

# A Thermodynamic Assessment of the Fe-Cr-Ni-C System

MATS HILLERT and CAIAN QIU

Since the Gibbs energy of formation of  $\text{Cr}_{23}\text{C}_6$ ,  $\text{Cr}_7\text{C}_3$ , and  $\text{Cr}_3\text{C}_2$  in the Cr-C system was modified in the recent assessment of the Cr-Ni-C system, it is not possible to continue with the previous description of the Fe-Cr-C system. In the present work, the Fe-Cr-Ni-C system was studied thermodynamically together with the Fe-Cr-C system, using the new descriptions of the Cr-Ni-C, Fe-Ni-C, and Fe-Cr-Ni systems. The descriptions of  $\text{M}_{23}\text{C}_6$ ,  $\text{M}_7\text{C}_3$ , body-centered cubic (bcc) ferrite, cementite, and liquid in the Fe-Cr-C system were reassessed. Particularly, attention was paid to improve the description of the solubility of  $\text{M}_{23}\text{C}_6$  in face-centered cubic (fcc) austenite. Composition-dependent interactions for  $\text{M}_{23}\text{C}_6$  and  $\text{M}_7\text{C}_3$  were introduced in order to get good agreement. After the new assessment, comparisons between experimental information and calculated results were made, which show that the agreement with experiments is satisfactory. Some phase diagrams are presented for practical use.

## I. INTRODUCTION

THE Fe-Cr-Ni-C system is the basis for austenitic stainless steels and also for important nickel-base alloys. The thermodynamic properties of this system and its phase relations have been discussed in many articles, but a complete assessment of the whole system has not been made. It was attempted in the present work.

It is important to first have a set of satisfactory descriptions for the four ternary systems based upon the same thermodynamic models and the same descriptions of the four unary and six binary systems. If such a consistent set is available, then the properties of the quaternary system can be predicted with considerable confidence. Small adjustment can be made by introducing quaternary interaction terms in order to improve the fitting to experimental information on the quaternary system.

When the present project started, a consistent set of three ternary assessments was available. The missing one was the Cr-Ni-C system, which had been partly assessed by Ansara *et al.*,<sup>[1]</sup> but the result was not quite consistent with the other three. The first stage of the project was thus devoted to the Cr-Ni-C system, and that work has been reported separately.<sup>[2]</sup> Unfortunately, during the course of that work, it became evident that the descriptions of the binary Cr-C system should be modified, taking new information into account. As a consequence, it is now necessary also to modify the Fe-Cr-C system, because it has Cr-C as one of its side systems. This work will be described in the present report, which also concerns the quaternary system.

Of the two remaining ternary systems, the Fe-Ni-C will be taken directly from Gabriel *et al.*<sup>[3]</sup> A description of the Fe-Cr-Ni system was available through two reports.<sup>[4,5]</sup> However, it has been criticized on some points, and a new assessment was thus carried out in the project. That result has been reported elsewhere.<sup>[6]</sup>

## II. METHOD OF ASSESSMENT

The present assessment of the Fe-Cr-C system will be based upon the previous study by Andersson.<sup>[7]</sup> However, due to the new descriptions of the Cr carbides, it was necessary to modify the descriptions of most of the phases.

Andersson<sup>[7]</sup> has reviewed the literature, and there does not seem to be any new ternary information that should be considered. Nevertheless, there is much information from Tuma<sup>[8]</sup> on the solubility of  $\text{M}_{23}\text{C}_6$  in face-centered cubic (fcc) with various Ni contents in the quaternary system, and some information can thus be obtained for the ternary system by extrapolation to the zero Ni content. That information is reproduced in Figures 1 and 2. Instead of making an extrapolation by hand, it was decided to assess the Fe-Cr-C system by taking into account this quaternary information directly. Consequently, it is required to have a reasonable description of the C activity in the quaternary fcc phase. Such experimental information is available from Tuma<sup>[8]</sup> and from studies by Greenbank,<sup>[9]</sup> as well as Natesan and Kassner.<sup>[10]</sup> All of this information was also included in the present assessment. Furthermore, it is necessary to describe the solution of Ni in  $\text{M}_{23}\text{C}_6$ , but this is not so critical because that solubility is rather low.

Having included these descriptions for the quaternary system, it is possible to use several other pieces of information on the solubility of  $\text{M}_{23}\text{C}_6$  in austenitic stainless steels. The Gibbs energy of each phase will be described with a mathematical model, and the best values of the model parameters will be found by using a computer-operated optimization program, PARROT, available in the Thermo-Calc database.<sup>[11]</sup> The optimization is made by minimizing the sum of the squares of the deviations between calculated and experimental values of various kinds. Each experimental value will be given a weight factor which may be changed until the overall result is satisfactory. During this work, individual sets of data for a particular case were often optimized separately, and finally, a simultaneous optimization was made with all of the data.

MATS HILLERT, Professor Emeritus, and CAIAN QIU, Graduate Student, are with the Division of Physical Metallurgy, Royal Institute of Technology, S-10044 Stockholm, Sweden.

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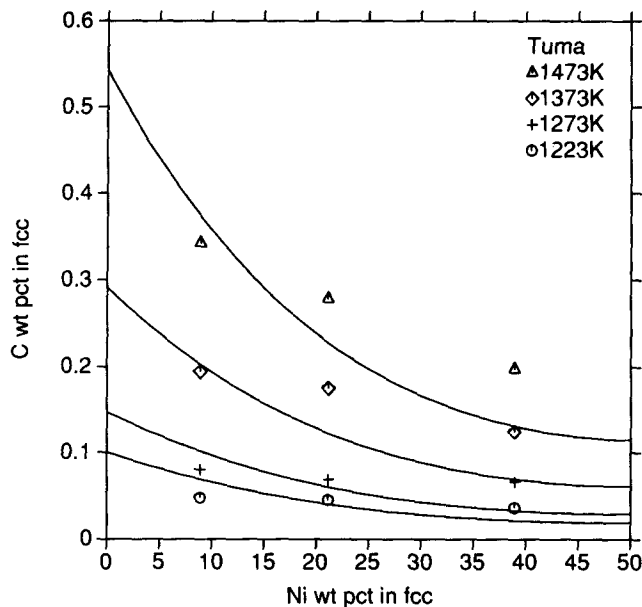


Fig. 1—Solubility of  $M_{23}C_6$  in Fe-Cr-Ni-C alloys with 17.5 wt pct Cr, evaluated from experimental curves published by Tuma.<sup>[8]</sup>

### III. THERMODYNAMIC MODELS

The fcc ( $\gamma$ ) and bcc ( $\alpha$ ) (body-centered cubic) phases were described with an interstitial model<sup>[12]</sup> yielding the following expression for one mole of formula unit,  $(Cr, Fe, Ni)_a (Va, C)_b$ :

$$G_m = ay_{Va} \sum y_M \circ G_M^h + y_C \sum y_M \circ G_{M,C}^b + a RT \sum y_M \ln y_M + b RT (y_{Va} \ln y_{Va} + y_C \ln y_C) + {}^E G_m + G_m^{mo} \quad [1]$$

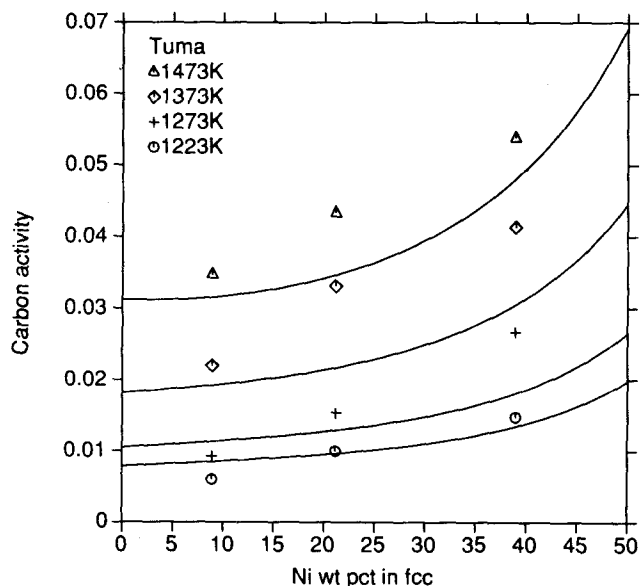


Fig. 2—Carbon activity of Fe-Cr-Ni-C alloys with 17.5 wt pct Cr at saturation with  $M_{23}C_6$ , evaluated from experimental curves published by Tuma.<sup>[8]</sup>

For fcc,  $a = 1$  and  $b = 1$ ; for bcc,  $a = 1$  and  $b = 3$ . The symbol  $y_i$  represents mole fractions evaluated for each sublattice separately, and it is often called site fraction. The term  $\circ G_M^h$  is the Gibbs energy of pure M in a hypothetical nonmagnetic state. The effect of magnetic ordering is represented by  $G_m^{mo}$ , using a model proposed by Inden<sup>[13]</sup> and modified by Hillert and Jarl.<sup>[14]</sup>  ${}^E G_m$  is the nonmagnetic excess term, and it is composed of several interaction terms,

$${}^E G_m = y_{Cr} y_{Fe} y_{Va} L_{Cr,Fe:Va} + y_{Fe} y_{Ni} y_{Va} L_{Fe,Ni:Va} + y_{Cr} y_{Ni} y_{Va} L_{Cr,Ni:Va} + y_{Cr} y_{Fe} y_C L_{Cr,Fe:C} + y_{Fe} y_{Ni} y_C L_{Fe,Ni:C} + y_{Cr} y_{Ni} y_C L_{Cr,Ni:C} + y_{Cr} y_{Fe} y_{Ni} y_{Va} L_{Cr,Fe,Ni:Va} + y_{Cr} y_{Fe} y_{Ni} y_C L_{Cr,Fe,Ni:C} \quad [2]$$

The subscripts give components on the same sublattice separated by a comma and on different sublattices separated by a colon. Each  $L$  coefficient may depend upon composition, and a Redlich-Kister polynomial was chosen for that purpose,

$$L = {}^0 L + {}^1 L (y_i - y_j) + {}^2 L (y_i - y_j)^2 + \dots \quad [3]$$

The liquid phase was treated as a substitutional phase, and C was thus included among the metals. Its Gibbs energy per mole of atoms can be expressed as follows:

$$G_m = \sum y_i \circ G_i^h + RT \sum y_i \ln y_i + {}^E G_m \quad [4]$$

where  ${}^E G_m$  includes all interactions among different components, and the magnetic term is neglected. Here, the site fraction  $y_i$  identical to the ordinary mole fraction  $x_i$  because there is only one sublattice.

