THERMODYNAMIC AND KINETIC BEHAVIOURS OF ASTALOY CrM

Yang Yu

Höganäs AB, SE-263 83 Höganäs, Sweden

Abstract - The phase diagram and some other properties of Astaloy CrM have been calculated based on thermodynamics. Experimental investigations on microstructures of the sintered samples were performed by means of metallography, X-ray diffraction and TEM, which indicate a great deviation from the calculated phase diagram. A very strong kinetic behaviour of this material is conformed. The CCT diagrams of Astaloy CrM with different carbon content (0.3%, 0.4% and 0.5%) are determined. Factors influencing diffusion behaviours of carbon as well as chromium and molybdenum are discussed. The effects of chromium and molybdenum on the formation of carbides and on the sintered microstructure are also discussed. In addition, the oxidation state during sintering and its temperature dependence is calculated and discussed.
KEYWORDS: ASTALOY CrM, THERMODYNAMIC EQUILIBRIUM, KINETIC EFFECT

I. INTRODUCTION

Astaloy CrM is a new prealloyed iron based powder (with 3%Cr and 0.5%Mo) developed recently at Höganäs AB. It has a combinative advantage for high compressibility, high mechanical performance, low cost and better for recycling. Since it is a new prealloyed material, the mechanism of its solution hardening effect, sinter hardening effect, diffusion and phase transformation behaviours during sintering process are needed to be more studied. In addition, it is necessary to compare the calculated phase diagram (including some of the calculated characteristics) with the experimental results in order to understand the mechanisms of the hardening effects after sintering, and other properties of this material.

In the present work, thermodynamic calculations and experimental works are both performed on the phase formation and transformation of Astaloy CrM. Discussions are concentrated on the thermodynamic and kinetic effects of this material, as well on its oxidation behaviours during the sintering.

II. THERMODYNAMIC CALCULATIONS ON ASTALOY CrM

All the thermodynamic calculations are performed using the program Thermo-Calc[1]. The phase diagram is shown in Fig. 1. Two features should be noted here concerning the calculated results. One is that the carbon content at the eutectoid point is about 0.25%C, which is much lower than that of the Fe-C system. The second is that when the carbon content is hypereutectoid, during cooling two carbides namely $M_{23}C_6$ and M_7C_3 should precipitate, as shown in Fig. 1

Phase constituent in sintered Astaloy CrM + 0.3%C is shown in Fig. 2, where it can be seen the mole fraction of each phase is varying with temperature. The variation of composition of the carbides ($M_{23}C_6$ and M_7C_3) with temperature is shown in Fig.3 and 4 respectively, which show an increase of Cr and decrease of Fe content for both phases during cooling. The oxidation state at different oxygen partial pressure and temperature is shown in Fig. 5, where NP representing the mole fraction of each phase in the solid and the lines No. 3 correspond the formation of Cr_2O_3 at different oxygen partial pressure (E-20, E-18 and E-16 from left to right). It is interesting to know with decreasing temperature (during cooling), the chromium oxide tends to be more ready to form. Therefore, the oxygen partial pressure (from E-16 to E-20 Atm.) should be more critical during cooling in order to avoid the formation of the oxide.

