Predicting Carbides in Alloy Steels by Computer

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Today there is an established technique to evaluate the thermodynamic properties of individual phases in an alloy system by assessing all the thermochemical information and the information on the phase diagram. This technique has been applied to a large number of binary and some ternary systems. From a practical point of view it would find its most important applications in higher order systems which are found in alloy steels. This lecture will report on an effort to build a thermodynamic database for iron-base alloys, suitable for predicting the formation of various alloyed carbides in steels.

KEY WORDS: phase diagram; computer calculation; consistent database; alloyed carbides; high speed steel; cemented carbides; stainless steel.

1. Introduction

Phase diagrams are of a considerable practical importance to metallurgists. They have been determined experimentally and can be used directly for making various kinds of predictions. In this respect a phase diagram may be regarded as a rationalization of experimental data which has proved itself very useful. However, the phase diagram is also a manifestation of the thermodynamic properties of the system, a fact which results in useful rules of construction to be applied when constructing a phase diagram from limited experimental information. On the other hand, there has been a relatively weak interest in the thermodynamic properties themselves, probably because the information obtained directly from the phase diagrams has been sufficient for most needs.

In the last decade there has been a growing interest in correlating the phase diagram with the thermodynamic properties. In many cases one has tried to derive the thermodynamic properties from the phase diagram and has been satisfied if it is possible to recalculate a phase diagram in reasonable agreement with the experimentally determined diagram. More ambitious evaluations also take thermochemical and thermophysical information into account and, in fact, the full name of the specialized journal for this field is "CALPHAD—computer coupling of phase diagrams and thermochemistry". Of course, CALPHAD is an abbreviation of CALculation of PHase Diagrams.

2. Advantages of the Calphad Technique

For binary and ternary systems the advantage of the Calphad technique is primarily that it results in more reliable phase diagrams but it should be realized that it may also give thermodynamic properties which were not available before. They can also be of considerable practical importance. They can be used for extrapolating phase boundaries into metastable ranges but also for evaluating driving forces for various

transformation or evaluating the heat of transformation, just to mention a few examples.

For higher order systems the Calphad technique is even more important. Here it is practically impossible to obtain more than a few scattered pieces of experimental information but by the Calphad technique one obtains the whole phase diagram and all the thermodynamic properties. However, there is a considerable uncertainty involved. In the first step, a quaternary system is obtained as a prediction by combining the thermodynamic descriptions of the four ternary side-systems. If there is some quaternary information available, it can be used to test the prediction and if a significant discrepancy is found, it may be eliminated by introducing and evaluating quaternary interactions.

After such a test and modification, the recalculated phase diagram will be more reliable but there may still be surprises if new information becomes available later on from regions not examined before. This is a very serious limitation if one wants to predict the properties of a ternary system from the three binary side-systems. It is really necessary to take into account ternary interactions and they cannot be evaluated without ternary information. It is a less severe limitation if one wants to predict a quaternary system from the four ternary side-systems because quaternary interactions, *i.e.*, interactions between four atoms of different kinds, are not so strong. It is an even less severe limitation if one wants to predict the properties of a quinary system from the five quaternary side-systems. On the other hand, it should be emphasized that the Calphad technique cannot predict the appearance of a new phase in a higher order system from the properties of the lower order systems.

There are many commercial steels where four or more elements play an important role and the only practical way to rationalize available information and to make predictions when no direct information is available, is to use the Calphad technique. The present lecture will describe an effort to build a database for alloyed steels made at the Division of Physical

Metallurgy at the Royal Institute of Technology (KTH) in Stockholm.

