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 論 文
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Relationships among Alloying Elements, Destabilization Conditions & Retained Austenite in Eutectic High Chromium White Cast Irons

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요 약

다섯 조성의 서로 다른 Mo, Ni 및 Mn 함량을 지닌 3 mass% C-20 mass% Cr 공정조성의 백주철을 질소분위기하에서, 1173, 1273 및 1373 °K의 온도로 3.6, 7.2, 14.4 및 28.8 ks 동안 불안정화열처리를 행한 후 공냉시켜 잔류오스테나이트를 측정하고 결과 합금원소함량, 불안정화열처리조건 및 V_γ 사이에 다음과 같은 관계를 얻었다. 즉 Mo, Ni 및 Mn을 첨가한 결과, 주방상태에서 79.89~91.65 vol.% 범위의 V_γ 가 얻어 졌으며 퍼얼라이트는 전혀 생성되지 않았다. 1173 °K에서 불안정화열처리를 한 경우에는 무수히 작은 이차탄화물이 석출하였으나 온도가 높아 질수록 그 수는 점차 감소하여 1373 °K에서는 거의 관찰되지 않았다. 1173 및 1373 °K에서 불안정화열처리를 한 경우, 불안정화열처리시간의 증가에 따른 V_γ 의 변화는 미미하였으나 1273 °K의 경우에는 감소하였다. 또한 Mo, Ni 및 Mn의 첨가량이 많아짐에 따라 V_γ 는 증가하였으며 이 두 함수사이의 관계식을 정립시키기 위하여 P인자를 도입하였다.

1. Introduction

High Cr white cast irons have an excellent resistance to abrasion, corrosion and oxidation because their microstructures consist of chromium-rich primary austenite and eutectic austenite, and eutectic chromium carbides[1-3]. However, a large amount of austenite is retained in the as-cast condition because of higher cooling rate after solidification and the presence of alloying elements such as Mo, Ni and Mn, whereby inferior properties are resulted. Therefore, the microstructure of matrix, particularly the amount of austenite in the matrix, should be controlled by the destabilization heat treatment in order to provide an optimum service performance for industrial applications such as hot strip mill rolls or mineral pulverizing mills.

In this research, the interrelation among alloying elements (Mo, Ni, Mn), destabilization condition (temperature and holding time) and V_γ was investigated.

2. Experimental Procedure

2.1 Preparation of specimen

Specimens were produced using a silica lined high frequency induction furnace with 15 kg melting capacity. Melts were super-heated to 1923 °K, and tapped

into a pre-heated teapot pouring ladle. After removal of any dross or slag, the melts were poured at 1823 °K into a pep-set mold consisted of 2 cylindrical bars of 20 mm ϕ and 165 mm in length.

2.2 Destabilization heat treatment

The size of specimens used for destabilization heat treatment were 10 mm $\phi \times$ 10 mm h. These specimens were destabilized at temperatures of 1173, 1273 and 1373 °K for 3.6, 7.2, 14.4 and 28.8 ks under nitrogen atmosphere, and subsequently air cooled to room temperature.

2.3 V_γ measurement

V_γ values were calculated from the peak areas of (200) and (220) for ferrite and those of (220) and (311) for austenite. The diffraction patterns were obtained by using the simultaneously rotating and swinging sample stage of X-ray diffractometer in order to minimize the effect of crystal orientation.

2.4 Metallographic examination

The specimens were ground, polished, etched and examined metallographically. The etching solutions used were Murakami's etchant (10 g of potassium ferricyanide, 10 g of potassium hydroxides and 100 ml of distilled water) and Villela's etchant (1 g of picric acid,

5 ml of hydrochloric acid and 94 ml of methyl alcohol).

2.5 Alloy design

In order to study the effect of Mo, Ni and Mn on V_γ , the eutectic series of 3 mass% C-20 mass% Cr high Cr white cast irons with different Mo, Ni and Mn contents were prepared as listed in Table 1.

3. Results and Discussion

3.1 Chemical analysis

A summary of the chemical compositions of the specimens from the five Heats is shown in Table 2.