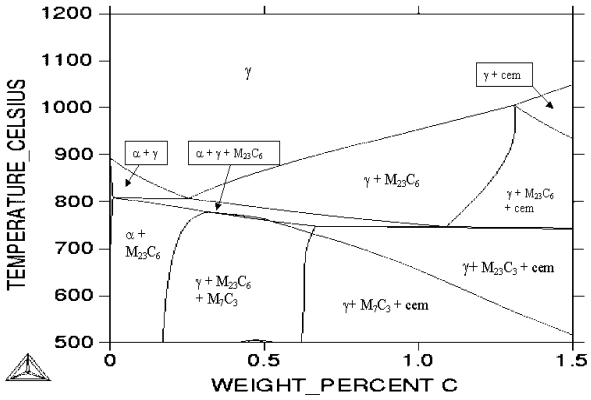


Fig.1 Phase diagram of (Fe-3Cr-0.5Mo) - C system

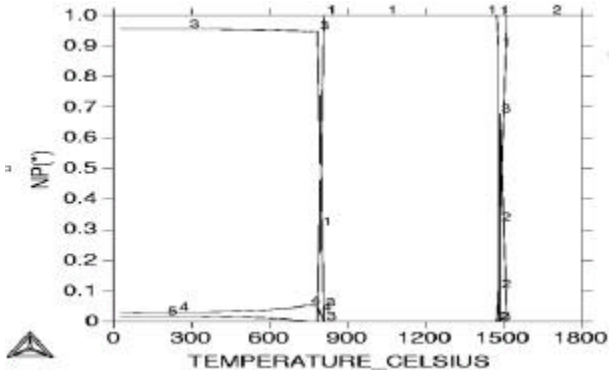


Fig.2 Mole fraction(NP) of each phase (1:FCC; 2:liquid; 3:BCC; 4:$M_{23}C_6$; 5:M_7C_3) of Astaloy CrM + 0.3%C varying with temperature

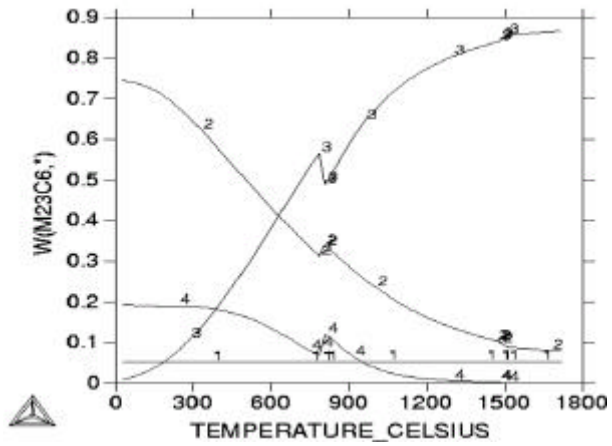


Fig. 3 Composition variations (1:C; 2:Cr; 3:Fe; 4:Mo) with temperature of the $M_{23}C_6$ carbide

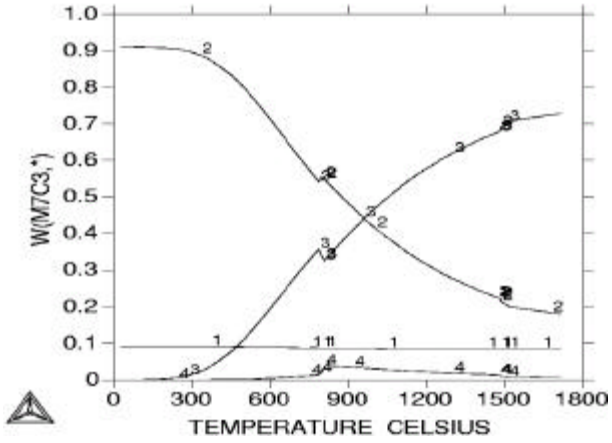


Fig 4 Composition variations (1:C; 2:Cr; 3:Fe; 4:Mo) with temperature of the M_7C_3 carbide

III. Experimental concerning micro-structure and phase constituent of sintered Astaloy CrM

1) Metallography The microstructure of sintered samples containing different carbon contents under different cooling rate are studied by the optical microscope. It is found in most cases, the microstructure of the sintered part is composed of bainite or martensite or both of them. The amount of the phase(s) is sensitive to both carbon content and the cooling rate. The results are summarised in Table 1, where F, B and M represents ferrite, bainite and martensite, respectively.

2) X-ray Diffraction (XRD) XRD tests on the as sintered specimen (1120°C/30min, 0.8°C/S for cooling rate) with the carbon content of 0.1-0.5% were performed suing an X-ray diffractometer, with only the Fe-bcc type structure being observed. This means the carbides are too dilute to be detected by X-ray.

