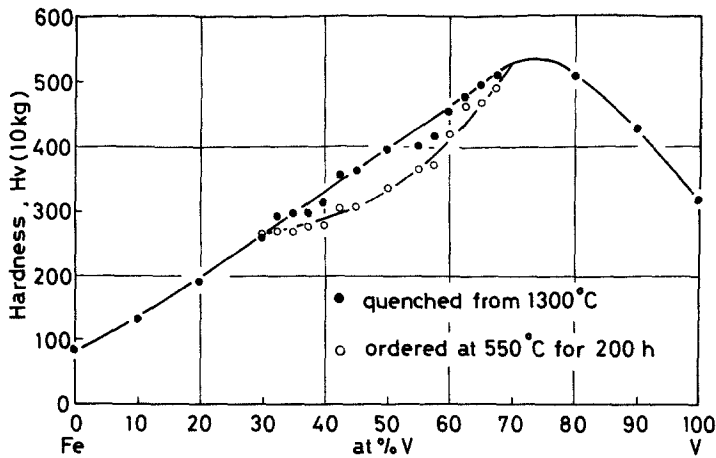*Figure 7* Change in the lattice constant with composition for ordered and quenched Fe–V alloys.

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Figure 8 Change in the hardness with composition for ordered and quenched Fe–V alloys.

composition in terms of the $\alpha \to \sigma$ transformation kinetics does not coincide with the equiatomic composition in the Fe–V binary system, which is the most stable thermally. The σ formation reaction in the Fe–V–Co and Fe–V–Ni ternary systems seems to be the most prominent along the lines from the composition of 40 at.% V in the Fe–V system to the σ phase regions of the V–Co and V–Ni systems. Thus, the substitution of a ternary alloying element for vanadium should traverse this line. As a result, T_σ is initially lowered and then raised with increasing the ternary elements.

Substitution of a ternary alloying element for either Fe or V in the equiatomic Fe–V alloy suggests a similar effect on the change in T_σ. That is, T_σ is lowered by the addition of Co and Ni, and is raised by Ti, Cr and Mn. Addition of Cr and Mn, which lie between Fe and V in the periodic table, is not so effective, but Ti, which lies to the left of V, is particularly effective in raising T_σ. Kichingman et al. [9] have shown that the addition of ternary alloying elements such as Mn, Zr and Re to the equiatomic compound tends to stabilize the b c c phase and slow the σ formation reaction, in agreement with the present results. The variations in T_σ produced by the addition of ternary alloying elements correspond clearly with the group numbers, and to some extent with the relative stabilities of the binary σ phases with iron or vanadium in terms of melting temperatures or maximum temperatures of stability in solid state [13].

According to Kichingman et al. [9], the T–T–T curves of the $\alpha \to \sigma$ transformation are not continuous but suggest that the σ formation reaction divides into two distinct parts above and below the temperature of 700 to 750° C. The σ formation reaction below that temperature commences earlier

than expected by the extrapolation from higher temperatures. In accordance with their observations, T_σ of the fully ordered alloys is lower than that of the quenched alloys, as shown in Fig. 6. This fact shows that the fully ordered state in the b c c phase before the transformation tends to enhance the σ formation reaction.

The order–disorder transition temperature T_c in the ternary region has been deduced by Hirone and Katayama [14], based on the Bragg–Williams approximation, and is given by

$$Lx_A x_B x_C - 2(\Omega_{AB} x_A x_B + \Omega_{BC} x_B x_C + \Omega_{AC} x_A x_C)RT_c + (RT_c)^2 = 0 \quad (1)$$

where $L = \Omega_{AB}^2 + \Omega_{BC}^2 + \Omega_{AC}^2 - 2\Omega_{AB}\Omega_{BC} - 2\Omega_{BC}\Omega_{AC} - 2\Omega_{AC}\Omega_{AB}$; x_A, x_B and x_C are the atomic fractions of the components A, B and
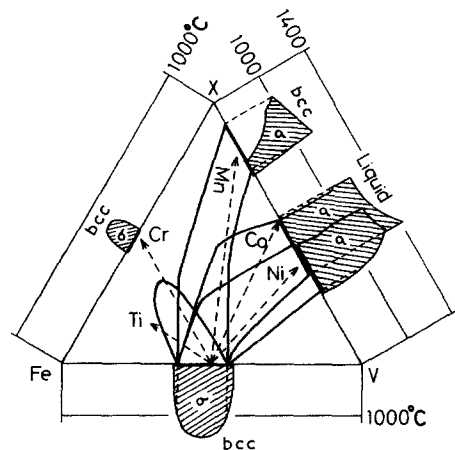

Figure 9 The homogeneity ranges of the σ phase in Fe–V–X ternary alloy systems at 1000° C, with lines drawn in to show the equivalent electron vacancy concentration, $N_v = 3.42$.

