

Ferrous High-Temperature Alloys for Exhaust Component Applications

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ABSTRACT

There is a wide spectrum of cast ferrous heat resistant alloys available for exhaust component applications such as exhaust manifolds and turbocharger housings. Generally speaking, the ferrous alloys can be divided into four groups including: ferritic cast irons, austenitic cast irons, ferritic stainless steels, and austenitic stainless steels. Selection of a suitable alloy usually depends on a number of material properties meeting the requirements of a specific application. Ferritic cast irons continue to be an important alloy for exhaust manifolds and turbocharger housings due to their relatively low cost. A better understanding of the alloying effects and graphite morphologies of ferritic cast irons are discussed and their effect on material behavior such as the brittleness at medium temperatures is provided. The nickel-alloyed austenitic cast irons, also known as Ni-resist, exhibit stable structure and improved high-temperature strength compared to the ferritic cast irons. Austenitic cast irons with varying nickel contents were evaluated in terms of microstructure stability, heat treatment, oxidation and thermal fatigue resistance. For the most demanding applications requiring even higher elevated-temperature strength, creep, and fatigue resistance, ferritic or austenitic stainless steels may be selected. The chemical composition, microstructures, and properties of cast stainless steels are reviewed. Synthesizing this information on material behavior provides a guide to aid in the selection of ferrous alloys for high temperature applications.

INTRODUCTION

High-temperature alloys broadly refer to the materials that provide strength, environmental resistance, and stability within the 260 to 1200 °C (500 to 2200 °F) temperature range [1]. Four groups of ferrous alloys are widely used for cast exhaust components: Group 1 - ferritic high-silicon based cast irons, Group 2 - austenitic high nickel irons (commonly

referred to as Ni-resist), Group 3 - ferritic stainless steels, and Group 4 - austenitic stainless steels. Over the past few decades, development of these temperature-resisting alloys has continued, resulting in improved high temperature strength and oxidation resistance, as well as to the development of superalloys [1]. These developments have been published in various reports. For example, in 1994, the SAE Exhaust Manifold Committee [2] compiled approximately 156 high temperature reference articles into two volumes. In 1999 SAE Iron and Steel Castings Committee wrote a report [3] on the four groups of ferrous alloys for exhaust manifold applications. A general description of mechanical, chemical, and thermophysical properties, temperature limits, and manufacturability of commonly-used alloys is provided in these reports. A series of high temperature property data of ferrous alloys were also published by the ASM International [4]. During the past few years, there have been more detailed evaluations of alloys tailored for specific applications, including manipulating the graphite morphologies in ferritic cast irons [5], further alloying of Ni-resist cast irons [6], and different formulae of nonstandard stainless steels [7].

More recently, comprehensive investigations of the four groups of alloys were conducted in Wescast. This paper draws on some examples from the company's material work to illustrate the advances that have been made with regard to alloying rules, microstructure control, and the elevated-temperature characteristics of these ferrous alloys. The results are presented within each group first, and then a brief comparison is made among the four groups.

EXPERIMENTAL PROCEDURES

A number of regression trials and a design of experiments on different alloy chemistries and processing techniques were performed at the Richard W. Levan Technical Center of Wescast Industries Inc. Heats weighing from 100 to 200 kg

were produced using air-melt induction furnaces. Ferritic cast irons were treated by using Fe-Si-Mg based nodulizers and Fe-Si based inoculants. Ni-Mg reagent was used for the treatment of austenitic Ni-resist cast irons. Except for microalloying, no special melt treatment was required for the stainless steels. Pour temperatures varied from 1350 to 1640 °C, mainly dependent on alloy type, casting geometry, and casting process. The alloy compositions were analyzed by an optical emission spectrometer. Optical microscopy and digital image analysis software were used in microstructural analysis of the cast samples. Further material evaluations included hot oxidation, linear growth, tensile, Brinell hardness, differential dilatometry, thermophysical, thermal fatigue [8], and component thermal durability testing [9].

