Sintered Fe-Cr-Mo-Si-C alloys produced from pre-alloyed Fe-Cr based powders admixed with 4% SiC for high performance applications

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Abstract
The use of pre-alloyed Fe-Cr based powders has been steadily increasing in the automotive industry. Mechanical properties can be tailored due to phase transformations controlled by alloying elements and cooling rates. Employing silicon carbide (SiC) as a source of alloying elements has been proved to be possible. In this study, three different pre-alloyed Fe-Cr based powders, namely Astaloy CrA, Astaloy CrL, and Astaloy CrM, were alloyed with 4 wt. % SiC powder. The powders were mixed and pressed into tensile test bars. The green compacts were sintered at 1250 °C for 45 minutes under the cracked ammonia gas and slowly cooled (<0.1°C/s) to room temperature. All experimental sintered alloys manifested a common feature resembling those of full pearlitic ductile irons, i.e., the feature consisted of black nodular particles enveloped with hyper-eutectoid steel matrix (grain boundary or pro-eutectoid cementite plus pearlite). The tensile testing indicated that Alloy-3 (Astaloy CrM + 4%SiC) was observed to have better mechanical properties in comparison with Alloy-1 (Astaloy CrA + 4%SiC) and Alloy-2 (Astaloy CrL + 4%SiC), apart from slightly lower elongation than Alloy-2. Regardless of SiC addition, the presence of chromium (Cr) content was observed to substantially influence mechanical properties and microstructure. According to the investigation of fracture surfaces by SEM, mixtures of shallow dimples and cleavage fractures were examined in the sintered alloys.

Keyword: Sintered alloys, SiC addition, Fully pearlitic matrix, Interlamellar spacing

1. Introduction
Powder metallurgy (PM) has been recognized as a cost-effective as well as sustainable manufacturing process over decades due to low energy consumption and less material waste [1]. Traditionally, nickel
(Ni), copper (Cu), and molybdenum (Mo) have been used as essential alloying elements in PM steels. However, these elements are recently getting replaced by cost-effective alloying elements such as chromium (Cr) and manganese (Mn) due to fluctuation of price, the difficulty of recycling, and health issues in recent years. One issue concerning Cr and Mn is that they are oxidation-prone unless a proper sintering atmosphere is employed [2]. Despite the concern on oxidation vulnerability, the sintering of chromium-containing pre-alloyed-powder compacts has already been proved to be possible at high temperatures (1120 to 1250°C) under the proper sintering atmosphere (hydrogen/nitrogen mixture) [3]. Therefore, the utilization of pre-alloyed powder has been steadily increasing for high-performance applications since their properties can be tailored by sinter hardening, high-temperature sintering, warm compaction, and alloying addition [4]. As SiC exhibits a wide range of properties in terms of excellent thermal stability, thermal shock resistance, hardness and wear resistance, there has been a lot of ongoing studies related to the sinterability of SiC with Fe and Fe based powders to produce metal matrix composites (MMC) [5-9]. Tensile strength and hardness of sintered Fe-SiC were observed to improve with increasing sintering temperature and smaller SiC particle size [7]. Likewise, the addition of SiC led to the improvement of strain at break in the case of sintered 316L+SiC composite, except for the reduction in sintered density [8]. It was previously reported that the interaction between SiC and iron (Fe) or Fe based powders above 1100 °C resulted in decomposition of SiC, and both Si and C atoms diffused into the Fe or Fe based powders, contributing to the formation of fully pearlite or ferrite/pearlitic microstructure [9]. Similar behavior was detected to exist when SiC was admixed into Fe-Mo-Si-C alloys [10-11]. In addition to that, sintering of Fe-Cr-Mo + SiC compacts followed by a slow cooling rate (0.1°C/s) was found to achieve a microstructure similar to that of fully pearlitic ductile iron [12].

In the present work, the authors aim to explore the effect of Cr content in pre-alloyed Fe-Cr based powders on microstructure and mechanical properties of sintered alloys produced from pre-alloyed Fe-Cr based + SiC powder compacts.

2. Experimental procedure

2.1 Material Preparation

The starting powders used in this study were water atomized pre-alloyed powder grades, namely Astaloy CrA, Astaloy CrL, and Astaloy CrM supplied by Höganäs AB, Sweden. As-received powder sizes were in the range of 45-150 µm. The pre-alloyed powders were admixed with 1% zinc stearate as a lubricant and 4% SiC as an alloying source of C and Si. Powder mixtures were blended in a mixer for 1 hr and pressed into tensile test bars using a uniaxial compaction machine at room temperature, according to MPIF-10 in Figure 1a. In the sintering process, the samples were delubricated by holding at 600 °C for 1 hour and 700°C for 30 minutes under the argon (Ar) atmosphere, and the samples were heated with a heating rate of 4.8°C/min up to isothermal sintering temperature. The isothermal sintering was conducted at 1250°C for 45 minutes under the cracked ammonia gas (75% Hydrogen and 25% Nitrogen). The sintered parts were cooled down to room temperature with a rate of 2.89 °C/min in the sintering furnace. The nominal composition of investigated materials is summarized in Table 1.

