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THE TECHNIQUE OF SUCCESSIVE PARTIAL EQUILIBRIA TO PREDICT PRECIPITATION
OF CARBIDES IN EQUILIBRIUM WITH A SOLUTION PHASE.

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ABSTRACT

The technique of successive partial equilibria has been employed to predict the equilibrium precipitation of carbides in iron-based alloy systems. To employ this technique, the principle that the equilibrium state is independent of the path followed, is utilized. The technique is illustrated with respect to the Fe-Cr-C system and also with respect to a steel containing several alloying elements. The technique is applicable to the precipitation of nitrides, oxides etc. also, in addition to that of carbides.

Introduction

The precipitation of carbides is an important phenomenon influencing the properties and, thereby, the application of steels for various structures and tools. An understanding of the nature of these precipitates is vital for the design of alloys to meet the requirements vis a vis the the desired properties during the service life of steels. A knowledge of the carbides appearing at equilibrium with different solid solutions is essential for this. Assessed thermodynamic data on the carbides and the solution phases are used to predict the equilibrium phases. Several systems based on iron and carbon and containing alloying elements like chromium, molybdenum, vanadium, manganese, nickel etc. have been assessed and phase diagrams derived from these data (1-5). Efforts are also being made to collate all the information available on the pertinent systems and predict precipitation of carbides in multicomponent systems using computers (6). The regions where different carbides are at equilibrium can be inferred from these phase diagrams.

The prediction of these phase diagrams is generally based on the principle that the free energy of a system is minimum at equilibrium. The total free energy of a system is a function of the chemical compositions of the various phases constituting the system and the masses of these phases. This technique of predicting the equilibrium state using the principle of free energy minimization has been described in literature (7,8). These methods exploit the mathematical definition of the minimum of free energy from which the magnitudes of the various parameters, i.e., the composition and the masses of the various phases, are evaluated. Graphical methods also use the same principle.

It is also possible to consider partial equilibrium in a thermodynamic system where the system is at equilibrium with respect to some of the components and some of the phases only. Though the concept of partial equilibrium is used to a good extent in analysing the behaviour of various systems, the possibility of using this to arrive at the total equilibrium state of a system remains unexplored. This communication uses the technique of partial equilibria to predict the equilibrium state in cases like the precipitation of carbides. In order to exploit this principle in a systematic

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manner to predict the equilibrium state of a system, one of the fundamental principles of thermodynamics, that the equilibrium state of a system is independent of the path followed to reach that, is used.

Partial Equilibrium

A system is at partial equilibrium when only some and not all of the components of the system have the same chemical potential in the different phases of the system. There will be other components which do not satisfy this requirement under conditions of partial equilibrium. When only some of the phases of the system are at equilibrium with respect to the components also, the system can be considered to be under partial equilibrium. There will be other phases which are not at equilibrium with these.

The Thermodynamic Path

In thermodynamics, a path represents a combination of sets of coordinates representing the various parameters required to define a state of a system and the direction in which the sets have to be traversed, to reach another defined state. Various paths can be employed to transfer a system from one state to another. An appropriate path can be adopted to reach the final state with the minimum number of operations.

A systematic definition of the state to be reached will provide the means of defining the path also in a systematic manner. The properties of the equilibrium state provide the means of defining the path. This will enable reaching the equilibrium state from any initial state. It is possible to generate several paths conforming to the criterion chosen to define the path.

Definition of Path to Reach The Equilibrium State

An essential property of the equilibrium state is that the chemical potential of any component constituting the system is the same in all the phases present in the system. To reach this state, the path can be so defined that at each stage of travel towards the desired state, the chemical potential of a component is the same in a pair of phases taken for consideration. All the phases that can be formed by the system are considered in succession by taking two of them at a time to compute the equilibrium state. At the end of the computation, the criterion for equilibrium, that the chemical potential of any component is the same in all the phases present at equilibrium, must be satisfied. If this condition is not satisfied, the computations are repeated by adopting this final state as the initial state for the next cycle of computations.

At each stage, partial equilibrium is reached between the two phases chosen with respect to the components taken for consideration. When such a partial equilibrium is reached, the components are distributed between them in a well defined manner. When the cycle of computation is repeated starting with a different initial state, this distribution is also altered. Depending on the path chosen, some of the phases that are present at the initial stages of computation may disappear and others that are not present initially, may gain in prominence and report as equilibrium phases. The sequence in which the various phases are considered gives one of the means of generating a number of paths. Some of these paths will be more efficient than the others in that they reach the equilibrium state with the minimum number of computation cycles or with minimum of computation time.

