The Role of Manganese on Microstructure of High Chromium White Cast Iron

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Abstract

To determine the effect of austenite stabilizer element on the microstructure and behaviour of as–cast high **Cr** white cast iron Fe-21Cr-3Ni-1.7Mo-2.4C, different percentages of Mn (0.4, 0.9, 1.3, 1.7, 2.2 and 2.6 wt%) were added. Detailed investigations were carried out using scanning electron microscopy, energy dispersive spectroscopy analysis (EDS), X-ray diffraction and hardness test. It showed that with increasing Mn addition, the austenite phase **(γ)** of the as-cast alloys refine clearly. The morphology of the austenite phase for all alloys is a mixture of dendrite and plate like. The austenite phase refines clearly with increasing manganese addition. The major carbide phase formed in the as- cast alloys is M_7C_3 with minor carbides of $(Fe,Cr)_{23}C_6$ and Mo_2C. Microstructure analysis showed the presence of small amounts of martensite and delta ferrite in all as-cast alloys. The hardness was decreased continuously with increasing Mn content. This is mainly attributed to the morphology of carbides rather than to small variation in carbides content. It was observed that considerable amounts of Mn were found in the carbides lower than that in the austenite matrix.

Keywords: As-cast white cast iron, Manganese, Austenite phase, EDS, Carbides, Austenite

1. Introduction

High alloyed chromium cast irons were used in applications with extreme demanding requirements such as abrasive, erosion, heat and corrosion resistance (Carpenter, Carpenter and Pearce, 2004; Komarov, Sadovski, Urbanovich and Lifshits, 2002). Also these cast irons were employed with unusual physical properties, such as low thermal expansion or non magnetic properties are desired (Ogi, Yamomoto and MiyaKawat, 2003; Chenje, Simbi and Navara, 2006; Tabrett and Sare, 2000). In the empirical development of alloyed cast irons the first prominent advance was the introduction of the Ni-hard cast iron in which the Ni and Cr are converted the pearlitic matrix to martensitic in the as cast state (Komarov and Sadovski, 2002; Asensio, Pero-Sanz and Verdiga, 2003; Zhou, Nilsson, Anderson and Stahi, 2004). In further modifications, the eutectic carbide was refined somewhat to give improved toughness (Baotong, Jingli and Stefano 2006). The M_7C_3 carbide is the predominant phase which is harder than M_3C present in unalloyed white cast irons and some Ni-hard cast irons, which cause a high abrasion resistance (Bedolla Jacuinde, 2001; Petrovic, Markovic and Pavlovic, 2003; Jun, Cong, Haohuai, Hongshan, Baoluo, Shenji and Sijiu, 2006).

Completely austenitic or completely martensitic matrix structure is desirable for wear resistance. High chromium white cast irons have usually complex mixed iron chromium carbides which are significantly harder than the cementite phase present in unalloyed and even low alloyed cast irons (Kuyucar and Liewiiyn, 2006; Alp, Wazzan and Imaz, 2005). The increase in the carbon content of high-chromium cast irons causes a decrease in the heat resistance and an increase in the rate of cracks propagation (Zhiping, Rulen and Baduo, 2002). On the other hand, chromium has a negative effect on the resistance of the hypoeutectic alloys to thermo-cycling loads (Bedolla, Correa, Quezada and Maldonado, 2005). Increasing manganese content will cause an increasing in retained austenite at room temperature and a decreasing in hardness. Manganese is soluble in M_7C_3 and M_3C carbides. It provides hardenabiliy increases and prevents pearlite formation.

2. Experimental Procedures

The alloys used were made in a silica lined coreless high frequency induction melting furnace with 45 kg capacity, 1.2 KHz frequency, 150 kW power. The charge materials consisted of pig iron, ferrochromium (Fe-72%Cr), ferromanganese (Fe-75%Mn), ferromolybdenum (Fe-65%Mo) and electrolytic nickel. The molten metal temperature was measured with type-S calibrated thermocouple (Pt-Pt/Re). The pouring temperature was 1450°C. The manganese element added to the molten as ferromanganese, in six series depending on the Mn percentage required. These alloys were poured into sand moulds to obtain square 12 mm×12 mm cross section area and 60 mm length bars. Table 1 lists the chemical composition for the six white cast irons produced. The only varied element is manganese from 0.4 to 2.6 wt%.