3.2 Effects of Mo, Ni and Mn on microstructure of as-cast specimen

Photo. 1 shows an as-cast microstructure of Heat 1 which is a typical eutectic microstructure of high Cr white cast iron which is consisted of eutectic γ and cellular M_7C_3 carbide. However, with the addition of Mo, Ni and Mn in different levels, the resulted microstructures of specimens from other Heats were almost similar to those observed in this Photo. In spite of the fact that the Cr/C ratios of the five Heats (average value=6.56) fell into a hypo-eutectic region in

Table 1. Heat series used in this research

Alloying elements	Mo (mass%)	Ni (mass%)	Mn (mass%)
1	1.0	0.0	1.0
2	1.0	1.0	1.0
3	2.0	0.0	1.0
4	1.0	0.0	2.0
5	2.0	2.0	1.0

Table 2. Chemical analysis for 5 Heats poured (mass%)

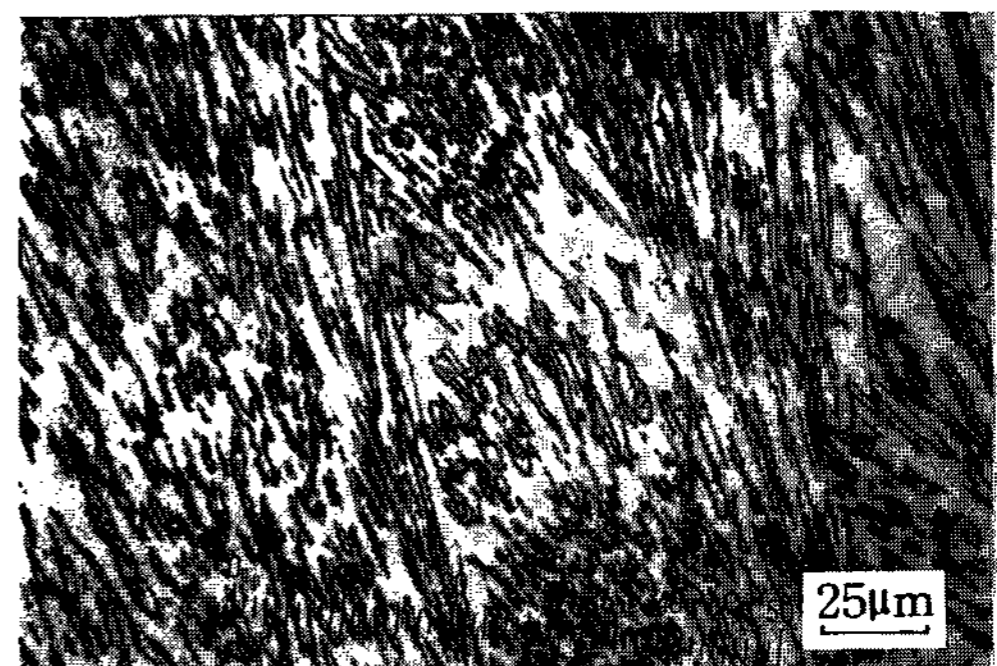
Chemical elements	C	Cr	Mo	Ni	Mn	Si
Heat No. 1	2.99	18.60	0.99	0.11	1.36	2.00
2	3.03	20.09	0.92	1.09	1.33	2.29
3	3.00	19.40	1.88	0.12	1.35	1.84
4	3.11	20.19	1.05	0.10	2.08	1.79
5	3.11	21.72	1.91	2.22	1.48	1.55

Jackson's phase diagram[4], all the resulted microstructures were eutectic because of the presence of Si up to about 2.0 mass%.

It is well known in Fe-C-Si alloy that Si increases the C activity, and the role of Si is equal to that of approximately 1/3 of the same amount of C. From this fact, Mo, Ni and Mn seem to have little influence on the solidification behaviour of eutectic-high Cr white cast iron. In stead, they are more concerned with the solid state transformation of the iron. As shown in Table 3, V_γ of each specimen was ranged from 79.89 to 91.65% and the remainder of the matrix might be



(a) Etched by Villela's reagent



(b) Etched by Murakami's reagent

Photo. 1. Microstructure of the as-cast specimen from Heat 1.