Prediction of Equilibrium Carbide Phases

Let us consider a system formed by the hypothetical chemical elements P, Q, R etc. and carbon. Each of the elements can form different carbides P₁, P₂, P₃ etc. These carbides are stoichiometric. There is only one solution phase 's', at equilibrium and it is known a priori. To predict the equilibrium state of the system, it is assumed that all the mass of carbon and all the mass of the element 'P' in the system react to form the carbide 'P₁', at equilibrium. From the standard free energy of formation of the carbide, the mass of the carbide formed and the masses of the element 'P' and carbon in solution at

equilibrium can be evaluated. In the next step, all the carbon and 'P' in solution are allowed to react to form the carbide 'P2'. Again, the mass of 'P2' and that of carbon and 'P' in solution at equilibrium can be evaluated. At each stage, the chemical potential of the elements at equilibrium are computed. The procedure is repeated until all the carbides that can be formed by 'P' have been considered in succession. In a similar fashion, the other elements 'Q,R...etc. and the carbides that can be formed by each element are considered and the chemical potentials of all the elements computed at each stage. When all the possible carbides have been considered, the chemical potentials of the various elements at equilibrium at the different stages are compared. For equilibrium, these values must be identical at the different stages for any chosen element. If this criterion is not satisfied, the next cycle of computation is initiated.

Let the carbide RX, formed at equilibrium with element 'R' and carbon be the carbide considered at the end of the first cycle. Some amount of 'P' and carbon are in solution at this stage. To this quantity of 'P' and carbon present in solution, the mass of 'P' and carbon precipitated in 'P1' in the first cycle, are added. This total masses of 'P' and carbon are allowed to react and form the carbide 'P1', again. The equilibrium masses are evaluated. The partial equilibrium reached at this stage will be different from the one attained earlier, in the first cycle, since the mass of carbon and that of the element 'P' available to form the carbide are different. In addition, the solution phase present now has a composition different from that present on the earlier occasion. As in the first cycle, the computations are repeated for all the elements and all the carbides that can be formed by these elements. At each stage, the total masses of the elements present in the corresponding carbide are combined with those in solution at the end of the previous stage, as described in the case of the carbide 'P1', above. The chemical potentials are computed at each stage and compared at the end of the cycle, when all the carbides that can be formed by the different elements have been considered. Equilibrium is given by the identity of the chemical potentials of any element at the different stages. If this condition is not satisfied, the next cycle of computation is initiated and carried out as above. The process is repeated until equilibrium is reached.

During the process of computation, the system is transferred from one state to another until equilibrium is reached. By altering the sequence in which the carbides are considered, it is possible to generate a number of paths. As the computation proceeds, the carbides that are stable at equilibrium gain in mass and those that are not stable disappear gradually.

A Multicomponent System

To illustrate this technique in the case of a real system, a steel containing vanadium, molybdenum, chromium and manganese as alloying elements apart from carbon is considered. The chemical composition of the steel is given in table 1. Precipitation of carbides in equilibrium with the α -phase is predicted. An understanding of the nature of the carbides precipitated in this steel is important for the design of alloys for better creep-resistance.

TABLE 1
Composition of Steel

Element	V	Mo	Cr	Mn	C
Wt %	0.25	0.5	0.5	0.5	0.12

To simplify the prediction procedure, it is assumed that the carbides are not complex, i.e., the metal sub-lattice in each carbide has only one type of element present. The carbides are taken to be stoichiometric. Various carbides that can be formed by the alloying elements in this system are listed in table 2.

