Sinter hardening – a big market and technology potential in China

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Abstract: Sinter hardening has been more and more applied in the PM component manufactures worldwide, due to its pronounced advantages: good hardening effect, cost saving, better dimensional control and environmental friendly. In this paper, the present situation of sinter hardening in mainland China is reviewed. The mechanism of sinter hardening is discussed in terms of both material and process effects. Among other sinter hardening materials, Cr-containing PM steels have shown a good market potential due to their high hardenability effect and low cost for raw materials. Combined with other technologies in PM such as warm compaction and high temperature sintering, Astaloy CrM can reach a tensile strength of 1400MPa, an elongation of 1.5%. A bending fatigue strength of 437MPa can also be reached after sinter hardening and tempering. In addition, sinter hardening gives a less dimensional change for this material. Finally, some suggestions are proposed regarding how to promote the sinter hardening technique in the Chinese PM market.

Introduction

Powder metallurgy (PM) is one of the most competitive methods to produce components with complicated shapes and large in quantity. During the last twenty years the PM industry, esp., the PM steel industry, has been developed greatly thanks to the highly development and increasing requests from the automobile industry. In practical PM production, many sintered components need to be heat treated in order to improve their mechanical performances. Due to the fact that PM parts contain many pores that can accelerate the corrosion effect inside the treated parts in case of water quenching, oil quenching has to be applied during heat treatment. The assimilated oil during quenching process has to be removed from the treated parts for effective tempering, which costs much not only for the equipment and energy but also for the environment.

Sinter hardening combines both sintering and hardening (quenching) in one process to produce martensite as the major phase in the microstructure of the sintered components. It is achieved by a gas quenching setup in the cooling zone of the sintering furnace, which can generate cooling rates of 2C/S-5C/S for the sintered components in the temperature range of 950C-200C. The main advantages of sinter hardening lie in cost saving and environmental protection.

In general, two conditions should be fulfilled to reach the sinter hardening effect: materials suitable for sinter hardening and furnaces equipped with gas quenching in the cooling zone. As shown in Fig.1 (a), if less alloying element is involved in the material the bainitic nose of the TTT diagram locates more to the left, as seen in curve 1. In such case, a conventional cooling rate will make the system generate large amount of bainite or even some pearlite. If alloying elements such as Mo, Cr, Mn, Ni, Si, ect., which are effective to the hardenability of steels, are added in the system as prealloy, the TTT curve will move to the right (see curve 2). Therefore, more martensite can be produced under the same cooling rate. The same effect can be achieved by increasing the cooling rate in the cooling zone of the sintering furnace, as shown in Fig.1 (b). In order to obtain the best sinter hardening effect, we need to balance the two factors discussed above, in terms of
material and process cost. Without or with too little amount of the above mentioned alloying elements, very little martensite can be obtained even the cooling rate is over 5°C/S. On the other hand, if too much above mentioned alloying elements are added in the system as prealloyed, two problems will appear although fast cooling can be avoid to a certain extent: Firstly, the material becomes harder due to the solution hardening effect, which results in a decrease in compressibility. Secondary, the cost of the base powder will increase due to the more expensive alloying elements such as Mo and Ni. Therefore in practical application, both factors (base powder and cooling rate) related to sinter hardening effect have to be carefully selected and balanced. In addition to these, factors such as density and carbon content also affect the sinter hardening and final mechanical properties of the components.

Fig.1 Schematic TTT diagram of PM steel with varying alloying elements (a) and cooling rate (b), where 1 represents low alloying amount in (a) and low cooling rate in (b); and 2 represents high alloying amount in (a) and high cooling rate in (b)

Case 1, Comparison of 4 different materials for sinter hardening

Materials

Four different base powders are used. Distaloy DH is based on a fully pre-alloyed powder with 1.5%Mo to which 2%Ni has been diffusion bonded. Astaloy 85Mo is a fully pre-alloyed powder with 0.85%Mo. Astaloy CrL is a fully pre-alloyed powder with 1.5%Cr, 0.2%Mn and 0.3%Mo whereas Astaloy CrM is pre-alloyed with 3%Cr and 0.5%Mo. In order to reach a better sinter hardening effect, 2%Cu (-325 mesh) is add mixed to Astaloy 85Mo and 1% and 2%Cu to Astaloy CrL. No Cu was added to Astaloy CrM. The graphite used in all cases was UF-4 and lubricant was Amide wax. The compositions of the mixes prepared are shown in Table 1.
Table 1. Compositions of powder mixes

