Prediction of Carbide Precipitation Using A Combined Partial Equilibrium- Para-Equilibrium - Lever Rule Approximation in Automobile Gear Materials

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Abstract. The carbide precipitation nature of an automobile gear material, i.e. Fe-C-Mn-Si-Cr-Mo alloy, during carburization and element addition process are investigated through PE+PA+LR prediction. Results show that, carburization process greatly increases the amount of cementite as well as the hardness index at the surface part. Besides, the addition of Ti and V helps to formation of TiC and (V,Mo)C carbides but suppress the precipitation of cementite, which contributes equivalent hardness at surface and lighter weight to the alloy.

1. Introduction
Automobile gear materials are well required for the wear-resistance around the surface and the toughness in the center. The basis composition of the gear material is 0.19wt%C, 1.20wt%Mn, 0.26wt%Si, 1.20wt%Cr, 0.021wt% Mo, 0.010wt%P, 0.020wt%S, 0.13wt%Ni, 0.021wt%Al, 12ppmO, 9ppmN. By using the gas carburization technique[1], it is possible to obtain a high carbon composition at the surface meanwhile maintain the original carbon composition over the bulk, which satisfies the dual industrial requirement for both surface and bulk of the alloy.

Recent years the demands in increasing of the gear hardness and at the same time reducing the weight of the automobiles have made it sound the addition of the substitutive elements into the traditional materials. Some VB group elements such as V and Nb etc, and IVB group elements like Ti and Zr etc are selected as the addition elements, for they promote the formation of MC type carbides with relatively lighter densities and much higher hardness[2,3] than usual M6C carbide.

In order to clarify the effects of carbide composition and amount on the hardness of the automobile gear materials with the gas carburization and the element addition techniques, the solidification path of the automobile gear materials was studied through partial equilibrium (PE)-para-equilibrium (PA)-lever rule (LR) approximation. The PE-PA-LR approximation[4,5] is preferred to predict the solidification path from liquid down to the room temperature with considering the back diffusion of interstitial elements such as C, O etc in solids and also retrieving peritectic as well as eutectoid transformations.

The paper firstly investigated the precipitation nature of the carbides after carburization process and V, Ti element addition at different positions of the automobile gear materials by PE-PA-LR approximation, and then analyzed the effects of carburization and element addition on the hardness of the automobile gear materials.

2. Carbon concentration distribution in a carburized sample by Dictra prediction
The carbon concentration as a function of the distance from the surface of a sample is obtained by solving Fick’s second law with the carbon flux prescribed at the carburized surface, \( J_C = f_C (a_C^{\text{eq}} - a_C^{\text{surface}}) \), where \( a_C^{\text{eq}} \) is the carbon activity at the steel in equilibrium with the gas. It is set as 0.64 corresponding to a carburizing carbon potential of 0.85 wt% according to the carburization condition\(^1\). \( a_C^{\text{surface}} \) is the actual carbon activity in steel close to the surface. \( f_C \) is mass - transfer coefficient for carbon in steel, chosen as 8.25\( \times 10^{-9} \) mol/s\(^6\). The diffusion coefficient and thermodynamic data are retrieved from Thermo-Calc/MOB2 mobility database\(^7\) and Thermo-Calc/TCFE6 steel database\(^8\). Then the distribution of carbon inside the sample can be predicted by Dictra \(^6\).

Figure 1 shows the carbon concentration distribution for JIS SCr420 alloy (chemical composition: 0.21wt%C, 0.79wt%Mn, 0.25wt%Si, 1.21wt%Cr, 0.029wt%Al, 0.015wt%P, 0.015wt%S, 0.012wt%N) after carburization by experimental measurement\(^1\) and by Dictra prediction. Reasonable agreement verifies the accuracy of Dictra prediction in carburization process.

![Figure 1](image1.png)  
**Figure 1** Predicted carbon concentration distribution after carburization for JIS SCr420 alloy and for the present Fe-C-Mn-Si-Cr-Mo alloy (0.19wt%C alloy) by Dictra. The measured data are from reference \(^1\).

Similar to JIS SCr420 alloy, a gear material Fe-C-Mn-Si-Cr-Mo alloy with 0.19wt%C base composition (0.19wt%C, 1.20wt%Mn, 0.26wt%Si, 1.20wt%Cr, 0.21wt% Mo) was adopted in the present carburization study. Through Dictra, its carbon composition distribution as a function of the distance from the surface is shown in figure 1, the carburization atmosphere, maintaining temperature and time are set same as those in reference\(^1\).

