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B. ALI<sup>\*,\*\*\*</sup>, S.H. CHOI<sup>\*,\*\*</sup>, S.J. SEO<sup>\*</sup>, D.Y. MAENG<sup>\*\*\*\*</sup>, C.G. LEE<sup>\*\*\*\*\*</sup>,  
T.S. KIM<sup>\*,\*\*\*#</sup>, K.T. PARK<sup>\*#</sup>**CARBON CO-DEPOSITION DURING GAS REDUCTION OF WATER-ATOMIZED Fe-Cr-Mo POWDER**

The water atomization of iron powder with a composition of Fe-3Cr-0.5Mo (wt.%) at 1600°C and 150 bar creates an oxide layer, which in this study was reduced using a mixture of methane (CH<sub>4</sub>) and argon (Ar) gas. The lowest oxygen content was achieved with a 100 cc/min flow rate of CH<sub>4</sub>, but this also resulted in a co-deposition of carbon due to the cracking of CH<sub>4</sub>. This carbon can be used directly to create high-quality, sinter hardenable steel, thereby eliminating the need for an additional mixing step prior to sintering. An exponential relationship was found to exist between the CH<sub>4</sub> gas flow rate and carbon content of the powder, meaning that its composition can be easily controlled to suit a variety of different applications.

*Keywords:* Water atomization, Fe-based powder, Oxide reduction, Powder metallurgy, Sinter-hardening alloys

**1. Introduction**

The relative abundance and low cost of iron (Fe) already makes it an essential element in daily life, but with increasing advancements in the field of powder metallurgy, Fe-based powders are becoming increasingly used in powder metal processing, welding rods, medicine, wastewater treatment and food production. Most iron powder is used in the production of high-strength steel components, which typically rely on alloying elements such as nickel (Ni), copper (Cu) and molybdenum (Mo) for their strength [1-2]. However, the high cost of these traditional alloying elements has created a need for cheap and efficient alternatives in order to reduce overall product costs. One such alternative is chromium (Cr), which is low in cost, relatively abundant, easy to recycle and offers good resistance to temper softening [1-3]. It is also particularly effective in improving sinter-hardenability [4], which is a process of transforming the whole part or some specific region to martensite by controlling the cooling rate during sintering. This offers many economic benefits as a one-step manufacturing process for achieving a good combination of strength, toughness and hardness [4]. Yet despite all these benefits associated with Cr, it is not currently being used to its fullest potential because of its very high affinity for oxygen [1-5].

The cheapest and most common method for the production of iron and steel powders is water atomization, which offers the important benefit of producing powders with an irregular shape. This facilitates powder compaction, gives good green body

strength and makes the powder suitable for near-net shaping of components [6]. However, the interaction of molten metal droplets with water or steam inevitably creates a surface oxide layer during atomization [6-7], and so subsequent reduction is needed to obtain high-purity powder. In this pre-alloyed state, Cr is usually present in solid solution with iron, and so its activity is roughly equal to its content [5].

The reduction of Fe oxides in a reducing gas environment has been widely studied due to its economic and industrial importance, with a number of studies looking at the kinetics of reduction with H<sub>2</sub> [8-14], CO [13-16] and CH<sub>4</sub> [17-20] gas. In a previous study, we briefly discussed the reduction of Fe-based oxides in an environment of H<sub>2</sub>, CO and CH<sub>4</sub> [21], and so the present study specifically focuses on the reduction of Cr-based oxides using CH<sub>4</sub> gas and the carbon that is co-deposited during reduction. Studies by Ostrowski et al [22] into the reduction of Cr<sub>2</sub>O<sub>3</sub> using CH<sub>4</sub> gas mixtures found that the extent of reduction increases with reduction temperature and CH<sub>4</sub> content. Ebrahimi-Kahrizsangi et al. [23] have also shown that the minimum temperature needed for the conversion of Cr<sub>2</sub>O<sub>3</sub> to Cr<sub>3</sub>C<sub>2</sub> in a 30% CH<sub>4</sub> gas mixture is 850°C. Similarly, Khoshandam et al. [24] have demonstrated that there is negligible carbon deposition during the conversion of Cr oxides to carbides in a CH<sub>4</sub> atmosphere, at least within a temperature range of 870-975°C. These previous studies used gas mixtures composed of CH<sub>4</sub>, H<sub>2</sub> and Ar, and mostly concerned the reduction of a single oxide of a given metal.