TABLE 2

Carbides Formed by Alloying Elements of Table 1

Element	Carbide
V	VC, V ₃ C ₂ , V ₂ C
Mo	MoC, Mo ₂ C
Cr	Cr ₃ C ₂ , Cr ₇ C ₃ , Cr ₂₃ C ₆
Mn	Mn ₇ C ₃ , Mn ₅ C ₂ , Mn ₃ C, Mn ₂₃ C ₆

To initiate the prediction scheme, all the vanadium in the steel is allowed to react with all the carbon available, to form the carbide 'VC'. The mass of the carbide formed and the masses of vanadium and carbon in solution in the α -phase at equilibrium are computed. In the next stage, the amount of vanadium and carbon in solution are allowed to react to form the carbide 'V₃C₂', at equilibrium. Again the masses at equilibrium are computed. The procedure is repeated for molybdenum, chromium and manganese, taking one carbide at a time. Some of the carbides may not form if the limit set by the solubility product for the carbide is not exceeded. After evaluating all the carbides possible in the system, the chemical potentials of carbon computed at the different stages are compared. These values must be identical, for equilibrium. Similarly, the chemical potential of each alloying element computed at the different stages must be identical. If these requirements are not satisfied, the next cycle of computation is initiated.

Table 3 lists the mass of the carbides formed and the masses of the different elements in solution in the α -phase, at each stage of computation in the first cycle. At the beginning of the second cycle, the mass of vanadium in solution at the end of the first cycle is added to the mass of vanadium in the carbide 'VC' formed in the first cycle. Similarly the mass of carbon in solution at the end of the first cycle is added to the mass of carbon in the carbide 'VC' formed in the first cycle. These total amounts of vanadium and carbon are allowed to react to form 'VC' in the second cycle. The mass of this carbide and that of carbon and vanadium in solution are computed. At the next stage, the mass of vanadium available at the end of the first stage is combined with the mass of vanadium present in the carbide 'V₃C₂' formed in the first cycle. The available mass of carbon is computed in a similar manner. The carbide 'V₃C₂' is allowed to form at equilibrium from the total vanadium and carbon thus available. The equilibrium masses are calculated. The procedure is repeated for other elements and carbides as outlined for the cases above. At the end of the cycle of computation, the test for equilibrium is applied as done in the first cycle. If equilibrium is not reached, the cycle of computations are repeated until equilibrium is reached. Table 4 lists the carbides formed at each stage of partial equilibrium in the second cycle. The data in tables 3 and 4 are provided for the purpose of illustration. The actual computation was carried out at a higher level of precision. Reporting at the same level of precision in tables 3 and 4 is felt to be not crucial for the purpose of understanding the technique. However, wherever necessary, a higher precision has been used in the reported data.

TABLE 3
 Carbides Formed in Cycle 1 for the Steel of Table 1
 Temperature = 773 K

Carbide	Initial mass (moles)				Mass in carbides (moles)	
	Alloying element		Carbon		Alloying element	Carbide
VC	4.9067	E-3	9.9999	E-3	4.906	E-3
V3C2	2.053	E-8	5.093	E-3	---	---
V2C	2.053	E-8	5.093	E-3	---	---
MoC	5.211	E-3	5.093	E-3	4.122	E-3
Mo2C	1.089	E-3	9.714	E-4	---	---
Cr3C2	9.613	E-3	9.714	E-4	1.425	E-3
Cr7C3	8.188	E-3	2.149	E-5	3.3599E-6	1.43996E-6
Cr23C6	8.185	E-3	2.005	E-5	---	---
Mn7C3	9.102	E-3	2.005	E-5	---	---
Mn5C2	9.102	E-3	2.005	E-5	---	---
Mn3C	9.102	E-3	2.005	E-5	---	---
Mn23C6	9.102	E-3	2.005	E-5	---	---

The same equilibrium state is reached irrespective of the order in which the carbides are considered in the computation cycles. Carbides formed in steels of this type are usually complex, containing more than one alloying element in the metal sub-lattice. They can be non-stoichiometric with respect to the ratio of the number of carbon atoms to that of the metal atoms in the carbide. Simplifying assumptions have been made regarding the nature of the carbides, as mentioned already, and regarding the thermodynamic nature of the solution phase. The aim of this exercise was to demonstrate that the same equilibrium state could be reached irrespective of the path, when several alloying elements and several possible carbides are involved in computation. This system offers a large number of paths to evaluate this technique.