The carbides were dealt without any vacancies on the C sublattice. Cementite,  $M_7C_3$ , and  $M_3C_2$  were described with a single sublattice for Cr, Fe, and Ni, and Eq. [1] can then be applied by setting  $y_{Va}$  to zero and  $y_C$  to unity. Again, the magnetic term was omitted.

Andersson<sup>[7]</sup> treated the  $M_{23}C_6$  carbide with two sublattices for the metallic components and one for carbon,  $(Cr, Fe)_{20}(Cr, Fe)_3C_6$ . This model stems from the consideration of higher order systems, and the purpose was to allow Mo and W to enter preferentially into the second sublattice. In order to make the present assessment consistent with higher order systems containing such elements, it is necessary to keep the two metallic sublattices separated. Assuming that the distribution of Cr and Fe is equal on the two sublattices, Andersson proposed the following relations:

$$23^\circ G_{Cr:Fe:C} = 20^\circ G_{Cr:Cr:C} + 3^\circ G_{Fe:Fe:C} \quad [5]$$

$$23^\circ G_{Fe:Cr:C} = 20^\circ G_{Fe:Fe:C} + 3^\circ G_{Cr:Cr:C} \quad [6]$$

Here,  $\circ G_{Cr:Cr:C}$  represents a compound with Cr on the first two sublattices and C on the third one. It is thus identical to  $\circ G_{Cr_{23}C_6}$ . Kajihara and Hillert accepted this proposal and added the following relations for the Cr-Ni-C system:<sup>[2]</sup>

$$23^\circ G_{Cr:Ni:C} = 20^\circ G_{Cr:Cr:C} + 3^\circ G_{Ni:Ni:C} \quad [7]$$

$$23^\circ G_{Ni:Cr:C} = 20^\circ G_{Ni:Ni:C} + 3^\circ G_{Cr:Cr:C} \quad [8]$$

Two more should be introduced in the present work:

$$23^\circ G_{\text{Fe:Ni:C}} = 20^\circ G_{\text{Fe:Fe:C}} + 3^\circ G_{\text{Ni:Ni:C}} \quad [9]$$

$$23^\circ G_{\text{Ni:Fe:C}} = 20^\circ G_{\text{Ni:Ni:C}} + 3^\circ G_{\text{Fe:Fe:C}} \quad [10]$$

These  $^\circ G$  quantities enter into the following expression for Gibbs energy per mole of formula unit:

$$G_m = \sum \sum y_i^s y_j^t {}^\circ G_{i:j:c} + 20RT \sum y_i^s \ln y_i^s + 3RT \sum y_j^t \ln y_j^t + \sum \sum y_i^s y_j^s y_l^t y_l^t L_{ij:ij:c} \quad [11]$$

where  $y_i^s$  represents the site fraction on the first sublattice and  $y_l^t$  on the second one.

The solubility of Ni in  $\text{Cr}_3\text{C}_2$  is very low, and it has been treated as a pure Cr carbide.<sup>[2,7]</sup> This was accepted in the present work, and Fe was not introduced into  $\text{Cr}_3\text{C}_2$ .

#### IV. ASSESSMENT

##### A. Fcc

An attempt was made to modify Andersson's description of the fcc phase in the ternary Fe-Cr-C system<sup>[7]</sup> in order to improve the agreement with experimental information on the C activity in fcc and on two-phase equilibria involving fcc. However, no real improvement was obtained, and it was decided to keep the fcc parameters proposed by Andersson. Then the fcc parameters from Cr-Ni-C<sup>[2]</sup> and Fe-Ni-C<sup>[3]</sup> were added, and the information on the C activity in the Fe-Cr-Ni-C system was fitted using a quaternary parameter

$$L_{\text{Cr,Fe,Ni:C}} = A + BT \quad [12]$$

Here,  $A$  and  $B$  are constants to be evaluated. In order to determine this parameter well, it is necessary to have experimental information for high Cr and Ni contents at the same time. Unfortunately, high Ni contents will increase the C activity, and high Cr contents will stabilize  $\text{M}_{23}\text{C}_6$  and also lower the solubility. Therefore, about half of the data reported by Natesan and Kassner<sup>[10]</sup> were suspected to be from the two-phase region fcc +  $\text{M}_{23}\text{C}_6$ , and they were excluded in the optimization. After the whole system had been optimized, a calculation was carried out in order to check where the solubility curves fall in Natesan and Kassner's diagrams. Figure 3 gives some examples. It is evident that there is a slight difference between their data at zero Cr and the description of the Fe-Ni-C system used here. In spite of this fact, there is a reasonable agreement up to the calculated solubility limit, where  $\text{M}_{23}\text{C}_6$  appears and the calculated values start to rise quickly. Most of the experimental data do not show the same strong increase inside the calculated two-phase region but fall well above values calculated by extrapolation from the one-phase region. It is possible that these data came from experiments in which the precipitation of  $\text{M}_{23}\text{C}_6$  has started but not yet come to an equilibrium. If that is so, then it would be quite incorrect to include them in the optimization as representing one-phase fcc. That would result in a prediction that C activity values at high Cr and Ni contents are too low. This has probably happened to the assessments of the C activity in fcc, presented by Natesan and Kassner<sup>[10]</sup> and by Hillert and Waldenström.<sup>[15]</sup>

Greenbank's data<sup>[9]</sup> were also used in the present assessment. Most of his data concern either fairly low Cr or fairly low Ni contents, and they were fitted reasonably well by the calculated results, as shown in Figures 4(a) and (b). Moreover, he also presented some data for high contents of both alloying elements at 1323 K. For these data, a comparison with the present assessment is given in Figure 4(c). It shows a consistent negative deviation. The calculated results seem to be a reasonable compromise between Natesan and Kassner's<sup>[10]</sup> and Greenbank's data.

##### B. Bcc

The solubility of C in bcc is very low, and the experimental information is scarce. Benz *et al.*<sup>[19]</sup> determined metallographically the solubility of  $\text{M}_{23}\text{C}_6$  in bcc from 1172 to 1424 K in the Fe-Cr-C system at  $u_{\text{Cr}} = 0.21$ . This information was fitted at 1323 K, but the variation with temperature was changed in order to make the solubility at low temperature low enough to satisfy an intuitive feeling.

The ternary parameters of the bcc phase in the Cr-Ni-C and Fe-Ni-C systems, where it is metastable except for a small region close to the Fe corner, were estimated by Kajihara and Hillert<sup>[2]</sup> and by Gabriel *et al.*<sup>[3]</sup> They have a very small effect on the phase diagrams, and Kajihara and Hillert simply took the same value for  $L_{\text{Cr,Ni:C}}^{\text{bcc}}$  that Andersson reported for  $L_{\text{Cr,Ni:C}}^{\text{bcc}}$ . Since the latter one had now been changed, the former was also changed. The value of  $L_{\text{Fe,Ni:C}}^{\text{bcc}}$  was not changed. No attempt was made to evaluate a quaternary parameter.

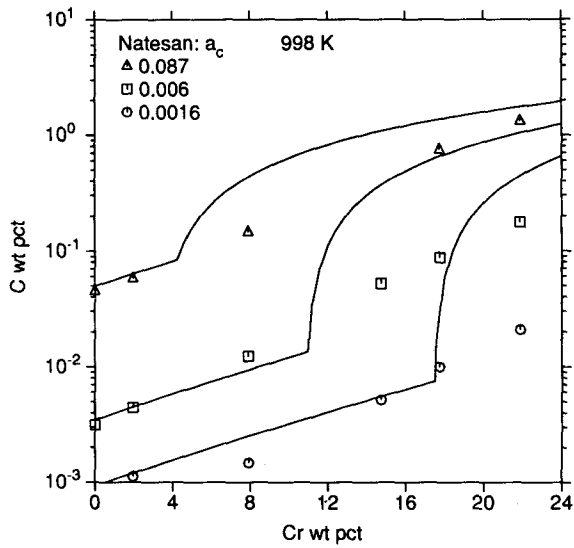
##### C. Cementite

The properties of cementite in the Fe-Cr-C system were assessed by Andersson<sup>[7]</sup> using the information on the distribution of Cr between cementite on one hand and bcc or fcc on the other hand. He also required that pure Cr cementite,  $\text{Cr}_3\text{C}$ , should not become stable in the Cr-C system. His results were essentially accepted, but a new value of the stability of  $\text{Cr}_3\text{C}$  was used, obtained by Kajihara and Hillert<sup>[2]</sup> in connection with their reassessment of the Cr-C system. Thus, it was necessary to allow the parameter  $L_{\text{Cr,Fe:C}}^{\text{cem}}$  to vary in the last optimization. The consistency for the distribution of Cr between bcc and cementite was almost the same as shown by Andersson in his Figures 2 and 3.