Based on the carbon composition distribution, the sample is divided into three regime- surface (0–0.1mm distance from surface, with the averaged composition 0.85wt%C), middle part (0.1–1.7mm, with the averaged composition 0.5wt%C) and base part (>1.7mm, with the original base composition 0.19wt%C). Acting as a gear material in automobiles, it is expected a great deal of carbides existing at the surface which benefits to the hardness required there meanwhile almost no carbide precipitating at the base part to keep the good toughness. Through carburization, the gradient distribution of the carbon composition is achieved.

3. **Prediction of solidification path to room temperature by PE+PA+LR approximation**

There are several thermodynamic approximations for predicting the solidification path in a multi-component alloy system. The lever rule, LR, and Gulliver-Scheil approximation, GS, are the two extreme cases. The actual solidification path goes in between these two cases. The partial equilibrium approximation, PE\(^9\), expands the GS model to distinguish the diffusivities of interstitial solutes as infinite and substitutionals as negligible respectively, but the prediction still terminate approaching to the solidus point. The para-equilibrium approximation, PA \(^4,10\), which makes it possible to retrieve the solid-solution transformation, predicts not only the mushy zone peritectic transformation but also the eutectoid transformation at solid state. These approximations show potentials in predicting the solidification path at total solidification range, i.e. from liquid down to the final room temperature. For
3.1. **PE+PA+LR approximation and its verification**

Considering the case that only carbon is regarded as an interstitial element.

The partial equilibrium (PE) of carbon among all the phases which includes liquid and solid phases $S_j, j=1, 2, \ldots, m$ should satisfy the following conditions: the equal chemical potential of carbon among all the phases and the mass conservation of carbon during PE procedure, considering the partial equilibrium of an interstitial element; the unchanged composition in $u$-fraction of substitutional elements and the mass conservation of the substitutional element in each phase during PE procedure regarding the negligible diffusion of the substitutionals.

Para-equilibrium (PA) approximation focuses on the local equilibrium merely between the solids. The generation of a new solid as well as its variation in amount and composition from the mother solid is constrained by the interface paraequilibrium, i.e. no driving force, condition. It requires the interstitials, e.g. carbon, to follow the equal chemical potential and the mass conservation among mother and generating phases. The substitutionals behave as a unity during the paraequilibrium process due to their negligible diffusion, which obey the following constraints: the unchanged composition in $u$-fraction for mother phase during PA procedure, the equal composition in $u$-fraction for mother and generating phases; as well as the equal combined chemical potential (i.e. the summation of the products of the composition in $u$-fraction and the chemical potential for substitutionals) for two phases, and the mass conservation throughout the two phases during PA.

The procedure is programmed at Thermo-Calc/TQ programming interface\[^{[11]}\] through coupling the thermodynamic equilibrium calculations. The temperature step adopted is $-1K$. The calculation finishes at room temperature.

In order to verify the calculation code, firstly the predicted solidification path by PE+PA and PE+PA+LR based on the composition of reference\[^{[4]}\] (0.21wt%C, 1.64wt%Mn, 0.24wt%Si, 0.09wt%Al, 0.032wt%P and 0.007wt%S) was given in figure 2. In what we called ‘PE+PA’ model, both the peritectic and eutectoid transformation are predicted by PE+PA model, as it did in literature \[^{[4]}\]. Meanwhile, in ‘PE+PA+LR’ model, the peritectic transformation is predicted by PE+PA model while the eutectoid transformation is predicted by a local equilibrium calculation between the matrix and the generation phase. This allows the austenite to transform to ferrite (or cementite) in a local equilibrium way. Comparatively, literature \[^{[4]}\] predicted the peritectic and eutectoid transformation through PE+PA or PE+LR approximation, and literature \[^{[5]}\] only made the PE+LR prediction around the peritectic transformation. As seen from figure 2, around the peritectic transformation regime, the predicted solidification path by PE+PA fits well with the results in literature\[^{[4]}\]. Around 800°C, both of them can retrieve the eutectoid transformation, although their starting points of transformation are a little bit different. As shown, the present prediction fits with the corresponding curves in reference\[^{[4]}\], and the predicted curves by PE+PA+LR model fit with the ones by PE+PA model in solid-state transformation. Thus the PE+PA+LR model is adopted in the following prediction since it is prompt to deal with the solid-state phase transformations.