<table>
<thead>
<tr>
<th>Base powder</th>
<th>Cu (%)</th>
<th>Mo (%)</th>
<th>Cr (%)</th>
<th>Gr (%)</th>
<th>Lub.(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astaloy 85Mo</td>
<td>2</td>
<td>0.85</td>
<td>0.65/0.8</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Distaloy DH</td>
<td>2</td>
<td>1.5</td>
<td>0.65/0.8</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Astaloy CrL</td>
<td>2</td>
<td>0.2</td>
<td>1.5</td>
<td>0.6/0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Astaloy CrM</td>
<td>-</td>
<td>0.5</td>
<td>3</td>
<td>0.4/0.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Processing conditions
Both tensile testing (TS) and impact energy (IE) specimens according to the ISO standards were compacted under pressure between 400MP and 800MPa to reach densities in the range 6.8-7.2g/cm using a laboratory press. Sintering was carried out in a laboratory belt furnace from Abbot. The furnace was equipped with a VARICOOL cooling system enable the cooling to desired cooling rates. Sintering temperature was 1120°C for 30 minutes and the sintering atmosphere was of 90% nitrogen and 10 % hydrogen. After sintering, the samples were tempered at 200°C for 60 minutes in air.

Testing
Rockwell hardness (HRC) was measured on the surfaces of each of the tempered samples. Tensile testing was performed in a MTS Sintech 20D tensile testing machine. Impact energy testing was carried out in a Charpy tester. Dilatometer studies were performed in the cooling range between 0.2C/S to 10C/S. Both the TS and the dilatometer samples were studied metallographically. The results are shown in the followings

Effect of cooling rate
The effect of cooling rate on hardness (HRC), tensile strength (UTS) and impact strength (IE) was summarised in Table. 2. It is clearly seen that both HRC and UTS increase with increasing cooling. This is because higher cooling rate produces more martensite which has positive effect on both HRC and UTS. The influence of cooling rate on the material toughness (IE) is not as pronounced as on the hardness and tensile strength. In case of Distaloy DH and Astaloy CrM as base powder, higher cooling rate even decreases the impact strength.

Among the four proposed materials, Distaloy DH and Astaloy CrM generate enough amount of martensite to make the materials a direct hardening effect even in conventional cooling rates (furnaces without fast cooling). Compared with Distaloy DH, Astaloy CrM reaches similar hardness and impact level, and a higher tensile strength with a good cost advantage of the base material. Recently research and industrial manufacture cases also proved that Astaloy CrM can keep a better dimension tolerance than other sinter hardening materials needed to mix with Cu for the final sinter hardening or direct hardening effect.

Table 2 Mechanical properties of the tested materials (sintered density 6.8-6.9g/cc) under different cooling rates

<table>
<thead>
<tr>
<th>Material</th>
<th>CR (C/S)</th>
<th>HRC</th>
<th>UTS (MPa)</th>
<th>IE (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astaloy 85Mo + 2%Cu + 0.7%C</td>
<td>2.5</td>
<td>27</td>
<td>834</td>
<td>13,2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37</td>
<td>896</td>
<td>14,3</td>
</tr>
<tr>
<td>Distaloy DH + 0.7%C</td>
<td>2.5</td>
<td>31</td>
<td>916</td>
<td>17,1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>39</td>
<td>1019</td>
<td>15,8</td>
</tr>
<tr>
<td>Astaloy CrL + 2%Cu + 0.6%C</td>
<td>2.5</td>
<td>30</td>
<td>821</td>
<td>13,4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>32</td>
<td>837</td>
<td>13,4</td>
</tr>
<tr>
<td>Astaloy CrM + 0.4%C</td>
<td>2.5</td>
<td>33</td>
<td>1026</td>
<td>15,5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>35</td>
<td>1067</td>
<td>11,4</td>
</tr>
</tbody>
</table>
Effect of carbon content and interaction between carbon and cooling rate