2.2 Material characterization

The tensile test was performed on a Universal Testing Machine (Instron 8801) at a cross speed rate of 0.1 mm/min in Figure 1b. The hardness value of sintered materials was evaluated by conducting on Rockwell B macro hardness tester. To observe the microstructure, the cross-section of tensile test bars was cut and hot mounted using thermoplastic resin for 15 minutes. The microstructure was analyzed by optical microscopy (OM) and scanning electron microscopy (SEM). The area fraction of microstructural components was evaluated by an image analysis software (Image-J) utilizing several OM micrographs taken on polished samples. In pearlitic steel, the interlamellar spacing and pearlite colony size are very important parameters that control the mechanical properties. Therefore, interlamellar spacing was measured by the circular grid test method [14], and pearlite colony size was determined by the linear
intercept method following the procedure of ASTM-E112 (2010). In the case of fractography analysis, the tensile fracture surface of each sintered alloy was studied by SEM.

![Image of tensile test bar and tensile testing](a) and (b)

**Figure 1.** MPIF-10 standard tensile test bar (a) [13] and an image of tensile testing (b).

### Table 1. The nominal composition of powder mixes (wt.%).

| Remark     | Base powder | Admixed alloying element | Fe  | Cr  | Mo  | Si  | C   |
|------------|-------------|--------------------------|-----|-----|-----|-----|-----|
| Alloy-1    | Astaloy CrA | SiC                      | Bal.| 1.8 | -   | 2.8 | 1.2 |
| Alloy-2    | Astaloy CrL | SiC                      | Bal.| 1.5 | 0.2 | 2.8 | 1.2 |
| Alloy-3    | Astaloy CrM | SiC                      | Bal.| 3.0 | 0.5 | 2.8 | 1.2 |

3. Results and discussion

#### 3.1 Microstructure

Even though the composition differed to some extent, the microstructure of all sintered alloys somehow unveiled a common feature closed to those of fully pearlitic ductile irons. The feature generally consisted of black nodular particles enveloped with pearlitic matrix in which pro-eutectoid cementite network (PCN) is precipitated along prior-austenite grain boundaries (PAGBs) in Figure 2a-2c and a small fraction of porosity. The area percentage of microstructure components is displayed in Figure 3.

Measurements of pearlite structure parameters including interlamellar spacing and pearlite colony size were conducted and given in Table 2. The measured pearlite interlamellar spacing decreases with increasing Cr content in sintered alloys (Table 2).

The sintered alloys with nominal compositions corresponding to those of Alloy-2 and Alloy-3, produced under sintering temperature of 1250°C and vacuum atmosphere also generated a fully pearlitic ductile iron-like microstructure [15], but with smaller PCN size and amount. The formation of PCN at PAGBs prior to pearlite transformation is a common phenomenon occurring in hypereutectoid Fe-C steels. In a previous study, austenitization temperature and transformation temperature affected PCN size and amount [15]. Large PCN was favored by large prior austenite grain sizes obtained at high austenitization temperatures. In our work, the sintering temperature, which is assumed to be equivalent to austenitization temperature, is 1250°C. Thus, it can be expected to have large prior austenite grain sizes in sintered alloys. The post-sintering cooling rate employed in our work was 2.89°C/min or 0.05°C/s, which was slow enough for C diffusion to form large carbide particles at high temperatures (in austenite (γ) + cementite (θ) filed). The slow cooling rate is unable to make the austenite phase bypass cementite precipitation. The disappearance of ferrite halo from all sintered Cr-containing alloys in this work, compared to sintered Fe-Mo-Si-C alloys [10-11], may imply that Cr addition suppresses the formation of ferrite halo around the black nodular particle in Figure 2d. In other words, Cr promotes pearlite transformation.

The reduction of measured pearlite interlamellar spacing with increasing Cr content in sintered alloys, as given in Table 2, is in good agreement with the analysis results using the neural network model.
The effect of alloying element concentration on interlamellar spacing \( (S_0) \), measured in µm, is shown in Equation (1):

\[
\log S_0 = -2.212 + 0.0514 \times [\text{Mn}] - 0.0396 \times [\text{Cr}] + 0.0967 \times [\text{Ni}] - 0.002 \times [\text{Si}] - 0.4812 \times [\text{Mo}] - \log \left( \frac{T_E - T}{T_E} \right)
\]

(1)

where \([\text{Mn}], [\text{Cr}], [\text{Ni}], [\text{Si}], \text{ and } [\text{Mo}] \) are alloying contents in wt. %, \( T_E \) is eutectoid temperature and \( \Delta T = T_E - T \) is the undercooling below the eutectoid temperature. The addition of Mo and Cr decreases the pearlite interlamellar spacing whereas that of Si slightly influences interlamellar spacing. The sintered alloy with higher Cr content has fine interlamellar spacing.