3.2. **Solidification path for automobile gear materials after carburization**

After carburization of a Fe-C-Mn-Si-Cr-Mo alloy sample, the carbide precipitation nature is checked according to the carbon concentration variation at surface, middle and base part through the prediction. As seen in figure 3, the existing carbides are cementite and $\text{M}_2\text{C}_3$. At 0.19wt%C content (figure 3(a)), the BCC-FCC phase transformation takes place and lasts from 1483°C to 1475°C. With the carbon content exceeding 0.5wt%, only FCC phase exists at this period (figure 3(b)). These three compositions all experience the FCC to BCC and FCC to cementite transformations at solid state. As seen in the figure, the carbide precipitation temperature rises up with the increase of the carbon content. At 0.19wt%C content, both $\text{M}_2\text{C}_3$ and cementite precipitate below the solidus (1164°C), that is, 750°C for $\text{M}_2\text{C}_3$ and 722°C for cementite, respectively, companying with the FCC to BCC transformation taking place at 809°C. With 0.85wt%C content, $\text{M}_2\text{C}_3$ forms at 1112°C which is above the solidus temperature.
1024°C, and cementite precipitates at 854°C which is also ahead of the FCC to BCC transformation point 738°C. The uprise of the precipitation temperature certainly increases the amount of the corresponding carbides. As shown in figure 4, with 0.19wt% C content, both the M7C3 and cementite are little in amount; their total mass fraction is around 0.022 (vf=0.0215). Then with the increase of carbon content, the amount of cementite rises up greatly and dominates the total amount of carbides, which are in mass fraction 0.064 (cementite, vf=0.067) and 0.071 (total, vf=0.074) at the middle part with 0.5wt% C content, and approaches in mass fraction 0.124 (cementite, vf=0.1306) and 0.125 (total, vf=0.131) near the surface with 0.85wt% C content; meanwhile, the M7C3 almost vanishes.

**Figure 3** Solidification path predicted after carburization at (a) base, (b) surface part of the basis gear material. FCC#2 in (a) has the similar constitution as FCC phase.

**Figure 4** Predicted carbide amounts in basis gear material after carburization.

### 3.3. Effect of C on precipitating carbide composition and hardness

Through solidification path prediction, the carbide composition variation with the increase of the carbon content is determined. In the base sample, the constitution of cementite is (Fe,Mn,Cr):C, in which Mn dominantly occupies 12wt% and Cr is 9.8wt%, whose Vickers hardness is around 1360-1570[1][2][3]: while in middle part, it changes to (Fe,Cr,Mn):C which contains 9.4wt%Cr and 6.7wt%Mn thus Vickers hardness increases to 1520-1890[1][2][3]. Up to the surface, the constitution alters to (Fe,Cr):C where Cr occupies 8.1wt%, Mn decreases to 4.6wt%, instead, the Mo content increases up to 0.7wt%. In a word, with the increase of carbon content the constitution of cementite changes from (Fe,Mn):C to (Fe,Cr):C, which increases its hardness.

Similarly, the M7C3 constitution in base part is (Fe,Cr):C3 which contains 40wt%Cr and corresponding Vickers hardness is 2080-2570[3]; meanwhile, in the middle, M7C3 alters to (Fe,Cr,Mo):C3 with 33.6wt%Cr and 7.4wt%Mo, its Vickers hardness changes to 2040 ~2570[3]; and at surface, its constitution changes to (Fe,Mo,Mn,Cr):C3 where Mo content is up to 30.7wt%, Mn 20.4wt% and Cr down to 7.4wt%. Vickers hardness keeps 2040 ~2570[3]. Totally, the increase of carbon content changes the M7C3 from (Fe,Cr):C3 to (Fe,Mo,Mn,Cr):C3, which leads variations to its hardness.

### 4. Addition of V and Ti content in automobile gear materials

#### 4.1. Effect of V on Carbide Precipitation

V helps to the formation of (V,Mo)C carbide (i.e. MC_eta). It precipitates approaching to the solidus temperature (1022°C) at 0.1wt%V addition, as shown in figure 5, although keeps precipitating in solid state, its amount is not too much.

With the addition of V content increasing from 0.1wt% to 1.0wt%, the total amount of carbide decreases at all part of the sample, even in the base part. Figure 6(a) shows the effects at surface of the sample. As shown, with 0.1wt% to 1.0wt%V addition, the total carbide amount decreases from 0.131 to 0.104 in volume fraction, decreased by 0.027, which is due to the large decrease of cementite, although the M7C3 and (V,Mo)C do increase at the same time, their amounts are not enough to compensate the decrease.

On the other hand, the composition of the carbide is strengthened with the V addition. Comparing 0.1wt%V and further 1.0wt%V addition with the basis sample at surface part, cementite constitution evolves from (Fe,Cr):C to (Fe,Cr,Mn):C. M7C3 constitution alters from (Fe,Mo,Mn,Cr):C3 to

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**Figure 5** Solidification path predicted after carburization at (a) base, (b) surface part of the basis gear material. FCC#2 in (a) has the similar constitution as FCC phase.

