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Metallography of High-carbon Ferrochromium

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The microstructure of high-carbon ferrochromium was analysed by means of optical and scanning electron microscopy, including energy-dispersive spectroscopy. Two different structures were observed: a two-phase structure consisting of primary M_7C_3 carbides and ferrite, and a three-phase structure consisting of primary M_7C_3 carbides and a ferrite–carbide eutectic. The two-phase structure, which formed during the slow cooling of cast ferrochromium is, in principle, a divorced eutectic structure. During slow cooling, the primary carbide grains continue growing until the liquid phase is depleted of carbon and is transformed into solid ferrite. The three-phase metastable structure comes about when cooling is rapid and the eutectic reaction takes place.

Both types of cast ferrochromium contained numerous cracks and cavities caused by thermal shrinkage and lack of liquid feed in the solidification process. However, they differed significantly in their friability properties. It was concluded that the two-phase equilibrium structure was highly susceptible to abrasion and disintegration into powdery particles, while the metastable three-phase structure was more resistant to these processes. The observed differences are attributed to the binding of the primary carbides by the eutectic in the three-phase alloy, while only limited binding occurs in the two-phase slowly cooled ferrochromium.

Some results of microanalyses are also presented, showing the partitioning of the principal elements (chromium, iron, and silicon) between the phases.

Introduction

High-carbon ferrochromium (HCFeCr) is normally regarded as a ferroalloy to be used exclusively as an additive in the production of chromium steels and, primarily, stainless steels. From this point of view, the only properties specified by customers and manufacturers alike are its composition and granulometry, i.e. the shape and size of the fragments. For this reason, the metallography of this alloy is generally considered to be uninteresting, and the available information on this subject is very sparse.

It is our belief, however, that a better understanding of the structure of ferrochromium is essential if its quality and marketing value are to be improved. The quality parameters, such as the overall contents of chromium, carbon, and iron, and also its resistance to disintegration during transportation, can be improved by suitable practices in the production process, and the development and possible introduction of such measures are based on the structure of the ferrochromium and its metallographic analysis.

The market value of ferrochromium increases with an increased content of chromium and decreased contents of carbon and iron. In terms of the observed phases, it can be said that the primary M_7C_3 carbide has a high chromium content but also a high carbon content; hence, its volume fraction must decrease if the carbon content is lowered.

The carbide $M_{23}C_6$ contains approximately 5,5 per cent carbon, having a lower carbon content than M_7C_3. It is known to dissolve a maximum of 30 per cent iron (by mass), compared with the 55 per cent iron that is soluble in the M_7C_3 carbide. It ought therefore to exhibit an even better Cr/Fe ratio. It can, however, never form directly from the melt, as the binary Cr–C diagram clearly shows (Figure 1). Solidification always starts with the formation of M_7C_3,

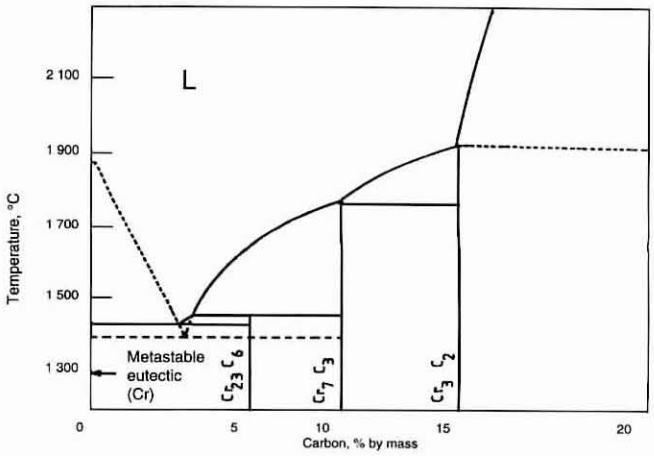

FIGURE 1. Cr–C binary-phase diagram [1]

which is then followed by the peritectic reaction yielding the $M_{23}C_6$ carbide (on slow cooling), or the eutectic reaction yielding either the stable eutectic ferrite $M_{23}C_6$ or the metastable eutectic ferrite M_7C_3.

