MODELING OF CHEMICAL WEAR IN FERROUS ALLOYS/SILICON NITRIDE CONTACTS DURING HIGH SPEED CUTTING

R. F. SILVA', F. J. OLIVEIRA', F. P. CASTRO* and J. M. VIEIRA'


Abstract—The wear resistance of Si₃N₄ in machining of iron alloys can be surprisingly low due to chemical affinity for dissolution in the metal. This limits the use of Si₃N₄ inserts in high speed machining of steels, while Si₃N₄ retains the best performance of all cutting materials in turning of grey cast iron, a different ferrous alloy. The chemical wear of several ceramics has been investigated on the basis of dissolution in pure iron by Kramer and Suh. Nevertheless, the influence of alloy elements was not studied. In the present work, solid solution thermodynamics is applied to predict chemical wear of Si₃N₄ by setting the influence of interaction coefficients of the alloy elements in the Henrian activity of Si and N in austenite. The model predicts the relative order of magnitude of the crater wear of Si₃N₄ inserts in machining of tool steels, carbon steels and grey cast iron. © 1998 Acta Metallurgica Inc.

1. INTRODUCTION

In the field of cutting tools it is most relevant to study processes of chemical or diffusion wear of Si₃N₄ because of the intimate and strong contact between the ceramic insert and the metal workpiece at high temperatures. Tool degradation results from a combination of mechanical and chemical processes, but in high speed machining of continuous chip forming workpiece materials like the steels, the dominant wear mode is chemical [1, 2]. Even when turning nickel based alloys, Si₃N₄ has only good performance at low speeds showing a quasi-exponential growth of the wear rates with increasing cutting speeds due to diffusion wear [3]. Interdiffusion between elements of the workpiece and tool, solution of tool material and formation of new phases by chemical reactions at the metal/ceramic interface leading to severe crater wear have been reported [1, 4–8]. Interdiffusion weakens the material structure allowing fast disruption of the tool surface [5]. Tonshoff and Barrsch [4] detected components of the ceramic tool material in the secondary flow zone of the metal chip. Depletion of tool elements such as Si and Y at the flank face of the tool confirms that the ceramic dissipates into the hot metal [9].

Thermodynamic calculations addressing the chemical stability of Si₃N₄ and other cutting tool ceramics in machining of iron alloys were performed by Kramer et al. [10, 11]. The solubility of the tool was calculated from the free energy of formation of the ceramic material and from the relative partial molar excess free energies of solution of its components in the pure metal. Data clearly showed that wear of oxide tools is not controlled by solubility whereas such wear mode dominates carbide tools. Aronsson [12], in comparative testing of silicon nitride and alumina based cutting tools attributes to chemical inertness the superior crater wear resistance of alumina. However, under conditions of high metal removal rate where toughness and hardness are definitively required, silicon nitride inserts perform better than some alumina tools [13]. Although the thermodynamic approach of Kramer et al. has ranked the cutting tool materials in order of the expected reactivity, it has some limitations. It is restricted to the equilibrium with pure iron by not considering the effects of alloying elements. Other authors [1, 7, 14] have explored Kramer's model but some chemical parameters used for the thermodynamic calculations were taken constant over a broad range of temperatures and concentration of alloying elements which is a rather crude approximation. The influence of steel composition in ceramic dissolution was recently investigated by static diffusion couples as a way of predicting chemical wear [7, 15]. The authors used the molecular nitrogen solubility and not the actual Si₃N₄ solubility in steels which can lead to large discrepancies in the final results.

In the present work a model to determine the Si₃N₄ solubility in different iron alloys is developed considering more realistic assumptions for the equilibrium conditions. Experimental values of the solubility products in the solid iron phases and interaction coefficients of all solute atoms were used to calculate the Si and N concentrations in the metal in equilibrium with Si₃N₄. Even conceding that the present thermodynamic model does not take into account reaction kinetics, it gives a realistic measure of the potential for chemical reaction,
the correlation between $Si_3N_4$ solubility and the crater wear rate of $Si_3N_4$ based cutting tools being further investigated.