**Figure 6** Predicted carbide amounts in basis gear material after carburization.
(Fe,Mn,Cr,Mo)-C and further to (Fe,Cr,V)-C, in which Cr content increases from 7.4wt% in basis to 16.7wt% (+0.1wt% V) and further to 31.9wt% (+1.0wt% V), V content is increased up to 8.8 wt%. In (V,Mo)C, the V, Mo content occupies from 41.3wt%V and 43.7wt%Mo at 0.1wt%V addition up to 62.0wt%V and 20.8wt% Mo with 1.0wt%V addition.

Figure 5 Predicted solidification path with 0.1%V addition at surface after carburization.

Figure 6 Predicted carbide amount at surface of the sample with the addition of (a)V and (b)Ti.

4.2. Effect of Ti on Carbide Precipitation

Ti addition is intended for the precipitation of TiC carbide. As seen from figure 7, TiC forms in the early stage of the solidification and precipitates both in liquid and solid state.

Figure 7 Predicted solidification path with 0.1%Ti addition at surface part after carburization.

From figure 6(b), Ti addition shows the similar changing tendency on carbide amount with V addition. However, TiC precipitation amount is larger than (V, Mo)C, thus at surface, the total carbide amount is decreased from 0.131 to 0.115 in volume fraction, decreased by 0.016, which is less than that in V addition. As cementite decreases by 0.038 in volume fraction, TiC forms up to 0.021 in volume fraction by 1.0wt%Ti addition; meanwhile, there is not much M7C3 left.

Ti doesn’t dissolve in cementite and M7C3, but it does change their constitution. Comparing the composition at surface, with 0.1wt%Ti and further 1.0wt%Ti addition, cementite constitution evolves from (Fe,Cr)C to (Fe,Cr,Mn)C. M7C3 constitution changes from (Fe,Mn,Mn,Cr)C3 to (Fe,Mn,Mn,Mo)C3 (+1.0wt%Ti), in which Cr content changes from 7.4wt% in basis (no Ti) increasing to 8.9wt% (+0.1wt%Ti) and up to 29.1wt% (+1.0wt%Ti). Ti is the dominant element in TiC, where the Ti content occupies from 73.5wt% at 0.1wt%Ti addition up to 79.0wt% with 1.0wt%Ti addition. Since no more data of the variation of Vickers hardness with the composition is available, regardless of the constitution change, the Vickers hardness 1520-1890\(^3\), 2040-2570\(^3\) and 3200\(^2\) are just adopted for cementite, M7C3 and TiC, respectively.
5. Hardness of automobile gear materials with C, V and Ti content variation

Considering the contributions of both the constitution and amount of the carbides to the alloy hardness, the hardness index of the alloy is plotted in figure 8. It is the summation of each carbide’s hardness weighted by its volume fraction, as illustrated in figure 6.

Figure 8(a) shows the hardness index at different part of the sample as a function of carbon content, the measured actual hardness in reference [1] is also plotted in the figure. As seen, both the measured data and the predicted hardness index have the same increasing tendency with the increase of the carbon content. However, the actual data increase in a larger slope. With carbon content ranging from 0.19wt% to 0.85wt%, the hardness index increases from 34–41 up to 200–250, increased by 166–209, while the actual hardness increases from 315 to 793, increased by 478. This hardness increase is mainly due to the great increase of the amount of the cementite, as shown in figure 4.

Figure 8(b) and 8(c) show the hardness index at surface with the change of V and Ti addition. As known, (V,Mo)C and TiC are high hardness carbide, whose Vickers hardness is 2100–2800[3] and 3200[2] respectively. Meanwhile, the density of (V,Mo)C, 5200–6200 kg/m³, and TiC, 4600–4800 kg/m³, is much less than that of cementite (7100–7500 kg/m³), thus they contribute both the higher hardness and the lighter weight to the gear materials. As shown from figure, with the addition of 0.1wt% ~1.0wt%Ti or 0.1wt%~0.5wt%V, the total hardness index at the surface equalizes the original hardness index there.

6. Conclusion

The carbide precipitation nature of an automobile gear material, i.e. Fe-C-Mn-Si-Cr-Mo alloy, during carburization and element addition process is investigated through PE+PA+LR prediction. Results show that, carburization, with the carbon content increasing from 0.19wt% to 0.85wt%, greatly increases the amount of cementite at the surface and the hardness index correspondingly rise up by 166–209. Besides, the addition of Ti and V helps to the precipitation of TiC and (V, Mo)C carbides, which favour in higher hardness and lighter weight comparing to cementite. It is found through prediction that with 0.1wt%~0.5wt%V addition or 0.1wt%~1.0wt%Ti addition, the total hardness index at the surface equalizes the original one there; meanwhile, the addition of Ti and V contributes less weight to the automobile gear material through suppressing the formation of cementite.

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