RESULTS AND DISCUSSION

HIGH-SILICON FERRITIC CAST IRONS

It is well known that graphite cast irons provide good service and low cost in exhaust applications. Numerous efforts [8, 10] have been made to improve these heat-resistant ferritic cast irons, mainly in four aspects:

1. Enhance the phase transformation temperature A_{c1} and hot oxidation resistance
2. Improve the elevated-temperature strength
3. Control the graphite morphologies, and
4. Reduce or eliminate the brittleness at medium temperatures (BMT)

Progress in these four aspects of improving the high temperature behavior of ferritic cast irons can be briefly described as follows.

Enhancing the phase transformation temperature A_{c1} and hot oxidation resistance can be achieved by adding small amounts of Al [10] and Cr [11], but principally by controlling the Si content from 4 to 5 wt.%. The A_{c1} temperature is defined as the critical temperature of the onset of phase transformation from ferrite to austenite during heating. It is known that the A_{c1} temperature increases with increasing Si, Al, and Cr content, as shown in Table 1. The same testing conditions were used for all A_{c1} measurements in this work. Previous work has also shown that the high temperature oxidation resistance is improved with the addition of these three elements, including less oxide thickness and more adherent oxide scales [8]. However, the ductility and casting process are adversely affected with increased Si, Al, and Cr contents, especially for Al and Cr.

Improved elevated-temperature strength can be achieved by adding some of the transition metals from Groups 5B and 6B of the Periodic Table, singly or in combination, leading to different iron formulae such as SiMo [12] and SiMoV [13]. It is well known that there is a continuous increase in the

strength at a given temperature with increasing Mo content. The most significant response to increased Mo content is realized over the range of 0.4 to 1.0 wt% Mo [8]. High Mo content tends to generate more primary interdendritic carbides and an increasing volume fraction of Mo-rich phases, thereby reducing the impact toughness, as shown in Figure 1. There has been increasing interest in the substitution of “low-cost” elements such as W and Cr for Mo due to the price of Mo. For example, Cr-alloyed graphite cast irons of up to 1.0 wt% Cr were investigated for the suitability of high-temperature use [11, 14]. As shown in Figure 2(a), Cr-alloyed samples formed a microstructure with significant carbides and lamellar pearlite. Therefore annealing heat treatment was required to disperse the grain boundary structures and improve the ductility, as shown in Figure 2(b). The tensile strength UTS at room temperature was slightly increased from 620 to 700 MPa as Cr content was varied from 0.04 to 0.80%. Thus, Cr increases both the A_{c1} temperature and the tensile strength.

Table 1. Indicative A_{c1} temperatures of different SiMo-based irons

Si (wt. %)	Cr (wt. %)	Al (wt. %)	A_{c1} (°C)
4.0	-	-	830 to 840
4.5	-	-	850 to 860
4.5	0.8	-	865 to 875
4.5	-	0.5	880 to 890

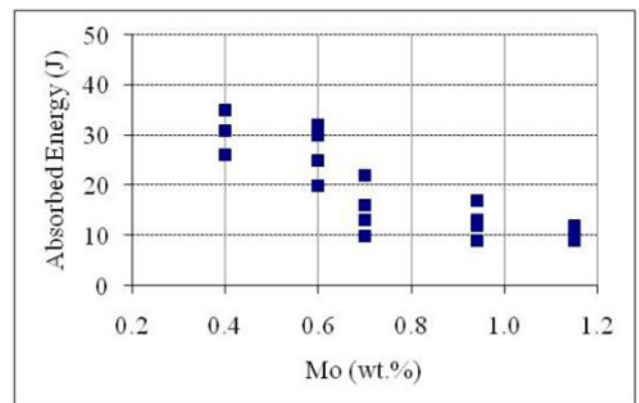


Figure 1. The effects of Mo on the absorbed energy of un-notched Charpy testing for SiMo samples.