3. Difficulty of Consistency

In some binary alloy systems there is direct experimental information on the properties of the liquid phase over the whole range of composition. Using a computer-operated optimization procedure one can then assess various types of information at the same time, *e.g.*, from calorimetric, emf and effusion studies, and evaluate model parameters to the best fit of the data. In the solid state this is rarely the case. There the compositional range of stability of each phase is usually limited but the model description of each phase may extend over the complete range of composition. Fig. 1 gives a simple example from the Fe–Cr system, where the fcc phase only exists up to about 11 % Cr but the thermodynamic description goes all the way to pure Cr. The assessment of the Fe–Cr system will thus result in a description of the properties of pure fcc Cr which cannot be studied directly. In the first instant, it does not matter if that description is realistic or not as long as the stable part of the diagram is well represented. However, one will meet the same situation in the Ni–Cr system and the two descriptions cannot be combined to yield the ternary Fe–Cr system unless the same descriptions of fcc Cr is used in both. This is demonstrated in Fig. 2.

As one goes from ternary systems to a quaternary, one realizes that any particular binary system appears in two of the ternary side-systems and they cannot be combined unless they are based on exactly the same descriptions of the binary. As a consequence, in order to build a database for higher order systems it is necessary to make the descriptions of all the lower order systems consistent. First, it is necessary to decide on the properties for each pure element in all possible states, at least bcc, fcc, hcp and liquid. Those descriptions are often called “lattice stabilities” after a proposal by Kaufman¹⁾ and a recommended set of lattice stabilities has recently been compiled by Dinsdale.²⁾ It would be a great advantage if all assessments could be based upon that compilation. Second, it is necessary to decide on the properties for each binary system but there we encounter the difficulty that different researchers often use different thermodynamic models and their assessments can not be combined.

Collaboration on a wide scale is only possible if there can be a general agreement on models to be used and, furthermore, on the actual numbers for each binary system. A very close contact between the collaborators is thus required and it may seem impossible ever to establish such a collaboration. However, an effort is made in Europe where seven laboratories collaborate under the name of SGTE (Scientific Group Thermodata Europe). That collaboration has been reasonably successful and a compilation of 129 binary phase diagrams has recently been completed.³⁾ All assessments of higher order

Fig. 1. Schematic molar Gibbs energy diagram for the Fe–Cr system at 1100°C.

Fig. 2. Schematic molar Gibbs energy diagram for the Fe–Cr–Ni system at 1100°C.

systems within SGTE should be based upon them and anybody who likes to contribute to a consistent database for higher order systems should base his or her work on these two compilations. In the future we can hope to see similar compilations of ternary systems.

4. Study of Ternaries at KTH

The study of ternary Fe–C–X systems at KTH started more than 25 years ago when first Drs. Tsuguyasu Wada and Harue Wada⁴⁾ spent a year in Stockholm and then Dr. Taiji Nishizawa^{5,6)} spent two years. They were followed by a number of graduate students. Over the years the group has produced some experimental information on ternary systems but it may be more important that it has developed thermodynamic models and also computer programs for any type of equilibrium calculation, POLY⁷⁾, and for optimizing the values of model parameters to the best fit of experimental information, PARROT⁸⁾. These programs are now parts of a databank, THERMOCALC⁹⁾. So far, ternaries of the type Fe–C–X with X being Si, Ti, V, Cr, Mn, Co, Ni, Nb, Mo and W have been completed. However, in order to combine them into higher order systems it is necessary to have descriptions of many other ternaries, without Fe or C. There is still a long way to go until we have a complete description of the Fe–C–Si–Ti–V–Cr–Mn–Fe–

Co-Ni-Nb-Mo-W system. In fact, that goal is still out of sight and cannot be reached without the collaboration of many other groups. On the other hand, a reasonable description of the Fe rich part of that multicomponent system may soon be obtained. In order to give an impression of this work, some higher order systems will now be discussed.

4.1. Fe-Cr-Mo-C

The Fe-Cr-Mo-C system contains two strong carbide formers, Cr and Mo, and, naturally, it was essential to assess the Cr-C and Mo-C binaries but also Fe-Cr, Fe-Mo and Mo-Cr. It then became evident that the accepted lattice stabilities for Cr and Mo should be modified¹⁰⁾ and the completed work thus comprised a complete reassessment of all the lower order systems except for Fe, C and Fe-C. As an example, Fig. 3 gives the Mo-C system¹¹⁾ with a comparison of experimental phase diagram data.