A lowering of the carbon concentration in the melt decreases the fraction of the primary M_7C_3 carbide. Chromium partitions considerably in the course of the eutectic reaction, and its content in ferrite is only approximately 35 per cent.

Materials Used

Both industrially produced HCFeCr and laboratory smelted HCFeCr were used for the metallographic investigation described here, which included optical and scanning electron microscope (SEM) techniques and energy-dispersive X-ray (EDX) techniques.

Industrially produced ferrochromium, after being smelted in an electric-arc furnace, is tapped into tetragonal cakes weighing about 6 t. As the cakes solidify, they are cooled in air, down to about 800°C, after which they are sprayed with water for faster cooling, and crushed into lumps for despatch to customers. The composition of the tested sample was as follows: 66% Cr, 26% Fe, 6,9% C, and less than 1% Si.

Laboratory-prepared ferrochromium was remelted in a 30 kW induction furnace, and cylindrical samples 2 cm in diameter and 2 cm high were obtained and cooled in water. The chemical composition was 63,8% Cr, 28,4% Fe, 6,59% C, and 0,7% Si. The resmelting of ferrochromium in the laboratory furnace was part of an investigation aimed at increasing the concentration of chromium and decreasing that of carbon by a reaction between a liquid charge and added chromite.

Microstructural Investigation

The equilibrium structure of HCFeCr consists of two phases: primary M_7C_3, which has a trigonal lattice, and ferrite. These transformation reactions are evident from Figure 1 and, as the solubility of iron in all the mentioned phases is high, the same processes occur during the solidification of ferrochromium. However, the temperatures, indicated in Figure 1 are significantly lowered by the presence of iron[2].

When ferrochromium solidifies under non-equilibrium conditions, the structure can contain three or two phases. The carbide $M_{23}C_6$ can form only by a peritectic reaction, which is normally completely suppressed. If the cooling is fast, the liquid gradually depleted in chromium reaches the eutectic composition, and then solidifies as a ferrite–carbide eutectic. Two different eutectics are described: the stable ferrite eutectic, $M_{23}C_6$, and the metastable ferrite eutectic, M_7C_3. The latter forms at a somewhat lower temperature if no $M_{23}C_6$ is allowed to nucleate. When the cooling is slow, the eutectic becomes divorced since the growth of the primary carbide grains continues and depletes the parent liquid by carbon until it solidifies as a pure ferrite.

The two-phase structure of industrially cast ferrochromium is shown in Figure 2. The primary M_7C_3 carbide prevails and contains internal cracks caused by shrinking during cooling subsequent to solidification. The minor ferrite phase is lighter in colour, and fills the space

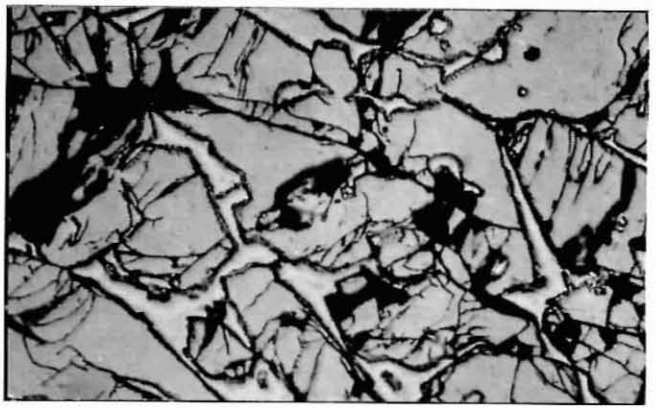

FIGURE 2. Industrially produced HCFeCr: primary M_7C_3 in a network of ferrite. 300x

between the primary faceted M_7C_3 crystals. The shrinkage porosity is not limited to cracks in the primary carbide crystals, but features also as pores at the phase and grain boundaries. The micrograph evidently reveals the equilibrium structure of a slowly cooled ferrochromium.