Table 3. V_γ in the as-cast specimen

Heat No.	V_γ (vol. %)
1	79.89
2	83.55
3	86.41
4	88.02
5	91.65

considered as martensite. In the previous study[5], a matrix structure composed of 60 vol.% V γ and 40 vol.% pearlite was obtained in the as-cast condition when the high chromium white cast iron was solidified to the room temperature without the addition of Mo, Ni and Mn. But, in this study, with the addition of Mo, Ni and Mn, no pearlite in the matrix was observed in all the specimens. Mo, Ni and Mn are reported to have an effect to move the CCT curve toward longer times and lower temperatures, and to stabilize austenite[6]. Therefore, it could be postulated that during the cooling of the iron after solidification, the cooling curve did not pass through the pearlite transformation region, and most of the austenite was stabilized in stead of being transformed into martensite. Therefore, with the addition of Mo, Ni and Mn, V γ in the as-cast specimens is higher than that of the specimens without them because of the fact that no pearlitic structure was found in the specimens alloyed with them. The Mo₂C carbide was also observed in the specimens from Heats 3 and 5 in which 2.0 mass% Mo was added. In this case, the eutectic reaction of [L= γ +Mo₂C] was followed by that of [L= γ +M₇C₃].

3.3 Effects of destabilization heat treatment on V γ

The effects of destabilizing temperature and time on

Table 4. The effects of destabilizing conditions on V γ (vol. %)

Destabilizing Conditions	Heat No.				
	1	2	3	4	5
1173 °K × 3.6 ks	2.23	1.19	2.79	1.75	2.34
1173 °K × 7.2 ks	1.99	1.61	3.92	1.24	2.49
1173 °K × 14.4 ks	1.46	1.92	1.48	1.75	4.10
1173 °K × 28.8 ks	1.57	1.03	1.62	2.14	2.74
1273 °K × 3.6 ks	24.23	26.61	28.97	52.16	53.70
1273 °K × 7.2 ks	24.35	27.21	26.91	40.20	50.70
1273 °K × 14.4 ks	25.43	23.48	25.11	28.13	36.83
1273 °K × 28.8 ks	6.15	12.64	13.33	23.36	27.67
1373 °K × 3.6 ks	78.31	77.15	80.35	86.81	83.45
1373 °K × 7.2 ks	77.13	79.15	81.46	87.57	86.95
1373 °K × 14.4 ks	77.23	78.27	82.50	83.72	86.37
1373 °K × 28.8 ks	74.89	75.41	76.36	84.91	88.79

V γ are shown in Table 4.

3.3.1 Effects of destabilizing temperature on V γ

The relationships between V γ and destabilizing temperature at the destabilizing time of 3.6, 7.2, 14.4 and 28.8 ks are shown in Fig. 1. It is clear from this figure that V γ was increased with the increased destabilizing temperature. While V γ values were very small when the specimens were destabilized at 1173 °K for all holding times, the higher values in V γ were observed at 1273 and 1373 °K. The variation of V γ values among the Heats destabilized at 1273 °K was relatively large in contrast with that destabilized at 1173 or 1373 °K. At 1273 °K, Heat 5 showed the highest V γ and Heat 1, the lowest. Numerous fine secondary carbides were observed in the specimens destabilized at 1173 °K. Less but coarse secondary carbides were obtained in the specimens held at 1273 °K. However, no precipitation of secondary carbides was occurred when the specimens were destabilized at 1373 °K. Because of the higher cooling rate after solidification encountered in the as-cast specimens, austenite is usually supersaturated with C and Cr, whereby Ms temperature decreases and V γ increases. Therefore, the destabilization heat treatment must be conducted to reduce C and Cr concentrations in the matrix by precipitating the secondary carbides, and consequently Ms temperature will be raised. The equilibrium concentration of C and Cr in the austenite is determined by Cr/C ratio and destabilizing temperature[7]. At the constant Cr/C ratio, the equilibrium concentration of C in the austenite decreases with a decrease in destabilizing temperature by which more secondary carbides are precipitated and less V γ is obtained in the matrix. On the other hand, the precipitated secondary carbides are dissolved again into the matrix by increasing the destabilizing temperatures, whereby more V γ results as shown in Fig. 1.