In order to investigate the carbide precipitation, the matrix of the as sintered specimen were dissolved in acid and the remains were studied using a Guinier-Hägg X-ray focusing camera with Cr-radiation and exposure time of 8-10 hours. The reference material used in the analysis was LaB_6. The results are listed in Table 2.

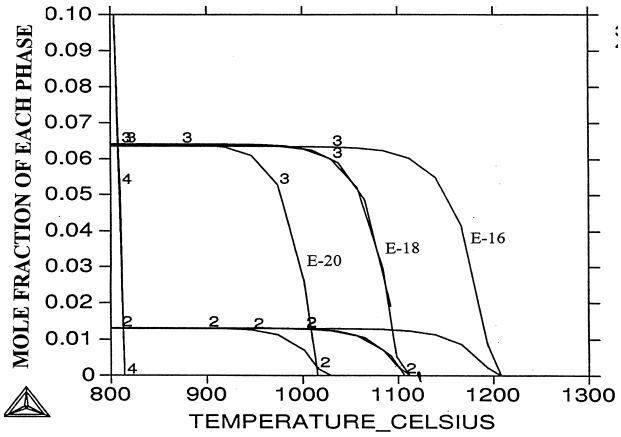


Fig. 5 Critical condition for the formation of Cr_2O_3 (lines No. 3 in the figure) under different oxygen partial pressure (10^{-20} to 10^{-16}Atm.) and temperature

Table 1 Metallurgraphic observation of sintered Astaloy CrM with different carbon content and cooling rate. No retained austenite was found at these carbon contents

Cooling Rate	Carbon Content		
Degree/s	0.3%	0.4%	0.5%
0.1	B +15% F	B + 1% F	B + < 1% F
0.25	B + 7% F	100% B	99.8% B + 0.2% M
0.5	B +0.5% F	90% B + 10% M	70% B + 30% M
1.0	100% B	60% B + 40% M	5% B + 95% M
2.0	90% B + 10% M	20% B + 80% M	1% B + 99% M
3.0	90% B + 10% M	5% B + 95% M	0.5% B + 99.5% M
5.0	80% B + 20% M	100% M	100% M
8.0	100% M	100% M	100% M
12.0	100% M	100% M	100% M
25.0	100% M	100% M	100% M

Table 2 Results of X-ray diffraction analysis on the extracted powders of each sintered part

Powder	Astaloy CrM				
C %	0.1	0.2	0.3	0.4	0.5
Phases obtained by X-ray	Fe_3O_4 Cr_2O_3 Fe-bcc	Fe_3O_4 Fe_2O_3 Fe-bcc	Fe_3O_4 Fe-bcc	Fe_3O_4 Fe_3C Fe-bcc	Fe_3O_4 Fe_3C Fe-bcc

It should be mentioned that the Fe-bcc phase found here are remains of the matrix after extraction. In addition, for Astaloy CrM plus 0.2/0.3 percent of carbon, some Fe_3C carbide should have formed. Since it is too small in amount, it may either be dissolved during the extraction or not be detected by X-ray.

3) Transmission Electron Microscope (TEM) TEM investigations were performed on two samples sintered from Astaloy CrM powder, one with 0.3%C and the other with 0.5%C. Both samples had the same sintering condition as those for the X-ray analysis.

The results show that for both samples, the matrix is composed of martensite and bainite, with the only carbide of Fe_3C-type being found. Its diffraction pattern is shown in Fig 6. The bainite is mainly lower bainite, as

shown in Fig. 7. Neither $M_{23}C_6$ nor M_7C_3 carbide was found, although they appear in the calculated phase diagram. Instead, cementite (M_3C) was observed as the majority of carbides in both samples, although this phase should be appeared when the carbon content is over 0.62% in case of thermodynamic equilibrium.