The three-phase structure is shown in Figures 3 and 4. Figure 3 shows the structure of a rapidly cooled part of an industrially produced cake, while Figure 4 shows that of a sample remelted in the laboratory. Both micrographs show the presence of white grains of primary M_7C_3 carbides and the eutectic mixture of ferrite and carbide. In the laboratory-prepared material, the hexagonal shape of the primary carbides is clearly seen, giving clear evidence of its M_7C_3 nature. The cracks and voids are overwhelmingly related to the primary crystals. The intercrystalline eutectic seems almost free of these defects, especially in the remelted materials. It can be assumed that ferrite, which forms the matrix of the eutectic, is sufficiently ductile and can accommodate the thermal stresses arising on solidification.

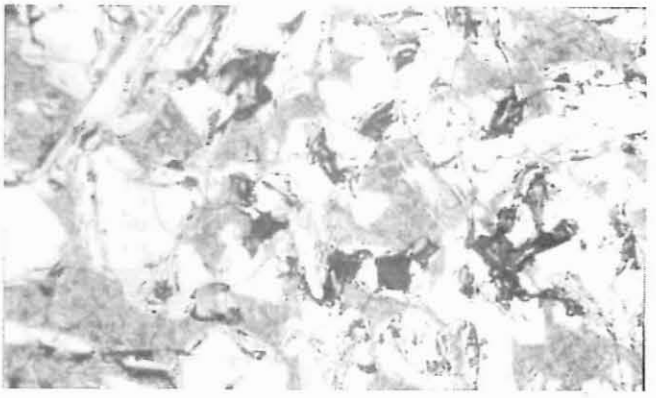

FIGURE 3. Industrially produced HCFeCr: primary M_7C_3 in a ferrite–carbide eutectic. 180x

The laboratory-remelted ferrochromium was cooled rapidly, and the microstructure of many samples frequently consisted of long needle-shaped primary carbides (Figure 5). They occurred in combination with equi-axed grains (Figure 6), which may be transverse sections of the needle-shaped primary carbides. The elongated shape of the primary crystals is obviously related to a steep thermal gradient during solidification. The rapid solidification

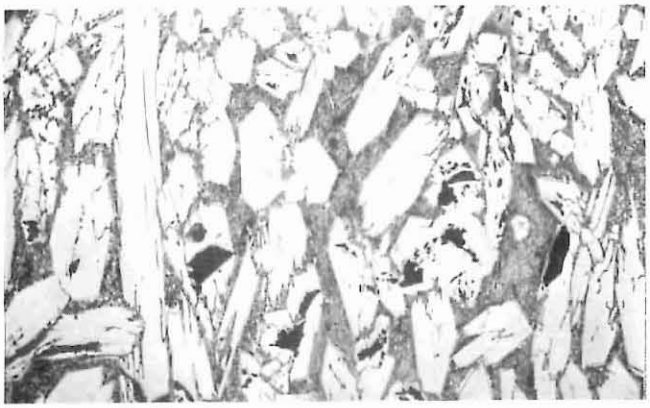

FIGURE 4. Laboratory-smelted HCFeCr: primary M_7C_3 in a ferrite–carbide eutectic. 90x