2. THERMODYNAMIC CALCULATIONS OF $Si_3N_4$ SOLUBILITY IN IRON ALLOYS

Iron alloys are multicomponent solid solutions in Fe where alloying elements strongly interact with one another. The solubility of $Si_3N_4$ in distinct iron alloys will be calculated at a reference temperature of 1000°C, which is representative of the conditions developed at the contact between the metal chip and the rake face of the ceramic tool during high speed cutting. Fe and $Si_3N_4$ react at 950°C and above [16]. Equilibrium within the $\gamma$-Fe phase is considered for thermodynamic evaluation of $Si_3N_4$ solubility in solid iron. Cast iron, carbon and chromium alloyed steels represent broad classes of iron alloys that have been investigated in relation to the benefits of high speed machining with ceramic cutting inserts [1-9].

In the analysis of crossed chemical interactions, Cr-N interaction competes with the dissolution of $Si_3N_4$ and molecular $N_2$ in austenitic iron. The chemical equilibria for phase compatibility in the $Si_3N_4$-CrN-$\gamma$-Fe$_3$ system are given in Table 1. By convenience, the activities of the alloying elements and Si and N from the $Si_3N_4$ ceramic tool in iron, will be defined on a weight percent basis using Henry’s law for dilute systems [17]:

$$\log(h_i) = \log(\%i) + \sum_j e_j(\%j)$$

where $h_i$ is the Henrian activity of the $i$ element, $\%i$ and $\%j$ are the concentrations in weight percent of the $i$ and $j$ elements dissolved in the alloy. The changes of chemical activity of those elements in the $\gamma$-Fe solid solution is expressed by the first order interaction coefficients $e_j$. Information on $e_j$ values, namely in $\gamma$-Fe, is scarce compared to data for liquid iron. However, as described below, values of $e_j$ were calculated from analysis of published phase diagrams or were estimated from numerical data available for $\alpha$-Fe. In some cases transposed $e_j$ values were assessed from the corresponding published values of $e_j$ parameters in $\gamma$-Fe, by applying a procedure given by Lupis [18]:

$$e_j = \frac{M_i e_j + \frac{1}{230} M_i - M_j}{M_j}$$

where $M$ is the atomic weight of the element. The complete set of interaction coefficients needed for the calculation of solubility in the different iron alloys was calculated as described in the following.

2.1. First order interaction coefficients $e_j$ in $\gamma$-iron

A summary of known values of first order interaction coefficients as a function of temperature is given in Table 2. $e_{Fe}^N$ for $\gamma$-Fe was considered the same as that for $\alpha$-Fe [16] due to the narrow two-phase transition between the $\gamma$ loop and and region in the Fe–Si phase diagram [19]. $e_{Fe}^N$, $e_{Cr}^N$ and $e_{N}^N$ were derived by Kunze et al. [16]. The Raoultian interaction coefficient in $\gamma$-Fe, $e_{Fe}^R = 0.05$ [20] was converted to the Henrian interaction coefficients, giving $e_{Fe}^H = 0.051$ and $e_{Cr}^H = 0.18$ were estimated from the Raoultian interaction coefficients at 1273 K, $e_{Cr}^R = -10.9$ [18] and $e_{Cr}^R = 8.7$ [18], respectively. No value of $e_{Cr}^N$ in $\gamma$-Fe was found in the literature, but self interaction coefficients are usually very small as it is the case of $e_{Cr}^N$ in liquid iron (~0.0003) [21]. So this value is approached to zero.

Kagawa et al. [22] measured the solubility of nitrogen in austenite in equilibrium with gaseous $N_2$ at 1 atm, in a Fe–C–N alloy, equation (6) in Table 2. By applying equation (1) the expression of the equilibrium constant $K_{IV}$ for equation (6) can be rearranged to:

$$\log(\%N) + 0.086(\%N) = \log K_{IV} - e_j(\%C)$$

where $e_j$ being given in Table 3. The first term of this equation is plotted against $[\%C]$ in Fig. 1 taking the values of $[\%N]$ and $[\%C]$ at the solubility limit in austenite [22]. Linear regression analysis gives $\theta_{N} = -0.75$, the transpose $e_j^N$ given by equation (2).

The interaction coefficients for the different alloys studied in the present paper are summarized in Table 3 for the temperature of 1273 K. Equation (2) was applied to calculate $e_j^N$, $e_j^N$, and $e_j^N$, respectively. The value of $e_j^N$ is enlev
lated in the section on chromium alloyed steels, below.

2.2. Dissolution of Si₃N₄ in pure iron

The concentration of Si and N in pure γ-iron at 1000°C in equilibrium with silicon nitride is calculated from data of the work of Kunze et al. [16].

