

Titre du document

**Review of the gas/Ni-base alloys interactions
in HTR impure helium**

MOTS-CLES : HTR, helium impurities materials

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RESUME – CONCLUSIONS

A review of the literature has been performed to summarise the basic mechanisms of the interaction between impure helium and metallic materials in HTR reactors. The reactivity of the helium environments and the basic reactions involved in the interaction between Ni-base alloys and impure helium are presented as well as their consequences on the behaviour of Ni-base alloys.

In this report, emphasis is given to the effect of environment chemistry in order to make recommendations for the specification of impurities in future HTRs to obtain the safest behaviour of Ni-base alloys.

The main points are the following ones :

- due to the low partial pressure of impurities, the impure helium is not in thermodynamic equilibrium because homogeneous reactions are much too slow and dwell time too short. In addition a limited number of surface reactions are possible,
- the interaction with the metallic surfaces may be rationalised by characterising the impure helium by 3 parameters that control the surface reactions :
 - the $\frac{P_{H_2O}}{P_{H_2}}$ ratio which is the "efficient" oxygen activity, even if the actual partial pressure of oxygen may be much lower than expected from this ratio,
 - the carbon activity, controlled either by the ratio $\frac{P_{CO}}{\sqrt{P_{O_2}}}$ or by the kinetic constant of methane and water decomposition on the surfaces,
 - the partial pressure of carbon monoxide P_{CO} , which controls the splitting of CO and the so-called "microclimate" reaction between chromium oxide and chromium carbide.
- These parameters may be used to build up "stability diagrams" which allow to predict the behaviour of the nickel base alloys in HTR helium. These diagrams depends on the temperature and on the composition of the alloy. They can be built from theoretical arguments and short term experiments. Thus a complete tool to establish the behaviour of Ni-base alloys in HTR environments is available.
- The interaction of impure helium with Ni-Cr-X alloys may lead to 5 types of behaviour corresponding to 5 domains of the "stability diagrams" :
 - formation of a protective chromium oxide that slows down the carburisation of the base metal (safest situation),
 - formation of a surface layer of carbides with underlying oxide and carburisation of the base metal
 - formation of a poorly protective oxide layer with decarburisation of the base metal
 - no oxide and rapid decarburisation
 - no oxide and rapid carburisation.

These three last cases occur in the domain of the so-called "microclimate reaction"

- To allow the formation of a protective oxide layer that strongly decreases the carburisation of the underlying material the helium impurities must satisfy the 3 following requirements:

the partial pressure of CO, the $\frac{P_{H_2O}}{P_{H_2}}$ ratio and the $\frac{P_{H_2O}}{P_{CH_4}}$ must be in excess of critical values

which increase with the temperature and decrease with the Cr and Mo content of the alloy.

- Minor, highly oxidizable elements (Mn, Al, Si, Ti) can significantly modify the behaviour of the Ni-base alloys but their effect can be complex and no predictive modelling is available.

I - BACKGROUND

The Helium coolant of the HTR reactors inevitably contains some impurities among them some are reactive and may interact with the core graphite and with the metallic materials and may cause some loss or damage of their properties.

The active impurities of Helium are species containing C, O and H i.e. O₂, H₂, H₂O, CO₂, CO and CH₄. The amount of these impurities is very low in the HTR helium with a total impurity content not exceeding few hundreds of μbars.

Basically these impurities can be separated in oxidising and carburising species:

Water may oxidise some metals and, in favourable circumstances, promote the formation of protective oxide layers which decrease the degradations of the underlying metal. Higher the temperature and higher the hydrogen content, less oxidising is the water.

Methane may be decomposed on metal surface leading to the formation of metal carbides. Higher the temperature, lower the stability of the methane and greater its carburising potential

Carbon monoxide can decompose to simultaneously cause metal oxidation and formation of carbides, leading to non-protective surface layers. Higher the temperature, more stable the carbon monoxide and less prone to oxidise and carburise the alloys.

Carbon dioxide can also be oxidising, but when the temperature exceeds 750/800° C, its content becomes negligible.

Depending on their relative concentrations and on the helium temperature, the interaction of these impurities with metallic materials may or may not lead to alloy oxidation and may cause alloy carburisation or decarburisation. Damages to the metallic materials may be surface damages with the formation of surface films involving oxide and/or carbides. But, due to the high temperature of the helium, carbon and oxygen may diffuse to significant depths into the metallic matrices and cause structural changes due to internal oxidation or, more commonly, to carburisation or decarburisation. Thus, damages may result from the loss of material as in most corrosion problems, but also from a loss of mechanical properties on significant thickness of material, with either a loss of strength or a local embrittlement which can favour the initiation of cracks. Intergranular damages can be particularly harmful because they can favour crack initiation.

II – ORIGIN OF HE IMPURITIES

The figure 1 summarises the main sources of impurities in the HTR reactors operating in the 70's.

Water [1, 2]

In the reactors operating with secondary water circuit, water originated from boiler leakages. Studies performed in Dragon and the experience gained from CO₂ cooled UK reactors indicate that the likelihood of steady state leaks is low: small leaks tend to seal [2, 3] whilst large leaks increase rapidly and require remedial actions. Water may also enter the circuit through porous welds in cooler circuits.

The use of water lubricated bearings in the circulators of GA HTR's has been reported as a possible source of steady state injection of water or a temporary injection during reactor start-up or shutdown [2].

In the early stages of operation of a reactor, water will be degassed from thermal insulation materials and from core and reflector graphite. Small quantities of water will also be introduced during refuelling, shutdown and maintenance periods.

Finally some water may be generated by the reduction of metal oxides (on structural materials) by hydrogen. This has been confirmed by injection experiments in the Dragon reactor.

In normal operation, small amounts of water of the order of μ bars or less are expected.

Hydrogen [1, 2, 4]

Hydrogen can arise in the primary circuit from the water side of boiler, cooling circuits, followed by proton diffusion through the wall of the tubes. In process heat reactors, hydrogen from a process stream may diffuse into the primary circuit through the heat exchanger walls.

Relatively high partial pressure of hydrogen of the order of hundreds of μ bars may be present in HTR helium [5].

Carbon monoxide [1, 2, 5]

It comes from the oxidation of graphite in the core by oxygen or water, from desorption of fresh fuel elements and from water-gas reaction. Partial pressures of several tens of μ bars are expected.

Carbon dioxide

Its concentration depends on the equilibrium with carbon monoxide (Boudouard reaction). No significant partial pressure of carbon dioxide is expected at high temperature ($> 750^{\circ}\text{C}$).

Nitrogen

Nitrogen is usually present in the impure Helium. Its role seems to be always negligible at least in the temperature range investigated in the 70's [4], even if Fujioka [6] mentions that alloy nitriding is a risk to be considered. From past experience, partial pressures of nitrogen of several tens of μ bars are expected [5].

Methane

The methane is produced by the radiolytic graphite-hydrogen reaction at low temperature, and it is decomposed by thermal cracking at high temperature in the core [5]

Oil [1, 2]

Some oil vapour may arise from the operation of circulators, compressors or pumps having oil lubricated bearings or diaphragms. The oil will pyrolyse in the core to produce H_2 and some CH_4

Degassing [1, 2]

The structural steel of the pressure vessel and other internal components will desorb H_2O at a rate which relates to temperature and time.

The graphite reflector and the other core components will desorb H_2O , H_2 , CO , CO_2 , N_2 , CH_4 , etc. again in quantities and proportions which relates to operating temperature and time. At low temperatures and early times H_2O together with CO , H_2 , .. will be desorbed. At higher temperatures and after extended operation, chemisorbed species will arise which in general will be dominated by H_2 and CO . This means that the balance of the impurities will progressively become more "reducing" with time.

A major source of water in the initial phase of operation will be associated with insulation materials such as mineral wool or fibres. The use of impure baked carbons such as "Kholstein" in the AVR reactor has led to lengthy degassing processes to remove several hundred kg of sorbed water.

Long term behaviour of impurity levels in helium [7]

From a study of the evolution of impurities in the AVR, Nieder shows that the impurity present in the helium exhibit some more or less constant ratios between hydrogen, water and carbon monoxide. These ratios are not those expected from thermodynamics or reaction kinetics because of absorption and desorption on porous graphite.

These ratios can be characterised by a "core reactivity" (defined as $R_C = \frac{\text{amount reacting}}{\text{amount present}}$ for a given reactive species) which is characteristic of the core structure, purification constant and temperature.