\* KOREA INSTITUTE FOR RARE METALS, KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY, INCHEON, SOUTH KOREA

\*\* DEPARTMENT OF ADVANCED MATERIALS ENGINEERING, IN-HA UNIVERSITY, INCHEON, SOUTH KOREA

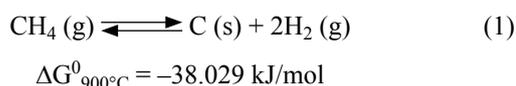
\*\*\* CRITICAL MATERIALS AND SEMICONDUCTOR PACKAGING ENGINEERING, UNIVERSITY OF SCIENCE AND TECHNOLOGY, DAEJEON, SOUTH KOREA

\*\*\*\* SAMSUNG ELECTRO-MECHANICS CO. LTD, SOUTH KOREA.

\*\*\*\*\* ADVANCED MATERIALS & PROCESSING CENTER, INSTITUTE FOR ADVANCED ENGINEERING, YONGIN-SI, SOUTH KOREA

# Corresponding authors: ktpark@kitech.re.kr and tskim@kitech.re.kr

The present study concerns powder particles with a surface layer that is composed of a number of different oxides of Fe and Cr, rather than just one. For this, a Fe-based powder with a composition of Fe-3Cr-0.5Mo (in wt.%) was fabricated, and any surface oxides produced during water atomization were reduced in a gas environment. Special attention was given to the reduction of Cr-based oxides by using a mixture of CH<sub>4</sub> and Ar. At the experimental temperature used (900°C), the CH<sub>4</sub> decomposes into C and H<sub>2</sub> gas according to following Eq. (1):



This H<sub>2</sub> gas that is generated helps to reduce the oxides, and so no extra addition of H<sub>2</sub> was considered necessary. However, as using CH<sub>4</sub> for reduction does result in excess carbon being deposited onto the powder, the effect of the gas flow rate on the deposited carbon was studied to develop a mathematical relationship for controlling the carbon content of the final product. Using this, high-carbon alloy powders can be produced directly without any further carbon addition, and once sintered can be used to create high-strength steel parts and wear resistant hardfacing coatings for various applications subject to harsh abrasive conditions, such as automobiles, hard-cased gears and tooling equipment.

## 2. Experimental procedure

A mother alloy with a composition of Fe-3Cr-0.5Mo (wt.%) was fabricated in an electric arc furnace, melted at 1720°C, and then atomized by a stream of water using a pressure of 15 MPa and a melt orifice diameter of 5 mm. Once the atomized powder was collected and dried, a 20 g sample was placed inside alumina boat and loaded into quartz tube under a vacuum of  $6.5 \times 10^{-2}$  Torr. This was placed into a horizontal vacuum-tube furnace, which was then purged with Ar gas (purity >99.99%) for around 40 minutes. A mixture of CH<sub>4</sub> and Ar gas with different flow rates was then introduced for reduction of the atomized powder. The different gas mixtures used are listed in Table 1 along with the corresponding gas flow rates and experimental parameters followed.

TABLE 1

Gas composition and experimental parameters used for reduction

	T (°C)	Heating Rate	Holding Time	Gas Flow Rate	Vacuum	Comments
1	900°C	5°C/min	1.5 h	CH <sub>4</sub> -100 cc/min	$6.5 \times 10^{-2}$ torr	Total flow rate was 100 cc/min in every condition
2				CH <sub>4</sub> -50 cc/min + Ar-50 cc/min		
3				CH <sub>4</sub> -20 cc/min + Ar-80 cc/min		

Different qualitative and quantitative techniques were used to characterize the initial and final materials. Inductively coupled plasma mass spectroscopy (ICP-MS) was used for chemical analysis of the mother alloy, while the morphology and chemical composition of the powders was analyzed by field emission-scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS), respectively. The composition of the surface oxide and its depth profile were analyzed by auger electron spectroscopy (AES). Phase identification of the atomized and reduced powder samples was performed by X-ray diffraction (XRD) analysis with Cu-K $\alpha$  radiation. The oxygen and carbon content of the reduced powder was estimated by nitrogen/oxygen and carbon/sulfur analysis, respectively. The standard Gibbs free energy variation with temperature during the reduction of Cr oxides was calculated with the help of HSC Chemistry [24] software.