The Fe-Cr-C system has been assessed several times but it was now necessary to evaluate it with the new lattice stabilities. From the assessment it was then possible to calculate various sections,¹²⁾ e.g., the vertical section at 13 wt% Cr given in Fig. 4.

Among the ternaries we also find the Fe-Cr-Mo system which contains several intermetallic phases. Here it was necessary to make many experimental measurements.¹³⁾ The final result for 1373 K is shown in Fig. 5. It contains four intermetallic phases, σ , χ , R and μ . A comparison with some data from the same temperature is given in Fig. 6 but it should be realized that the result presented in Fig. 5 is the result of data from other temperatures, as well.

When all four ternaries had been assessed and were combined into the quaternary system, it became evident that one needs new information in order to describe the alloyed carbides.¹⁴⁾ As an example, quaternary information shows that Cr dissolves in the ksi carbide which is present in the Fe-Mo-C system. In principle, that effect can be represented by choosing a value for the Gibbs energy of the ksi carbide in the

Cr-C system where it is metastable and has never been observed. As another example, $M_{23}C_6$ may be mentioned for which the quaternary information made

Fig. 4. Computer-calculated vertical section of the Fe-Cr-C system at 13 wt% Cr.

Fig. 5. Computer-calculated isothermal section of Fe-Cr-Mo at 1273 K.

Fig. 3. Computer-calculated Mo-C phase diagram, compared with experimental information.

Fig. 6. Computer-calculated isothermal section of Fe-Cr-Mo at 1273 K, compared with experimental tie-lines.

Fig. 7. Experimental tie-lines and tie-triangles in the Fe-Cr-Mo-C system at 1273 K and $a_C=0.33$.

it necessary to evaluate Gibbs energy for a mixed carbide, $\text{Fe}_{21}\text{Mo}_2\text{C}_6$, and for the interaction inside the quaternary system. A similar assessment had to be made for the M_6C carbide.

In the assessment of the Fe-Cr-Mo-C system it was particularly valuable to have quaternary information on the phase equilibria at constant values of the C activity. As an example, Fig. 7 shows experimental data at 1273 K and $a_C=0.33$ and Fig. 8 shows the recalculated diagram. This quaternary diagram looks like an isothermal section of a ternary diagram because it has been sectioned at a constant carbon potential. By the same reason, it is possible to make reaction schemes at constant T where the C activity varies vertically. See Fig. 9 which resembles a Scheil diagram for a ternary system where T varies vertically.

4.2. Fe-Cr-Mo-W-C

In a continuation of the work on the Fe-Cr-Mo-C system, an assessment of the Fe-Cr-W-C system was made¹⁵⁾ and then the quinary system Fe-Cr-Mo-W-C was predicted by calculation.¹⁶⁾ However, it was then desirable to have assessments of three additional quaternary systems which were not available. An attempt was made to base their descriptions on the ternary systems and estimated values for the new parameters appearing in the quaternary systems.

The result for the quinary system was of particular interest in connection with high-speed steels. The result could thus be checked by comparing with some information obtained with well defined synthetic high-speed steels.¹⁷⁾ That information gave the constitution of several steels at 1473 K and a constant C activity. Most of them contained austenite and M_6C . It was possible to obtain reasonably good agreement with this information. It thus seems that a description is now available for predicting the constitution of high-speed steels with some confidence. As an example, Fig. 10 shows a vertical section at 4 wt% Cr, 6 wt% Mo and 6 wt% W. The dashed line indicates the composition of a typical high-speed steel. How-

Fig. 8. Computer-calculated isothermal and isoactivity section of the Fe-Cr-Mo-C system at 1273 K and $a_C=0.33$.

Fig. 10. Computer-calculated vertical section of the Fe-Cr-Mo-W-C system at 4 wt% Cr, 6 wt% Mo and 6 wt% W.

ever, it must be emphasized that the important effects of V and Co have not yet been included.