III – POSSIBLE INTERACTION OF METALLIC ELEMENTS WITH He IMPURITIES

The metallic alloying elements exhibit different behaviours with the Helium impurities [4, 5, 8] :

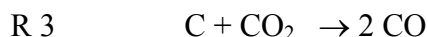
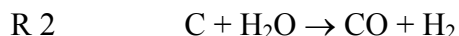
- Fe, Ni and Co can never be oxidised nor carburised and cause no problem regarding their interaction with impure Helium; However, Co is undesirable due to the formation of active isotopes,
- Cr may or may not react depending on the conditions and it is able to form both oxide (Cr_2O_3) and carbides (Cr_7C_3 , Cr_{23}C_6 or even Cr_3C_2). The behaviour of most alloys is controlled by the behaviour of chromium and more precisely, by the ability to form a protective film of chromia,
- Mn may be oxidised and it is found associated with chromium oxides,
- Mo and W form stable carbides but no oxides. In particular the volatile MoO_3 oxide is not formed at the oxygen potential of the impure He [4]. Mo can enter chromium carbides M_6C which can have a wide range of composition and are more stable than the pure chromium carbides,
- Al and Si may form stable oxides which cannot be reduced,
- Ti and Nb may form oxides and carbides. However neither surface carbides nor NbO oxide have been found. The role of Ti is rather complex: it may have an important effect in preventing internal oxidation of Al [5, 8, 9] but it is also claimed to be deleterious [4] because behaving like Aluminium. High Ti and Al alloys have been reported to suffer accelerated oxidation [10] . The effect of temperature on the role of Titanium should be looked in more detail. Niobium could be an important alloying element for alloys used in HTRs [4]

IV – REACTIVITY OF IMPURE HELIUM

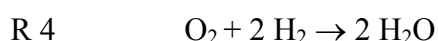
Gas phase is not in thermodynamic equilibrium

One specificity of the helium environment is that the partial pressure of the impurities is very low (of the order of few Pa to few tens of Pa) and this makes very low the probability of collision of impurity particles and thus the gas/gas reaction rates are very low [11]. Indeed, it has been verified up to 1050°C that, in the absence of metal surface, no measurable change of impurity composition occurs in an experimental helium loop with a dwell time of about 10 s, i.e. much greater than the dwell time in a HTR reactor [12]. This is why, the gas phase is not in thermodynamic equilibrium and reactions which should not occur simultaneously may be possible. This is also why Brenner [11] claims that it is not possible to describe the helium environment by the classical thermodynamic potentials of carbon and oxygen. The reasons for that are that:

1. the reaction R 1, R 2 and R 3, which occur in the core, are much faster on the high temperature graphite surfaces in the reactor core than the corresponding reverse reaction in the cooler metallic surfaces of the circuits [1, 2]. Thus, owing the very short dwell times in each part of the circuit there is no chance for the equilibrium to be reached out of the core.



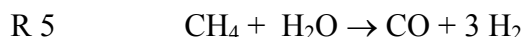
2. In the core, the reaction R 1 is quite fast and it eliminates most of the oxygen in the helium. However, the reaction R 2 is slower and leaves some traces of water [13] in the gas and thus, the $\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$ ratios may be much higher than expected from the equilibrium of the reaction R 4:



This is why, when evaluating the oxidizing potential of the impure Helium it is necessary to take into account not the actual partial pressure of oxygen but rather the ratio $\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$. This is what Quadakkers [14] uses to do even though he expresses this ratio as an oxygen activity:

$$(1) \quad p_{\text{O}_2} = K_4 \cdot \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^2$$

Similarly, the equilibrium of the reaction R 5 is not reached in the gas and the partial pressure of CH_4 present in the gas can be far in excess of the equilibrium.



In practice, the impurity content of the Helium will result from the dynamic equilibrium of impurity ingress, reactions in the core, purification process [11], and, to some extent reactions on metal surfaces.

Surface reactions

In the literature, most of the discussions only refer to Cr reactions which are those which control the behaviour of high chromium Ni(Co) based alloys in high temperature gaseous atmospheres. In this report the metal/gas interaction will be described in more detail for chromium and few elements will be given for other elements such as Mo, Al, Ti and Si, mainly in terms of modification of the behaviour of Ni-Cr alloys.

Several authors have attempted to describe the surface reaction in high temperature helium (see for example Menken et al. [5]), but the most comprehensive approaches come from two main series of papers respectively from Brenner and Quadakkers that present two self consistent approaches of the surface reactions on metallic materials which can be directly used to predict the behaviour of Ni based alloys in HTR environments.

The Brenner approach [11, 15]

In impure Helium atmospheres no homogeneous reactions are possible (see above) but surface reactions on metallic surfaces are possible. However, the "low partial pressure principle" [11] implies the following points:

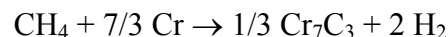
1. the only possible reactions are those which combine one gaseous molecule with one solid species to form one or more gaseous and/or solid species,
2. solid compounds which require more than one molecule of gas for their formation are built by

surface diffusion and combination of simple chemisorbed complexes, formed through above processes. For example the formation of Cr_2O_3 occurs from Cr via Cr-O complexes.

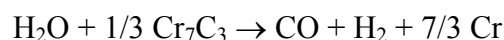
This lead Brenner to define 5 possible surface reactions which are possible in the Helium on Cr bearing materials :

R 6 – Chromium oxidation by water vapour $\text{H}_2\text{O} + 2/3 \text{Cr} \leftrightarrow 1/3 \text{Cr}_2\text{O}_3 + \text{H}_2$

R 7 – Decomposition of methane and formation of chromium carbides¹



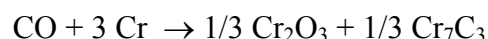
R 8 – Attack of carbides by water with formation of carbon monoxide



R 9 – Attack of carbides by water with formation of methane



R 10 – Splitting of CO



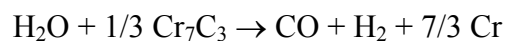
Due to the limitations presented above, some of these reactions are possible in the two directions (R 6) but most are unidirectional due to the lack or to the excessive number of intermediate adsorbed compounds required by the reverse reaction.

The reaction R 10 requires more attention. It is not directly possible in the reverse direction because it would involve two solid species, but fast reverse reaction may result of the simultaneous occurrence of two other reactions involving H_2O and H_2 . This has been called by Brenner "the microclimate reaction" because it is of major importance in the pores of the surface layers of metallic materials.

The two relevant reactions are:

Reversed R 6 – reduction of chromium oxide by hydrogen $1/3 \text{Cr}_2\text{O}_3 + \text{H}_2 \rightarrow \text{H}_2\text{O} + 2/3 \text{Cr}$

R 8 – Attack of carbides by water with formation of carbon monoxide



Adding these two reactions leads to the reversed reaction R 10:

R 11 = Reversed R 10 – the "microclimate reaction" $1/3 \text{Cr}_2\text{O}_3 + 1/3 \text{Cr}_7\text{C}_3 \rightarrow \text{CO} + 3 \text{Cr}$

Although no significant gas/gas reaction can occur, a consequence of the "microclimate reaction", is that local thermodynamic equilibrium of the reaction R 5 can be reached close to the reacting metal surface provided chromium oxide and carbide are simultaneously in contact with the gaseous phase.

R 5 $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2$

The diffusion controlled layer of gas, which must contains H_2 and H_2O , bridges the gap between

¹ The decomposition of methane as well as the splitting of carbon monoxide result in the formation of carbides because, according to Brenner [11], the carbon deposition at the temperature of interest is not thermodynamically possible. But no justification of this assertion is given and other authors seems to consider the possibility of carbon deposition.

Cr₂O₃ and Cr₇C₃ allowing these species to be reduced into Cr and to form CO even if they are not in close contact.

Critical conditions for the surface reactions

At a given temperature, this "microclimate reaction" R 11 occurs only if the partial pressure of CO is lower than a critical value P_{CO}^* . Conversely, at a given partial pressure of CO, this reaction occurs above a critical temperature called the "microclimate temperature" T_A .

In the same way, the oxidation of chromium R 6 occurs only if the oxidising power is in excess of a critical value expressed by a critical $\frac{P_{H_2O}}{P_{H_2}}$ ratio.

According to Brenner, the "interference" of carbide and oxidation due to R 7 and/or R 10 result from a competition between these reactions and the oxidation of chromium(R 6) and, thus they occur when critical ratios $\frac{P_{CH_4}}{P_{H_2O}}$ and/or $\frac{P_{CO}}{P_{H_2O}}$ are exceeded. Similarly, the attack of carbides by water (reactions R 8 and/or R 9) occur as soon as $\frac{P_{CO}}{P_{H_2O}}$ and $\frac{P_{CH_4}}{P_{H_2O}}$ are lower than critical values.

According to Brenner [11], all these critical values or ratio require experimental determination either because the lack of precise thermodynamic data (for example the actual activity of chromium in complex alloys [15]) or because they result from kinetic constants.

The Quadakkers approach [14, 16, 17]

The Quadakkers approach is quite close to the Brenner approach when considering the main reactions even if the formulation is somewhat different and the surface reactions are not as clearly identified as in the work of Brenner. The main difference with the Brenner approach is that besides thermodynamics considerations Quadakkers goes into kinetics considerations which allow a better description of the limits between carburisation and decarburisation of the materials.

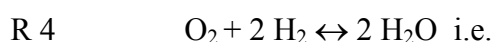
In the original papers, Quadakkers does not specify the detail of surface reaction involving the carbon and he uses the notation [C] for the "carbon deposited on the surfaces" whatever its form may be. In actual atmospheres, we have seen that carbon cannot be deposited on the metallic surfaces as a carbon phase but rather as metallic carbides (usually chromium carbides). Thus in the following paragraph, and following Brenner, we have replaced in all the surface reactions, the general notation [C] used by Quadakkers by the one of the chromium carbides most frequently formed in Ni-base alloys i.e. Cr₇C₃.