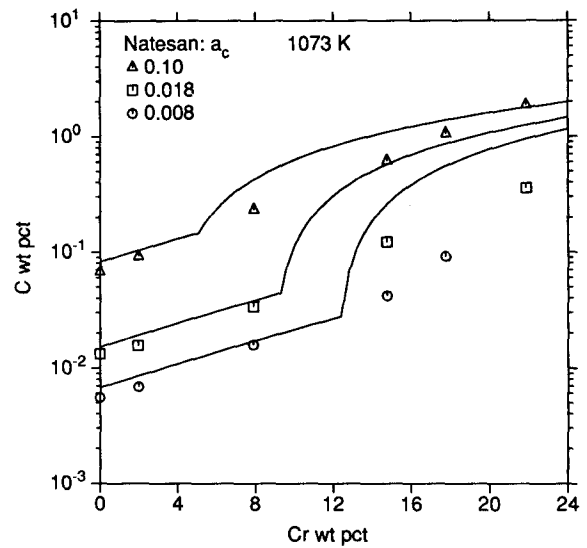
Because cementite is not stable in the Cr-Ni-C system, the parameter  $L_{\text{Cr,Ni:C}}^{\text{cem}}$  was quite arbitrarily set to zero in the present work. The description of cementite in the Fe-Ni-C system, given by Gabriel *et al.*,<sup>[3]</sup> was kept. No quaternary parameter was introduced.

##### D. $\text{M}_7\text{C}_3$

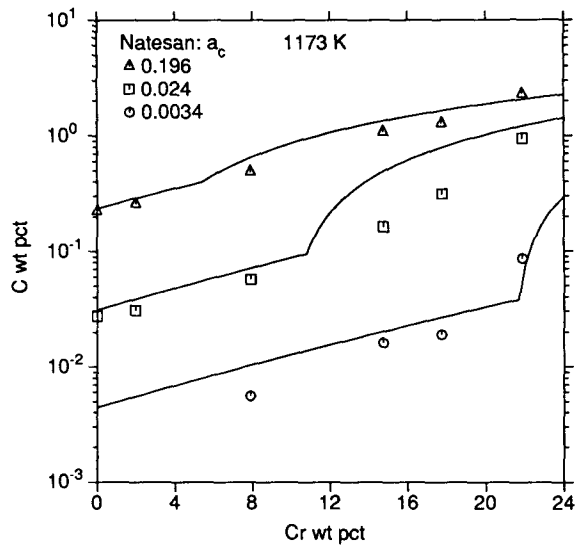
The parameters for  $\text{M}_7\text{C}_3$  in the Fe-Cr-C system optimized by Andersson<sup>[7]</sup> must now be reassessed due to the change of the Gibbs energy of formation of  $\text{Cr}_7\text{C}_3$ . There is experimental information on the distribution of Cr between bcc or fcc and  $\text{M}_7\text{C}_3$  at the Fe-rich side of the system.<sup>[16-20]</sup> There is also information on the liquidus temperature of  $\text{M}_7\text{C}_3$ .<sup>[21]</sup> Andersson evaluated  $^\circ G_{\text{Fe,C}_3}$  and a constant interaction parameter  $L_{\text{Cr,Fe:C}}$ . With



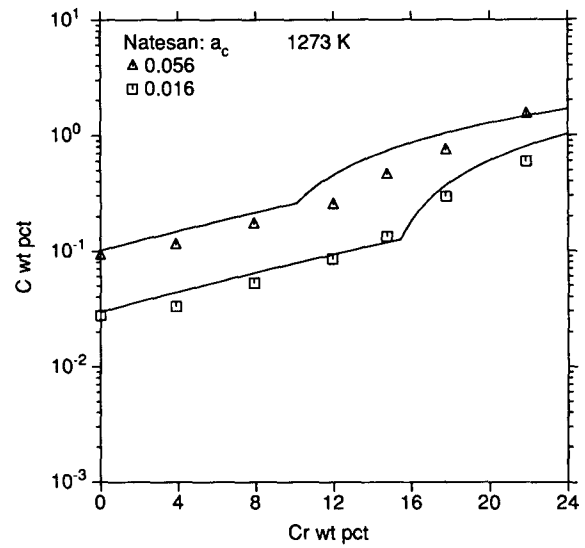
(a)



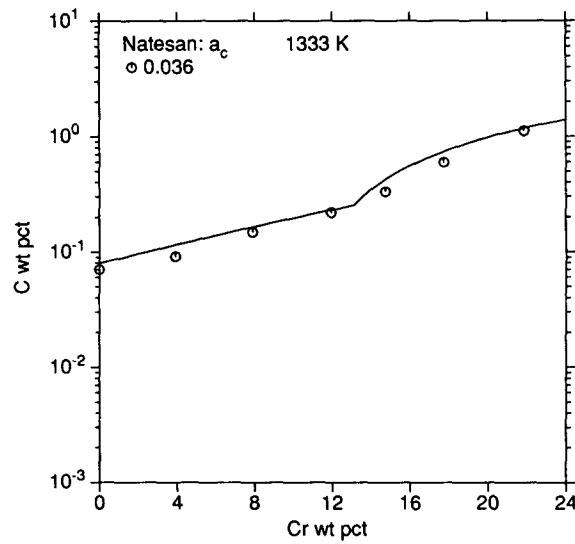
(b)



(c)



(d)



(e)

Fig. 3—(a) through (e) Carbon isoactivity lines of Fe-Cr-Ni-C alloys with 8 wt pct Ni at a series of temperatures according to Natesan and Kassner's experiments<sup>(10)</sup> and the present calculation.

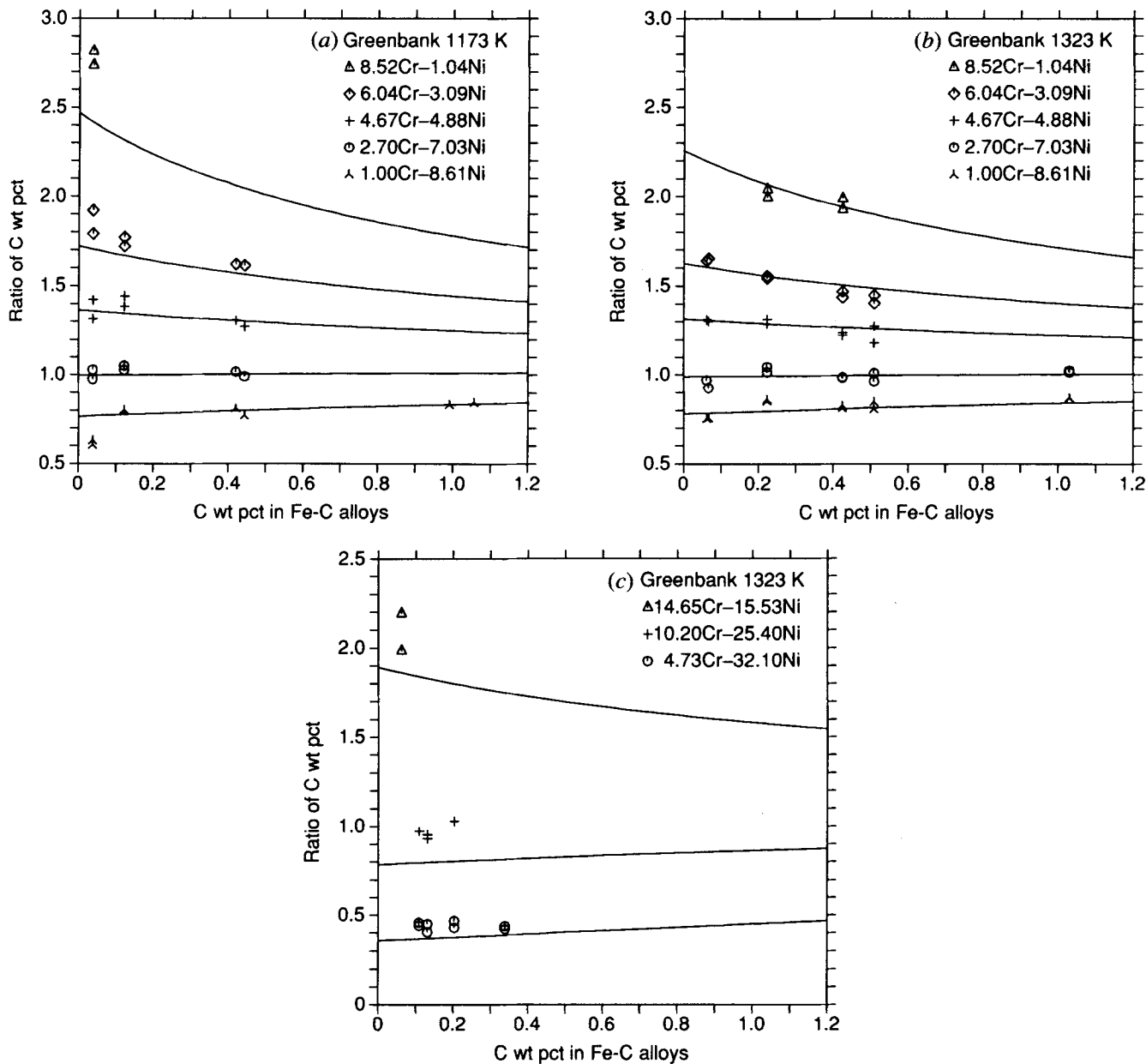


Fig. 4—Distribution of carbon between Fe-Cr-Ni-C alloys and pure Fe-C specimens at (a) 1173 K, (b) 1323 K, and (c) 1323 K according to Greenbank's experiments<sup>(9)</sup> and the present calculation.

the new values for  $^{\circ}G_{Cr_7C_3}$ , it was now found that it was not necessary to change  $^{\circ}G_{Fe_7C_3}$ , but the interaction parameter must be allowed to vary with composition. Equation [3] was applied to this case, and two terms were used. A comparison between calculated and experimental solubility of Cr in  $M_7C_3$  in equilibrium with bcc is shown in Figure 5. The experimental data are fairly well reproduced, considering the discrepancy between the two sets of data. The calculated curve at low Cr contents, however, may be too steep. This may not be too serious for practical applications, because the  $M_7C_3$  carbide is not stable under such conditions.