## 3. Results and Discussion

### 3.1. Atomized powders

The ICP analysis of the mother alloy, the results of which are shown in Table 2, showed that the concentration of elements was very homogenous and close to the starting composition. After atomization, average oxygen content of as-atomized powder was found to be 2.09 wt.%. Pseudo-binary phase diagram of a Fe-3Cr-0.5Mo and H<sub>2</sub>O system showed that three kinds of oxides exist in the high temperature, low H<sub>2</sub>O concentration region, namely: AB<sub>2</sub>O<sub>4</sub>-spinel (Fe<sub>3</sub>O<sub>4</sub>, FeO·Cr<sub>2</sub>O<sub>3</sub>), MeO-type monoxide (FeO), and Mo oxide (MoO<sub>2</sub>). At high temperature, FeO and AB<sub>2</sub>O<sub>4</sub>-spinel (Fe<sub>3</sub>O<sub>4</sub>) are the dominant phases, whereas Fe<sub>2</sub>O<sub>3</sub> is the dominant oxide at low temperature and high concentrations of H<sub>2</sub>O. After atomization, the powder consists of Fe, Fe<sub>3</sub>O<sub>4</sub> and FeO phases, as can be seen from the XRD result in Figure 1 [21].

TABLE 2

ICP analysis of mother alloy

Element (nm)	Concentration (Fe-3Cr-0.5Mo)	
	Weight (%)	Atomic %
Cr (283.5)	2.99	3.11
Fe (259.9)	96.49	96.65
Mo (202.0)	0.52	0.24

Reduction process follows different chemical pathways based on the reduction temperature. At low temperatures (below 570°C) reduction proceeds in single step from Fe<sub>3</sub>O<sub>4</sub> to Fe because FeO is not stable below this temperature, whereas above this temperature, reduction proceeds in two steps from Fe<sub>3</sub>O<sub>4</sub> to FeO and then to Fe [21,26].

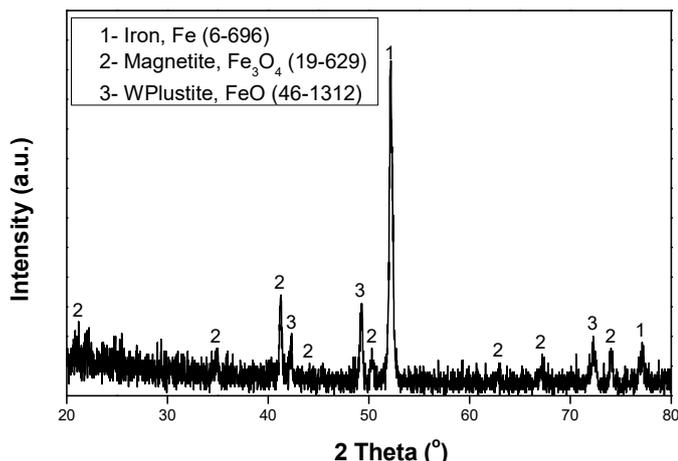
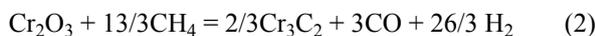


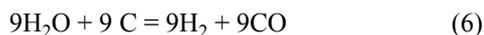
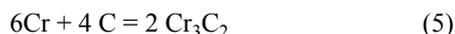
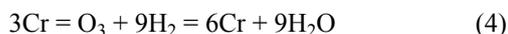
Fig. 1. XRD analysis result of as-atomized powder showing three distinct phases of Fe, Fe<sub>3</sub>O<sub>4</sub> and FeO present in the powder [20]