Altering the melt treatment process allows the graphite morphology to be controlled to generate structures that contain predominantly compacted graphite (CG), spheroidal graphite (SG) [8], or mixed graphite (MG) [15]. The SAE Iron and Steel Castings Committee [12] recommended that the nodularity of CG should be less than 20% for C-grades

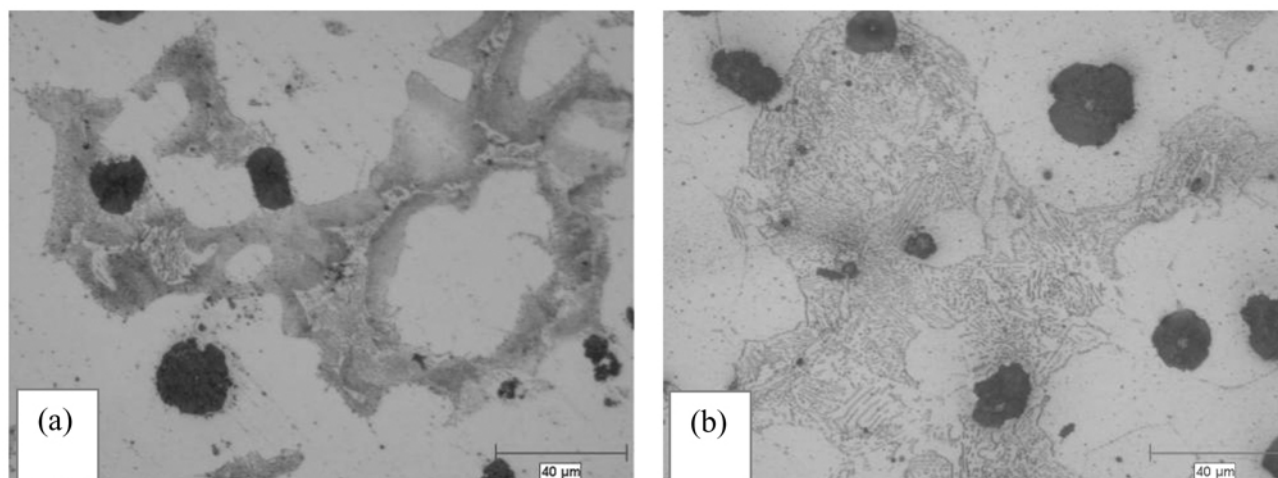


Figure 2. Micrographs of SiMo iron with 0.85 % Cr: (a) as-cast, and (b) heat treated condition.

and from 20 to 50 % for the C-HN grades. On the other hand, the SG SiMo microstructure should consist of at least 80% nodularity as specified in SAE J2582. The graphite morphologies exert a significant impact on cast iron properties, apart from the chemical compositions mentioned above. Both SG and CG irons are used for turbocharger housings and exhaust manifolds. However CG irons are more widely specified for use in Europe than in the United States or elsewhere [8]. Recently, we proposed a compromise, namely the mixed graphite (MG) irons with the nodularity ranging from 30 to 80% [15], in order to improve the material properties and manufacturability. The mixed graphite is defined as a mixture of SG and CG in a certain ratio, including graphite forms ASTM I, II, and IV, or ISO III, V, and VI. Much less nodulizers and inoculants are utilized for MG than SG iron during the melt treatment. Additionally, MG structure may not require anticompatizing elements such as Ti which is often added into conventional CG iron. As a result, there is a decreased possibility for inclusions, dross, and Ti-induced defects for MG irons. Figure 3 shows micrographs of SiMo cast iron with different graphite morphologies in which (a) and (d) represent CG and SG microstructures respectively, and (b) and (c) illustrate two different MG structures. Certainly, there is a crossover in microstructure between CG and MG, and between MG and SG cast irons. Testing results [15] have repeatedly shown that MG iron offers benefits for both cost savings and improved material performance, as compared to conventional CG and SG cast irons.