A similar comparison for the equilibrium between fcc and various carbides at 1273 K is given in Figure 6. Again, the experimental data for  $M_7C_3$  are fairly well

fitted. It can also be seen that the data for cementite are well reproduced.

The description of  $M_7C_3$  in the Cr-Ni-C system was accepted from Kajihara and Hillert.<sup>[2]</sup> The  $M_7C_3$  carbide is not stable in the Fe-Ni-C system, and the interaction parameter  $L_{Fe,Ni:C}$  was put to zero quite arbitrarily. Based on the information by Waldenström<sup>[22]</sup> on the Cr and Ni contents of  $M_7C_3$  in equilibrium with fcc in the Fe-Cr-Ni-C system and on the C activity of the same equilibrium, an attempt was made to evaluate a quaternary parameter  $L_{Cr,Fe,Ni:C}$ . The Ni and Cr contents were reproduced with reasonable success, but the scatter was considerable. Some of the C activity values were well fitted, but in most of the cases, the calculated values were too low.

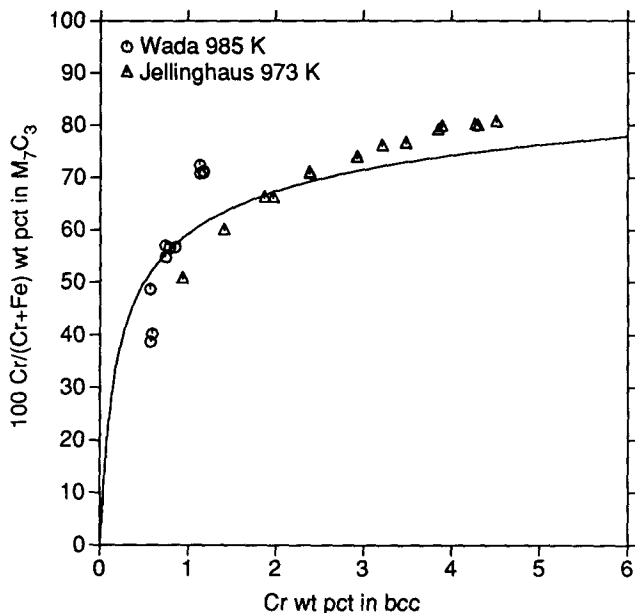


Fig. 5—Calculated distribution of Cr between  $M_7C_3$  and bcc at 973 K in the Fe-Cr-C system in comparison with two sets of experimental data.

### E. $M_{23}C_6$

The properties of  $M_{23}C_6$  in the Fe-Cr-C system were assessed by Andersson,<sup>[7]</sup> and they must also be reassessed due to the new value of the Gibbs energy of formation of  $Cr_{23}C_6$ . There is experimental information on the distribution of Cr between bcc or fcc and  $M_{23}C_6$  at the Fe-rich side of the system.<sup>[18,19]</sup> Furthermore, there is information on the three-phase triangles bcc + fcc +  $M_{23}C_6$ ,<sup>[23]</sup> and fcc +  $M_{23}C_6$  +  $M_7C_3$ .<sup>[7]</sup> However, the solubility of  $M_{23}C_6$  in fcc did not seem to be well established in the Fe-Cr-C system, and the assessment was

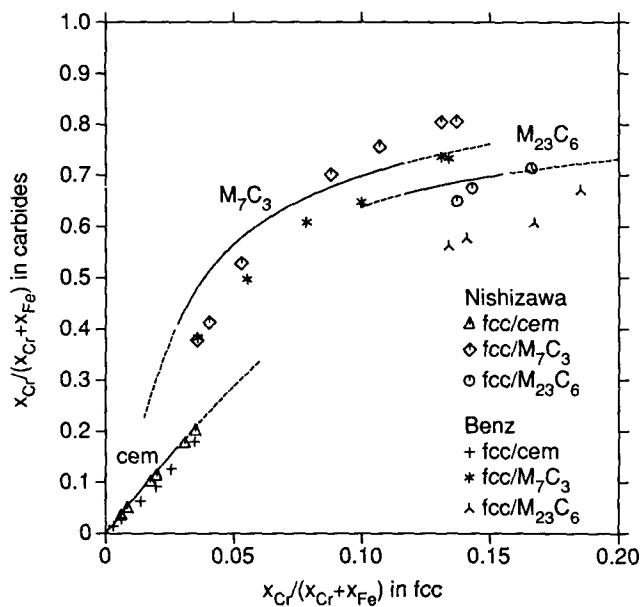


Fig. 6—Calculated distribution of Cr between various carbides and fcc at 1273 K in the Fe-Cr-C system in comparison with experimental data.

thus made together with the Fe-Cr-Ni-C system, where the solubility has been studied more carefully due to the great practical importance. Andersson used a constant interaction parameter  $L_{Cr,Fe:Cr,Fe:C}$  which was evaluated together with  $^{\circ}G_{Fe_{23}C_6}$ . In order to establish the latter parameter with some certainty, he combined the Fe-Cr-C information with that from the Fe-Cr-W-C and Fe-Cr-Mo-C systems, where  $M_{23}C_6$  can form with high Fe contents. That information was not included in the present work, and in order to get a result which can later be used in the assessments of those two quaternary systems, Andersson's value of  $^{\circ}G_{Fe_{23}C_6}$  was accepted. In the present work, it was found that  $L_{Cr,Fe:Cr,Fe:C}$  must be allowed to vary with composition. The following expression was chosen for the Fe-Cr-Ni-C system:

$$L_{Cr,Fe:Cr,Fe:C} = {}^0L + {}^1L(y_{Cr}^s - y_{Fe}^s) + {}^2L(y_{Cr}^i - y_{Fe}^i) \quad [13]$$

but  ${}^1L$  and  ${}^2L$  were put equal.

The description of  $M_{23}C_6$  in the Cr-Ni-C system<sup>[2]</sup> was accepted. For the Fe-Ni-C system, there is no information on  $M_{23}C_6$ , because it is not stable there. Consequently,  $L_{Fe,Ni:Fe,Ni:C}$  was set to zero quite arbitrarily.

As already mentioned, there is much information on the solubility of  $M_{23}C_6$  in the quaternary Fe-Cr-Ni-C system. There is also some information from that system regarding the Cr and Ni contents of  $M_{23}C_6$  in the equilibrium with fcc and the C activity of that equilibrium.<sup>[22]</sup> During the optimization for fitting this information, it was found that it is not necessary to introduce a quaternary parameter because of the low Ni contents of  $M_{23}C_6$ . The calculated Ni content of  $M_{23}C_6$  was considerably lower than the experimental ones, around 1.0 compared to around 2.5 wt pct. The C activity values were fitted better. It was not possible to fit both types of data at the same time.

A comparison between the assessment and the experimental distribution of Cr between  $M_{23}C_6$  and fcc is given in Figure 6 in the Fe-Cr-C system at 1273 K. It shows good agreement with Nishizawa and Uhrenius<sup>[18]</sup> but about 10 pct higher than Benz *et al.*'s data.<sup>[19]</sup> for the bcc/ $M_{23}C_6$  equilibrium, the corresponding comparison is given in Figure 7. There is again good agreement at Cr contents of about 70 at. pct, but at higher Cr contents, the calculated values are too low, and there is an indication that the calculated values at low Cr contents would be too high. This situation seems to be similar to the one for bcc/ $M_7C_3$ . Andersson<sup>[7]</sup> reported the same discrepancy for  $M_7C_3$  at low Cr contents. On the other hand, it should be noticed that Nishizawa and Uhrenius were able to reproduce the data in Figure 7 very well over the whole composition range when assessing the Fe-Cr-C system at 1273 K.<sup>[18]</sup>

The curves in Figure 1 give the calculated solubility of  $M_{23}C_6$  in fcc as a function of the Ni content at 17.5 wt pct Cr. The agreement with Tuma's data<sup>[8]</sup> is satisfactory, in particular at 8 wt pct Ni, and Tuma's results may thus be looked upon as support for the calculated limit of solubility shown in Figure 3. On the other hand, it may be argued that the calculation predicts a decrease with the Ni content, which is too strong. Tokareva *et al.*<sup>[24]</sup> also reported the solubility of  $M_{23}C_6$  in fcc for the

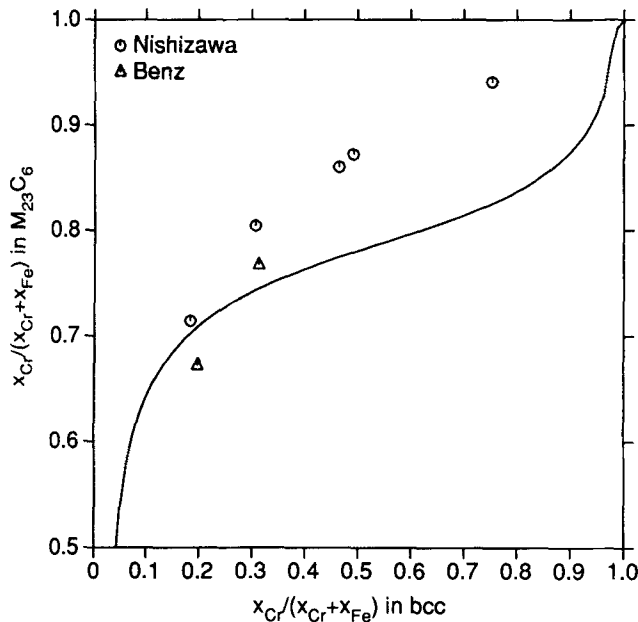


Fig. 7—Calculated distribution of Cr between  $M_{23}C_6$  and bcc at 1273 K in the Fe-Cr-C system compared to experimental data.