### 3.2. Thermodynamics of chromium oxide reduction

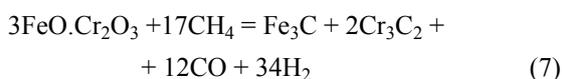
As mentioned earlier, the atomized powders were predicted to contain FeO, Fe<sub>3</sub>O<sub>4</sub> and complex Cr oxides (Cr<sub>2</sub>O<sub>3</sub>, FeO, Cr<sub>2</sub>O<sub>3</sub>). Although the formation of Cr oxides is unlikely when in a prealloyed state the possibility does still exist, and so the thermodynamics of Cr<sub>2</sub>O<sub>3</sub> and FeO.Cr<sub>2</sub>O<sub>3</sub> reduction were studied. Only CH<sub>4</sub> gas was considered as a reductant, as our previous study demonstrated that this gives the optimum oxygen value and helps convert Cr<sub>2</sub>O<sub>3</sub> to carbide by the following reaction Eq. (2) [27-29]:



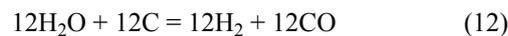
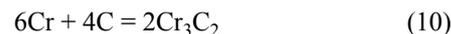
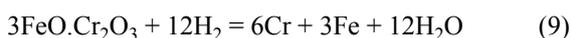
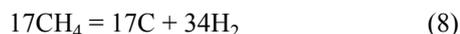
Thus, CH<sub>4</sub> gas supplies carbon that helps convert the oxide into a carbide through diffusion. However, this represents a complicated and complex process, as at temperatures >570°C the decomposition of CH<sub>4</sub> into H<sub>2</sub> and CO becomes feasible. Read et al. [28] studied the reduction of Cr<sub>2</sub>O<sub>3</sub> with CH<sub>4</sub> and found that this decomposition causes reduction to follow a path from Eq. (3) to (6) as:



Qayyum and Reave [29], on the other hand, suggested that at low temperatures chromite is reduced by the Eq. (7):



Whereas at high temperature, the reaction follows chemical pathway from Eq. (8) to (12) as shown below:



According to Anacleto et al. [27], the reduction of Cr oxides to metallic Cr with H<sub>2</sub> or CO needs a much higher temperature, especially CO gas addition of which retards the reduction rather than promoting it. This implies that CH<sub>4</sub> has greater potential for the economic reduction of Cr oxides. For this reason, a mixture of CH<sub>4</sub> and Ar was used in this study.

### 3.3. AES analysis

The AES spectrum of the as-atomized Fe-3Cr-0.5Mo powder (mean size: 50.32 μm) has been shown in Figure 2. The spectrum shows main peaks for Fe, Cr, Mo and O. The strength of the latter indicates that the surface of the powder was covered with an oxide layer, which likely consisted mostly of Fe oxides based on the strength of the Fe peak. The minute Cr peak does, however, suggest that at least some Cr oxide was also present, with the lower peak intensity likely caused by interference from the O and Fe peaks [6]. Depth profiling by AES can be used to determine the extent to which this oxide layer extends from the surface, with Figure 3 showing the change in Fe, O and Cr with analysis time and particle depth. This demonstrates that the concentration of Fe increases with depth, while the concentration of O and Cr decreases, thus indicating that only a surface layer of oxide is present. This oxide layer is likely a complex Cr-based oxide such as Cr<sub>2</sub>O<sub>3</sub> or FeO.Cr<sub>2</sub>O<sub>3</sub>, as the AES results confirm the presence of both Fe and Cr on the surface of the as-atomized particles.