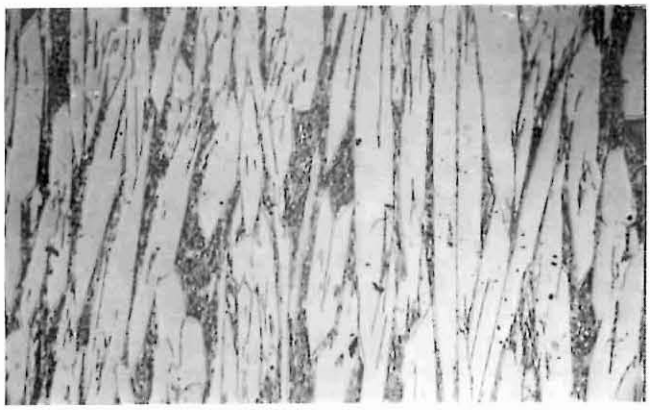

FIGURE 5. Laboratory-smelted HCFeCr: elongated primary carbides in the eutectic. 90x

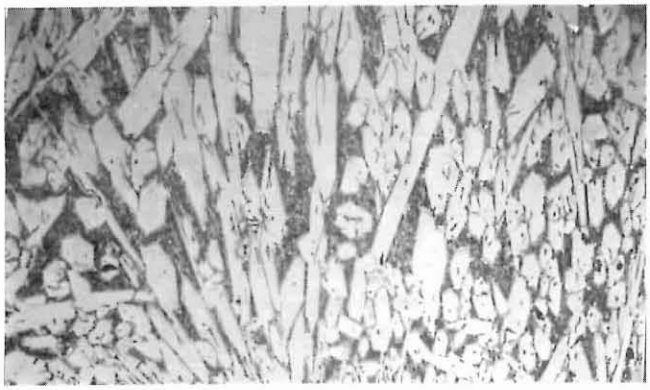

FIGURE 6. Laboratory-smelted HCFeCr: mixed-shape primary carbides in the eutectic. 90x

resulted in a non-equilibrium phase composition, consisting of primary M_7C_3 crystals (note their hexagonal shape) and a eutectic. The cracks and pores in the primary crystals can be attributed to shrinking on subsequent cooling, and also to the lack of liquid-metal feed during solidification.

Friability Analysis

Friability is a frequently discussed physical property of ferrochromium. By definition, it is a measure of the tendency of the material to break down into smaller fragments and particles under applied and abrasive loads. Friable ferrochromium disintegrates into more or less fine powder when crushed, transported, or simply handled, and friability is therefore an important property affecting the material's export value.

Slow cooling of HCFeCr yields primary hard carbides, which are usually cracked as a result of shrinking, and a small volume fraction of ferrite, while rapid cooling leads to a structure in which the primary carbides are embedded in a eutectic consisting of a plastic, inherently tough ferrite and discrete, finely distributed carbide platelets. The eutectic may well serve as a binder for the primary carbides, significantly reducing the friability of the ferrochromium. This assumption was put to a test similar to the standard ASM test used to assess the friability of coal[3].

Samples of ferrochromium were tumbled in iron cylindrical jars with a diameter of 22 cm and a length of 26 cm, which were rotated for 4 hours at 80 r/min, giving a total number of revolutions of 19 200. The samples consisted of 1 kg of industrially produced ferrochromium and of material remelted in the laboratory and rapidly cooled. Both samples consisted of lumps over 8 mm in size. After the tumbling test, it was found that 14,5 per cent (by mass) of the industrial sample passed through the 8 mm sieve, while only 1,8 per cent of the laboratory-melted and cooled sample was smaller than 8 mm.

The results of subsequent sieve analyses of the abraded material from both tumbling tests are shown in Figure 7. The major portion of both materials is in the fraction smaller than 75 µm. This indicates that most of the abraded material consists of particles comparable in size with the spacing of the cracks and pores in the carbide grains. The mechanism of the comminution process can thus be described as an abrasion breakdown of the surface resulting from existing internal cracks. However, if the carbide grains are bonded together by the eutectic binder phase, the disintegration rate under the same conditions is considerably slower than that of the two-phase material. The faster cooling rate of cast ferrochromium obviously brings about a significant improvement in its friability.