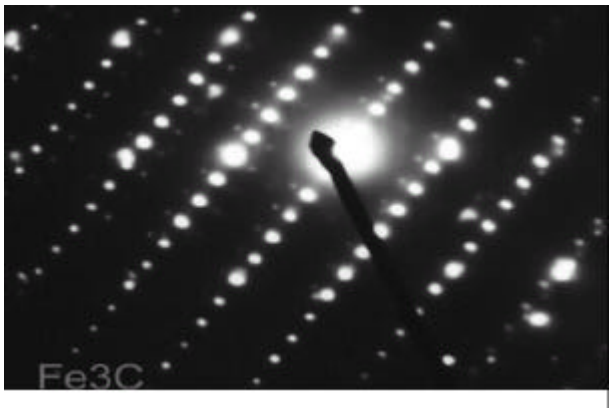


Fig. 6 Electron diffraction pattern of Fe_3C

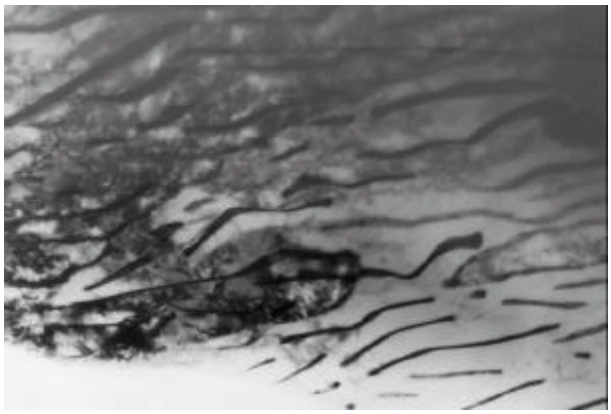


Fig. 7 TEM image of lower bainite in Astaloy CrM with 0.3%C sintered at 1120°C/30min

4) CCT diagrams of Astaloy CrM The CCT diagrams of Astaloy CrM with 0.3%, 0.4% and 0.5% of carbon have been determined from the dilatometer measurements and metallurgraphy observations. The results are shown in figures 8 to 10.

IV. DISCUSSION

1) Deviation of the experimental results from the theoretical calculation. The deviations of the experimental results from the theoretical calculations are mainly in two aspects: microstructure and carbide formation. The former is mainly controlled by the carbon diffusion behaviour and the latter by the diffusion of chromium and molybdenum atoms.

It is known from last section that the microstructure of the sintered samples are mainly composed of bainite and martensite, which indicates that this system is far from the thermodynamic equilibrium state under normal carbon content (0.2%-0.5%) and cooling rates (0.5-5 °C/s).