3.3.2 Effects of destabilizing time on V γ

The relationships between V γ and destabilizing time in the Heats destabilized at 1273 and 1373 °K are shown in Fig. 2. The graphical presentation of the Heats destabilized at 1173 °K was omitted because all the values of V γ and the variation of it with the destabilizing time were very small. While the variation of V γ with the destabilizing time in all the Heats was small at 1373 °K, V γ showed a tendency to decrease

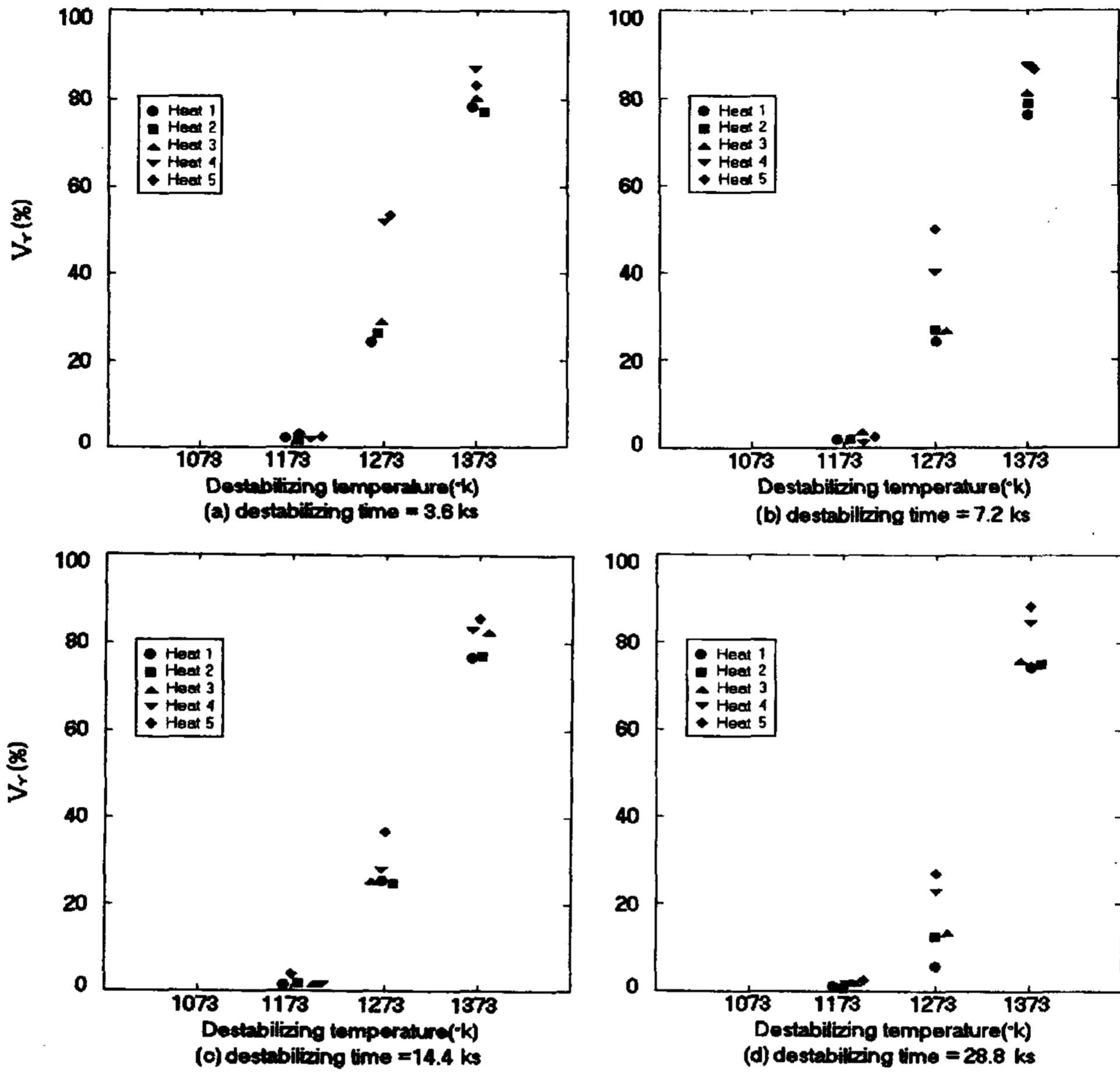


Fig. 1. The effect of destabilizing temperature on V_γ in four different destabilizing times.