Energy-dispersive X-ray Micro-analysis

Samples of laboratory-smelted HCFeCr were subjected to energy-dispersive X-ray micro-analysis using a scanning electron microscope with an EDX analyser. In addition, the usual wet-chemical analysis of the material was carried out with the following result: 6,6% C, 64% Cr, 28% Fe, 0,7% Si, and 0,06% S. A profound partitioning of the chromium, iron, and silicon in the two structural constituents (carbide and eutectic) was thus revealed. Figure 8 shows the data from 20 points equally spaced on a line straddling a carbide–eutectic grain boundary.

Figure 8 indicates that the ratio Cr/Fe is just under 5 in the primary Cr_7C_3 carbide. The eutectic ferrite, in contrast, contains approximately 65% Fe, 35% Cr, and evidently all the silicon present in the alloy. The analysis of the eutectic carbide indicates that chromium prevails over iron, but the grains are too small to yield reliable results since the analysed volume most probably contains some adjacent ferrite. The apparent scatter of data points in the eutectic is caused by arbitrary scanning of the eutectic by the electron beam. This may have hit areas dominated by either the ferrite or the carbide.

At this stage, we cannot determine whether the carbide in

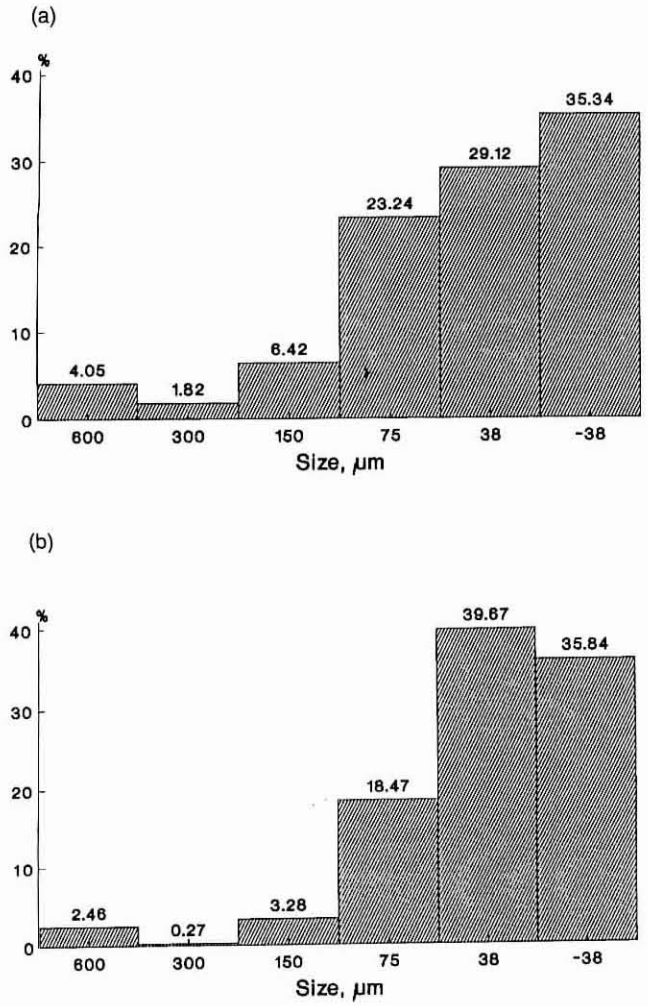

FIGURE 7. Size analysis of abraded material after the tumbling tests
(a) Laboratory-smelted ferrochromium
(b) Industrially smelted ferrochromium

the eutectic of our rapidly cooled samples was M_7C_3 (metastable eutectic) or $M_{23}C_6$ (stable eutectic) since the particles were too small for accurate micro-analysis. Transmission electron microscopy would probably be needed in order to obtain the diffraction pattern, which would resolve the issue.

It can be calculated that the chemical formula of the primarily solidified carbide can be written as $(Cr_{5,8\text{-}5,85}Fe_{1,2\text{-}1,15})C_3$. Hence, its iron content is well below the solubility limit, which is believed[2] to be a minimum of 30 per cent. The percentage (by mass) of carbon in this carbide is about 8,6.