Samples for metallographic were prepared using abrasive paper grades 220, 320, 400, 500, 800 and 1000 respectively and then polished with 1 μm diamond paste. The specimens were etched using nital. Quantitative and qualitative determinations of chemical composition of the phases in as cast and heat treated samples were made by using the energy dispersive microanalyses. To aid in the identification of the phases present in the castings, X-ray diffraction was performed. Carbide fraction computing was made to study the effect of manganese content on the carbide fraction for the as cast. Average hardness of the as cast and heat treated specimens measured was using HRC. δ-ferrite content determination for the as cast specimens was also carried out by ferrite Content Meter (FCM).

3. Results and Discussion

High chromium white cast irons are usually produced as hypoeutectic composition, with austenite dendrites, either partially or substantially transformed to martensite and eutectic containing carbides an*d austenite. Figure 1 illustrates the microstructure of the as cast high chromium alloyed cast irons with different amounts of manganese addition. They compose of primarily proeutectic austenite dendrites and eutectic which consists* of eutectic austenite and eutectic carbides (mainly M_7C_3 type). It appears that the solidification of these kinds of alloys starts by austenite dendrites formation, and as the temperature decreases these dendrites grow, till the remaining liquid reaches the eutectic composition. At this stage the eutectic austenite/$(Fe, Cr)_7C_3$ carbide are formed. The austenite phase and $K_2(M_7C_3)$ carbides developed from liquid phase around the primary austenite dendrite which grows and formed as eutectic cells. The dendrites and the dendrites arm spacing differ with increasing manganese content and the regularity of the grains increases positively with manganese content. These structures which improved by the nucleation and growth of the austenite grain size are affected by the manganese content.

XRD analysis showed that there is small amount of martensite appeared as a thin dark-etching layer in the interface between the eutectic phase and primary γ phase. This is because, during eutectic solidification the M_7C_3 carbide which grows along the austenite absorbs carbon from its surrounding and narrow areas at the austenite/carbide interphase become impoverished in carbon. The lack of carbon in these zones of austenite increases the M_s temperature which allows these areas of austenite to transform to martensite during subsequent cooling down. Therefore, it is common to find eutectic M_7C_3 carbides are surrounded by martensite.

Due to the nucleation and growth kinetics of γ phase and M_7C_3 carbides in the eutectic, "rosette" morphology forms as a result of the early formation of a carbide crystal followed by rapid formation of γ around the former (Fig. 1). It appears that the eutectic solidified with a colony structure is consisting of a matrix of fine globular carbides in the central region, string-like or granular. They developed towards the boundary and large massed in the boundary area. At a higher percentage of manganese, the shape of the colony will differ and take another shape as indicated in (Fig. 1) which represents 2.6% Mn-alloy.

The nucleation and growth of the eutectic chromium carbides lead to the depletion of its content in the remaining liquid. This depletion is account for the chromium content of the subsequent and smaller carbide. In addition to eutectic carbides, secondary carbides where precipitated from the austenite matrix during slow cooling. These carbides precipitate due to decrease in C and Cr from the matrix and the destabilized the austenite as confirmed from the energy dispersive spectroscopy (EDS). It transformed to martensite which causes an increase in the bulk hardness. Besides martensite, the secondary carbides play important role in increasing the bulk hardness by their dispersion hardening effect on the matrix.

Presence of molybdenum in the alloys of high chromium white cast irons leads to the formation of Mo_2C carbides. Molybdenum is soluble in M_7C_3 carbide, so most of it partitions to the eutectic M_7C_3 carbide and some dissolve in austenite. It is also possible that small part of Mo also forms M_2C carbide (Mo_2C) due to the presence of carbon in the alloys. This type of carbide is found joined together with M_7C_3 as a lamellar shape (Fig. 2). It demonstrates that Mo_2C recrystalizes in a finely dispersed form as a eutectic in the final stage of solidification.

The shape and the size of eutectic M_7C_3 differ with manganese content. Hexagonal M_7C_3 eutectic carbides type beginning to appear as the manganese content increases especially at 1.3 and 1.7% Mn (Figs. 1 and 2). Also the average size of the carbide phase was increased with increasing manganese content in the alloys. The energy dispersive spectroscopy analysis showed that the manganese percentage in the austenite and carbide increases as its addition increases in the alloys. This leads to increase the retained austenite in the prepared white cast irons. Also, it indicates that the manganese percentage in the austenite is more than its percentage in the carbides. This means that the partition of manganese to the austenite is more than its partition to carbide (Table 2). Manganese affects the austenite dendrites and the austenite dendrite arm spacing. Also the Cr percentage in the carbide phase is more than 50% and its percentage in the γ phase is around 15% except specimen of 2.6%Mn. This is because the analysis is made near the carbide phase. X-Ray diffraction analysis illustrates that the austenite (γ) is the predominant phase in all the prepared high chromium white cast alloys with different manganese additions. Besides γ phase, $(Fe, Cr)_7C_3$ eutectic carbides also exist. Also there is a small amount of martensite and molybdenum rich carbide (Mo_2C) present.