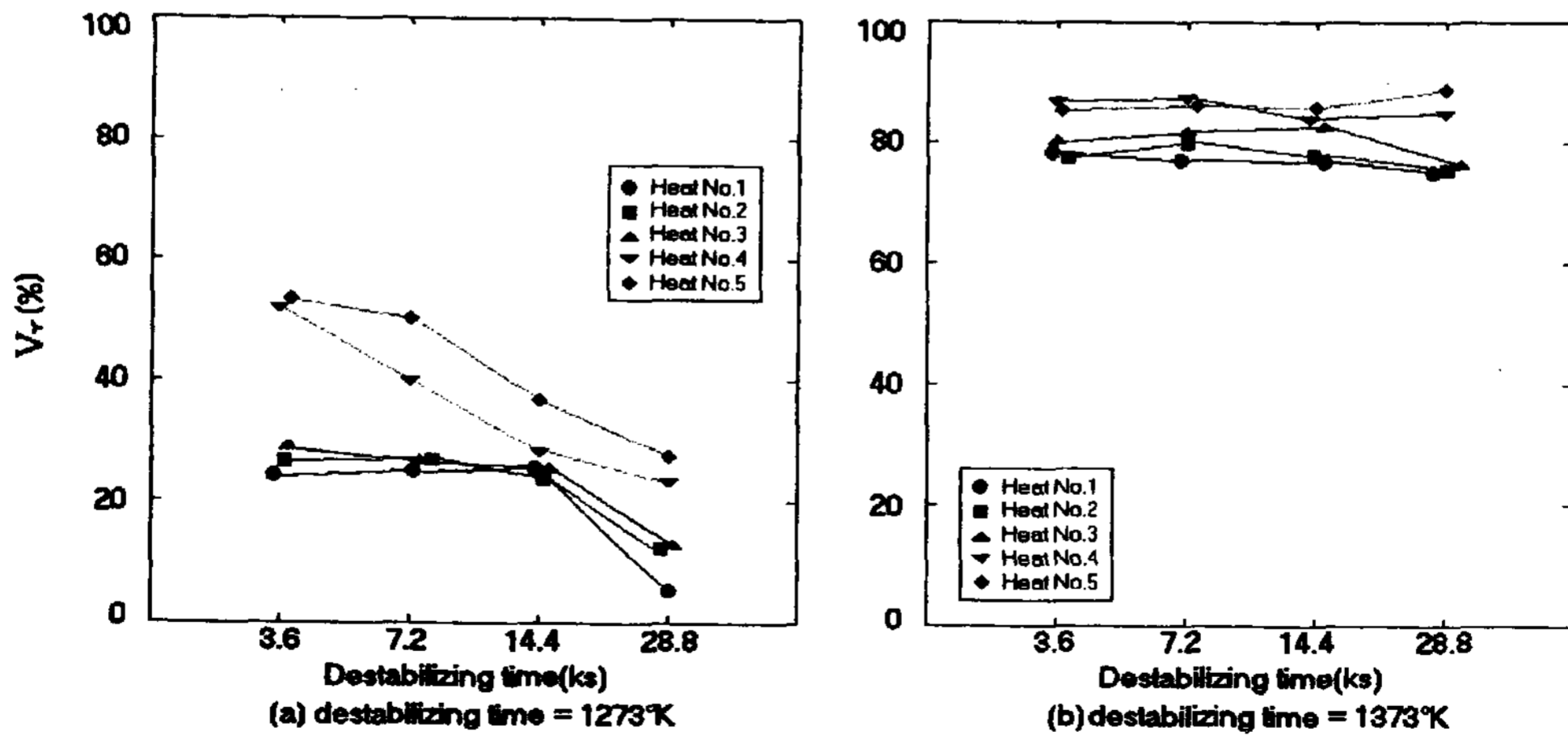


Fig. 2. The effects of destabilizing time on V_γ at two different destabilizing temperatures.

with an increase in destabilizing time at 1273 °K. Especially, Heats 4 and 5 showed a sharp decline with the

destabilizing time. From the fact mentioned above, it can be postulated that even in the specimens des-