TABLE 4
Carbides Formed in Cycle 2 for the Steel of Table 1

Carbide	Initial mass (moles)		Mass in carbides (moles)	
	Alloying element	Carbon	Alloying element	Carbide
VC	4.9067 E-3	4.9268 E-3	4.9025 E-3	4.9025 E-3
V3C2	4.246 E-6	2.427 E-5	---	---
V2C	4.246 E-6	2.427 E-5	---	---
MoC	5.211 E-3	4.146 E-3	3.523 E-3	3.523 E-3
Mo2C	1.688 E-3	6.227 E-4	---	---
Cr3C2	9.610 E-3	1.572 E-3	2.320 E-3	1.547 E-3
Cr7C3	7.293 E-3	2.500 E-5	1.767 E-6	7.573 E-7
Cr23C6	7.291 E-3	2.424 E-5	---	---
Mn7C3	9.102 E-3	2.424 E-5	---	---
Mn5C2	9.102 E-3	2.424 E-5	---	---
Mn3C	9.102 E-3	2.424 E-5	---	---
Mn23C6	9.102 E-3	2.424 E-5	---	---

The Iron-Chromium-Carbon System

The present technique has been employed to predict the carbides precipitated in the Fe-Cr-C system. Assessed thermodynamic data from reference (1) have been used. In this system, the carbides formed are complex in nature with the metal sub-lattice of the carbide containing both iron and chromium in varying ratios. The carbides $(\text{Cr,Fe})_{23}\text{C}_6$ (M_{23}C_6) and $(\text{Cr,Fe})_7\text{C}_3$ (M_7C_3) are reported to be in equilibrium with the Γ -phase at 13 wt % Cr in the temperature range 1173-1473 K (1). M_3C_2 and M_3C are the other carbides that can form in this system. Initially, the equilibrium was predicted considering only the carbides M_{23}C_6 and M_7C_3 . Subsequently, the same equilibrium could be predicted identically, considering all the carbides that can form in the system, in the computation scheme. In addition to predicting the carbide, the ratio of iron to chromium in the carbide also was obtained at each stage of partial equilibrium. A suitable algorithm was used for this purpose.

The equilibrium predicted was independent of the path. Tables 5-8 give the partial equilibria reached at different stages in the first two cycles for two different paths. Table 9 lists the carbides precipitated at equilibrium at different temperatures for different levels of carbon. The various phase boundaries obtained are consistent with those reported in literature (1) and reproduced in figure 1, in this communication. It has also been possible to verify the liquid-carbide equilibrium projected in the same reference, using the present technique.

TABLE 5

Masses of Carbides Formed in the First Cycle
Starting With the Precipitation of Cr_{23}C_6 (Path-1)
System : Fe-Cr-C Temperature : 1173 K

(13 wt %Cr and 0.26 wt% C)

$\text{M23C6} = (\text{Cr,Fe})_{23}\text{C}_6$ $\text{M7C3} = (\text{Cr,Fe})_7\text{C}_3$

Element	Carbide	Masses of elements (gm.atom)		
		Initial solution	Final solution	Carbide phase
Fe		1.553088	1.549870	0.0032185
Cr	M23C6	0.249952	0.228196	0.0217557
C		0.0216667	0.0109635	0.01070132
Fe		1.549870	1.549823	0.0000467302
Cr	M7C3	0.228196	0.228102	0.0000942979
C		0.0109635	0.0109267	0.0000367899

TABLE 6

Masses of Carbides Formed in the Second Cycle
Starting With the Precipitation of Cr_{23}C_6 (Path-1)
(System and temperature as in table 5)

Element	Carbide	Masses of elements (gm.atom)		
		Initial solution	Final solution	Carbide phase
Fe		1.549823	1.549836	0.00320558
Cr	M23C6	0.22811	0.22836	0.0216821
C		0.0109267	0.01096	0.0106662
Fe		1.549836	1.549789	0.0000936475
Cr	M7C3	0.228176	0.228081	0.000188604
C		0.0109637	0.0109269	0.0000936475

TABLE 7

Masses of Carbides Formed in the First Cycle
Starting With Cr_7C_3 (Path-2)
(System and temperature as in table 5)

Element	Carbide	Masses of elements (gm.atom)		
		Initial solution	Final solution	Carbide phase
Fe		1.553088	1.539282	0.0138067
Cr	M23C6	0.249952	0.223000	0.0269519
C		0.0216667	0.011034	0.0106327
Fe		1.539282	1.539274	0.0000082415
Cr	M7C3	0.223000	0.222945	0.0000547319
C		0.011034	0.011007	0.0000269886

TABLE 8

Masses of carbides formed in the second cycle
starting with Cr_7C_3 (Path-2)
(System and temperature as in table 5)