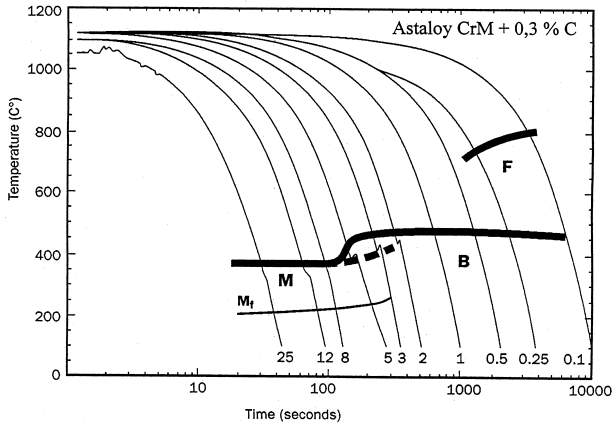


Fig. 8 CCT diagram of Astaloy CrM with 0.3%C

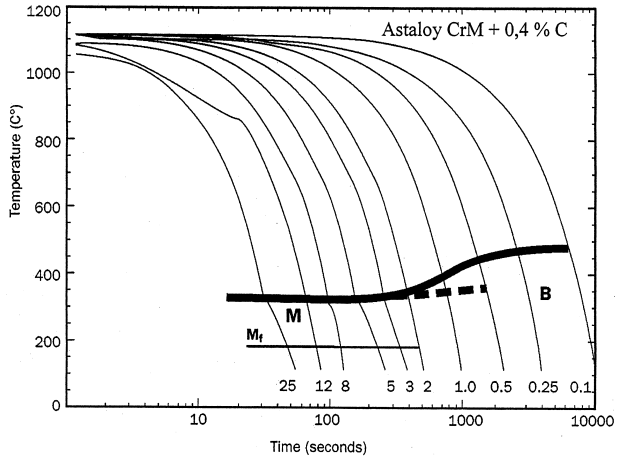


Fig. 9 CCT diagram of Astaloy CrM with 0.4%C

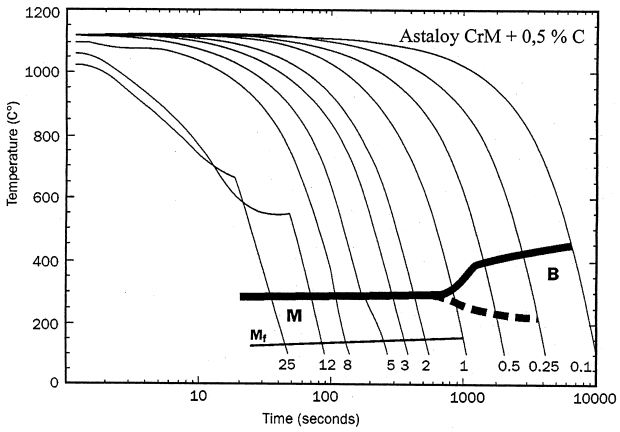


Fig. 10 CCT diagram of Astaloy CrM with 0.5%C

In the case of carbides formation, three carbides corresponding to the carbon content of 0.3% to 0.5% should appear according to the thermodynamic calculation, namely $M_{23}C_6$, M_7C_3 and M_6C. However, none of them was found in the sintered parts. From the calculation, cementite should appear at a carbon level of above 0.62%, as stated in the previous section. However, in all sintered parts with carbon contents in the range of 0.3% to 0.5%, cementite was found as the unique carbide. The reason why no other carbides (except of Fe_3C) is obtained in this material will be discussed in the next section.

2) Different diffusion behaviours in the Fe-C system and the Fe-Cr-Mo-C system. Previously, intensive studies have been performed on the Fe-C system due to the fact that this system is very important in the iron and steel industry. Since it is a binary system and the carbon diffusion coefficient is several orders higher than that of iron, the phase transformation process in the Fe-C system is mainly controlled by the diffusion of carbon atoms. Under lower and medium cooling rates, carbon diffusion is almost complete. Thus thermodynamic equilibrium microstructures are obtained, such as ferrite and pearlite. Under medium high or high cooling rate, carbon diffusion is partially complete, and over-saturated ferrite type phase is obtained. Thus bainite microstructure is found (upper bainite in case of high temperature and lower bainite in case of low temperature). In case of super-high cooling rate, no carbon diffusion can occur. Phase transformation takes place from FCC to BCC in the way that all the carbon atoms are frozen in the distorted BCC crystal structure. Thus the over-saturated ferrite-type martensite is formed.