Oxygen and carbon activities

Contrarily to Brenner, Quadakkers defines activities of oxygen and carbon in the helium gas as follows:

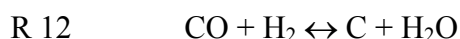
1. In the absence of methane

- the activity of oxygen (expressed as P_{O_2}) comes from the equilibrium of the reaction R 4:



$$(2) \quad p_{O_2} = K_4 \cdot \left(\frac{P_{H_2O}}{P_{H_2}} \right)^2$$

- the activity of the carbon comes from the equilibrium of the reaction:



$$(3) \quad a_c = K_{12} \cdot \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

The carbon activity a_c can be written in the following form:

$$(4) \quad a_c = K_{12} \cdot \sqrt{K_4} \cdot \frac{P_{\text{CO}}}{\sqrt{P_{\text{O}_2}}} = \frac{1}{\sqrt{K_1}} \cdot \frac{P_{\text{CO}}}{\sqrt{P_{\text{O}_2}}}$$

where K_1 is the equilibrium constant of the reaction R 1



Thus, in helium, P_{O_2} , a_c and P_{CO} are not independent variables since they are bound by the relation (4). In addition a thermodynamic calculation shows that between 800 and 950° C the equilibrium partial pressures of CO_2 and CH_4 are negligible.

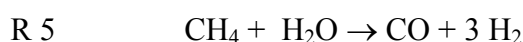
It is worth noticing that **this formulation does not assume that the equilibrium is reached** in the helium gas but rather **it allows to calculate free energies for the possible surface reactions** by calculating P_{O_2} and a_c from the actual values of CO , H_2 and H_2O partial pressures in the helium environment,

From these definitions of carbon and oxygen activity and their relation with CO content, Quadakkers introduces a very convenient stability diagram to plot the thermodynamic description of the helium environments (figure 2).

In these diagrams, the fact that P_{O_2} , a_c and P_{CO} are not independent variables implies that the point corresponding to a helium atmosphere lies on a oblique line corresponding to the partial pressure of CO in the environment.

2. In the presence of methane

If equilibrium would be reached, methane would completely decompose water according to the reaction R 5:



And the remaining methane would lead to the carburisation reaction R 13:



This would yield to theoretical carbon activity far over 1 (actually values of the order of 10^3 can be calculated in some instances) which would lead to a strong carburisation potential with an effective carbon activity of 1.

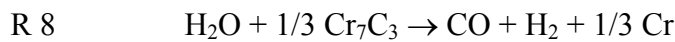
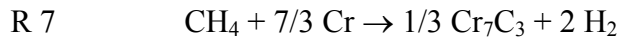
In this case, the oxygen partial pressure which can still be related to the carbon activity through the relation (4) becomes (see the corresponding point on the diagram of the figure 2):

$$(5) \quad P_{\text{O}_2} = \frac{1}{K_1} (P_{\text{CO}})^2$$

In fact, the reactions leading to methane decomposition are relatively slow and a better estimation of the carbon activity on the reacting surfaces can be obtained from kinetic arguments.

3. Kinetic approach of surface reactions involving carbon

Regarding the carbon transport to or from the metal surfaces, two competing reactions occurs in the presence of methane and water, the reaction of decomposition of methane R 7 and the attack of carbides by water R 8.

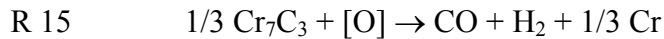
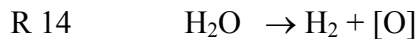


The fact that the kinetic of the reaction R 7 is much lower than that of the reaction R 8 may dramatically lower the activity of carbon on reacting surfaces in a flowing gas, as shown by Williams et al. [18]. The actual activity of carbon may be obtained from kinetic calculations but this requires experimental data on the kinetics of both R 7 and R 8 reactions.

Quadackers, following an approach identical to that of Williams et al., derived an expression of the carbon activity as a function of the $\frac{P_{\text{CH}_4}}{P_{\text{H}_2\text{O}}}$ ratio and kinetic factors.

This approach involves the following assumptions:

1. the reaction R 8 is in fact the result of two partial reactions :



From experimental results [19], Quadackers assumes that the reaction R 15 is fast and, thus, the kinetics of the reaction R 8 is controlled by that of the decomposition of water on the metal surfaces R 14.

2. the reactions R 7 and R 14 are of first order regarding the partial pressure of respectively methane and water. It is worth noticing that Williams et al. found more complex kinetic laws for the same reactions on nickel and iron in presence of much higher partial pressures of methane and water.

According to these assumption, Quadackers is able to derive an expression of the carbon activity on metal surfaces a_c^{ss} in a flowing gas containing low partial pressure of reactive species :

$$(6) \quad a_c^{\text{ss}} = a_c^{\text{eq}} \frac{1}{\left(1 - \frac{k_7 P_{\text{CH}_4}}{k_{14} P_{\text{H}_2\text{O}}}\right)}$$

where a_c^{eq} is the carbon activity in the absence of methane, given by the equation (4)

and k_7 and k_{14} are the rate constant of the reactions R 7 and R 14.

From specifically designed experiments, Quadackers [19] confirmed that the rate constant k_7 is much lower than k_{14} , the ratio $\frac{k_{14}}{k_7}$ being in excess of 100 in the conditions of the experiments performed at 900 and 950° C. As a consequence, methane has no large effect on the carbon activity on metal surfaces

as long as the $\frac{P_{CH_4}}{P_{H_2O}}$ ratio does not exceed the $\frac{k_{14}}{k_7}$ ratio i.e. values in excess of 100 (figure 3). This result accounts for the general observation that the presence of water strongly decreases the carburising potential of the methane in impure helium [5, 10, 18-23] and the use of $\frac{P_{CH_4}}{P_{H_2O}}$ ratio as the main parameter controlling the carbon activity in the helium atmosphere is in agreement with the Brenner analysis.

V – INFLUENCE OF HELIUM IMPURITY CONTENT ON THE INTERACTION HELIUM/METALLIC MATERIALS.

Molybdenum based materials may exhibit a good resistance to degradation by helium atmospheres, with no formation of oxides and, if the carbon activity is high enough, the formation of a Mo_2C scale and some carburisation of the underlying metal on a very limited thickness [8, 24] but no more detail will be given about these alloys owing to few mentions in the available literature.

Besides Ni base alloys which are protected by a chromium oxide film, alloys with lower Cr and high Al and/or Ti contents are considered for use at very high temperature [25, 26]. As the formation of chromium oxides in atmospheres with low oxidising potential becomes more and more difficult as the temperature increases, the resistance to carburisation of these materials rely on the formation of a Ti or Al oxide layer. The effect of helium chemistry on these materials will only be shortly mentioned in the part of paragraph V.2 dealing with the minor oxidizable elements.

Thus, the following paragraph only deals with nickel-base, high Cr materials, but this could apply to cobalt base alloys as Co and Ni do not interfere with the helium atmosphere.

V.1 – Effect of the helium impurities in the interaction with Ni base alloys with high Cr content

To describe these effects, two graphic representations have been proposed by Brenner (TEA diagrams – see figure 10) and by Quadakkers (see figure 2). These representations are based on the stability diagram of chromium oxide and chromium carbides as a function of the impurity content of the helium expressed as :

- P_{H_2O}/S , P_{CH_4}/S and P_{CO}/S (where $S = P_{H_2O} + P_{CH_4} + P_{CO}$) for a given P_{H_2} by Brenner
- the carbon and oxygen activity a_c and P_{O_2} by Quadakkers (figure 2).

This last diagram is more convenient as it involves directly the two main potentials of interest for material behaviour i.e. the oxidising and the carburising potentials.

In addition, the use of TEA diagrams is made difficult by the fact that the diagram depends both on the hydrogen partial pressure and on the parameter $S = P_{H_2O} + P_{CH_4} + P_{CO}$. Thus, it is impossible to represent environment changes (for examples local changes in surface layer pores, or in crevices) on a single diagram, even for a given temperature.

For these reasons, and for the sake of simplicity of the presentation we will only use the Quadakkers stability diagrams to describe the different possible kinds of damages that can be expected from helium impurities on a Cr bearing material.

Stability diagrams and behaviour of Ni-Cr alloys

The behaviour of Ni-Cr alloys in HTR helium is primarily controlled by the Cr compounds which are stable in the relevant conditions, as they will determine the possible surface reactions.

The figure 2 shows, for a temperature of 950° C, the domains of stability of:

- metallic chromium, at low a_c and P_{O_2} levels,
- chromium oxide at high P_{O_2} levels and
- chromium carbides at high a_c levels.

In fact, the stability diagram is more complex since several chromium carbides may be stable (figure 4). However, in the following discussion only one chromium carbide will be considered.

At lower temperature, the figure 5 shows that metallic chromium exhibits a smaller area of stability, that means that the formation of oxide and carbide requires respectively increasing oxidising and carburising potentials when the temperature increases.