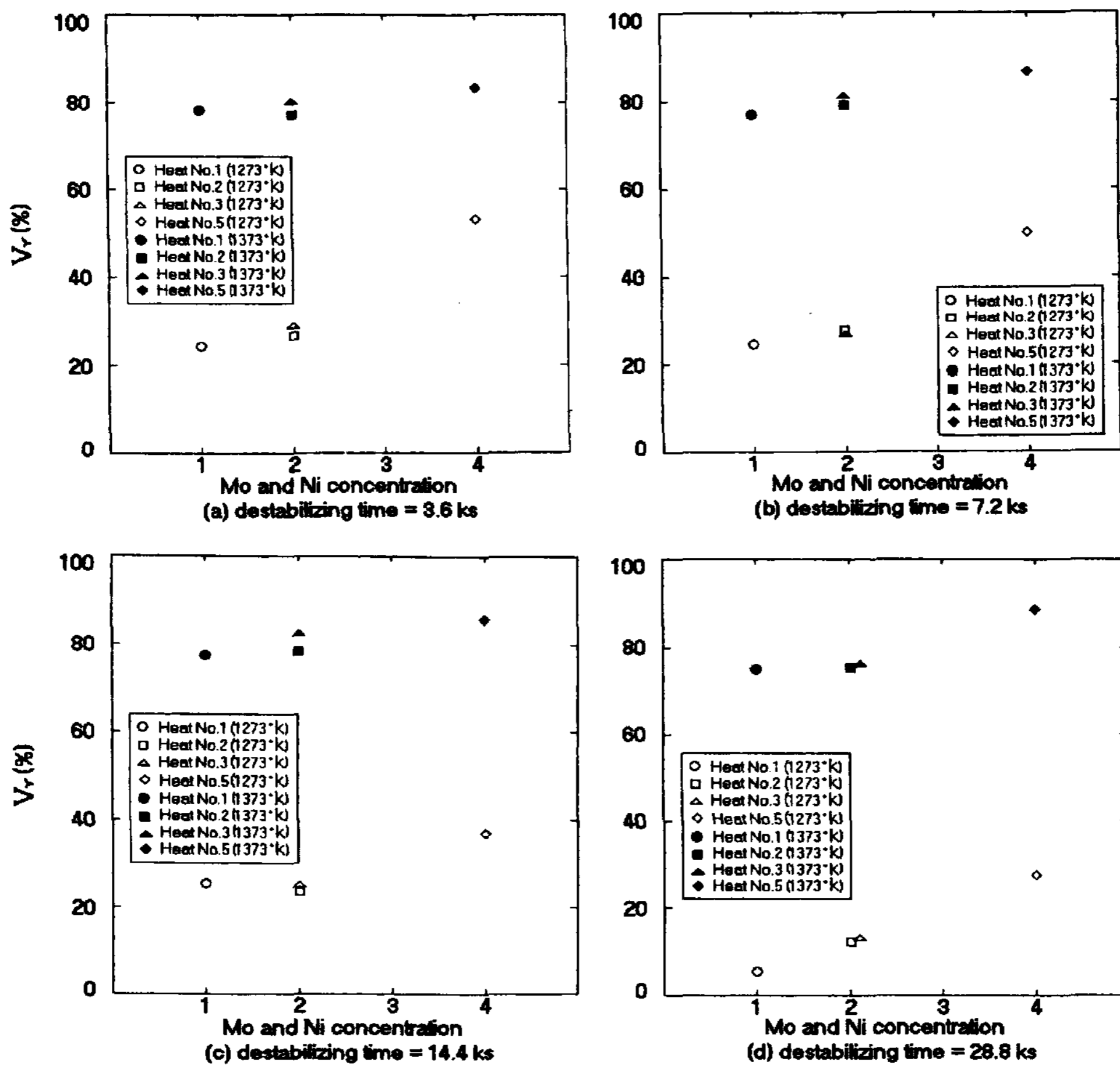


Fig. 3. The effects of Mo and Ni on V_γ for four different destabilizing times.