Carbon plays a very important role in the process of sinter hardening. In many systems, esp. the prealloyed system, a small variation of the carbon content can make a significant change of the sinter hardening effect. Take Astaloy CrM, for instance. As seen in Fig. 2a, when the carbon content in the sintered material is 0.4%, the martensite/bainite ratio is around 40/60 for the cooling rate of 1°C/S. If the combined carbon is increased to 0.5%, however, the martensite/bainite ratio is changes to 95/5 under the same cooling rate, as shown in Fig. 2b. This indicates that the carbon content is very sensitive to the sinter hardening effect of this material. In other word, there is a certain interaction between the cooling rate and the carbon content in most sinter hardening materials. Therefore, in practical production both carbon content and cooling rate should be well controlled to get a good sinter hardening effect. As shown in Fig 3, with increasing cooling rate the optimised combined carbon content corresponds to the best UTS decreases from 0.45% down to 0.38%.
Case 2, Effect of sinter hardening in combination of warm compaction and high temperature sintering of Astaloy CrM

If other process methods such as warm compaction and high temperature sintering are applied on convention production process, the mechanical properties are improved pronouncedly in terms of tensile strength and elongation. As seen in Fig. 4, starting from 1120°C/30min sintering with sintered density of 7.0g/cm³, Astaloy CrM + 0.35%C can reach a TS of 800MPa and a elongation of 1%. If high temperature sintering is applied (1250°C/60min), the TS and elongation of the same part lie in 950MPa and 2.4%, respectively. With warm compaction (sintered density 7.2g/cm³) and high temperature sintering, both TS and elongation improved further more to the level of 1140MPa and 3.9%. Now, sinter hardening is applied to the warm compacted and high temperature sintered part, the TS is pronouncedly increased to 1320MPa with a decrease of elongation to less than 1% due to the fast cooling. If this part is tempered in air for 1 hour, the mechanical properties are further improved to a TS of over 1400MPa and elongation of 1.5%.

Fig. 4 Properties of Astaloy CrM + 0.4%C under different process conditions

Recent publications [] show that AstaloyCrM + 0.4%C sintered at 1120°C/30min with a sintered density of 7.1g/cm³ can reach a bending fatigue strength (un-notched state with R=−1) of 437MPa under a sinter hardening condition (cooling rate of 2°C/sec). It indicates that this material is a candidate for high fatigue loaded components which also gives a good wear resistance due to its fully martensitic microstructure at the surface.

Sinter hardening in China

Sinter hardening, as an industry manufacture process for large scale PM parts, has been introduced into mainland China during the last 3-4 years. A general survey recently in mainland China shows that 5-7 sinter hardening furnaces are available in mainland China apparently, among which one of them was produced by a domestic furnace manufacture. Further investigation indicates that none of these furnaces are fully used for sinter hardening purposes. The real application of the fast cooling function in these furnaces is less 30% and the rest of the time they are just used for conventional sintering.
Reasons why sinter hardening is not well applied in China so far are summarized as followings:

- Too little education and information exchange in Chinese language to the local PM industry on sinter hardening
- No academic activity in China on sinter hardening
- Problems in dimensional control, since sizing can not be applied after sinter hardening
- Most of the Chinese PM manufactures are, by far, passive in introducing sinter hardening technique in their production process
- Lack of cooperation among the material suppliers, part manufactures and the end users in the product chain

Looking towards the future, we are fully optimistic that the application of sinter hardening will be increased in mainland China due to the two fast growing markets: high performance and good tolerance PM parts for automotive industry and high strength PM parts for high quality electrical power tools. According to a survey performed by an European furnace manufacture on about 35 medium size PM component manufactures in mainland China, 75 percent of these visited companies have the interests to invest in new furnaces with sinter hardening functions. According to the present situation, we have the following suggestions to “WORK TOGETHER” in order to promote the sinter hardening activities in China:

- Bring more education and information exchange in Chinese language to the local PM industry on sinter hardening
- Encourage more international cooperation with Chinese academia on sinter hardening
- Work together with Chinese PM industry on application of sinter hardening
- Encourage more close cooperation among the material suppliers, part manufactures and the end users in the product chain

**Conclusions:** Sinter hardening is a more economical, effective and environmental friendly process in PM component manufacture. It shows a high potential in its application in China. Among other sinter hardening materials, Cr-steels will be more and more applied due to their good hardenability, low material cost and better dimensional stability.