<figure 2 here>

<figure 3 here>

The brittleness at medium temperatures (BMT) has long been known as a detrimental phenomenon in ferritic ductile irons [16, 17]. It was suggested [16] that the BMT was caused by

the grain boundary segregation of impurities, which could be a result of the magnesium-assisted sulfur segregation. The MG iron has shown a reduction of BMT due to reduced use of Mg-bearing nodulizers during the treatment process. Also, the BMT can be further reduced by adding a small amount of phosphorus into SG irons [18]. Kirby et al. [19] reported a beneficial effect of P to the creep behavior of α -iron, since P suppressed cavity nucleation at high temperatures to the extent that the alloy showed no ductility minima. Figure 4 shows the elongation at room temperature and 425 °C as a function of P content. The microstructure and chemical composition (including C, Si, Mo, S, and Mg) were controlled at the same levels among the tested SG SiMo samples. For example, the residual Mg was approximately 0.035% in all cases. BMT was observed when the P content was lower than 0.02%; however the elongation at 425 °C was dramatically increased up to 21% with 0.031% P, as seen in Figure 4. The Mg/P ratio was recommended to be approximately 1 to eliminate the BMT for ductile irons [18, 20]. Figure 5 shows the SEM fracture surfaces of two samples which were tensile tested at 425 °C. For sample (a) with 0.016% P, the elongation at 425 °C was only 3.0% and the micrograph revealed approximately 20 to 30% of cleavage fracture surface. However, for sample (b) with 0.030% P, the fracture surface was characteristically ductile, with no cleavage fracture surface observed, and elongation of 18% at 425 °C was achieved for this sample.

Much work has been carried out to optimize ferritic high-Si cast irons for high temperature use, including evaluations of the chemical compositions, alloy strengthening, carbon equivalent, graphite morphologies, and foundry practices. Ferritic high-Si based irons have many positive features that make them attractive for the production of exhaust components. Nevertheless, the use of ferritic cast irons for exhaust components is essentially limited by the relatively low strength at high temperatures, phase transformation, and