4.3. Fe-Ni-W-C

The Fe-Ni-W-C system is particularly interesting as a possible system for making cemented carbides with Fe-Ni replacing Co as the binder phase in WC tools. Due to the similarity between Fe and Ni, the phase diagram is not very complicated and its main features could be obtained by prediction from the four ternary side-systems.¹⁸⁾ However, it was necessary to introduce and assess two quaternary interactions for the liquid in order to fit some information on the liquidus.

A typical vertical section through the phase diagram is shown in Fig. 11. It is made at 17 wt% Fe and 3 wt% Ni. It is of some practical interest because it shows the conditions for producing a material of WC+fcc and preventing the formation of graphite

Fig. 9. Reaction scheme of the Fe-Cr-Mo-C system at 1273 K.
The numbers give the C activity values.

if the carbon content is too high and M_6C if it is too low, both of which are detrimental to the mechanical properties. One may conclude that the C content should be adjusted between the values 5.03 and 5.16 wt%. Fig. 12 shows how these limits vary with the Fe:Ni ratio.

4.4. Co-Fe-Ni-W-C

In a continuation of the work on the Fe-Ni-W-C system, a calculation was made of the quinary system Co-Fe-Ni-W-C.¹⁹⁾ It was based on assessments of the Fe-Ni-W-C, Co-Fe-Ni-C and Co-Ni-W-C systems. The Co-Fe-Ni-W system was not assessed due to the lack of information but it is probably not too unrealistic to assume that its quaternary interactions

are small. Nor was the Co-Fe-W-C system assessed because of lack of information but due to the similarity between Fe and Co it was assumed that its quaternary interactions can be neglected. Assessments of all the 10 ternary and 10 binary side-systems were used. With the description of the Co-Fe-Ni-W-C system available, it is now possible to calculate diagrams like Fig. 12 for any Co-Fe-Ni binder phase. As an example, Fig. 13 gives a vertical section at 5 wt% Fe, 4 wt% Co and 1 wt% Ni. The possibility of predicting such phase diagrams can drastically decrease the experimental cost in alloy development.

Fig. 11. Computer-calculated vertical section of the Fe-Ni-W-C system at 17 wt% Fe and 3 wt% Ni.

Fig. 12. Temperature projection of a section of the Fe-Ni-W-C system calculated at 20 wt% Fe+Ni.

5. A Problem of Consistency

The Fe-Cr-Ni-C system is the basis for austenitic stainless steels but also for heat-resistant Ni base alloys. It is thus important to have a good description across the whole system but when work was to start on this system it was found that there was no ambitious assessment of the Cr-Ni-C system. The work thus started with that ternary side-system but after many attempts it was concluded²⁰⁾ that the solubilities of the Cr rich carbides in the Ni rich fcc phase could not be fitted with the present description of the Cr-C system. It was thus necessary to go back to that binary. In recent years there has been new information on the properties of the Cr carbides²¹⁾ and when an assessment was now made, based upon that information, it was also possible to fit the solubility data in the Cr-Ni-C system.

Fig. 14 gives a comparison between different reports on Cr_3C_2 . The scatter is very large and the previous assessment was based upon the dashed line which may be regarded as a reasonable choice. The new assessment is based upon the solid line. Considering the large scatter of the experimental information one may think that the difference between the two choices is small. This example is an illustration of the fact that information on phase equilibria is sometimes more critical for the determination of thermodynamic properties than direct thermochemical measurements. However, this is not always true. For example, in the present case the Cr-C phase diagrams calculated from the two assessments look almost the same. It was thus necessary to go to a higher order system in order to decide on the properties of the Cr carbides.

The decision to accept a new assessment of the Cr-C system was a difficult one because the old assessment had been used as a basis for assessments of a number of ternary systems, Fe-Cr-C, Mo-Cr-C,

Fig. 13. Computer-calculated vertical section of the Co-Fe-Ni-W-C system at 4 wt% Co, 5 wt% Fe and 1 wt% Ni.