Element	Carbide	Masses of elements (gm.atom)		
		Initial solution	Final solution	Carbide phase
Fe		1.539274	1.539289	0.0137911
Cr	M23C6	0.2229453	0.223028	0.0268692
C		0.011007	0.0110327	0.0106070
Fe		1.539289	1.539282	0.00000158789
Cr	M7C3	0.223028	0.222975	0.000107471
C		0.0110327	0.0110068	0.0000528644

TABLE 9

Carbides Precipitated at Different Temperatures
for Different Levels of Carbon at 13 wt % Cr in
the Fe-Cr-C System, at Equilibrium

M23C6 = (Cr,Fe) ₂₃ C ₆ (M7C3) = (Cr,Fe) ₇ C ₃		
Temperature (K)	Wt % carbon	Carbide precipitated
1173	0.25	M23C6
	0.26	M23C6+M7C3
	0.28	M7C3
1273	0.27	no carbide
	0.28	M23C6
	0.39	M23C6+M7C3
	0.41	M7C3
1373	0.55	no carbide
	0.56	M7C3
	1.0	M7C3
1473	0.97	no carbide
	0.98	M7C3
	1.05	M7C3

Discussion

A technique is presented in this communication to predict equilibrium precipitation of carbides exploiting the principle of partial equilibrium and that the ultimate equilibrium state is independent of the path followed to reach that state. This technique can be applied to systems involving the precipitation of carbides, nitrides, oxides etc. The algorithm used in the present case predicts the carbides in equilibrium with a single solution phase like the α -, β -, Γ - or the liquid phase which is declared a priori. Work is in progress to develop a scheme that can predict the solution phase also, apart from the equilibrium carbides.

Summary

It is demonstrated that the principle of successive partial equilibria can be successfully employed to predict the equilibrium precipitation of carbides in steels. The predictions made using this technique are consistent with published information in the Fe-Cr-C system which has been considered for illustration.

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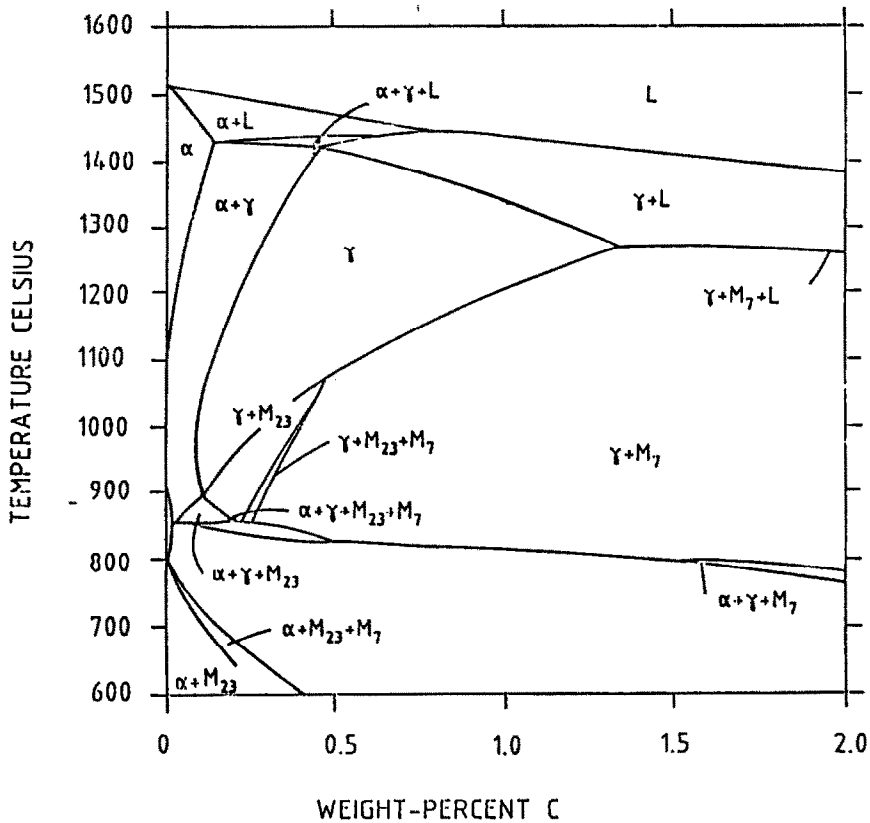


FIG. 1

The Vertical Section of the Fe-Cr-C System at 13 wt% Cr (from ref.1)