In the stability diagrams, 7 different domains combining the different possibilities regarding the phase stability and the possible surface reactions have to be considered to

as regards the corrosion behaviour of Ni-Cr materials. The figure 6 shows these regions and summarises the corresponding behaviour of the Ni-Cr materials:

- In the region III-a, chromium oxide is stable ($P_{O_2} > P_{O_2}^s$). Thus, the formation of a protective layer on the alloy is possible. In addition, the carbon activity is in excess of the critical value for the formation of carbides ($a_c > a_c^s$). Thus, chromium carbides can be formed below the oxide, where the oxygen activity is low enough. Thus, both alloy oxidation and carburisation are possible, but, in many instances, the oxide film can limit the carburisation by limiting the access of carburising species to the metal surface. Provided that the oxide film is protective, **this region of the diagram is the safest region regarding the material degradation**, with light formation of carbides below the oxide layer.
- In the region III-b, chromium oxide is still stable but the carbon activity is too low for the chromium carbide to be stable. Thus, reduction of the carbide by water is possible. Decarburisation of the base metal may occur but it will be slow if the oxide layer is compact.

However, according to Quadackers (figure 7), the practical situation may be different in the domain III-b, depending on the porosity of the oxide layer. If the oxide pores are so large that the local gas composition is the same as that of the bulk, the expected severe decarburisation will occur (left side of the figure 7). But if the oxide pores are small, the gas in the pore is not rapidly renewed and it can be equilibrated at the metal/oxide equilibrium, i.e. at an oxidising potential lower than in the bulk gas phase (right side of the figure 7). Due to the relation (4) between a_c and P_{O_2} at constant CO partial pressure, the local decrease of oxygen activity causes a local increase of carbon activity which makes the decarburisation impossible. Thus, like the region III-a, the region III-b maybe a safe region, provided the oxide layer exhibits small pores (which is of course also a requirement for this layer to offer some protection against oxidation).

- In the region IV-a, chromium carbide is stable and a non-protective surface layer of chromium carbides may be formed that allows internal carburisation of the material. However, at the carbide/alloy interface, the carbon activity is lower than in the bulk gas and, since $P_{O_2} > P_{O_2}^s$, a chromium oxide film may be formed below the carbide surface layer. However, this oxide is not very protective and cannot hinder further internal carburisation. Thus, this region is not safe for the Ni-Cr materials.
- In the region IV-b, carbon activity is high and carburisation may occur. If the porosity of the carbide surface layer is not too large, an oxide layer may be formed below the carbide layer due to a similar mechanism which have been described for the region III-b (local decrease of carbon activity to a_c^s and local increase of oxygen activity over $P_{O_2}^s$). In this case, the behaviour of the alloys are quite similar in regions IV-a and IV-b.

- In the region I, metallic chromium is stable, no protective layer can be formed and a strong decarburisation will occur.
- In the region II, chromium oxide is stable, but the low carbon activity will result in alloy decarburisation. Due to the gas evolution resulting from the decomposition of the carbides the protective character of the oxide layer cannot be maintained [11].

It is worth noticing that the material may exhibit safe behaviour only if the partial pressure of carbon monoxide exceeds a **critical value** P_{CO}^* . Below this critical partial pressure no protective layer can be formed and the alloys exhibits severe damages either by carburisation or by oxidation and decarburisation. This corresponds to the "microclimate" reaction of Brenner [11, 15]. Below the critical partial pressure of CO, chromium oxide and carbide cannot coexist. If oxide are stable the decomposition of matrix carbide cause CO evolution which does not allow a compact oxide film to be maintained [11]. If oxide is not stable, the base metal is not protected and severe carburisation or decarburisation occurs according to the carbon activity.

Effect of chromium depletion of the substrate

On the diagram of the figure 6, the limits of the domains are somewhat modified by the fact that the oxidation or the carburisation changes the chromium activity of the surface material in contact with helium atmosphere. Since the stability region of the metallic chromium increases when the chromium activity decreases (figure 8), the critical partial pressure of CO (P_{CO}^*) increases with the surface chromium depletion. Deeper the surface chromium depletion, larger the shift of P_{CO}^* . Taking into account this effect leads to stability diagrams like the one of the figure 9. On these modified diagrams the value of the shift in P_{CO}^* results from kinetic factors:

- the diffusion coefficient of the chromium in the base metal,
- the oxidation or carburisation rate of the alloy.

Quadackers [19] has developed an experimental and theoretical approach based on the classical Wagner theory of oxidation to calculate the chromium activity at the metal oxide interface and to predict the subsequent modification of the stability diagrams in the region III which is of practical interest. In the region IV the same approach could be used but the kinetics of the formation of the carbides layers is not well known and the prediction are less accurate.

TEA diagrams and material behaviour

The analysis performed by Brenner [11, 15] is summarized in the figure 10. Like in the stability diagrams, different material behaviours are separated by several critical lines. Even though each line corresponds either to a possible reaction, no kinetic argument is invoked to predict the position of these lines as long as the reactions are not fast enough to be considered at the equilibrium (particularly in the case of the decomposition of methane) and to predict the effect of surface chromium depletion. Thus, these diagrams must entirely be obtained from experiments [15].

V.2 – Effect of other alloying elements on Ni-Cr alloys with high Cr content

Among the alloying elements of Ni-Cr base alloys, those which are reactive in the HTR environment must be taken into account when analysing the gas/metal interaction.

The **molybdenum** cannot be oxidised but it can form carbides (in Mo alloys) and in Ni-Cr alloys it can enter the M_6C chromium carbides. This has two consequences:

- the domain of stability of chromium carbide is significantly increased towards lower carbon activity, and this increases the resistance to decarburisation. In particular, the critical partial pressure of CO (P_{CO}^*) required to avoid the "microclimate" reaction and to allow a fair protection of

the alloy surface is decreased by the presence of molybdenum in the Ni-Cr alloy [19].

- the M_6C carbides have a large composition domain. Thus, the stability lines of carbides change with the Mo activity (figure 11). In particular, the stable coexistence of pure chromium oxide and carbide is not possible in Ni-Cr but it becomes possible in Ni-Cr-Mo alloys (between the lines 4 and 6 of the diagram of the figure 11) and indeed mixture of oxide and carbides have been obtained in helium atmospheres on Ni-Cr-Mo alloys [8].

The very oxidizable elements (Mn, Al, Ti and Si) strongly increase the stability of the chromium oxide, may change the morphology of the oxide films and, in particular situations, may form their own oxide layer (alumina):

- **Manganese** may enter the chromium oxide layer [19, 27]. High Mn contents [27] and/or high temperature ($> 950^\circ \text{C}$) [19] causes the formation of spinel oxides $MnCr_2O_4$. There are some discrepancies in the appreciation of the effect of Mn. According to Shindo et al. [27], the effect of Mn is always beneficial, particularly at high levels when the spinel phase may be formed. According to Quadackers [19], the effect of Mn which is beneficial at low temperature but it becomes deleterious above 950°C because of the formation of spinel oxide whiskers that are very prone to spallation [28]. Huddle [4] considers that Mn should be avoided for use in HTR environments.
- **Aluminium** is always oxidizable but it does not form carbides. At low levels it causes internal oxidation [4, 29], particularly intergranular oxides [27, 29, 30]. For very low levels of water, i.e. for very low oxygen activity, protective layers of Al_2O_3 can be formed [4, 8, 23].
- **Titanium** has a very complex and controversial effect. It can enter the chromium oxide [17, 20] and it is mentioned that this makes the oxide film less protective [20] and/or more porous (ref to retrieve). It also can form a Ti oxide when the oxygen activity is very low or if high concentrations of Ti are present in the alloy [31]. But it can also stimulate the formation of intergranular network of oxides in conjunction with aluminium [29]. By reacting with carbon, it can participate to the formation of harmful plate-like carbides in the matrix below the surface depleted zone [4]. Thus, in many circumstances, it is considered to be deleterious either as regards the oxidation [10] or the carburisation, particularly at high temperature when diffusion is fast [4].
- **Silicon** seems to behave very similarly to aluminium [4, 19] as regards internal oxidation. However, Shindo [27] found a beneficial effect as it increases the adherence and the resistance to spallation on Hastelloy X.

A particular effect of the very oxidizable species is they cause transient behaviour to occur in the early times of exposure to helium. This is related to their low concentration and their high reactivity. As soon as the material is exposed to the impure helium, these elements are rapidly oxidised. When they do not form a protective layer, their surface activity becomes rapidly much lower than that of the bulk alloy. This effect is very similar to the chromium depletion effect previously mentioned and it may significantly change, not only the mechanical properties of the alloy [29], but also the stability of chromium oxides and carbides on the alloy surface. In some instances, this leads to the change from initial carburisation to subsequent decarburisation of the alloy [10, 19]

VI – RECOMMENDATIONS FOR THE SPECIFICATION OF HTRS ENVIRONMENTS

From the above analysis of the available knowledge of the interaction of metallic materials with impure helium, very basic rules can be derived to specify the acceptable impurity levels in HTR helium for the Ni base alloys with high Cr content.

Basically, the safest conditions are those that allow the formation of a stable oxide layer on the alloy.