W-Cr-C, and several quaternary systems involving them. It will thus be necessary now to reassess most of the systems discussed in the previous sections of this lecture in order to get a consistent database. One may wonder if consistency in the database could be worth such a large effort. The answer is that without consistency the database would be of little use. There is really no alternative. Rather than accept inconsistency, one should accept an inferior fit of some information. As a consequence, in the present situation it will be necessary to have two separate databases, one based on the old Cr-C assessment and a separate one based on the new. This second database will primarily be used for stainless steels but may be extended gradually as the other systems are being reassessed.

Fig. 14. Gibbs energy of formation of Cr_3C_2 , according to various authors and two assessments.

It is important to notice that a reassessment is much quicker than the first assessment. Thanks to the computer-operated procedure of the assessment, all the information is already in the computer and the thermodynamic models are already defined. There is still a problem of finding the new optimum when parameter values for a lower order system are changed but the experience gained in the previous assessment is of considerable help. It would be even better if the experience could be stored in the computer and brought to use again in the new assessment. This is something we still have to learn how to do.

5.1. Fe-Cr-Ni-C

The assessment of the Fe-Cr-Ni-C system continued with a reassessment of the Fe-Cr-C system.²²⁾ It was then found that the solubilities of Cr rich carbides in austenite are not very well established experimentally, especially not at temperatures below 1 000 °C. On the other hand, these solubilities are very important for the austenitic stainless steels and additional information could thus be obtained from the Fe-Cr-Ni-C system. As a consequence, the Fe-Cr-C system was assessed together with the Fe-Cr-Ni-C system.

The assessment of the Fe-Cr-Ni-C system has now been used for some calculations of the tendency of a steel to be sensitized for intercrystalline corrosion.²³⁾ The idea is that, during an unintentional heat treatment, C may diffuse to the grain boundaries and there cause a precipitation of Cr rich carbides, thus causing a Cr depleted zone along the grain boundaries. If the Cr content falls below a value of about 12 wt%, then the corrosion resistance is low.

Fig. 15 gives a comparison between the solubility of M_{23}C_6 in steels with 8 wt% Ni and various Cr contents and the critical C content for sensitization. To the left of the first line there will be no precipitation of M_{23}C_6 from the austenitic material. Between the

Fig. 15. Computer-calculated precipitation of M_{23}C_6 in austenitic stainless steel with 8 wt% Ni and various Cr contents. Precipitation can occur to the right of the first curve but makes the steel sensible for corrosion only to the right of the second curve.

Fig. 16. Computer-calculated curves for the critical conditions for sensitization of austenitic stainless steels of 8 wt% Ni and various Cr contents.

lines there will be precipitation and the zone along the grain boundaries will be more and more depleted of Cr until it falls below 12 wt% Cr to the right of the second line. It is interesting to note that the difference between the two lines increases with the Cr content.

Fig. 16 shows the critical condition for sensitization as function of temperature and it is important to notice that extremely low C contents are required in order to eliminate the risk of making a steel sensitized by a long enough heat treatment at 600°C. Before leaving this topic it should be emphasized that the

phenomenon of sensitization is more complicated than indicated here. It may be stated that the present arguments apply at a very large grain size.

6. Conclusions

Even if a database is not perfect and does not give quite accurate predictions, it may be very useful in predicting the effect of a change in composition or temperature. It may thus be used in order to eliminate much experimental work in alloy development. However, it is a requirement that the database is consistent.

Our experience is that the construction of a consistent database requires much more work than separate assessments of the same number of systems. However, the practical use of a consistent database is so much larger that the larger effort is justified.

It is important to continue developing the computer-operated procedures of assessment. At present, many subjective decisions are taken by the assessor during the course of the assessment. That situation may never change and may even be a guarantee of a good result. However, it should be possible to impose such decisions on the computer in a logical language, such that it may be retrieved, considered and applied in a later reassessment.

There will always be a need of reassessments.

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