Significance of the Results

The phase composition of the slowly cooled HCFeCr was a simple mixture of carbide and ferrite. In addition, cracks and voids in the carbides made the alloy very friable since its fracture toughness was inherently low. The volume fraction of ferrite was very low, and hence its network was discontinuous. Therefore, the binding capacity of ferrite was very limited. Low levels of stress, which could have been caused by mere vibration of the material, sufficed to propagate the existing cracks and cause disintegration of

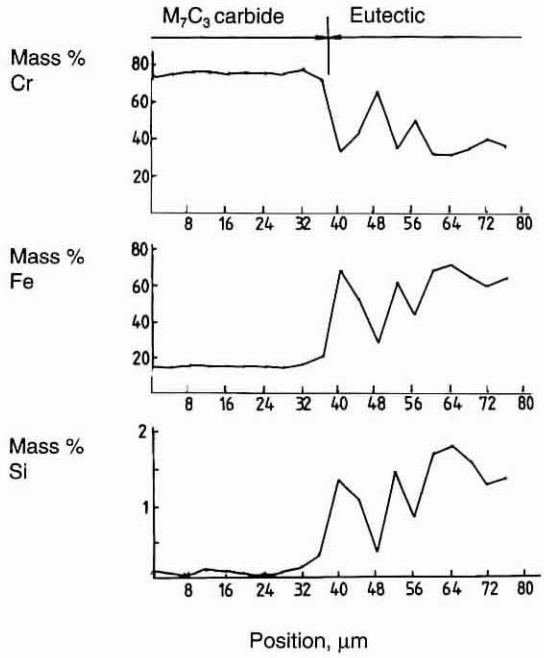

FIGURE 8. Partitioning of the elements Cr, Fe, and Si in M_7C_3 carbide and eutectic

the ferrochromium into powder.

In contrast, the rapidly cooled ferrochromium contained a eutectic, which, in turn, contained the ductile ferrite. The eutectic had a much higher fracture toughness than any carbide, and a crack in it would not propagate unless the material was subjected to a much higher stress than that needed to propagate a crack in a carbide. Hence, the ferrite acted as a crack arrestor or a binder to the primary carbide crystals. This structure is inherently far more resistant to disintegration by forces encountered in the transportation of this material. The microstructural analysis proves that friability is exclusively dependent on the material's structure, and not on its composition within the accepted limits of the elements chromium, iron, carbon, sulphur, and silicon.

This reasoning was confirmed qualitatively by the laboratory tumbling test. The sieve analysis of the disintegrated material indicated that the active mechanism was surface abrasion, resulting in the formation of a powder having a particle size comparable with the spacing between the observed cracks, pores, and interfaces of the material. The weak interfaces probably existed only in the slowly cooled material, and not in the rapidly cooled material, which contained the eutectic binder. Admittedly, the results of the tumbling test have yet to be verified by practical tests during the handling and transportation of ferrochromium. However, the susceptibility to disintegration was certainly much lower in the rapidly cooled ferrochromium than in the slowly cooled material.

In practice, e.g. during handling and transportation, the dynamic loads may be much higher than those in the laboratory test, which will cause the material to disintegrate into larger lumps. However, the mechanism of the process is similar, i.e. the growth of cracks initiated by existing microcracks. Although much work is needed to solve some of the detailed problems, it can be concluded that metallographic analysis of solidified ferrochromium provides a powerful tool for controlling the quality of the

product. With the aim of reducing the carbon content in the material, an optimum fraction ought to be found for the primary carbide that will yield the best metallurgical and mechanical properties of the material. In addition, metallography allows monitoring of the kinetics of the reactions taking place in the smelting process, and permits evaluation of the behaviour and effects of different kinds of ores, reductants, and fluxes.

Acknowledgements

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