C; and Ω_{AB}, Ω_{BC} and Ω_{AC} are the regular solution parameters in the b c c binary solid solutions AB, BC and AC respectively. The unknown parameters Ω can be estimated by the measurements of T_c over a wide region of the ternary system and then T_c in the binary system can be extrapolated theoretically, even if the binary ordered phase is metastable or unstable. In fact, the parameters of each binary system concerned could be determined consistently by the results of the measured T_c in the Fe–V–Cr, Fe–V–Mn and V–Mn–Cr ternary systems [4]. From the results the parameter of the Fe–V system has been estimated as $\Omega_{FeV} = -4520 \pm 60$ cal mol^{-1}. Such a theoretical extrapolation is shown in Fig. 5 as the solid line, which is a parabola symmetrical with respect to equiatomic composition. It can be seen in Fig. 5 that all the data from the different sources are in good agreement with each other.

As shown in Fig. 1, T_c could not be detected for addition of titanium. All the Fe–V–Ti alloys containing less than 10 at% Ti, however, have a single b c c phase upon quenching from 1300° C and transform to the CsCl-type ordered phase by the ordering heat-treatment without precipitation of any kind of second phase. This has been confirmed by the detection of (1 0 0) superlattice reflections and by the exothermic peak at around 600° C in the DTA curves as shown in Fig. 1. Detection of the superlattice lines is easily done using CrKα radiation, which has a frequency close to the absorption edge of iron and vanadium. The reason why we could not observe T_c in the Fe–V–Ti alloys might be understood in terms of rapid increase of the T_c as stated below.

Differentiation of the expression for T_c in Equation 1 with respect to x_A, taking $x_A \approx x_B$ and $x_C \ll 1$, leads to the displacement of a binary critical temperature T_{crit} by a small addition of a ternary alloying element,

$$\frac{\partial T_{crit (AB)}}{\partial x_C} = \frac{1}{2R\Omega_{AB}}\{\Omega_{AB}^2 - (\Omega_{AC} - \Omega_{BC})^2\}$$

(2)

According to Equation 2, $T_{crit(FeV)}$ is raised if $|\Omega_{FeTi} - \Omega_{VTi}| > |\Omega_{FeV}|$ and lowered if $|\Omega_{FeTi} - \Omega_{VTi}| < |\Omega_{FeV}|$. Ω_{FeTi} seems to have a large negative value because of the occurrence of the stable CsCl-type compound in the Fe–Ti system [1]. On the other hand, Ω_{VTi} seems to

have a small absolute value due to the presence of the continuous b c c solid solution in the V–Ti system [1]. In fact, a relatively small, positive deviation in the activity is observed in the V–Ti system [15]. Thus, the absolute value of $|\Omega_{FeTi} - \Omega_{VTi}|$ becomes so large that $T_{crit (FeV)}$ is expected to be raised drastically by a small addition of titanium. If T_σ is raised faster than T_c by the titanium addition, the T_c might be detected at temperatures greater than 1000° C.

The broad endothermic trough, denoted as T_a in Fig. 1, corresponds obviously to the peak called "the 550° C anomaly" in the Fe–Co ordered alloys and " the 730° C anomaly" in the V–Mn ordered alloys [16]. The measured and extrapolated anomaly temperatures T_a are summarized in Fig. 5. In the Fe–Co [17], V–Mn [18] and Fe–V alloys, T_a does not depend greatly on the compositions but on heating rate. According to Sato and Kikuchi [19], and others [20, 21], the anomaly in the Fe–Co alloys has been interpreted as due to a relaxation effect, that is, the consequence of "melting" of the "frozen-in" state. Although we might say the Fe–V ordered alloys also have 650° C anomaly", the relevant effect can be expected to be common to any ordered alloy system.

The negative deviation of the lattice constant from ideality is shown in Fig. 7. This negative deviation in the Fe–V system implies that the Fe–V bond is stronger than the Fe–Fe or V–V bond, which is consistent with the presence of the CsCl-type ordered phase and with a marked negative deviation in the activity [22–24]. Moreover, a closer inspection of Fig. 7 reveals that the lattice constant of the quenched state in the middle of the system deviates slightly from the values obtained by interpolation from both sides of the system. This result indicates that the quenched state may be partly ordered and that it is difficult to obtain the perfect disordered state by quenching into iced brine. Nevitt has reported that ordering in 57Fe–43V alloy cannot be prevented by quenching [25].

5. Conclusions

The metastable CsCl-type order–disorder transition temperature in the binary Fe–V system was studied using several methods to supress the stable σ phase formation. Based on this study, the following conclusions may be drawn:

(1) The order—disorder transition temperature is found to be between 850 and 880° C for the equiatomic composition and decreases parabolically as the composition deviates from stoichiometry.

(2) The "650° C anomaly", which corresponds to the 550° C anomaly in Fe—Co alloys and the 730° C anomaly in V—Mn alloys, is observed in the ordered Fe—V alloys during continuous heating.

(3) The σ formation reaction does not commence most easily at the composition where the σ phase has the maximum temperature of stability, but rather on the iron-rich side of the 40 at.% V alloy.

(4) The influence of the addition of ternary alloying elements on the σ formation reaction is dependent on the group numbers and hence to a degree on the relative stability of the binary σ phase with iron or vanadium.

(5) The existence of a fully ordered state in the b c c phase before the σ formation tends to enhance markedly the σ formation reaction as compared to the disordered state.

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