![Figure 2. SEM micrographs of sintered Alloy-1 (a, d), Alloy-2 (b), and Alloy-3 (c).](image)

**Table 2.** Evaluated interlamellar spacing and pearlite colony size.

| Remark   | Interlamellar Spacing (nm) | Pearlite colony size (µm) |
|----------|-----------------------------|---------------------------|
| Alloy-1  | 194.93                      | 9.42                      |
| Alloy-2  | 278.68                      | 9.65                      |
| Alloy-3  | 152.13                      | 8.48                      |

3.2 Mechanical properties

All experimental sintered alloys showed high ultimate tensile strengths (UTS) in the range of 700-800 MPa with yield strengths (YS) in the range of 300-400 MPa (Figure 4a). Both strengths varied slightly with Cr content in sintered alloys. The hardness value and elongation varied with Cr content (Figure 4b). Since the sintered alloys exhibited composite microstructure consisting of black particles, pores, and PCN-containing pearlite matrix (Figures 2 and 3), it was supposed that all microstructural
components should have contributions to tensile strength. Taking the area fractions of microstructural components (Figure 3) into account, the pearlite matrices may be considered as the most important contributor to the mechanical properties of sintered alloys. As given in the literature [17-20], the strength and hardness of pearlite structure relied on refinements of interlamellar spacing and pearlite colony size, as given by the Hall-Petch relationship (Equation 2):

$$
\sigma = \sigma_0 + KS_0^{1/2}
$$

where $\sigma$ is the stress, $\sigma_0$ is the friction stress, $K$ is the Hall-Petch constant. With a comparison between tensile strength and hardness, given in Figure 4, it is noticed that the hardness is quite sensible to the Hall-Petch relationship. For the elongation value, it is also sensible to interlamellar spacing values of the pearlite structure (Figure 4b). The relative elongation of the steels with coarse lamellar pearlite is higher than that of the steels with fine lamellar pearlite [21]. However, microstructural parameters, such as interlamellar spacing, austenite grain size, and pearlite colony size are not sufficient to fully describe the structure and the mechanical strength of pearlite [22]. Further studies on the effects of strengthening mechanisms in pearlite will be needed.

Figure 3. % Area fractions of microstructural components in sintered alloys.

Figure 4. Mechanical properties of sintered alloys (a) strengths and (b) hardness and %elongation.
3.3 Fractography Analysis

The fracture surface of the experimental sintered alloys is shown in Figure 5. All sintered alloys exhibited a large portion of cleavage characterized by a river pattern, small fractions of quasi-cleavage, and micro-dimples with sizes comparable to interlamellar spacing. The sites of black particles can be seen as empty holes in Figure 5. The fracture surface characters are related to tensile properties. As all sintered alloys have low elongation values but high tensile strengths, the fracture surfaces are dominated by cleavage, and smaller areas with dimples were observed. Some areas with quasi-cleavage are observed in Alloy-2 (Figure 5c) due to its highest elongation values among all experimental sintered alloys.

![Fractography images of Alloy-1 (a-b), Alloy-2 (c-d), and Alloy-3 (e-f).](image)

**Figure 5.** Fractography of sintered Alloy-1 (a-b), Alloy-2 (c-d), and Alloy-3 (e-f).
4. Conclusions
The microstructure of all sintered alloys shows a common feature similar to that of fully pearlitic ductile iron, i.e., the feature consists of black nodular particles enveloped with hyper-eutectoid steel matrix (grain boundary or pro-eutectoid cementite plus pearlite). Even though the ferrite halo around black particles (core-shell structure) was discovered to exist in sintered Fe-Mo-Si-C composites [10-11], this phenomenon was not found in this study. Therefore, it can be concluded that the existence of a small portion of molybdenum (Mo) in this work might not substantially influence the final microstructure. Instead, the presence of chromium suppressed the ferrite halo formation around black nodular particles and might promote pearlite formation in some ways.

Surprisingly, although the fabrication and sintering were conducted under the same condition, refining of the interlamellar spacing by increasing chromium (Cr) content was observed in this work. Moreover, sintered Alloy-3 achieved higher strength and hardness values in comparison with Alloy-1 and Alloy-2. All experimental sintered alloys have a microstructure-property relationship explained by the Hall-Petch relationship. Fractography analysis confirmed that sintered alloys exhibited a large portion of cleavage fracture characterized by a river pattern, small fractions of quasi-cleavage, and micro-dimples with sizes comparable to the interlamellar spacing.

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