tabilized at 1173 °K for 3.6 ks, most of the supersaturated C and Cr in the matrix were precipitated as tiny secondary carbides because of the low C equilibrium concentration at this temperature, whereby V_γ was low and remained almost constant with the longer destabilizing times upto 28.8 ks. At the constant Cr/C ratio, the equilibrium concentration of C in the austenite increases with an increase in destabilizing temperature. Therefore, it is thought that all the C and Cr present except for in the M_7C_3 carbides were dissolved in the matrix when the specimens were destabilized at 1373 °K for 3.6 ks, whereby V_γ was high and did not change with the destabilizing time. The equilibrium concentration of C in the matrix at 1273 °K lies between the values of 1173 and 1373 °K. The diffusion is necessary in order to C and Cr be precipitated as secondary carbides. The diffusion rate is

known to be dependent upon the temperature and time. Therefore, one can approach the equilibrium concentration of C by extending the destabilizing time, and finally can reach it in the infinitely longer destabilizing time, where the minimum value of V_γ is obtained.

3.3.3 Effects of Mo, Ni and Mn on V_γ

At 1.0 mass% Mn level, the effect of Mo and Ni on V in the Heats destabilized at 1273 and 1373 °K for 3.6, 7.2, 14.4 and 28.8 ks are shown in Fig. 3. As shown in this figure, V_γ increased with an increase in alloying contents at both destabilizing temperatures. At the same alloy concentration, the Heat destabilized at 1373 °K showed a higher V_γ value than that of the Heat destabilized at 1273 °K. A similar result was also observed when V_γ was plotted as a function of Mo and Mn contents(Heats 1, 3, 4), or Ni and Mn contents