This requires three conditions :

- **the partial pressure of CO must be in excess of a critical value P_{CO}^* ,**
- **the oxygen activity must be large enough** for the chromium oxide to be stable in the bulk environment, even on chromium depleted surfaces. This implies that the water level of the environment is high enough, i.e. the ratio $\frac{P_{H_2O}}{P_{H_2}}$ has to be in excess of the equilibrium value of the reaction of oxidation of chromium by water R 6
- **the ratio $\frac{P_{CH_4}}{P_{H_2O}}$ has to be lower than a critical ratio** related to the kinetic constants of the reactions R 7 and R 14. This ratio is estimated to be in excess of 100 around 900/950° C but it obviously depends on the temperature and the nature of the reactive surfaces [18].

These critical values are dependant on :

- **the temperature of the helium** : higher the temperature, higher the required partial pressures of CO and water,
- **the nature of the alloy**:
 - higher the Cr and Mo content, lower the critical CO partial pressures and $\frac{P_{H_2O}}{P_{H_2}}$ ratio,
 - the presence of minor oxidizable element will also change these critical values but no predictive capability is available.

In specifying the impurity levels of helium, it is also necessary to specify that the design should avoid crevice zones in high temperature areas, particularly in the presence of methane. Since the partial pressure of water will be low, it can be rapidly consumed in areas of restricted mass transport and the $\frac{P_{CH_4}}{P_{H_2O}}$ ratio can sharply increase and cause the local environment to be located in the area IV of the stability diagram resulting in a severe carburisation. This effect has been observed in laboratory experiments [21].

The use of low Cr, High Ti or Al alloys in the hottest components, such as turbine blades where chromium oxide becomes less stable require different helium specifications with an upper limit of the $\frac{P_{H_2O}}{P_{H_2}}$ ratio, since their protective layer is better formed in very dry atmospheres,

Thus, the simultaneous use of both type of alloys at different temperatures would rely on a compromise on the oxygen activity of the helium and a tight control of the water content.

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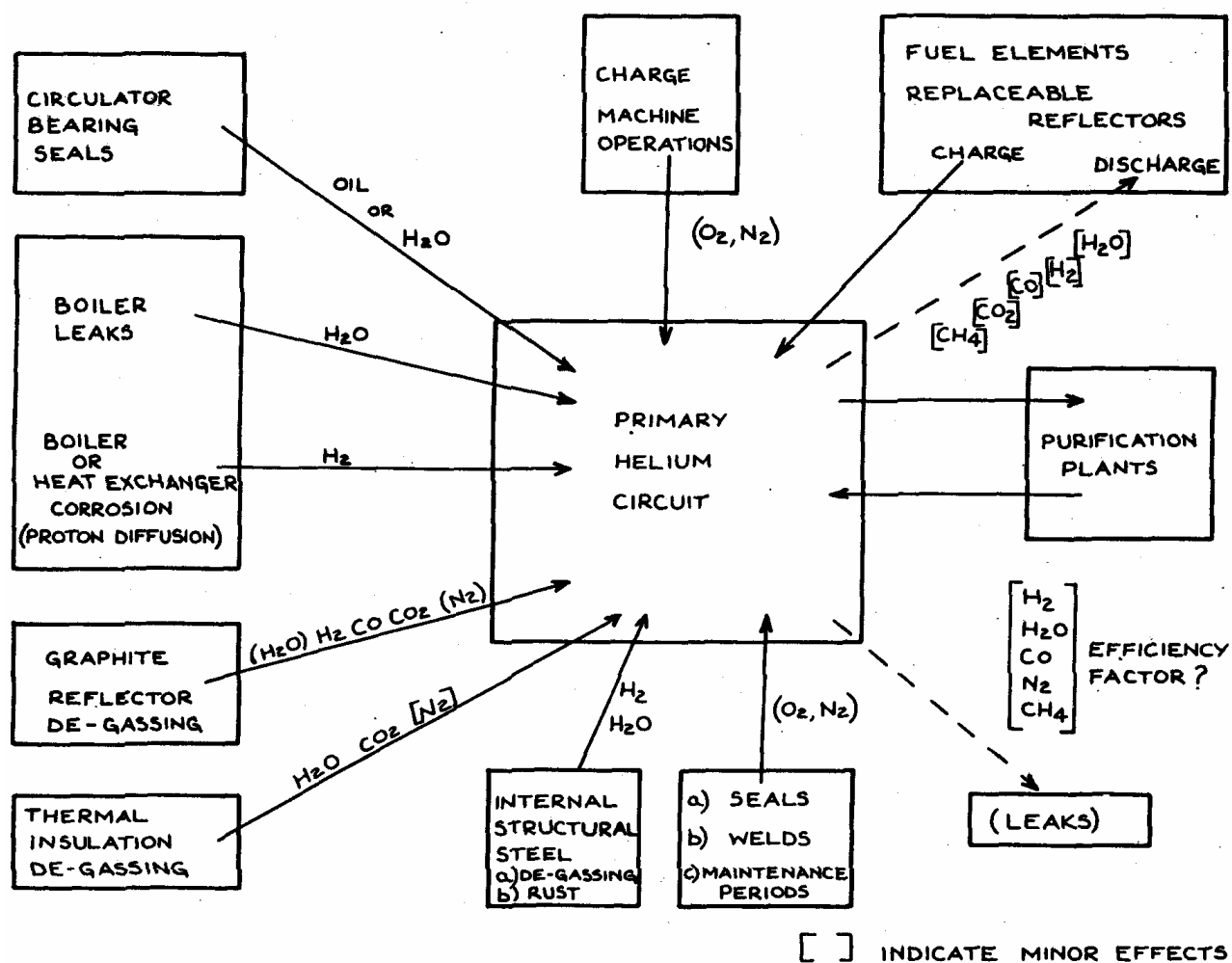


figure 1: main origins of the impurities in the HTR reactors operating in the 70s [1, 2]

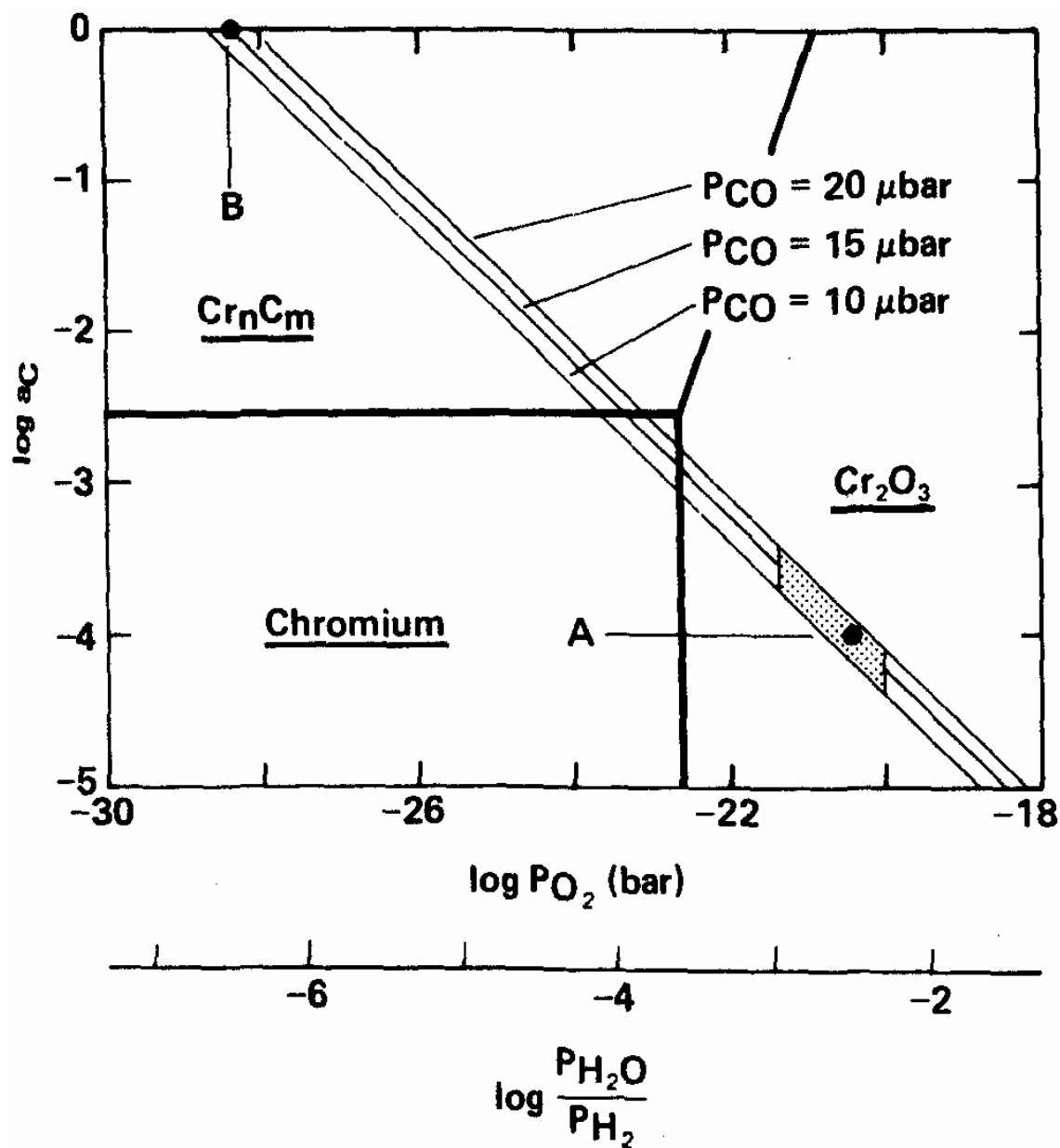


figure 2: diagram used by Quadakkers to describe the helium environment: at 950° C

1. this diagram has been plotted for a chromium activity of 0.6 which correspond to the order of magnitude of the chromium activity of alloys containing 22 to 25 % Cr with some Mo addition (ex: alloy 617) [19, 32]
2. Each oblique line represents the environments with the same partial pressure of CO.
3. Point B ($a_c = 1$) corresponds to an environment with a large partial pressure of methane and corresponding low oxidising potential.
4. On this diagram stability domains of chromium metal, chromium oxide and chromium carbide have also been plotted.