Figure 3 shows that the hardness decreases with increasing manganese content. The hardness does not depend on the carbide fraction only but also on the austenite shape and the percent of manganese content in this grain. The shape of carbides was changed from rosette shape to large plate kind. The δ-ferrite content decreases as the manganese content increases (Fig. 4). This indicates that increasing manganese content reduces the effect of chromium in the content of δ- ferrite; with consideration that δ-ferrite is also affected by casting variables.

4. Conclusion

1) With increasing manganese content, the austenite matrix of the alloys refine considerably.

2) Presence of manganese in high Cr-white cast irons does not affect the tendency of chromium to stabilize the carbides, but increasing in the amount of austenite.

3) There was also found that manganese has a high tendency to change the morphology of carbides formed and decreasing the carbide fraction.

4) All cast alloys contain a small amount of martensite distributes on the interphase between austenite and M_7C_3 carbide.

5) The hardness of alloys decreased continuously with increasing manganese content which attributes mainly to the morphologies of carbides rather than their content.

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Table 1. Chemical composition of alloyed cast iron studied (wt%)

Specimen No.	% C	% Cr	% Mo	% Ni	% Mn	% Si	% S	% P	% Fe
1	2.48	21.76	1.79	3.17	0.4	1.88	0.0026	0.045	rem.
2	2.60	21.52	1.75	3.14	0.9	2.03	0.033	0.049	rem.
3	2.38	21.41	1.80	3.12	1.3	1.91	0.028	0.048	rem.
4	2.37	21.22	1.76	3.13	1.70	1.93	0.023	0.047	rem.
5	2.39	20.63	1.72	2.91	2.20	1.81	0.014	0.015	rem.
6	2.39	20.66	1.73	2.97	2.6	1.79	0.017	0.019	rem.

Table 2. EDS analysis of Mn and Cr in austenite (γ) and carbide phase (wt%)

% Mn in alloy	% Mn in γ	% Mn in carbide	% Cr in γ	% Cr in carbide
0.4	0.76	0.23	14.89	56.81
0.9	1.01	0.52	14.7	57.67
1.3	1.4	1.17	15.45	56.16
1.7	1.81	1.4	15.18	57.78
2.2	2.6	2.14	14.17	51.95
2.6	3.0	2.2	29.17	57.83