The equations for nitrogen concentration in austenitic and ferritic iron and the solubility product of Si₃N₄ in ferritic iron are summarized in Table 4. Equations (8)–(10) can be rearranged to the form of equation (11):

$$\log[\%Si] = -1.300 - 1.333 \log[\%N] - 0.114[\%N]$$

By assuming Henry's law, equation (1), the equation of the solubility constant $K_I$ for Si₃N₄ dissolution in γ-Fe, equation (3) in Table 2 expands to:

$$\log K_I = 3 \log[\%Si] + 4 \log[\%N]$$

Rearranging equation (13) with equation (11) and $e_i^N$, $e_i^N$, $e_i^N$ and $e_i^N$ in Table 3 gives:

$$\log K_I = -1.5541.6 \frac{1}{T} - 37.432$$

where $T$ is the concentration in γ solid solution for the reason presented above that the effect of Si solubility on the thermodynamic properties of both crystalline structures is virtually the same [19]. At 1273 K, equation (11) becomes:

$$\log[\%Si] = -1.300 - 1.333 \log[\%N] - 0.114[\%N]$$

By assuming Henry's law, equation (1), the equation of the solubility constant $K_I$ for Si₃N₄ dissolution in γ-Fe, equation (3) in Table 2 expands to:

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Rearranging equation (13) with equation (11) and $e_i^N$, $e_i^N$, $e_i^N$ and $e_i^N$ in Table 3 gives:

$$\log K_I = -1.5541.6 \frac{1}{T} - 37.432$$

which is the equation for the solubility constant of silicon nitride dissolution in pure γ-Fe. The range

<table>
<thead>
<tr>
<th>Chemical equilibrium</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log[%N] = -1.5541.6 \frac{1}{T} - 37.432$</td>
<td>(8)</td>
</tr>
<tr>
<td>$\log[%N] = 2188 \frac{2188}{T} - 0.845[%Si]$</td>
<td>(9)</td>
</tr>
<tr>
<td>$\log[%Si] = -1.300 - 1.333 \log[%N] - 0.114[%N]$</td>
<td>(10)</td>
</tr>
</tbody>
</table>

Note: $[\%i]$ and $[\%j]$ are the concentrations by weight percent of $i$ element in ferrite and austenite, respectively.
of solubility measurements used to derive equations (8)–(10) was \(0.48 < \%[\text{Si}] < 0.75\) [16]. For the mean silicon concentration of \(\%[\text{Si}] = 0.61\%\) and the resulting value of \(\%[\text{N}] = 0.15\) by equation (12), equation (14) gives \(\log K_I = -3.27\) at 1273 K.

2.3. \(\text{Si}_3\text{N}_4\) dissolution in chromium alloyed steels

The interaction of chromium with nitrogen from the \(\text{Si}_3\text{N}_4\) ceramic tool is very strong for a chromium alloyed steel and \(\text{CrN}\) precipitates in \(\gamma\)-Fe phase for concentrations well below 13 wt\%Cr at 1273 K [23]. Equation (4) in Table 1 must be added to the solubility [equation (3)] of the ceramic, leading to global equation (5).

The equilibrium constant \(K_{II}\) depends on the Cr and N concentrations in \(\gamma\)-Fe and on the interaction coefficients, equation (1) as follows:

\[
\log K_{II} = - \log[\%\text{Cr}] - \log[\%\text{N}]
- (e_{S}[\%\text{Cr}] + e_{N}[\%\text{N}])
- (e_{S}[\%\text{N}] + e_{N}[\%\text{Cr}])
\]  

Using equation (2) to express \(e_{S}\) as a function of \(e_{C}\) and replacing \(e_{S}\) and \(e_{N}\) by their respective values at 1273 K, Table 3, equation (15) is rearranged to:

\[
\log[\%\text{Cr}] + \log[\%\text{N}] + 0.086[\%\text{N}] - 0.0032[\%\text{Cr}]
= - \log K_{II} - ([\%\text{N}]
+ 0.2692[\%\text{Cr}]e_{N})
\]  

The values of \(\log K_{II}\) and \(e_{N}\) are obtained by linear regression analysis from the \(\%\text{Cr}\) and \(\%\text{N}\) values at the solubility limit line of \(\text{CrN}\) in \(\gamma\)-Fe field of the Fe–Cr N phase diagram at 1273 K [23].