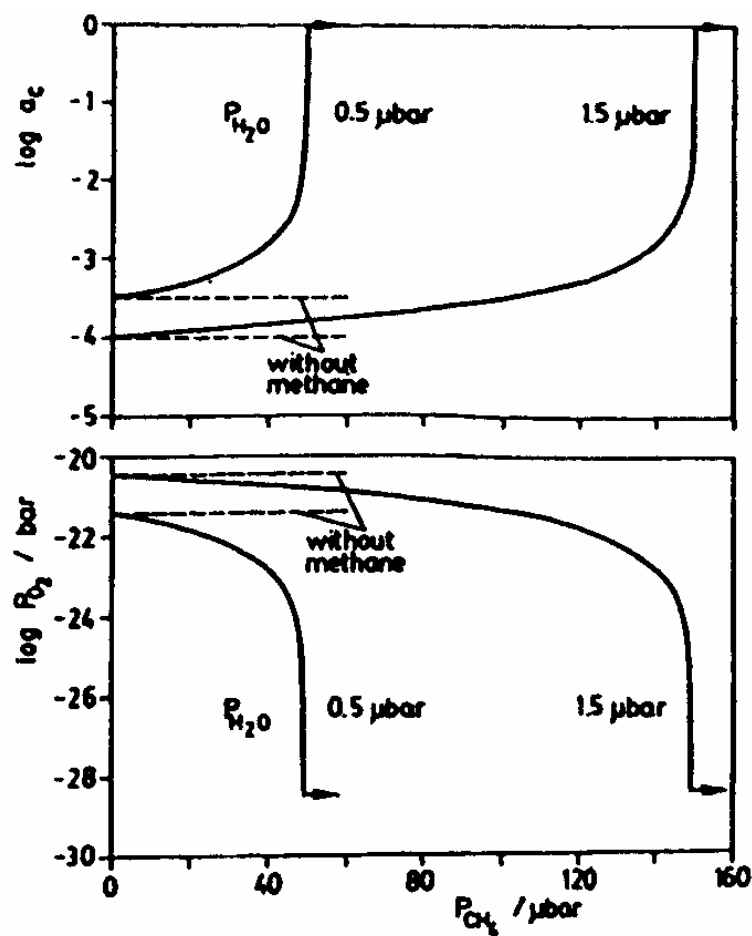


figure 3: Effect of methane content on the steady state activity of carbon on metal surface:
temperature= 950° C, $p_{H_2} = 500 \mu\text{bar}$, $P_{CO} = 15 \mu\text{bar}$ and $P_{H_2O} = 0.5$ and $1.5 \mu\text{bar}$.

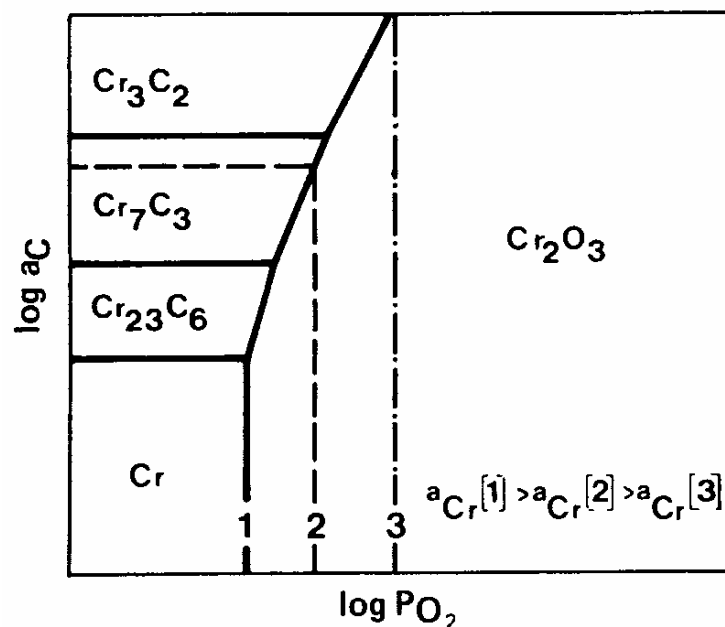


figure 4: sketch of a stability diagram involving the different chromium carbide

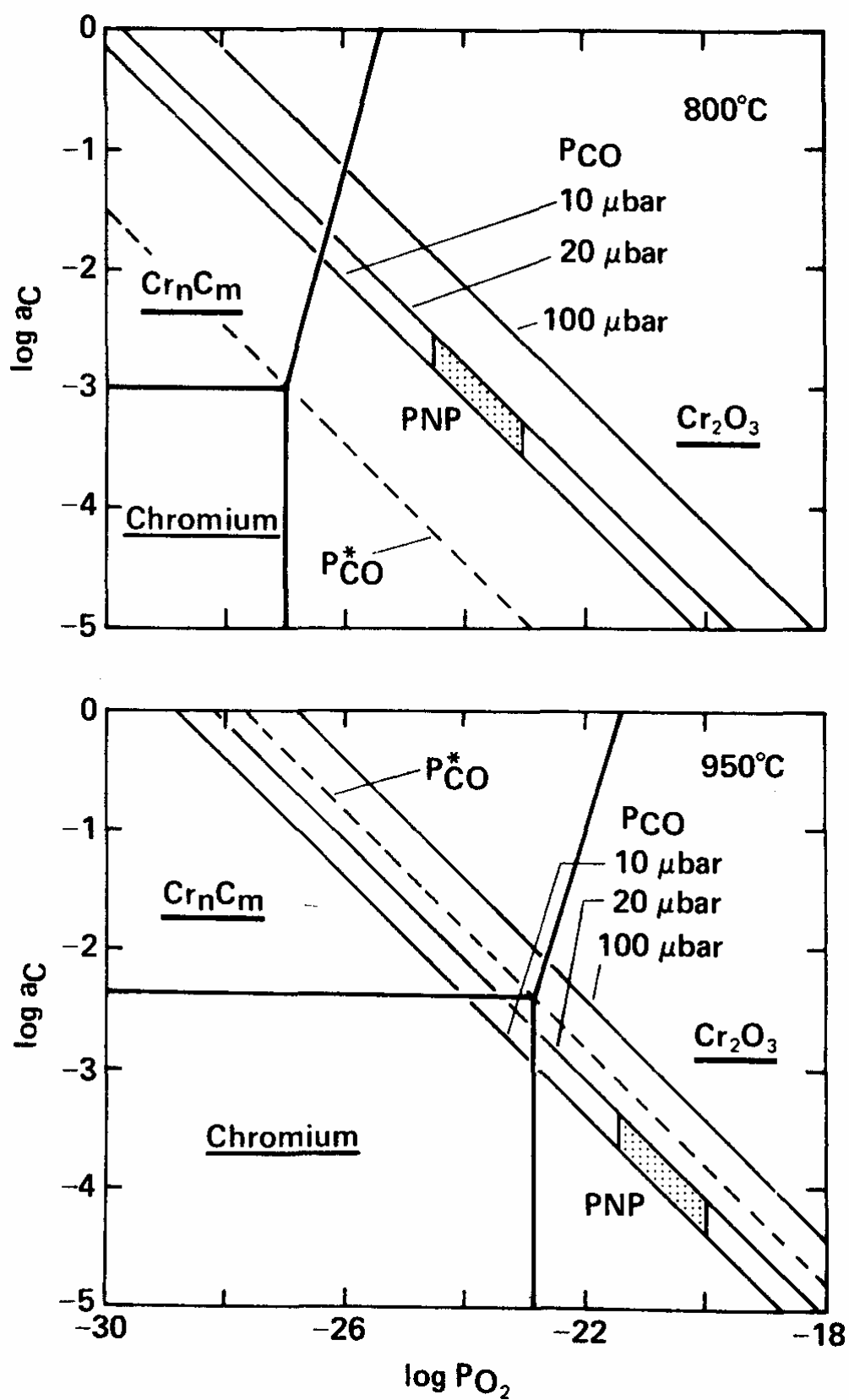


figure 5: stability diagram of Cr species at 950 and 800° C [16, 19]