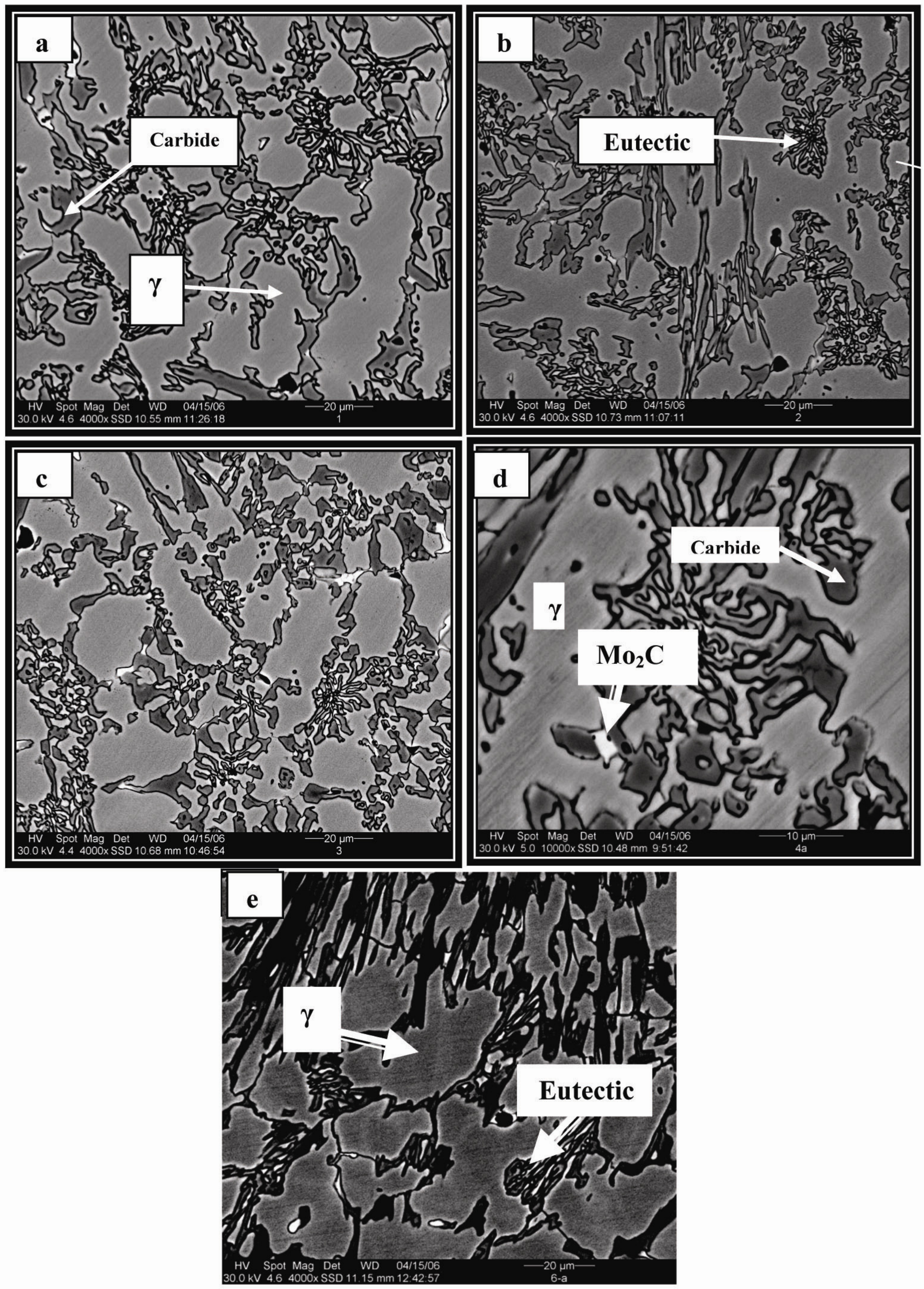

Figure 1. SEM micrographs showing the colony shapes with rosette morphologies of high chromium white cast irons with different percentages of manganese (a) 0.4 wt%, (b) 0.9 wt%, (c) 1.3 wt%, (d) 1.7 wt% and (e) 2.6 wt%.