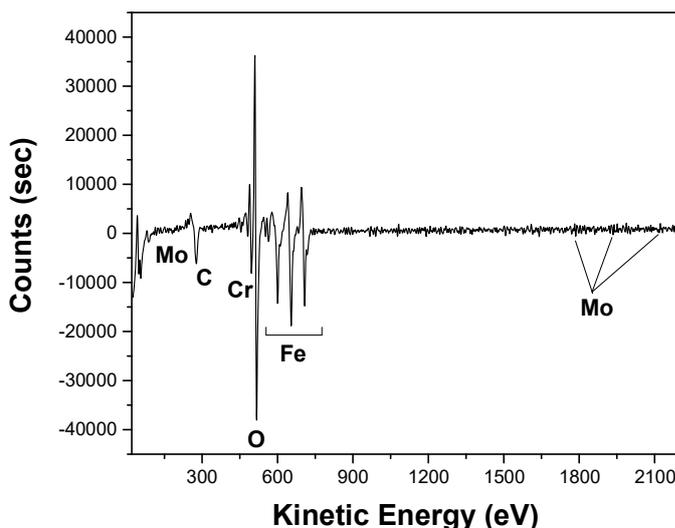


Fig. 2. AES spectrum for as-atomized Fe-3Cr-0.5Mo powder

Powders of Fe alloyed with Cr are typically soft annealed at 800-1000°C under a H<sub>2</sub> atmosphere in order to minimize O<sub>2</sub> and prevent the formation of Fe oxides [30]. This use of H<sub>2</sub> as

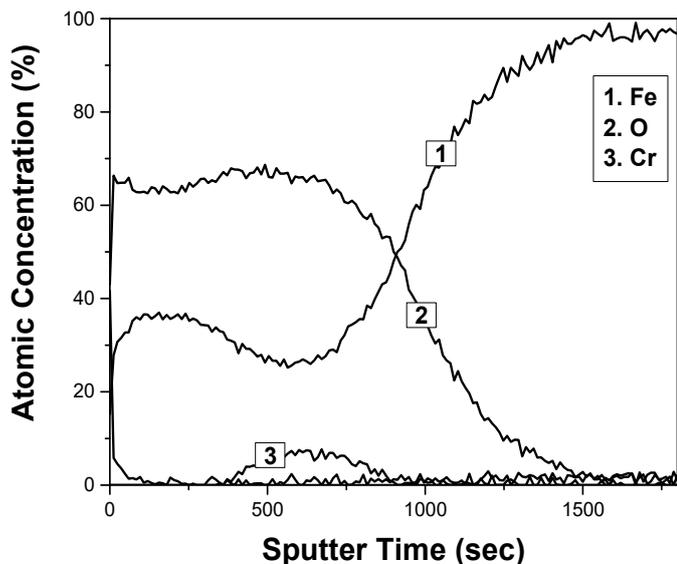


Fig. 3. AES spectrum sputter time and atomic concentration for as-atomized Fe-3Cr-0.5Mo powder

a reducing agent can, however, produce compact Fe layers that can slow the overall reduction rate [8]. Moreover, the reduction of Cr-based oxides by  $H_2$  requires very high temperatures. Figure 4 presents a graph showing the effect of increasing temperature on the Gibbs free energy ( $\Delta G^\circ$ ) for the reduction  $Cr_2O_3$  with  $H_2$  gas. This shows that even at very high temperature, the  $\Delta G^\circ$  value remains positive, indicating that the reaction is not feasible. In this situation  $CH_4$  plays a vital role, as Anacleto et al. [27] have shown that it can increase the rate of Cr oxide reduction by facilitating the formation of Cr carbides, which are then reduced to Cr metal by  $H_2$ . However, as this process results in the deposition of carbon onto the particles, it is necessary to study both the role of  $CH_4$  in reduction and its decomposition to carbon.