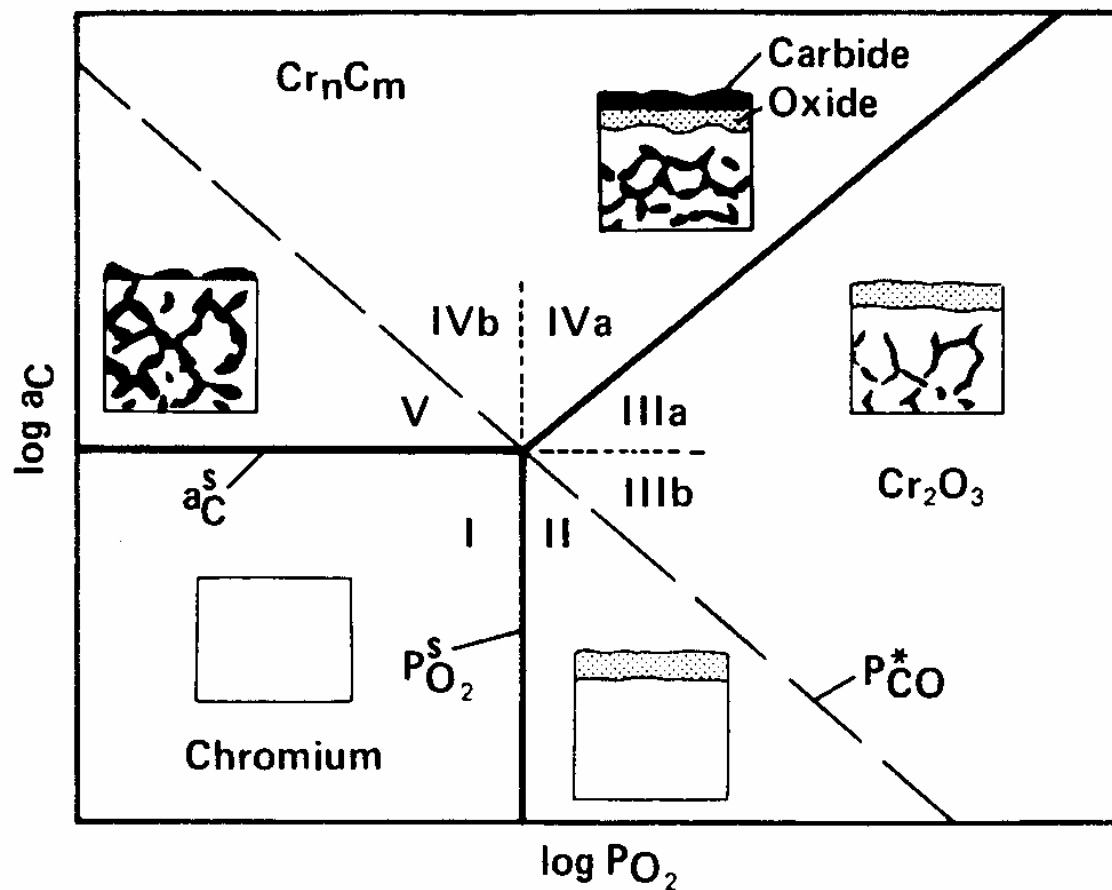


figure 6: different regions of the stability diagram and corresponding types of behaviour of Ni-Cr based alloys [16, 19] :

- regions I and II – severe decarburisation
- region V severe carburisation
- region IV carburisation
- region III – formation of a protective oxide layer, slight carburization – safest region

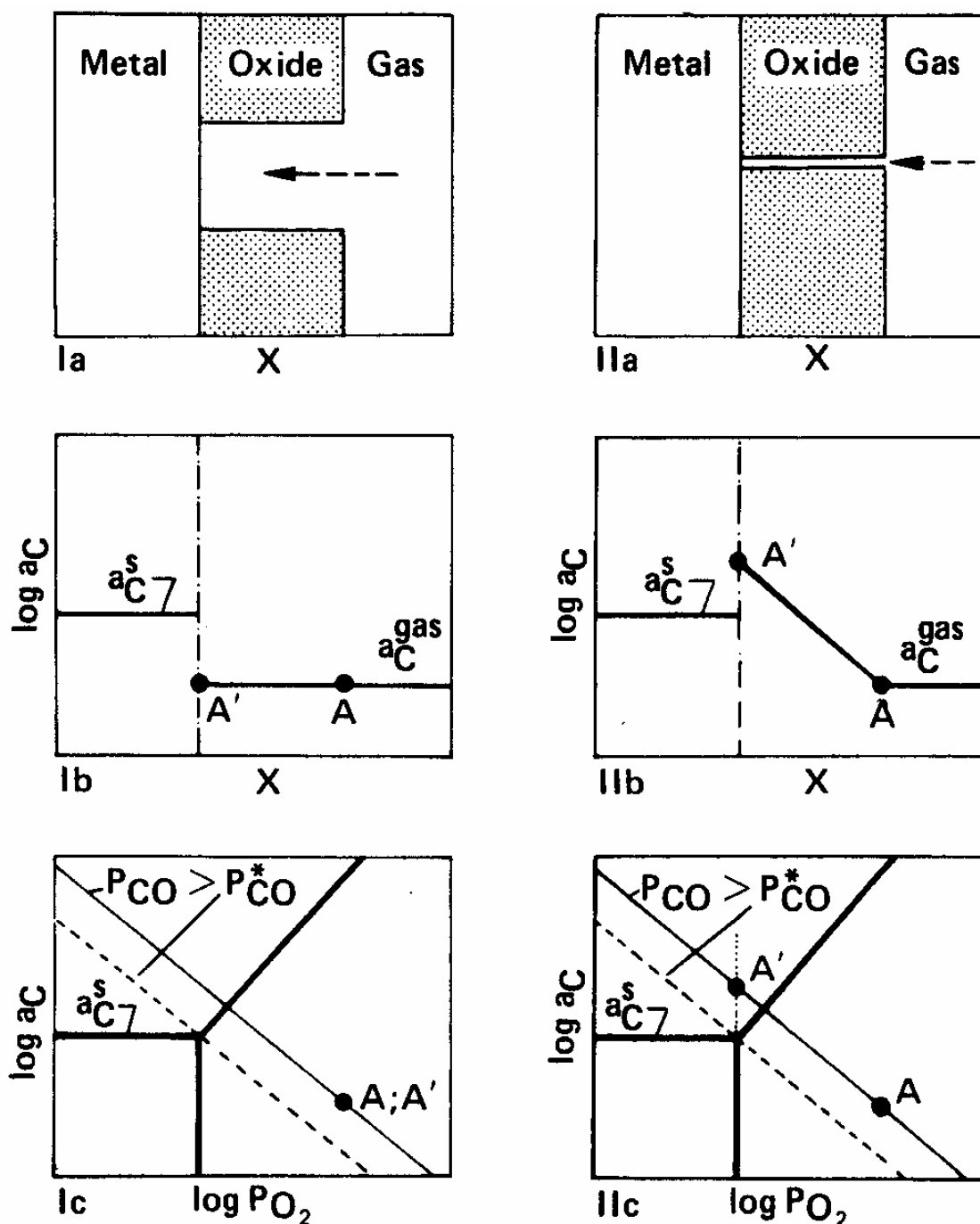


figure 7: influence of the pore size on the local gas chemistry and local alloy/gas interaction [16, 19]

- In part I of the figure (left) pores are large enough for the gas to have free access to the metal surface – the low carbon activity causes the decarburisation of the alloy;
- In part II of the figure (right), pores are thin and the gas has a restricted access to the metal surface. The local oxygen activity is lowered to the equilibrium with the metal and oxide ($P_{O_2}^s$) and thus the carbon activity is raised to higher values (point A' in II-b and c) and no decarburisation occurs.