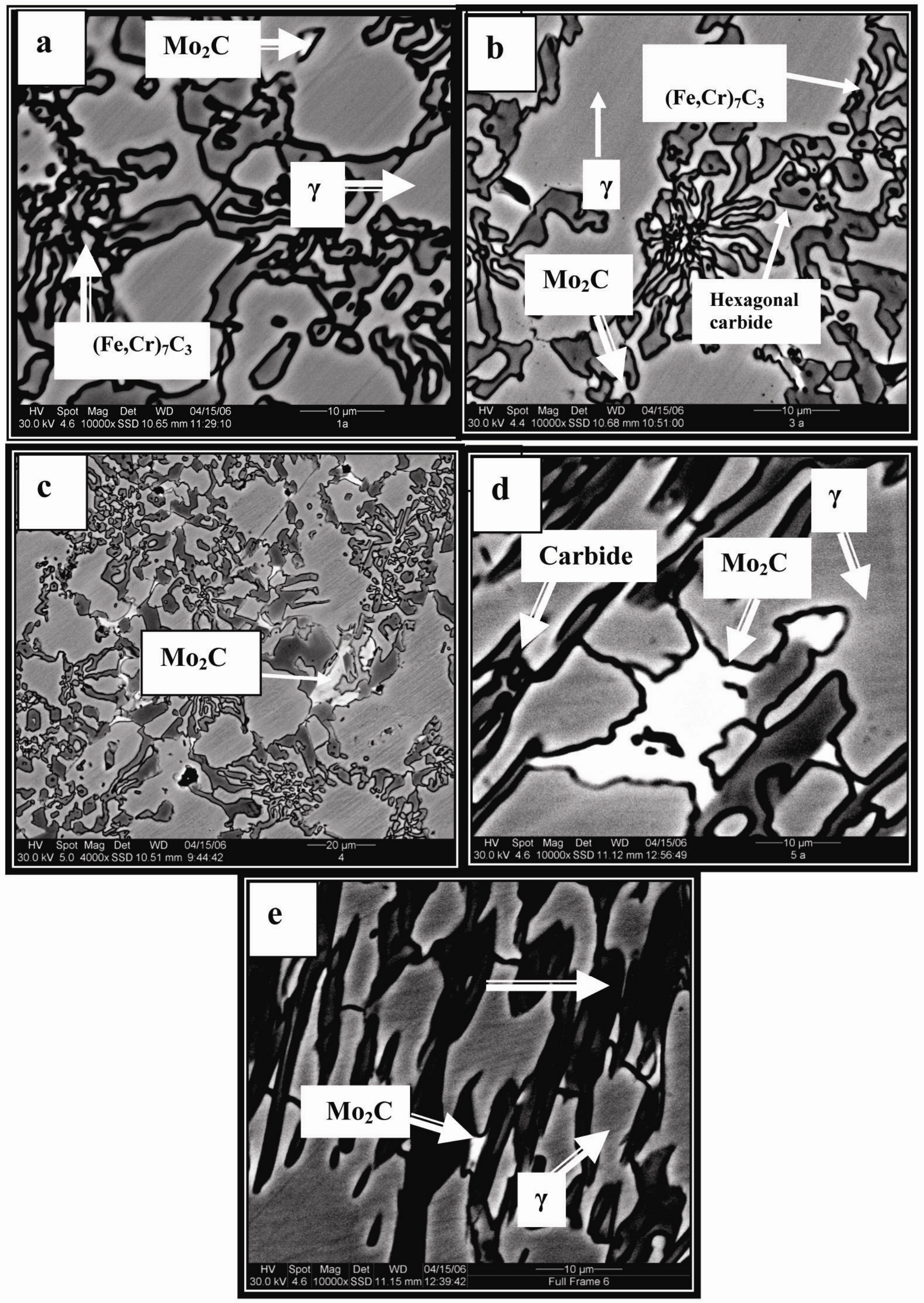

Figure 2. SEM micrographs showing the presence of molybdenum carbide in the high chromium white cast irons at different percentages of manganese (a) 0.4 wt%, (b) 1.3 wt%, (c) 1.7 wt%, (d) 2.2 wt% and (e) 2.6 wt%.

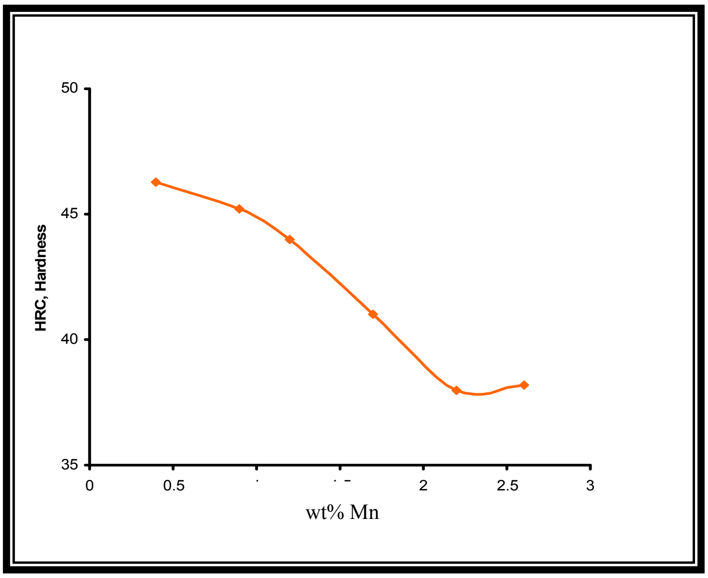

Figure 3. Effect of percentage of manganese on hardness in the as-cast high chromium white cast iron

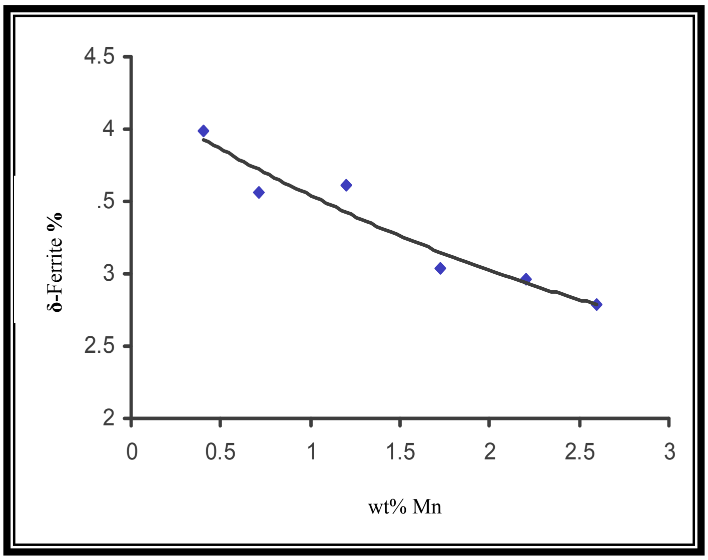

Figure 4. Effect of % Mn on δ –Ferrite in the as-cast high chromium white cast iron