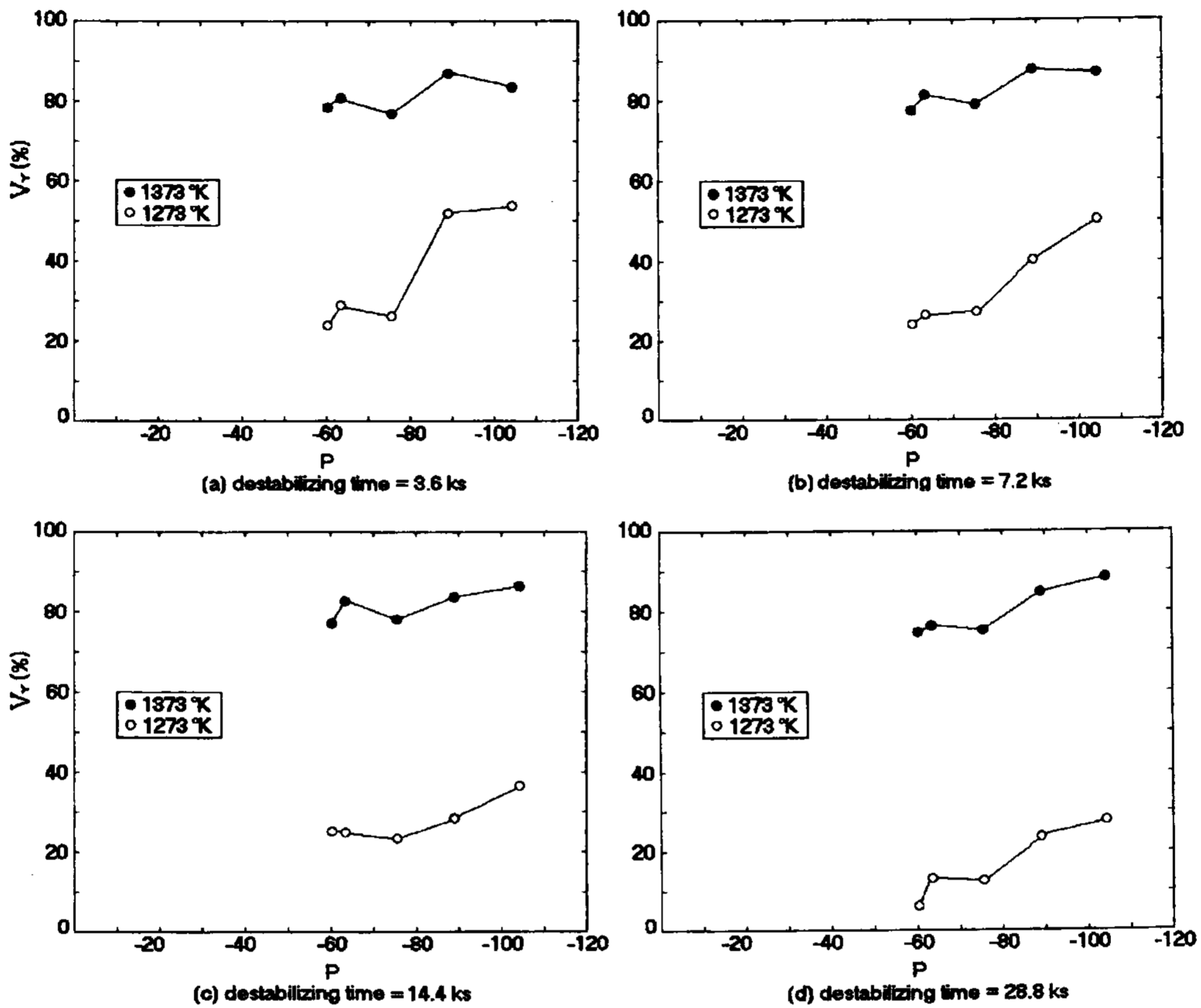


Fig. 4. The effects of parameter (P) on V_γ in four different destabilizing times

(Heats 1, 2, 4). V_γ is closely related to the M_s temperature of the cast irons, and M_s temperature is determined by alloy concentrations in the matrix just after destabilizing or just before the start of air hardening. However, it is difficult to analyze the alloy concentration exactly by EPMA method because many fine carbides are precipitated in the matrix during holding at the destabilizing temperature. In alloy steels, on the other hand, a convenient equation obtained experimentally has been used to estimate the M_s temperature; $M_s(^{\circ}C) = 550 - (350 \times \%C) - (40 \times \%Mn) - (35 \times \%V) - (20 \times \%Cr) - (17 \times \%Ni) - (10 \times \%Cu) - (10 \times \%Mo) - (10 \times \%W) - (15 \times \%Co)$

Supposing that Cr and C concentrations in the matrix are about same because both contents in the irons are almost same, the M_s temperature changes mainly depending on the concentrations of Mo, Ni and Mn. Almost all Ni and Mn, and 40 mass% of Mo are reported to be dissolved in the matrix[8]. Here, the fol-

lowing parameter(P) is introduced as a factor affecting the M_s temperature and in addition $V_\gamma: P = 0.4 \times (-10 \times \text{mass}\% \text{ Mo}) - (17 \times \text{mass}\% \text{ Ni}) - (40 \times \text{mass}\% \text{ Mn})$

The relationship between V_γ and P at two different destabilizing temperatures in four destabilizing times is shown in Fig. 4. It is clear from this figure that V_γ decreases with an increase in P and this relationship is more distinct at 1273 than 1373 °K. This might be attributed to the fact that more effective alloying elements such as C and Cr are dissolved in the matrix at 1373 °K whereby the effect of Mo, Ni and Mn on V_γ becomes smaller.

4. Conclusion

1) In as-cast condition, V_γ of each specimen was ranged from 79.89 to 91.65 vol.% with the addition of Mo, Ni and Mo, and no pearlitic structure was observed.

2) While $V\gamma$ values of all the Heats were very small when the specimens were destabilized at 1173 °K for four different destabilizing times, a significant increase in $V\gamma$ was observed at 1273 and 1373 °K.

3) Numerous fine secondary carbides were observed in the specimens destabilized at 1173 °K. Less but coarse secondary carbides were obtained in the specimens held at 1273 °K. However, no precipitation of secondary carbides was occurred when the specimens were destabilized at 1373 °K.

4) While the variation of $V\gamma$ with the destabilizing time in all the Heats was small at 1173 and 1373 °K, $V\gamma$ decreased with an increase in destabilizing time at 1273 °K.

5) $V\gamma$ increased with an increase in Mo, Ni and Mn concentrations at the destabilizing temperatures of 1273 and 1373 °K, but was almost constant at 1173 °K.

6) The parameter(P) was proposed as a factor to relate the alloying elements with $V\gamma$. $V\gamma$ decreased with the increased in P and this relationship was more dis-

tinct at 1273 than 1373 °K.

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