In the system of Fe-Cr-Mo-C, however, phase transformation process (and thus the final sintered microstructure) is controlled by the diffusion behaviours of both carbon and the alloying metal atoms. Here, it is very important to understand how the alloying elements (Cr and Mo) influence the carbon diffusion behaviour. As we know, the γ to α phase transformation in steels is mainly controlled by the carbon diffusion behaviour during the cooling process. In the Fe-C system (without other alloying element), the temperature of the γ to α phase transformation is at around 720^{o}C. From the dilatometer measurements of Astaloy CrM, however, it is known that the γ to α phase transformation temperature is in the range of 350^{o}C to 500^{o}C, which is well below that of the Fe-C system. This means that the additional alloying elements Cr and Mo have a very strong influence to the γ-α transformation by varying the diffusion behaviour of the carbon atoms: they hinder the diffusion of the carbon atoms in the CrM matrix. Under such circumstance, a higher driving force (over cooling) is needed for the Fe-Cr-Mo-C system to start the γ to α transformation during the cooling process, as compared to that of the Fe-C system. This explains why a relative low γ to α transformation temperature is needed for the Fe-Cr-Mo-C system. At such a low transformation temperature (350^{o}C to 500^{o}C), the carbon activity is relatively low, thus the diffusion length of the carbon atoms is very limited. Therefore, the thermodynamic non-equilibrium lower bainite and martensite is obtained as the main microstructure constituent of the sintered Astaloy CrM component, although a conventional cooling rate (0.8^{o}C/s – 2^{o}C/s) is applied after sintering. This is the main reason why Astaloy CrM has a relatively high hardening effect after sintering.

As to the reason why no $M_{23}C_6$ and M_7C_3 carbide is obtained in the sintered Astaloy CrM component, it is necessary to study the diffusion behaviours of the alloying elements (Cr and Mo).

From Fig. 3 and Fig. 4, it can be seen that a certain concentration of Cr and Mo is needed for the formation of these carbides: about 30% of Cr and 10% of Mo in case of $M_{23}C_6$; about 40% of Cr and 5% of Mo in case of M_7C_3. The concentration of Cr and Mo in the CrM matrix is, however, 3% and 0.5% respectively. This means that ten times of Cr and ten to twenty times of Mo atoms have to be concentrated at the carbide ($M_{23}C_6$ or M_7C_3) nucleation positions by the diffusion of these atoms in the CrM matrix. As a matter of fact, the diffusion of both Cr and Mo atoms are relatively slow at the carbide formation temperature (their diffusion coefficients are in the range of 10^{-14} cm^3/s to 10^{-12} cm^3/s). Therefore, the time in the cooling process is not enough for these metallic atoms to reach such a high concentration which fulfils the condition for the carbides nucleation. This explains why no $M_{23}C_6$ and M_7C_3 carbide is obtained in the sintered Astaloy CrM component.

3) Oxidation state during sintering and its temperature dependence. It can be seen from Fig. 5 that the critical condition for the formation of Cr_2O_3 is dependent of the oxygen partial pressure and the temperature. At 1120C, if the oxygen partial pressure of the sintering atmosphere is below 10^{-18} Atm., no oxidation takes place. This calculated result is in good agreement with the experimental and earlier calculated ones, where the critical oxygen partial pressure is $5*10^{-18}$ Atm. [2]. It can also be seen that under the same oxygen partial pressure, the tendency to form the chromium oxide is decreasing with increasing temperature.

This result is of significance for choosing the right sintering temperature and atmosphere to prevent the sintering from oxidation. For instance, if the sintering is performed at 1210C, even the oxygen partial pressure is around 10^{-16} Atm., no oxidation takes place. This indicates that the sintering of Astaloy CrM at high temperatures is not so sensitive to the atmosphere as to that at low temperatures. On the other hand, if the oxygen partial pressure is around 10^{-18} Atm., and the sintering temperature is decreasing from below 1110C, oxidation will take place.

V. Conclusions

1) The Fe-Cr-Mo-C system has a much higher kinetic effect than the Fe-C system.
2) Carbides such as $M_{23}C_6$, M_7C_3 and M_6C do not appear in the sintered Astaloy CrM with 0.1-0.5%C.
3) High temperature sintering of Astaloy CrM is less sensitive to the sintering atmosphere than low temperature sintering

References

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[2] J. Arvidsson and O. Eriksson, Proc. Powd. Metall. World Congr., **2**(1998) 253.