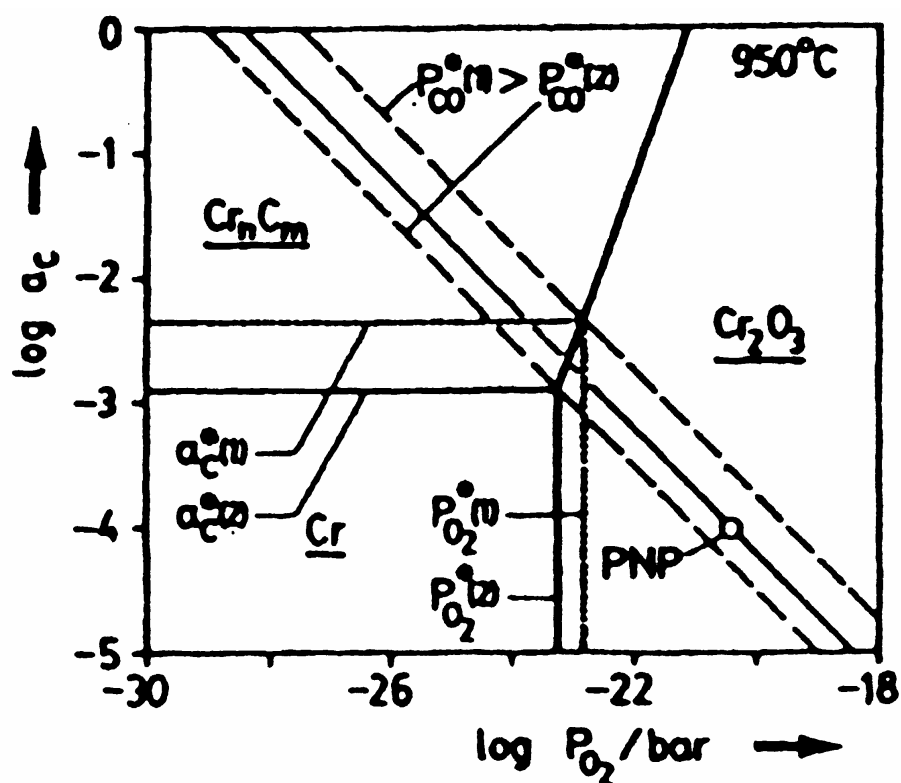


figure 8: influence of the chromium activity on the stability domains of chromium oxide and carbide
[17] - $a_{\text{Cr}(1)} = 0.6$ - $a_{\text{Cr}(2)} = 0.8$

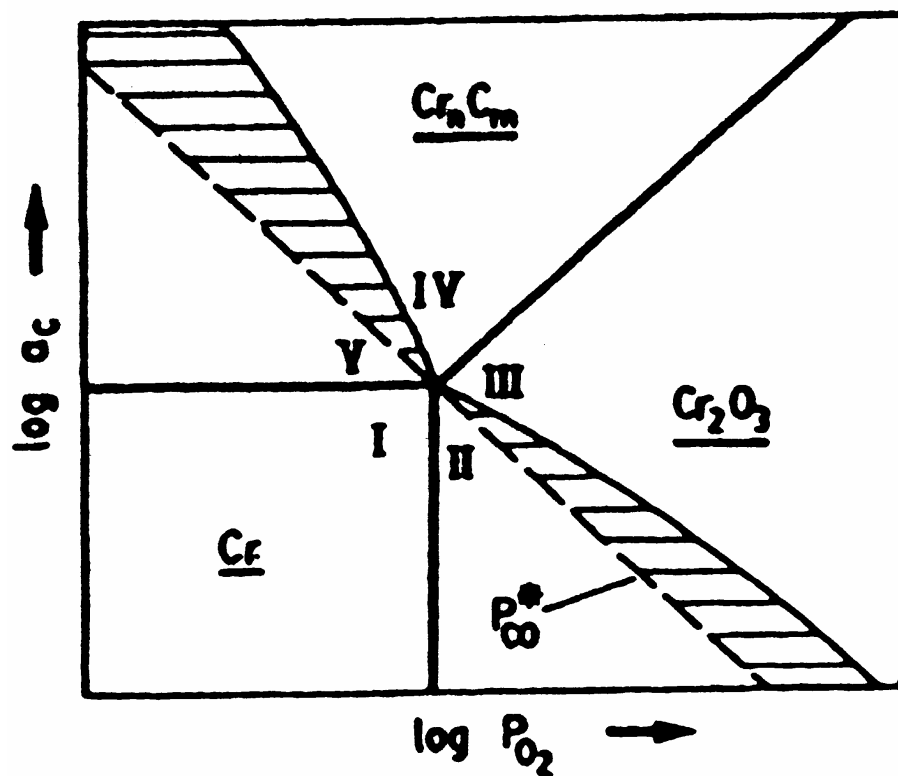


figure 9: modified stability diagram to take into account the chromium depletion of the base material due to formation of chromium oxide or carbide [17, 19]

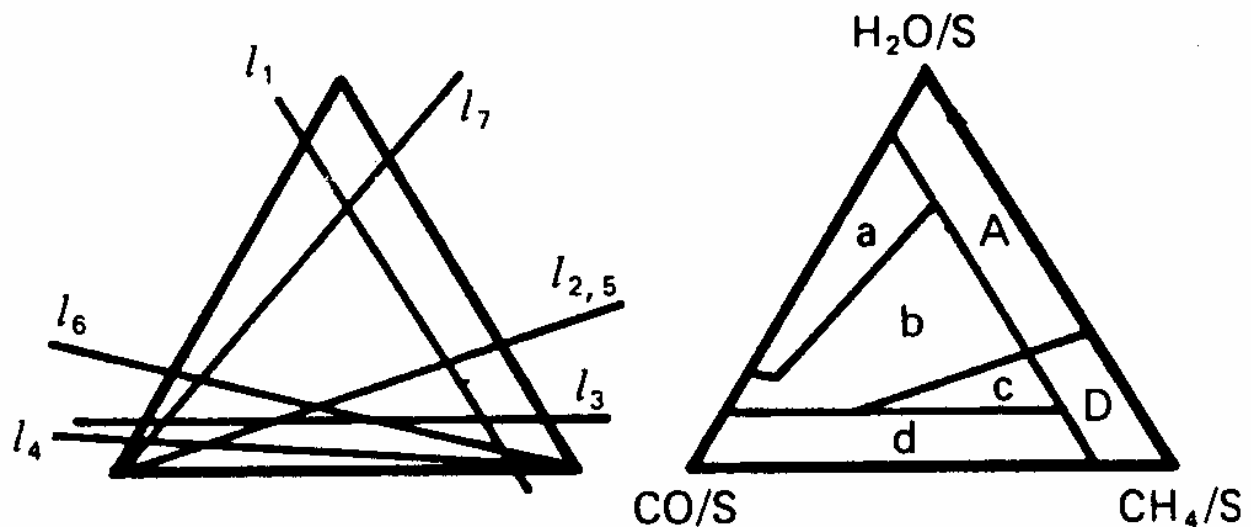


figure 10: TEA diagrams [11, 15]

- line 1 corresponds to the microclimate reaction (occurs on the right side of the line)
- line 3 defines the region where chromium oxidation by water occurs (above the line)
- line 2 and 5 defines the region of carburisation from methane decomposition (occurs below the line)
- line 4 defines the region of carburisation from CO splitting (occurs below the line)
- lines 7 and 6 define the regions of decarburisation due to attack of carbides by water to form CO (line 6) or methane (line 7) (decarburisation occurs above these lines).

Six different kinds of behaviour of Ni-Cr materials can be defined:

- A and B are region where the microclimate reaction occurs and promotes severe oxidation (A) or carburisation D).
- "Active" corrosion will occurs in zones a, c and d
- Decarburisation occurs in region a
- Carburisation occurs in regions c and d
- "Passive" behaviour will prevail in the region b which is the safe region for a Ni-Cr material exposed to HTR environment.

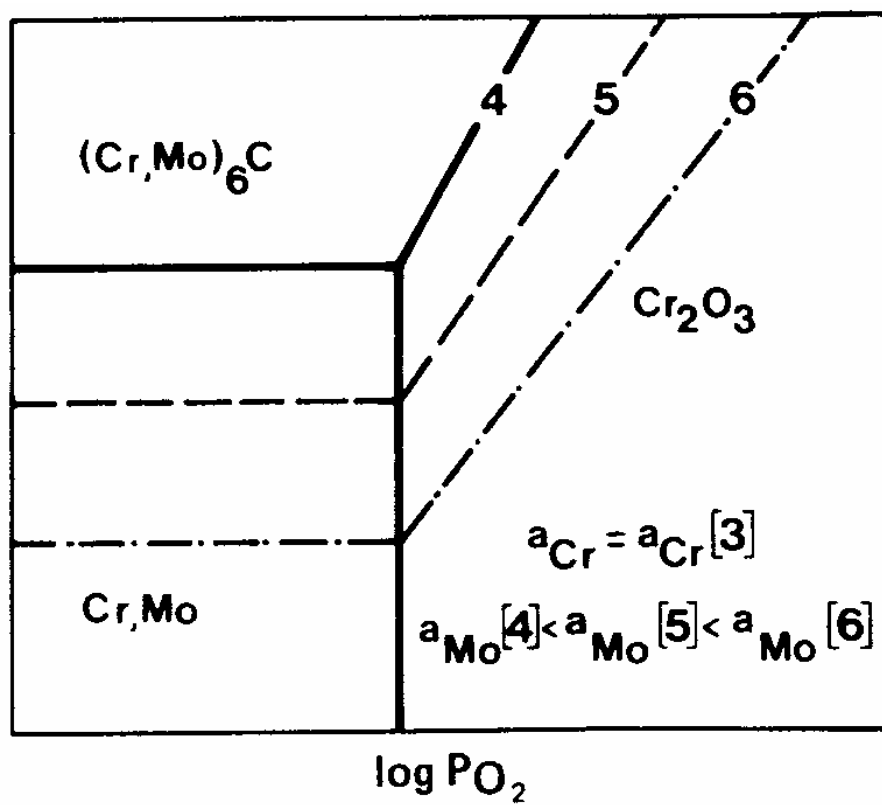


figure 11: sketch of stability diagrams of M_6C carbide with different Mo activity