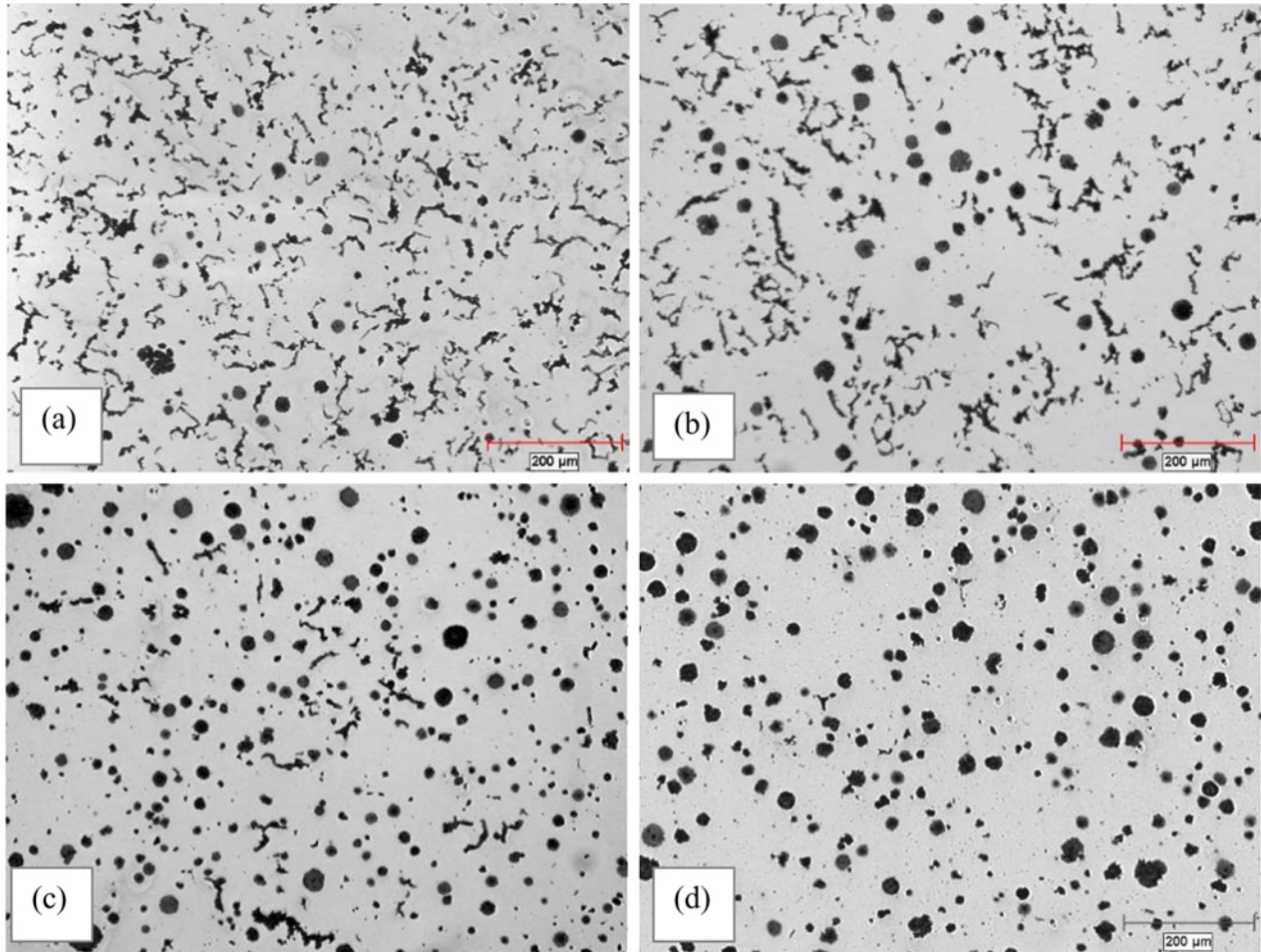


Figure 3. Micrographs of SiMo samples with different graphite morphologies. The indicative graphite nodularity is (a) 30%, (b) 50%, (c) 70%, and (d) 90%.

more than 10% volume fraction of graphite as voids. Alternatively, austenitic Ni-resist cast irons can be used to withstand greater loads and higher temperatures which exceed the limits of ferritic cast irons.

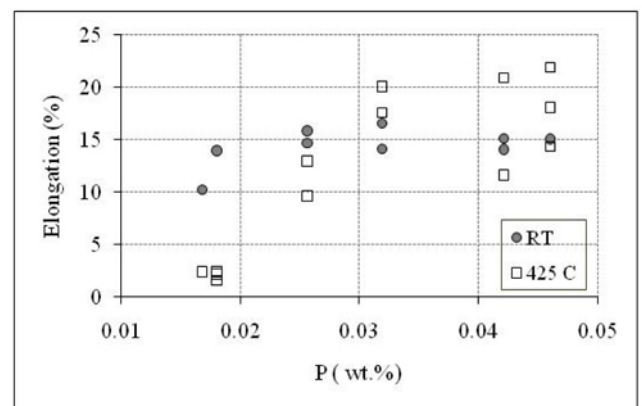


Figure 4. The effect of phosphorus on the elongation at room temperature and 425 °C for SiMo samples.