Fe-Cr-Ni-C system, but their values are much lower and were not included in the present assessment. Figure 2 shows the corresponding C activity. Again, the agreement with Tuma is reasonable, but here the predicted effect of Ni seems to be too weak.

Figure 8 demonstrates the temperature dependence of the solubility of  $M_{23}C_6$  in fcc for an alloy with 25 Cr and 20 Ni wt pct, and Nishino and Kagawa's<sup>[25]</sup> results were reproduced very well. The specimens from the three lowest temperatures were reported to contain some  $\sigma$  phase in addition to fcc, so the final optimization was performed without using those results. However, this did

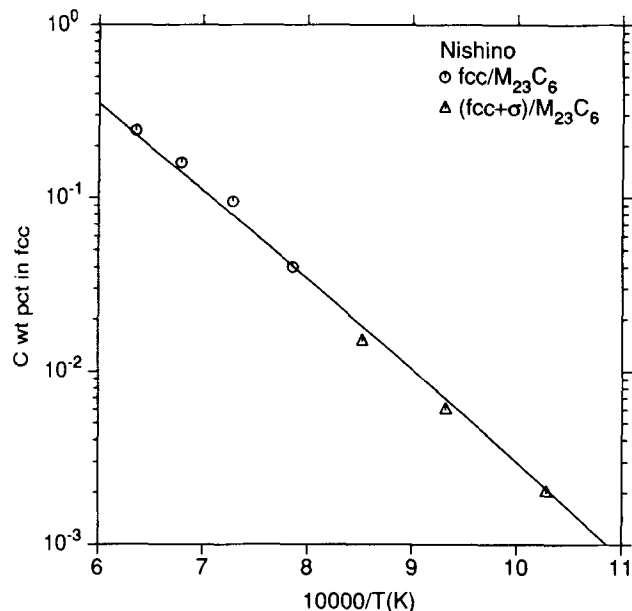


Fig. 8—Calculated solubility of  $M_{23}C_6$  in fcc with 25 wt pct Cr and 20 Ni vs temperatures together with experimental data.

not change the calculation appreciably, and there is still good agreement with those results.

Figure 9 shows the calculated extension of the fcc one-phase field in the Fe-Cr-C system at various temperatures. After comparing, it was concluded that the boundaries are in reasonable agreement with the experimental information.

Figure 10 shows the whole isothermal section of the Fe-Cr-C system at 1273 K. The point fcc/ $M_{23}C_6$  +  $M_7C_3$  falls at 10.9 wt pct Cr and 0.30 wt pct C according to the present calculation and at 12.2 wt pct Cr and 0.30 wt pct C according to Andersson's assessment.<sup>[7]</sup> The calculated point fcc/bcc +  $M_{23}C_6$  falls at 14.5 wt pct Cr compared to Andersson's value of 15.1. The maximum solubility of Cr in cementite was calculated to 14.8 wt pct, which is a little lower than the experimental value 17.6 reported by Nishizawa and Uhrenius.<sup>[18]</sup>

#### F. Liquid

Because new values have been adopted for the Cr carbides and they affect the position of the liquidus in the Fe-Cr-C system, the properties of the liquid phase, which were assessed by Andersson,<sup>[7]</sup> must be reassessed. The new assessment was based upon liquidus data for bcc, fcc,  $M_7C_3$ , and cementite by Thorpe and Chicco,<sup>[21]</sup> as well as for graphite by Chimpman<sup>[26]</sup> and by Griffing *et al.*<sup>[27]</sup>

In comparison with those experimental data, the calculated temperatures of the liquidus for bcc were between 10 and 20 K lower; for fcc, they usually were about 10 K higher, except for several points with around -10 K; for cementite, some were as much as 15 K lower; and for  $M_7C_3$ , there were both positive and negative deviations, most of which were less than 20 K. Finally, for the graphite liquidus which is very steep, an attempt was made to fit the C contents. The experimental data

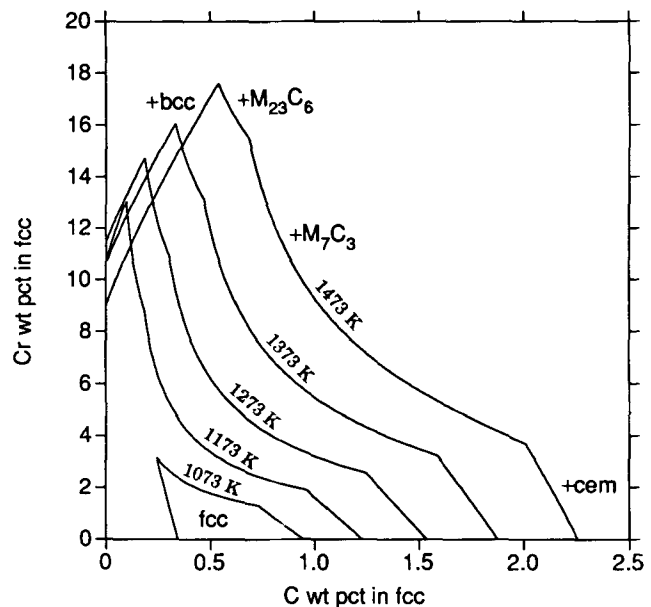


Fig. 9—Extension of the fcc phase field in the Fe-Cr-C system at various temperatures according to the present assessment. The phases outside the boundaries are indicated.

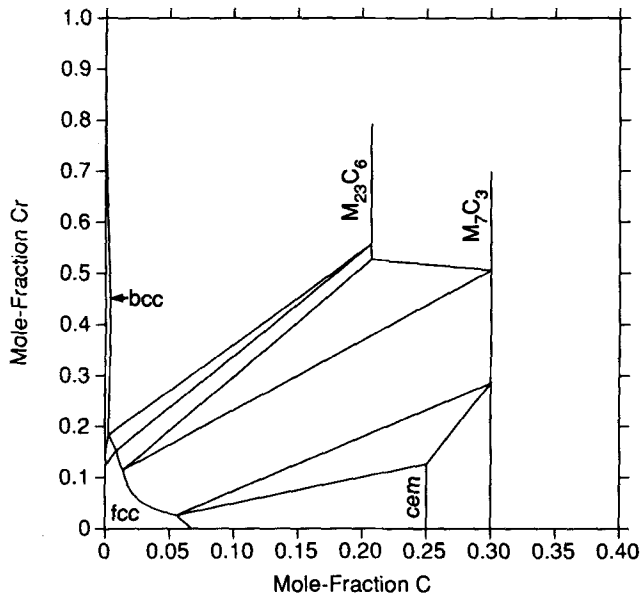


Fig. 10—A calculated isothermal section of the Fe-Cr-C system at 1273 K.

ranged from 5 to 11 wt pct C, and all of the calculated values were about 1 wt pct C higher.

For experimental tie lines from Kundrat and co-workers in the Fe-Cr-C<sup>[28]</sup> and Fe-Cr-Ni-C<sup>[29]</sup> systems, the fit was rather good and comparable to Andersson's<sup>[7]</sup> for the Fe-Cr-C system.

The calculated projection of the liquidus surface is presented in Figure 11. It is very similar to that obtained by Andersson,<sup>[7]</sup> but the liquidus of  $M_{23}C_6$  is somewhat wider. It shows the same phase relations and thus supports Andersson's suggestion that the liquids of  $M_{23}C_6$  and fcc should meet.

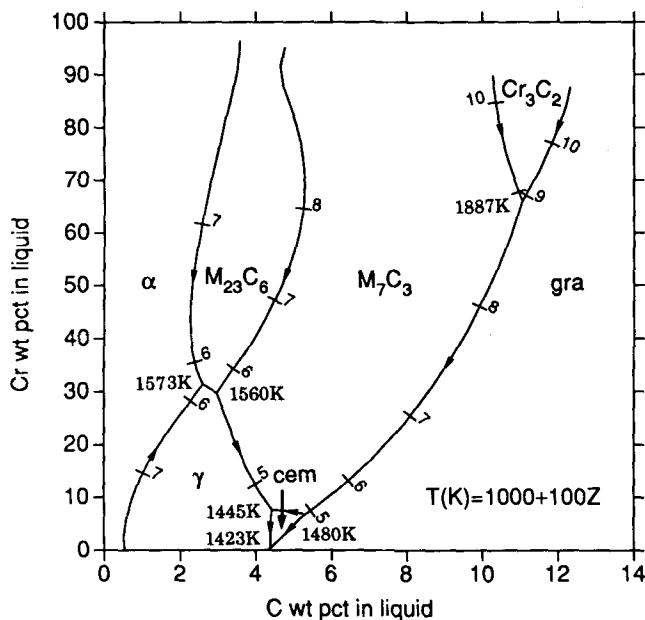


Fig. 11—Calculated projection of the liquidus surfaces in the Fe-Cr-C system. The numbers Z give the temperatures according to  $T(K) = 1000 + 100Z$ .