The first member of equation (16) is plotted against \([\%\text{N}] + 0.2692\ [\%\text{Cr}]\) as shown in Fig. 2, giving the values of \(K_{II} = 0.86\) and \(e_{N} = -0.40\).

From the chemical equilibria I, II and III in Table 1, and the above values of \(K_I\) and \(K_{II}\) at 1273 K,

\[
\log K_{III} - \log K_{II} + 4 \log K_{II} - 0.17
\]

On the other hand, \(\log K_{III}\) can be written as:

\[
\log K_{III} = 3 \log[\%\text{Si}] - 4 \log[\%\text{Cr}]
+ 3(e_{S}[\%\text{Si}] + e_{N}[\%\text{N}])
- 4(e_{C}[\%\text{Cr}] + e_{N}[\%\text{N}])
+ e_{C}[\%\text{C}] + e_{N}[\%\text{Si}])
\]  

Replacing all the known parameters in equation (18), the general equation for Si and N solubilities in the \(\gamma\) phase of chromium alloyed steels thus becomes:

\[
\%[\text{N}] = 0.076 - 1.35 \log[\%\text{Si}]
- 0.20[\%\text{Si}] + 1.79 \log[\%\text{Cr}]
- 0.74[\%\text{C}]
\]

The carbon and chromium content in the first chromium alloyed steel in Table 5, the DIN 1.2080 tool steel, are above the solubility limit in \(\gamma\)-Fe at 1273 K, while these same alloying elements are fully dissolved in the DIN 1.4021 steel at the reference temperature [24]. The saturation contents of carbon and chromium in \(\gamma\)-Fe at 1273 K for the 2.0 wt\%C,
12 wt% Cr steel were determined from the isothermal section of the Fe-Cr-C phase diagram at 1273 K [24]. For the approximate saturation values of [%C] = 0.9 and [%Cr] = 4.4, the final relationship between the concentrations of Si and N in γ-Fe for the DIN 1.2080 tool steel becomes:

\[ [%N] = 0.56 - 1.35 \log [%Si] - 0.20 [%Si] \]  
(20)

For a 0.2 wt% C, 13 wt% Cr steel, the isothermal section of the Fe-Cr-C phase diagram at 1273 K shows that all the carbon and chromium are dissolved in γ-Fe [24]. By straightforward replacing the nominal [%C] and [%Cr] values of the alloy in equation (19), yields:

\[ [%N] = 1.92 - 1.35 \log [%Si] - 0.20 [%Si] \]  
(21)

### 2.4. Si₃N₄ dissolution in grey cast iron and carbon steels

The solubility constant, \( K_i \), for the dissolution of silicon nitride in γ-Fe phase of grey cast iron and carbon steels can be expressed by equation (13) with addition of the first order interaction coefficients of carbon on silicon and nitrogen, in due proportions. Replacing \( K_i \) for its value at 1773 K (\( K_i = 3.27 \)), \( e_{Si} \) and \( e_{N} \) for the values given in Table 3, the final equation is obtained:

\[
\log [%Si] + 0.3 [%Si] = -1.09 - 1.333 \log [%N] - 0.325 [%N] - 0.33 [%C] 
\]

(22)

As before, grey cast iron represents an alloy where the alloying elements exceed the solubility limit in γ-Fe, while they are fully dissolved in carbon steels. The solubility saturations for carbon and silicon in γ-Fe at 1273 K were graphically determined from an isothermal section of the Fe-Si-C phase diagram at 1273 K [24]. The approximate value of [%C] = 1.0 was found for the nominal Si content of the grey cast iron composition in Table 5 (\( [%Si] = 2.9 \)). The remaining carbon precipitates as graphite. The elements Mn and S of the cast iron composition precipitate as MnS and should not interfere with the equilibria set in Table 1. By replacing these values of [%C] and [%Si] in equation (22), the calculated value of the solubility of N in γ-Fe phase of grey cast iron becomes [%N] = 0.009.