<figure 5 here>

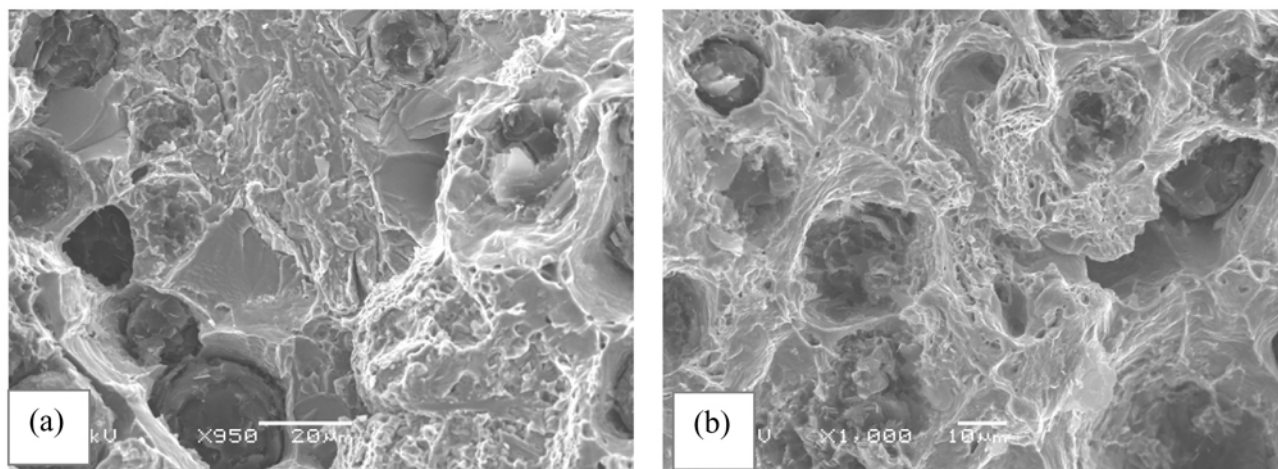


Figure 5. The SEM (Scanning Electron Microscopy) micrographs showing the fracture surface of tensile tested at 425 °C for SG SiMo iron samples: (a) some cleavage fractures for the samples with 0.016% P, and (b) no cleavage fracture for the sample with 0.030% P.

AUSTENITIC NI-RESIST CAST IRONS

The Ac1 temperature is considerably decreased by adding Ni into ferritic cast irons. In the range of 1 to 5% Ni, the Ac1 is reduced by 20 to 30 °C per 1% Ni addition [14], also confirmed by the work at Wecast. When the Ni concentration exceeds 18%, the Ac1 temperature may be reduced much below room temperature so that the ferrite-austenite phase transformation is suppressed, thereby leading to austenitic Ni-resist iron. Grade D5S with nominal 35% Ni has excellent microstructural stability, oxidation resistance, and thermal deformation resistance at high temperatures. However, due to the high nickel cost in D5S it is of interest to understand how Ni-resist irons with lower nickel content compare to D5S. For screening purposes, cast irons at compositions of 15, 20, 25, 30, and 35% Ni were investigated, respectively. Based on the outcomes of the screening experiments and referencing ASTM Standard A439, three grades of Ni-resist irons, as listed in Table 2, were further assessed for high temperature applications in which ferritic high-Si based irons cannot be used.

Satisfactory as-cast microstructures can be produced for these three Ni-resist grades by employing foundry best practices for carbon equivalent, melt treatment, post inoculation, and pour temperature. The lower Ni irons allow for slightly higher carbon content, as indicated in Table 2, which may be beneficial for castability. The as-cast microstructure typically consists of an austenite matrix with 5 to 6% volume fraction of spheroidal graphite having approximately 90% nodularity, and 5 to 10% chromium carbides, as shown in Figure 6.

Table 2. Indicative chemical compositions of three Ni-resist irons tested in this work

Alloy ID	Ni	Si	Cr	Mn	C
Ni25	25.0	5.5	1.9	0.6	2.1
D4A	28.0	5.5	1.9	0.6	2.1
D5S	35.0	5.0	1.9	0.6	2.0

<figure 6 here>

<figure 7 here>

Cooling curves were recorded for different Ni-resist samples, as shown for instance in Figure 7. Figure 7(a) shows a liquidus thermal arrest of primary austenite at 1220 °C. This is undesirable because the formation and growth of primary austenite dendrites increases the tendency for porosity defects in castings. In Figure 7(b), the solidification started at 1180 °C and no primary growth occurred. This curve exhibits fairly smooth cooling to the low eutectic temperature where the bulk growth started with a few degrees of recalescence. The cooling curve of Figure 7(b) can result in a uniform graphite distribution with a lower shrinkage tendency, and it's often referred to as a “good curve.” The measurements also show that the liquidus or eutectic temperature of Ni-resist is appreciably higher than that of SiMo-based irons, which is approximately 1140 °C. Different foundry practices are recommended with respect to gating, risering, melting, pouring, and finishing for Ni-resist.