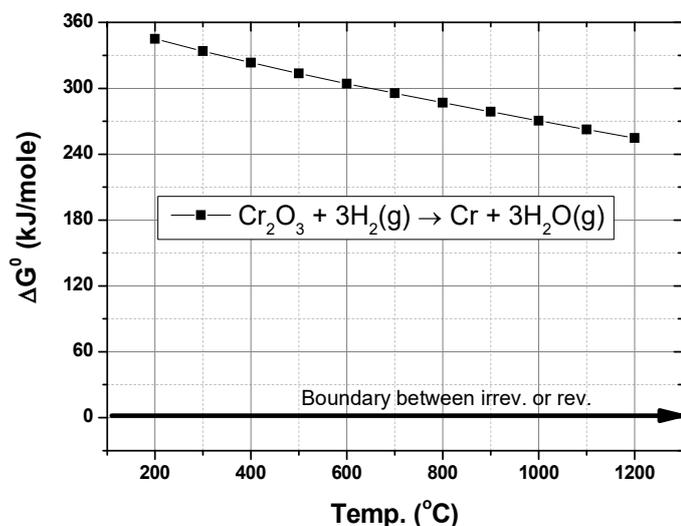


Fig. 4. Gibbs free energy ( $\Delta G^\circ$ ) vs. temperature for the reduction of  $Cr_2O_3$  with  $H_2$  gas

### 3.4. Post reduction

In the XRD patterns of powders reduced using three different flow rates of  $CH_4$  given in Figure 5, two distinct phases (Fe and  $Fe_3C$ ) were detected. The  $Fe_3C$  peak intensity was highest when 100 cc/min of  $CH_4$  was used, and decreased with a decrease in  $CH_4$  flow rate. As explained earlier, this  $Fe_3C$  is produced as a result of the decomposition of  $CH_4$  into C and  $H_2$  at high temperature. No elemental carbon was detected because this is present in an amorphous state and XRD can only be used for the detection of crystalline materials.

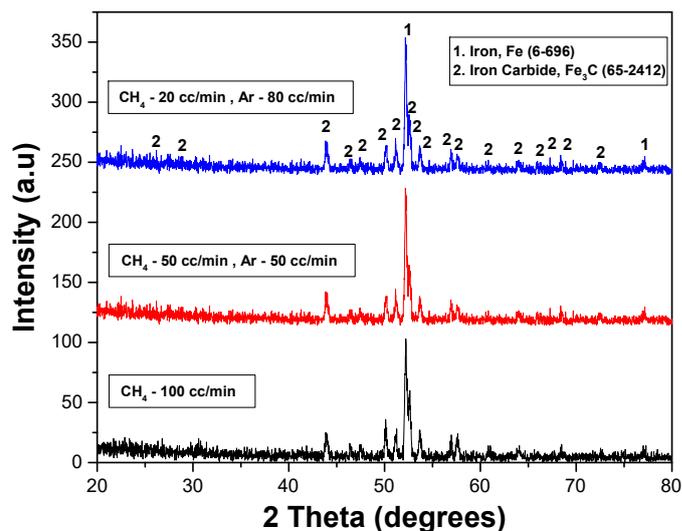


Fig. 5. XRD patterns of powders after reduction with a mixture of  $CH_4$  and Ar gas

The results presented in Table 3 show that the lowest O concentration (0.498 wt%) and highest C concentration (7.998 wt%) occurred in the sample reduced with 100 cc/min  $CH_4$ . When compared to the initial O concentration of the as-atomized powder (2.09 wt.%), this represents a very promising decrease in the extent of oxidation. Lower  $CH_4$  flow rates resulted in a decrease in C concentration and increase in O concentration.

Figure 6 presents SEM and EDS analysis results for powders reduced using different flow rates of  $CH_4$ . It is evident from this that the particles were generally irregular in shape, and were high in carbon due to the decomposition of  $CH_4$ . The absence of oxygen in the EDS results is promising in terms of achieving reduction. The sample reduced with 100 cc/min of  $CH_4$  had the highest Cr and C content, whereas a 20 cc/min flow rate produced the lowest values, indicating that these values are directly related to the amount of  $CH_4$  in the gas mixture used.