The silicon and nitrogen solubilities in carbon steels can be calculated by replacing the carbon content [%C] in equation (22). For a 0.42 wt% C carbon steel, Table 5, this relationship is thus:

\[
\log [%Si] + 0.3 [%Si] = -1.229 - 1.333 \log [%N] - 0.325 [%N] 
\]

(23)

### 3. DISCUSSION

The results of the precedent section can lead to the estimation of the chemical wear of silicon nitride in contact with ferrous alloys. The Si and N saturation in the metal chip is given by equations (12), (20), (21) and (23) for pure iron and for chromium alloyed and carbon steels, respectively. The relationship between Si and N equilibrium concentration for each alloy is plotted in Fig. 3, together with the point representative of the nitrogen solubility in the gray cast iron as calculated in Section 2.4. The concentrations of Si and N in iron in equilibrium with the Si and N source, the Si₃N₄ ceramic, is given by the interception points of the saturation curves with the straight line representing the stoichiometric Si₃N₄ composition. The resulting solubility values span into a range of two orders of magnitude showing that the composition of the ferrous alloy strongly affects the wear resistance of the silicon nitride cutting tools.

Table 5 gives the equilibrium solubilities of Si, N and the concentration of dissolved Si₃N₄ in equilibrium with the selected alloys at 1273 K as well as the values of the crater wear parameter \( \kappa \) obtained in a previous work for DIN 1.2080 tool steel and gray cast machining [5] and from literature, for 0.42 wt% C carbon steel turning [6]. \( \kappa \) is defined as \( \kappa = T/M \), the ratio between the crater wear rate, \( (T = KM.KT/t; KM \text{ being the distance between the tool edge and crater center, KT the crater depth and } t \text{ the cutting time}) \) and the metal removal rate \( (M = \text{cutting speed } \times \text{feed}) \) [5]. The Si₃N₄ solubility is normalized to the lowest value, the value in the gray cast iron in Table 5. It becomes evident that additions of C or Si to the Fe alloy decrease Si₃N₄
solubility, the alloying with Cr having the opposite effect. These results corroborate the observations that silicon nitride tools present the highest resistance to wear by dissolution when machining gray cast iron [1,4,5,13] as given by the low value of $\kappa$. In Fig. 4 the wear parameter $\kappa$ is plotted against $\text{Si}_3\text{N}_4$ solubility in a log-log scale, resulting in a straight line of slope unity, the two variables being directly proportional. The scatter of crater wear parameter $\kappa$ for each type of alloy in Fig. 4 are mostly due to differences of secondary phases used as sintering aids of the silicon nitride insert materials [5], Table 5. It is thus possible to predict relative wear rates of $\text{Si}_3\text{N}_4$ cutting tools when machining different ferrous alloys using the chemical wear model.

Although other models [1,7,10,11,14,15] were developed to predict relative wear rates of ceramic cutting tools based on thermodynamics, there are some important differences with respect to the pre-
sent model that are highlighted. The early studies of Kramer et al. [10, 11] have only considered tool wear by solution in pure \(\alpha\)-Fe and postulated that the \(\alpha\)-Fe is preserved in the metastable form at the high temperatures developed during cutting. Since seizure conditions occur at the contact between the chip and the tool rake face [5, 25], the equilibrium high temperatures developed during cutting. Since seizure model that are highlighted. The early studies of calculation of solubilities. It should be pointed out couples was tentatively correlated to chemical wear structure, \(\gamma\)-Fe, is used in the present study for the calculation of solubilities. It should be pointed out that the results of static ceramic/metal interaction diffusion couples are often performed above 1273 K, where no doubts exist about the \(\alpha/\gamma\)-Fe transformation. The reactivity of the diffusion couples was tentatively correlated to chemical wear in turning by using Kramer’s model [1, 7].

The \(\text{Si}_3\text{N}_4\) solubility in pure iron calculated by the model of Kramer has a value of 0.74 cm\(^3\)/mol Fe [10] which is much higher than the value in Table 5. The discrepancy cannot be attributed to differences of the iron crystalline structures adopted in the two models because a calculation made with the solubility constant as experimentally determined in \(\alpha\)-Fe, yields a value of 0.04 cm\(^3\)/mol Fe [16]. In the model of Kramer the relative partial molar excess free energies of Si and N were estimated at 1273 K, where no doubts exist about the \(\alpha/\gamma\)-Fe transformation. The reactivity of the diffusion couples was tentatively correlated to chemical wear in turning by using Kramer’s model [1, 7].

This thermodynamic tool also allows the calculation of \(\text{Si}_3\text{N}_4\) solubility lines in iron alloys phase diagrams. The concept can be adopted to alloying elements other than Si, N, C and Cr. This method is restricted so far to \(\text{Si}_3\text{N}_4\) but it can be extended to sialons, composites or even to other ceramic materials giving a more consistent approach than those reported.

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