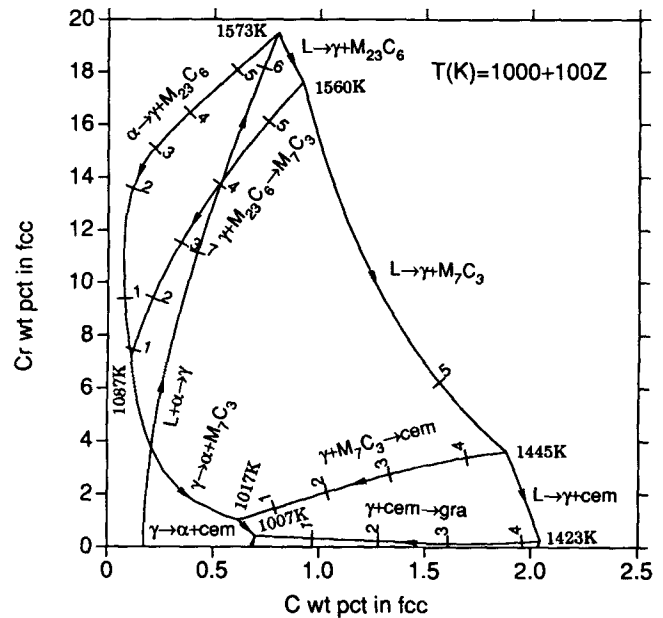


Fig. 12—Calculated projection of the solvus surfaces of fcc in the Fe-Cr-C system. The numbers Z give the temperatures according to  $T(K) = 1000 + 100Z$ .

Figure 12 shows a similar projection of the solvus surfaces with fcc. It is also very similar to Andersson's.<sup>[7]</sup> The main difference is the Cr content of fcc in equilibrium with bcc,  $M_{23}C_6$ , and  $M_7C_3$ . All of the calculated invariant points in the Fe-Cr-C system are presented in Table I.

All of the parameter values used are listed in Table II. Those obtained in the present assessment are marked with an asterisk.

## V. DISCUSSION

The main impression of the present work is that it is possible to base an assessment of the Fe-Cr-C system on the new values of Gibbs energy for the Cr carbides recommended by Kajihara and Hillert,<sup>[7]</sup> although concentration-dependent interactions must be used. The result is rather similar to what Andersson obtained with constant interactions. However, it should be emphasized

Table I. Calculated Invariant Equilibria in the Fe-Cr-C System

Phases				T (K)
bcc	$M_7C_3$	$Cr_3C_2$	gra	608
bcc1	bcc2	$M_{23}C_6$	$\sigma$	785
bcc	cem	$M_7C_3$	gra	941
fcc	bcc	cem	gra	1007
fcc	bcc	cem	$M_7C_3$	1017
fcc	bcc	$M_{23}C_6$	$M_7C_3$	1087
liq	cem	fcc	gra	1423
liq	$M_7C_3$	fcc	cem	1445
liq	$M_7C_3$	gra	cem	1480
liq	fcc	$M_{23}C_6$	$M_7C_3$	1560
liq	bcc	fcc	$M_{23}C_6$	1573
liq	$Cr_3C_2$	$M_7C_3$	gra	1887



**Table II. Summary of Thermodynamic Parameters Describing the Fe-Cr-Ni-C System in SI Units (J, mol, K)\***

**Liquid**

One sublattice, site 1 constituents: C, Cr, Fe, Ni

$$\begin{aligned}
 {}^{\circ}G_C^{\text{liq}} &= {}^{\circ}G_C^{\text{gra}} + 117,369 - 24.63T \\
 {}^{\circ}G_{\text{Cr}}^{\text{liq}} &= {}^{\circ}G_{\text{Cr}}^{\text{hbcc}} + 24,335.93 - 11.42T + 2.37615 \cdot 10^{-21} T^7 && 298.15 < T < 2180 \\
 &= H^{\text{SER}} - 16,459 + 335.618T - 50T \ln T && 2180 < T < 6000 \\
 {}^{\circ}G_{\text{Fe}}^{\text{liq}} &= {}^{\circ}G_{\text{Fe}}^{\text{hbcc}} + 12,040.17 - 6.55843T - 3.6751551 \cdot 10^{-21} T^7 && 298.15 < T < 1811 \\
 &= H^{\text{SER}} - 10,839.7 + 291.302T - 46T \ln T && 1811 < T < 6000 \\
 {}^{\circ}G_{\text{Ni}}^{\text{liq}} &= {}^{\circ}G_{\text{Ni}}^{\text{hfcc}} + 16,414.686 - 9.397T - 3.82318 \cdot 10^{-21} T^7 && 298.15 < T < 1728 \\
 &= H^{\text{SER}} - 9549.775 + 268.598T - 43.1T \ln T && 1728 < T < 6000 \\
 {}^0L_{\text{C,Cr}}^{\text{liq}} &= -90,526 - 25.9116T \\
 {}^1L_{\text{C,Cr}}^{\text{liq}} &= 80,000 \\
 {}^2L_{\text{C,Cr}}^{\text{liq}} &= 80,000 \\
 {}^0L_{\text{C,Fe}}^{\text{liq}} &= -124,320 + 28.5T \\
 {}^1L_{\text{C,Fe}}^{\text{liq}} &= 19,300 \\
 {}^2L_{\text{C,Fe}}^{\text{liq}} &= 49,260 - 19T \\
 {}^0L_{\text{C,Ni}}^{\text{liq}} &= -110,160 + 34.6T \\
 {}^0L_{\text{Cr,Ni}}^{\text{liq}} &= -1276 - 5.3873T \\
 {}^1L_{\text{Cr,Ni}}^{\text{liq}} &= 2699 \\
 {}^0L_{\text{Fe,Ni}}^{\text{liq}} &= -18,378.86 + 6.03912T \\
 {}^1L_{\text{Fe,Ni}}^{\text{liq}} &= -9228.1 - 3.54642T \\
 {}^*0L_{\text{C,Cr,Fe}}^{\text{liq}} &= -530,395 \\
 {}^*1L_{\text{C,Cr,Fe}}^{\text{liq}} &= 49,287 \\
 {}^*2L_{\text{C,Cr,Fe}}^{\text{liq}} &= 43,461 \\
 {}^0L_{\text{C,Fe,Ni}}^{\text{liq}} &= 122,200 - 58.8T \\
 {}^1L_{\text{C,Fe,Ni}}^{\text{liq}} &= 92,200 - 58.8T \\
 {}^2L_{\text{C,Fe,Ni}}^{\text{liq}} &= 152,200 - 58.8T \\
 {}^0L_{\text{Cr,Fe,Ni}}^{\text{liq}} &= 13,022 \\
 {}^1L_{\text{Cr,Fe,Ni}}^{\text{liq}} &= 13,177 \\
 {}^2L_{\text{Cr,Fe,Ni}}^{\text{liq}} &= 3313
 \end{aligned}$$

**Bcc**

Two sublattices, sites 1:3 constituents: Cr, Fe, Ni:C, Va

$$\begin{aligned}
 {}^{\circ}G_{\text{Cr}}^{\text{hbcc}} - H^{\text{SER}} &= 8851.93 + 157.48T - 26.908T \ln T + 0.00189435T^2 \\
 &\quad - 1.47721 \cdot 10^{-6} T^3 + 139,250T^{-1} && 298.15 < T < 2180 \\
 &\quad = -34,864 + 344.18T - 50T \ln T - 2.88526 \cdot 10^{32} T^{-9} && 2180 < T < 6000 \\
 {}^{\circ}G_{\text{Fe}}^{\text{hbcc}} - H^{\text{SER}} &= -1224.83 + 124.134T - 23.5143T \ln T - 0.00439752T^2 \\
 &\quad - 5.89269 \cdot 10^{-8} T^3 + 77,358.5T^{-1} && 298.15 < T < 1811 \\
 &\quad = -25,384.451 + 299.31255T - 46T \ln T + 2.2960305 \cdot 10^{31} T^{-9} && 1811 < T < 6000 \\
 {}^{\circ}G_{\text{Ni}}^{\text{hbcc}} &= {}^{\circ}G_{\text{Ni}}^{\text{hfcc}} + 8715.084 - 3.556T \\
 {}^{\circ}G_{\text{Cr:C}}^{\text{hbcc}} &= {}^{\circ}G_{\text{Cr}}^{\text{hbcc}} + 3{}^{\circ}G_{\text{C}}^{\text{gra}} + 416,000 \\
 {}^{\circ}G_{\text{Fe:C}}^{\text{hbcc}} &= {}^{\circ}G_{\text{Fe}}^{\text{hbcc}} + 3{}^{\circ}G_{\text{C}}^{\text{gra}} + 322,050 + 75.667T \\
 {}^{\circ}G_{\text{Ni:C}}^{\text{hbcc}} &= {}^{\circ}G_{\text{Ni}}^{\text{hfcc}} + 3{}^{\circ}G_{\text{C}}^{\text{gra}} + 400,000 - 100T \\
 {}^0L_{\text{Cr:C,Va}}^{\text{bcc}} &= -190T \\
 {}^0L_{\text{Fe:C,Va}}^{\text{bcc}} &= -190T \\
 {}^0L_{\text{Cr,Fe,Va}}^{\text{bcc}} &= 20,500 - 9.68T \\
 {}^*0L_{\text{Cr,Fe:C}}^{\text{bcc}} &= -1,226,000 + 570T \\
 {}^0L_{\text{Cr,Ni,Va}}^{\text{bcc}} &= 21,310 - 13.6585T \\
 {}^1L_{\text{Cr,Ni,Va}}^{\text{bcc}} &= 25,800 - 7.8927T \\
 {}^*0L_{\text{Cr,Ni:C}}^{\text{bcc}} &= -1,226,000 + 570T \\
 {}^0L_{\text{Fe,Ni,Va}}^{\text{bcc}} &= -956.63 - 1.28726T \\
 {}^1L_{\text{Fe,Ni,Va}}^{\text{bcc}} &= 1789.03 - 1.92912T \\
 {}^0L_{\text{Fe,Ni:C}}^{\text{bcc}} &= -956.63 - 1.28726T \\
 {}^1L_{\text{Fe,Ni:C}}^{\text{bcc}} &= 1789.03 - 1.92912T \\
 {}^0L_{\text{Cr,Fe,Ni,Va}}^{\text{bcc}} &= 1390 \\
 G_m^{\text{mo}} &= RT \ln (\beta + 1)f(\tau) \quad \tau = T/T_C
 \end{aligned}$$