Commercially available Fe-based powders need to be mixed with carbon prior to sintering, but as carbon is deposited during reduction with  $CH_4$ , this can potentially eliminate a step in the process and greatly reduce the cost of manufacturing. The small amount of oxygen still present in the sample (Table 3) should be reduced by the deposited carbon during sintering of the powder, as this is normally conducted at temperatures of 1000-1200°C. The remaining carbon can then form ferrite, austenite and other

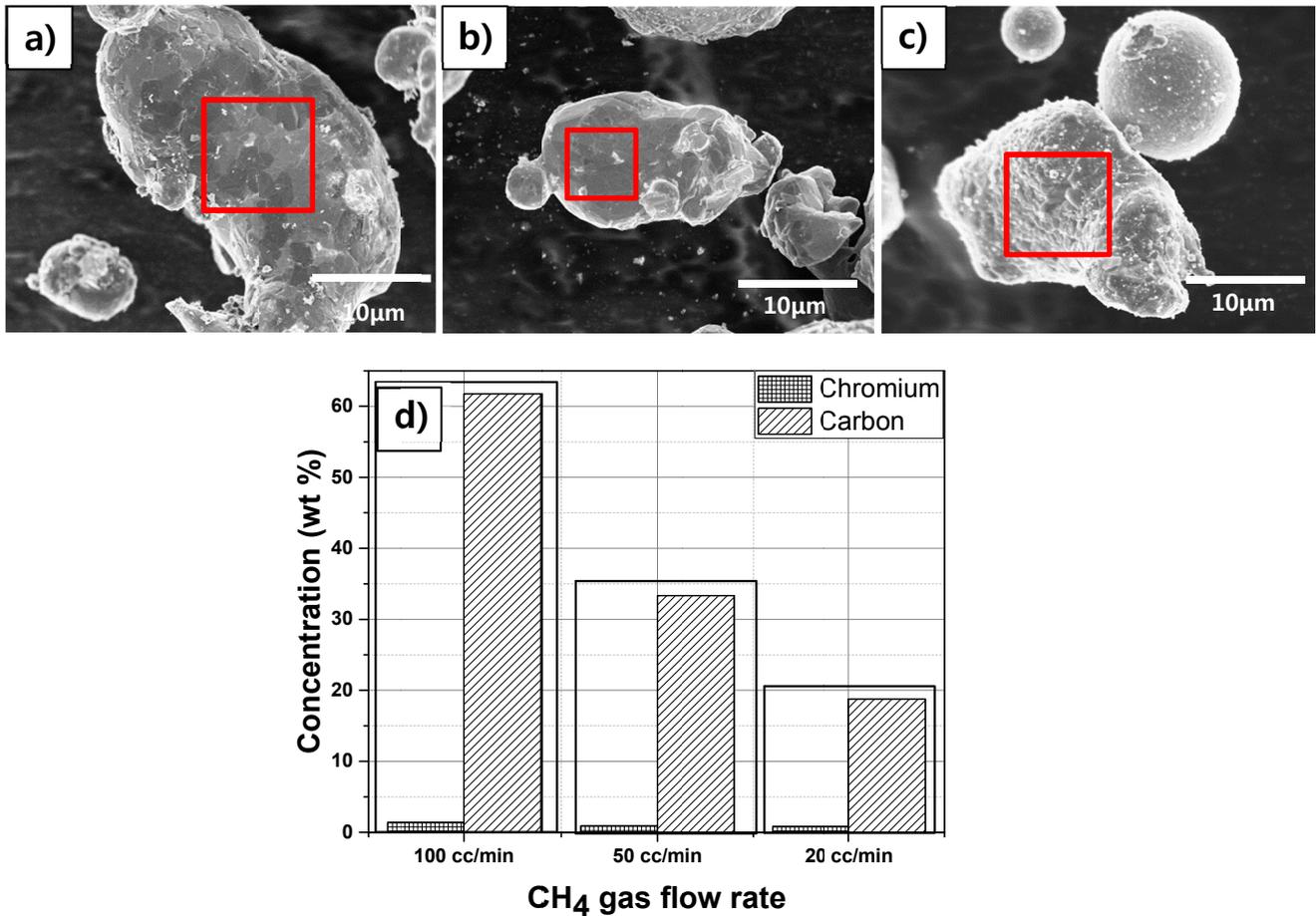


Fig. 6. SEM and EDS analysis results for powders reduced with: a) 100 cc/min CH<sub>4</sub>, b) 50 cc/min CH<sub>4</sub> and 50 cc/min Ar, and c) 20 cc/min CH<sub>4</sub> and 80 cc/min Ar. d) Comparison of C and Cr content in highlighted area

steel phases, or very hard carbides like Fe<sub>3</sub>C, Cr<sub>23</sub>C<sub>6</sub>, and Cr<sub>7</sub>C<sub>6</sub> [31-32]. As these carbide phases should be dispersed inside the microstructure of the sintered steel, they should have a significant effect in terms of increasing the strength, hardness and wear resistance of the final component.

Where in Eq. (13),  $y$  is the carbon content of the reduced sample and  $x$  is the CH<sub>4</sub> gas flow rate. Using this expression, the amount of carbon can be carefully controlled so as to minimize the cost and time of processing.

TABLE 3

Carbon and oxygen content of powder reduced at different CH<sub>4</sub> flow rates

Gas Flow Rate	Carbon (%)	Oxygen (%)
CH <sub>4</sub> – 100 cc/min	7.998	0.493
CH <sub>4</sub> – 50 cc/min, Ar – 50 cc/min	5.04	0.513
CH <sub>4</sub> – 20 cc/min, Ar – 80 cc/min	3.83	0.702

Powders with a high carbon content often have a detrimental effect on the properties of sintered parts (high carbon content induces embrittlement and reduces hardenability [31]), thus making control over the carbon content during reduction by varying the CH<sub>4</sub> flow rate is very beneficial from an industrial point of view. The graph of CH<sub>4</sub> flow rate and retained carbon content in Figure 7 shows exponential behavior, and so a mathematical expression was derived using the general form of an exponential function ( $y = ab^x$ ):

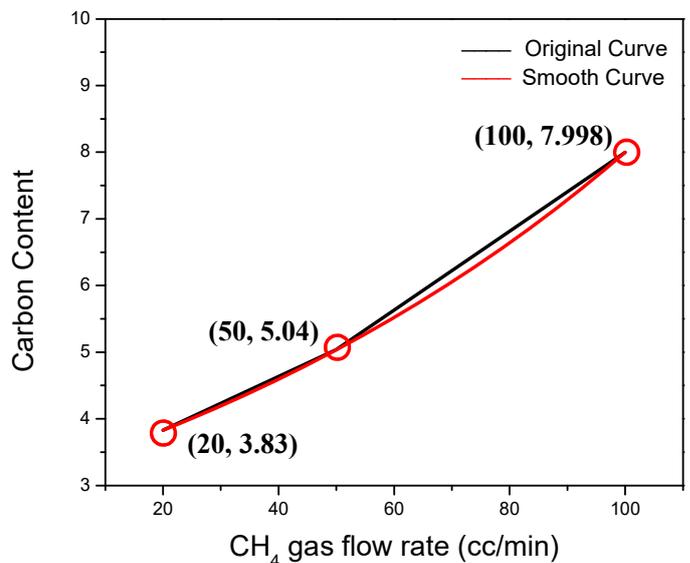


Fig. 7. Curve showing exponential relationship between co-deposited carbon and CH<sub>4</sub> gas flow rate

$$y = (3.19)(1.0092)^x \quad (13)$$

#### 4. Conclusions

A Cr-based prealloyed Fe powder with a composition of Fe-3Cr-0.5Mo was successfully fabricated via water atomization, but found to have a surface oxide layer composed of Fe- and Cr-based oxides. A literature survey revealed that gas mixtures containing CH<sub>4</sub> are the most suitable for the reduction of Cr-based oxides, and so a mix of CH<sub>4</sub> and Ar was used to reduce the as-atomized powder at 900°C. At this temperature CH<sub>4</sub> decomposes into H<sub>2</sub> and carbon, with the latter converting Cr oxides into carbides. The H<sub>2</sub> then reduces these carbides to metallic Cr. At the same time, excess carbon is co-deposited onto the particle surface during reduction. As the amount of carbon deposited increases exponentially with the CH<sub>4</sub> flow rate, it can be easily controlled to provide sufficient carbon for direct sintering. This could eliminate the need to pre-mix powders with carbon prior to sintering, thereby drastically reducing the processing costs and time needed for sintering.

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