**Table II. Cont. Summary of Thermodynamic Parameters Describing the Fe-Cr-Ni-C System in SI Units (J, mol, K)\***

$$f(\tau) = \frac{1}{\tau A} \left[ \tau A - \frac{79}{140p} - \frac{158}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{\tau^4}{2} + \frac{\tau^{10}}{45} + \frac{\tau^{16}}{200} \right) \right] \quad \text{for } \tau < 1$$

$$f(\tau) = -\frac{1}{A} \left[ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right] \quad \text{for } \tau > 1$$

$$\text{where } A = \frac{518}{1125} \left[ 1 + \frac{790}{497} \left( \frac{1}{p} - 1 \right) \right]$$

$$p = 0.4$$

$$T_C = -311.5(y_{Cr}y_{Va} + y_{Cr}y_C) + 1043(y_{Fe}y_{Va} + y_{Fe}y_C) + 575(y_{Ni}y_{Va} + y_{Ni}y_C) \\ + y_{Cr}y_{Fe}(y_C + y_{Va}) [1650 + 550(y_{Cr} - y_{Fe})] + y_{Cr}y_{Ni}y_{Va}[2373 + 617(y_{Cr} - y_{Ni})]$$

$$\beta = -0.008(y_{Cr}y_{Va} + y_{Cr}y_C) + 2.22(y_{Fe}y_{Va} + y_{Fe}y_C) + 0.85(y_{Ni}y_{Va} + y_{Ni}y_C) \\ - 0.85y_{Cr}y_{Fe}(y_C + y_{Va}) + 4y_{Cr}y_{Ni}y_{Va}$$

Whenever the calculated value of  $T_C$  or  $\beta$  is negative, it should be divided by  $-1$  when inserted in  $G_m^{mo}$  and  $f(\tau)$ .

### Fcc

Two sublattices, sites 1:1 constituents: Cr, Fe, Ni:C, Va

$${}^{\circ}G_{Cr}^{fcc} = {}^{\circ}G_{Cr}^{hbcc} + 7284 + 0.163T$$

$${}^{\circ}G_{Fe:Va}^{fcc} = {}^{\circ}G_{Fe}^{hbcc} - 1462.4 + 8.282T - 1.15T \ln T + 6.4 \cdot 10^{-4} T^2 \quad 298.15 < T < 1811 \\ = H^{SER} - 27,098.266 + 300.25256T - 46T \ln T + 2.78854 \cdot 10^{31} T^{-9} \quad 1811 < T < 6000$$

$${}^{\circ}G_{Ni}^{fcc} = H^{SER} - 5179.159 + 117.854T - 22.096T \ln T - 0.0048407T^2 \quad 298.15 < T < 1728 \\ = H^{SER} - 27,840.655 + 279.135T - 43.1T \ln T + 1.12754 \cdot 10^{31} T^{-9} \quad 1728 < T < 6000$$

$${}^{\circ}G_{Cr:C}^{fcc} = {}^{\circ}G_{Cr}^{hbcc} + {}^{\circ}G_C^{gra} + 25,000$$

$${}^{\circ}G_{Fe:C}^{fcc} = {}^{\circ}G_{Fe}^{hbcc} + {}^{\circ}G_C^{gra} + 77,202 - 15.877T$$

$${}^{\circ}G_{Ni:C}^{fcc} = {}^{\circ}G_{Ni}^{hbcc} + {}^{\circ}G_C^{gra} + 45,000 + 1.88T$$

$${}^0L_{Cr:C:Va}^{fcc} = -29,686 - 18T$$

$${}^0L_{Fe:C:Va}^{fcc} = -34,761$$

$${}^0L_{Cr,Fe:Va}^{fcc} = 10,833 - 7.477T$$

$${}^1L_{Cr,Fe:Va}^{fcc} = 1410$$

$${}^0L_{Cr,Fe:C}^{fcc} = -26,586 - 18T$$

$${}^0L_{Cr,Ni:Va}^{fcc} = 8347 - 12.1038T$$

$${}^1L_{Cr,Ni:Va}^{fcc} = 29,895 - 16.3838T$$

$${}^0L_{Cr,Ni:C}^{fcc} = -81,265 + 81.8T$$

$${}^0L_{Fe,Ni:Va}^{fcc} = -12,054.355 + 3.27413T$$

$${}^1L_{Fe,Ni:Va}^{fcc} = 11,082.1315 - 4.45077T$$

$${}^2L_{Fe,Ni:Va}^{fcc} = -725.805174$$

$${}^0L_{Fe,Ni:C}^{fcc} = 49,074 - 7.32T$$

$${}^1L_{Fe,Ni:C}^{fcc} = -25,800$$

$${}^0L_{Cr,Fe,Ni:Va}^{fcc} = 1618$$

$${}^*0L_{Cr,Fe,Ni:C}^{fcc} = -8215$$

$$p = 0.28$$

$$T_C = -1109y_{Cr}y_{Va} - 201(y_{Fe}y_{Va} + y_{Fe}y_C) + 633(y_{Ni}y_{Va} + y_{Ni}y_C) \\ - 3605y_{Cr}y_{Ni}y_{Va} + y_{Fe}y_{Ni}y_{Va}[2133 - 682(y_{Fe} - y_{Ni})]$$

$$\beta = -2.46y_{Cr}y_{Va} - 2.1(y_{Fe}y_{Va} + y_{Fe}y_C) + 0.52(y_{Ni}y_{Va} + y_{Ni}y_C) - 1.91y_{Cr}y_{Ni}y_{Va} \\ - y_{Fe}y_{Ni}y_{Va}[9.55 + 7.23(y_{Fe} - y_{Ni}) + 5.93(y_{Fe} - y_{Ni})^2 + 6.18(y_{Fe} - y_{Ni})^3]$$

Whenever the calculated value of  $T_C$  or  $\beta$  is negative, it should be divided by  $-3$  when inserted in  $G_m^{mo}$  and  $f(\tau)$ .

### Graphite

Constituent: C

$${}^{\circ}G_C^{gra} - H^{SER} = -17,369 + 170.73T - 24.3T \ln T - 4.723 \cdot 10^{-4} T^2 + 2,562,600T^{-1} \\ - 2.643 \cdot 10^8 T^{-2} + 1.2 \cdot 10^{10} T^{-3}$$

### Cementite

Two sublattices, sites 3:1 constituents: Cr, Fe, Ni:C

$${}^*0G_{Cr:C}^{cem} = 3{}^{\circ}G_{Cr}^{hbcc} + {}^{\circ}G_C^{gra} - 29,392 + 41.65T - 9.32T \ln T + 2.6282 \cdot 10^{-3} T^2$$

$${}^{\circ}G_{Fe:C}^{cem} - H^{SER} = -10,745 + 706.04T - 120.6T \ln T$$

$${}^{\circ}G_{Ni:C}^{cem} - H^{SER} = 3{}^{\circ}G_{Ni}^{hbcc} + {}^{\circ}G_C^{gra} - 34,700 - 20T$$

$${}^*0L_{Cr,Fe:C}^{cem} = 20,976 - 20.3144T$$

$${}^0L_{Fe,Ni:C}^{cem} = 29,400$$

**Table II. Cont. Summary of Thermodynamic Parameters Describing the Fe-Cr-Ni-C System in SI Units (J, mol, K)\***

**Cr<sub>3</sub>C<sub>2</sub>**

Two sublattices, sites 3:2 constituents: Cr:C

$$^{\circ}G_{Cr:C}^{Cr_3} - H^{SER} = -92,138 + 632.1755T - 105.6289T \ln T - 0.022348T^2$$

**M<sub>23</sub>C<sub>6</sub>**

Three sublattices, sites 20:3:6 constituents: Cr, Fe, Ni:Cr, Fe, Ni:C

$$^{\circ}G_{Cr:Cr:C}^{M_{23}} - H^{SER} = -462,844 + 3200.2837T - 550.0669T \ln T - 0.2043663T^2$$

$$^{\circ}G_{Cr:Fe:C}^{M_{23}} = 20/23^{\circ}G_{Cr:Cr:C}^{M_{23}} + 3/23^{\circ}G_{Fe:Fe:C}^{M_{23}}$$

$$^{\circ}G_{Fe:Cr:C}^{M_{23}} = 20/23^{\circ}G_{Fe:Fe:C}^{M_{23}} + 3/23^{\circ}G_{Cr:Cr:C}^{M_{23}}$$

$$^{\circ}G_{Fe:Fe:C}^{M_{23}} = 23/3^{\circ}G_{Fe:C}^{cem} - 5/3^{\circ}G_C^{gra} + 66,920 - 40T$$

$$^{\circ}G_{Fe:Ni:C}^{M_{23}} = 20/23^{\circ}G_{Fe:Fe:C}^{M_{23}} + 3/23^{\circ}G_{Ni:Ni:C}^{M_{23}}$$

$$^{\circ}G_{Ni:Fe:C}^{M_{23}} = 20/23^{\circ}G_{Ni:Ni:C}^{M_{23}} + 3/23^{\circ}G_{Fe:Fe:C}^{M_{23}}$$

$$^{\circ}G_{Ni:Ni:C}^{M_{23}} = 23^{\circ}G_{Ni}^{hfcc} + 6^{\circ}G_C^{gra} + 212,988$$

$$^{\circ}G_{Cr:Ni:C}^{M_{23}} = 20/23^{\circ}G_{Cr:Cr:C}^{M_{23}} + 3/23^{\circ}G_{Ni:Ni:C}^{M_{23}}$$

$$^{\circ}G_{Ni:Cr:C}^{M_{23}} = 20/23^{\circ}G_{Ni:Ni:C}^{M_{23}} + 3/23^{\circ}G_{Cr:Cr:C}^{M_{23}}$$

$$*0 L_{Cr,Fe:Cr,Fe:C}^{M_{23}} = 604,852 - 158.6196T$$

$$*1 L_{Cr,Fe:Cr,Fe:C}^{M_{23}} = -1,914,930$$

$$*2 L_{Cr,Fe:Cr,Fe:C}^{M_{23}} = -1,914,930$$

**M<sub>7</sub>C<sub>3</sub>**

Two sublattices, sites 7:3 constituents: Cr, Fe, Ni:C

$$^{\circ}G_{Cr:C}^{M_7} - H^{SER} = -177,506 + 1471.6421T - 249.2091T \ln T - 0.024006T^2$$

$$^{\circ}G_{Fe:C}^{M_7} = 7^{\circ}G_{Fe}^{hbcc} + 3^{\circ}G_C^{gra} + 113,385 - 78.37T$$

$$^{\circ}G_{Ni:C}^{M_7} = 7^{\circ}G_{Ni}^{hfcc} + 3^{\circ}G_C^{gra} + 193,000$$

$$*0 L_{Cr,Fe:C}^{M_7} = -131,281 + 53.4926T$$

$$*1 L_{Cr,Fe:C}^{M_7} = -41,451$$

$$*0 L_{Cr,Fe,Ni:C}^{M_7} = -323,854$$

**Sigma**

Three sublattices, sites 8:4:18 constituents: Fe, Ni:Cr:Cr, Fe, Ni

$$^{\circ}G_{Fe:Cr:Cr}^{\sigma} = 8^{\circ}G_{Fe}^{hfcc} + 22^{\circ}G_{Cr}^{hbcc} + 92,300 - 95.96T$$

$$^{\circ}G_{Fe:Cr:Fe}^{\sigma} = 8^{\circ}G_{Fe}^{hfcc} + 4^{\circ}G_{Cr}^{hbcc} + 18^{\circ}G_{Fe}^{hbcc} + 117,300 - 95.96T$$

$$^{\circ}G_{Fe:Cr:Ni}^{\sigma} = 8^{\circ}G_{Fe}^{hfcc} + 4^{\circ}G_{Cr}^{hbcc} + 18^{\circ}G_{Ni}^{hbcc}$$

$$^{\circ}G_{Ni:Cr:Cr}^{\sigma} = 8^{\circ}G_{Ni}^{hfcc} + 22^{\circ}G_{Cr}^{hbcc} + 173,460 - 188T$$

$$^{\circ}G_{Ni:Cr:Fe}^{\sigma} = 8^{\circ}G_{Ni}^{hfcc} + 4^{\circ}G_{Cr}^{hbcc} + 18^{\circ}G_{Fe}^{hbcc}$$

$$^{\circ}G_{Ni:Cr:Ni}^{\sigma} = 8^{\circ}G_{Ni}^{hfcc} + 4^{\circ}G_{Cr}^{hbcc} + 18^{\circ}G_{Ni}^{hbcc} + 175,400$$

\*The parameters marked with \* were assessed in the present work.

that he instead used the properties of the Cr carbides as adjustable parameters, which was natural in view of the large experimental scatter and possible because he did not consider the Cr-Ni-C system.

For the Fe-Cr-Ni-C system, it has been possible to represent the solubility of M<sub>23</sub>C<sub>6</sub> very well, although there is some discrepancy for the Ni dependence of the C content and of the C activity according to Tuma's results.<sup>[8]</sup> These quantities depend upon the variation of the C activity of fcc with the Cr and Ni contents. After excluding experimental information which falls inside the fcc + M<sub>23</sub>C<sub>6</sub> region, the remaining data were fitted well, and the present description should be better than previous ones by Natesan and Kassner<sup>[10]</sup> and by Hillert and Waldenström.<sup>[15]</sup>

Most of the experimental data on the Fe-Cr-C and Fe-Cr-Ni-C systems have been fitted reasonably well in the present assessment. In particular, it seems that it could

be used for realistic predictions of the solubility of M<sub>23</sub>C<sub>6</sub> in Fe-rich alloys. No information from the Ni-rich region was used for the optimization because of scarcity. However, an expression was proposed<sup>[30]</sup> for the solubility of M<sub>7</sub>C<sub>3</sub> in an alloy with 16.74 at. pct Cr, 9.42 at. pct Ni, and 0.15 at. pct C (similar to the INCONEL\* 600 alloy).

\*INCONEL is a trademark of Inco Alloys International, Inc., Huntington, WV.

$$\ln(\text{wt pct C}) = 9.0 - 14,713/T \quad [14]$$

In Figure 13, this expression is compared with values predicted from the present calculation. The agreement is satisfactory in the experimental range, but the slopes are different. The slope mainly depends upon quantities which are reasonably well established, and one could probably trust the calculated slope.

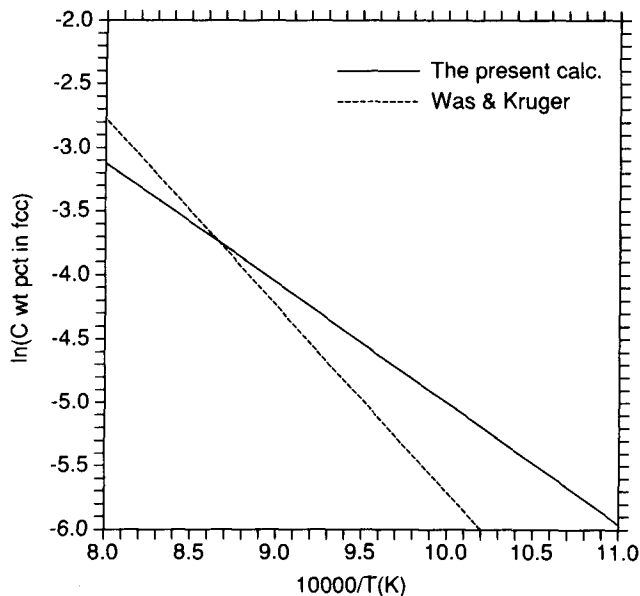


Fig. 13—The solubility of  $M_7C_3$  in an alloy with 16.74 at. pct Cr and 9.42 Fe vs temperatures according to the present (full line) and a previous assessment (dashed line).

Among the experimental information, which has not been fitted very well, are the dependence on the Ni content of the C activity and solubility of  $M_{23}C_6$  in fcc, the distribution of Cr between  $M_7C_3$  or  $M_{23}C_6$  and fcc or bcc at very high and at very low Cr contents in the carbides, and finally, much of the information on the liquidus temperatures. The assessment could undoubtedly be improved on these points by using more complex models and by reassessing all of the lower order systems together with the Fe-Cr-Ni-C system in the same optimization. However, it seems that such an assessment should not be undertaken until much of the experimental information has been confirmed by independent experimental studies.

## VI. CONCLUSIONS

From the present work, it can be concluded that the recent assessment of the Cr-Ni-C system<sup>[2]</sup> can be used as a basis for a reasonable assessment of the Fe-Cr-C system. However, composition-dependent interactions must be introduced in the carbides.

The phase relations involving the liquid, formed in the previous assessment by Andersson,<sup>[7]</sup> appeared again.

The experimental information on the C activity in fcc may partly fall in the fcc +  $M_{23}C_6$  region in the Fe-Cr-Ni-C system. When that part of the information is omitted, the assessed C activities at high Cr and Ni contents are lower than ones indicated previously.

In the Fe-Cr-Ni-C system, it has been possible to fit very well the experimental solubility of  $M_{23}C_6$  in fcc within the high Fe region and of  $M_7C_3$  in fcc within the high Ni region.

## ACKNOWLEDGMENTS

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