CHEMISTRY, METALLURGY AND MECHANISM OF MICROSTRUCTURAL TRANSFORMATION IN HADFIELD STEEL, HIGH CHROMIUM CAST IRON AND AUSTEMPERED DUCTILE IRON

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Abstract

Three ferrous materials; Hadfield steel, high chromium white cast iron and austempered ductile iron (ADI) exhibit a similar phenomenon in which soft stabilised austenite transforms to hard martensite on the worked surface. This property is desirable in applications where toughness is required in the bulk of the component while the surface needs to be hard-wearing. Thus, the microstructure of the component may consist of meta-stable austenite, which is meant to change to martensite by strain-induced transformation as a result of impact or wearing loads applied to the surface. The chemistry of alloys is very different while the metallurgy and transformation mechanisms are closely similar. In this paper, the differences, similarities as well as the most appropriate applications of the materials are discussed.

Keywords: Hadfield, chromium, ADI, austenite, martensite

1. INTRODUCTION

The mechanical properties of toughness and strength have been known for be mutually exclusive in most ferrous materials. An attempt to gain toughness is almost invariably accompanied by loss of hardness and strength and vice versa. Metallurgists have had to compromise on the properties in a delicate balance that cannot be shifted, unless expensive alloying and heat treatments are employed. Sustained research has culminated in three special alloys that are manipulated to allow a component to exhibit the desired combination of toughness and strength during use. Hadfield steel, high chromium cast iron and austempered ductile iron (ADI) are alloys, which possess a rare and unique characteristic that is atypical of most ordinary ferrous alloys. The chemistry, microstructure as well as mechanisms by which toughness and strength are made to co-exist are reviewed in this paper. In application however, the materials are not necessarily interchangeable, particularly ADI, which has limitations in product size and working conditions. The scientific goal of the present paper is to explain that although the materials exhibit similar metallurgical behaviour, they are not exactly interchangeable. Thus this paper helps practitioners in material selection for application in appropriate circumstances.

2. LITERATURE REVIEW

2.1. Properties and behaviour of materials

The conventional feature in the properties of ferrous alloys and other materials is the inverse relationship between hardness (and strength), and toughness (and ductility). As hardness increases, toughness decreased and vice versa [1]. Hardness (H) is the resistance to penetration or deformation, which is related to the strength of the material, while on the other hand toughness (K_c) is a measure of how much a material can deform before fracture. These two competing properties pose a challenge to metallurgists, who have no option other than strike a compromise between them, depending on the requirement for a particular application. The ratio H/K_c was proposed by Lawn and Marshall in 1979 [2] as an index of brittleness. A high index favours high hardness while compromising toughness and vice versa. The index of brittleness underscores the behaviour of materials where deformation occurs at low loads, materials deform leading to fracture at high loading events. The extent of deformation before fracture is dependent on the magnitude of the H/K_c ratio. However, this index would not be applied in some rare cases where hardness and toughness can be increased simultaneously, as is the case in the three materials under investigation in this paper.

Attaining both high strength and toughness is crucial for most structural steels [3] but this is not possible in conventional ferrous materials. The quest to maximise both H and K_c is an ever compelling subject for research to find materials that will defeat the age long conflict between strength and toughness.

2.2. Microstructural phases in ferrous materials

The phases found in ferrous materials consist of soft phases and hard phases depending on the thermo-mechanical treatment of the component. **Table 1** shows relative hardness of common phases found in microstructures of ferrous alloys.

Table 1 Typical hardness values of some phases found in ferrous alloys

Phase	**Ferrite**	**Austenite**	**Pearlite**	**Martensite**	**Cementite (carbide)**
Description	Soft	Soft	Hard	Hard	Hard
Hardness	80B HN (37R_B)	**110** BHN estimated (62 R_B)	400 BHN (41 R_C)	700 BHN (63 R_C)	>794 BHN (68 R_C)

BHN = Brinell Hardness Number R = Rockwell Hardness

The hardness of the component depends on the proportion of the phases and constituents in the microstructure. The preponderance of ferrite or austenite has low hardness while the microstructure of cementite (carbides) and martensite is hard. In most cases ferrous microstructures consist of a combination of phases resulting in a compromise of hardness value depending on the proportion of hard and soft phases. Consequently it is ordinarily not possible to maximise two properties of strength and toughness [3].

2.3. Hadfield steel

Hadfield steel was invented by Sir Robert Hadfield in 1882. The original chemical composition of Hadfield steel contained about 1.2% C and 12% Mn, but other formulations with essentially minor modifications have been developed. In some variants however, significant increases in carbon and manganese have been made up to 1.4% and 20% respectively, in combination with chromium additions for purposes of achieving high initial hardness, maximum hardness after work hardening and wear resistance [4]. The manganese to carbon ratio should be greater than 10 in Hadfield steel grades [5]. However, if manganese content is too high the casting does not completely work-harden [6] leading to particularly low wear abrasion resistance. The chemistry of low manganese grades can be modified by addition of grain refining elements that form nitrides and carbides such as NbN and Nb_2C [6].

The fundamental significance of Hadfield steel is its work-hardening behaviour from an initial low hardness of 240 BHN (23 Rc) in the austenitic phase to high hardness well in excess of 500 BHN (51 Rc) in martensite [7]. Thus Hadfield steel is a hard wearing steel widely used for rock crushing in mining and stone quarrying e.g. crushers and hammers, dredge buckets, power shovel buckets and teeth [8] and military applications such as tank track pads [9] as well as diggers and railroads [4]. However, where service applications devoid of severe impact such as in the attrition of friable ores and in secondary crushing of particulate ore; transformation of austenite to martensite is limited resulting in lower-than-expected wear resistance. Hadfield steel used for this purpose lacks the necessary wear resistance and need be strengthened by precipitation hardening of vanadium and chromium carbides [10].

2.4. High chromium white cast iron

The family of high chrome white cast iron can be classified in four groups of chromium content namely; 11% to 14% Cr, 14% to 18% Cr, 18% to 23% Cr and 23% to 28% Cr with carbon content ranging between 1.6% and 3.4% [11]. However, there are some though commonly used grades with Cr content up to 34%. For the hypoeutectic composition of high chromium cast iron, solidification proceeds by a eutectic process where the austenitic phase precipitates from the liquid phase until the composition reaches eutectic, then the eutectic reaction occurs forming austenite and faceted crystals of $(Cr,Fe)_7C_3$ type carbide [11]. The microstructure of the as-cast condition depicts primary dendrites of austenite in a matrix of eutectic. The large volume fraction eutectic carbides in the matrix is responsible for the high hardness necessary for crushing and grinding applications. The microstructure can be adjusted by alloying and heat treatment to strike a balance between abrasion resistance and the toughness required to withstand repeated impact loading. Class **III** irons containing 23 to 28% **Cr are** austenitised at temperatures ranging between 1010 to 1090°C and cooled in a fan-generated draught in order to by-pass the TTT curve knee at 550 and 600°C Subsequent slow cooling from 600°C to room temperature either in still-air or even in a furnace is highly recommended to reduce stresses that are caused by the volumetric expansion occurring when austenite transforms to martensite. Stress relieving at suitable temperature is often necessary. Too high temperatures in excess of 540°C will severely compromise abrasion resistance, and tempering between 200°C and 230°C substantially improves fracture toughness by up to 20% [12].

2.5. Austempered ductile iron

ADI is a versatile material with a combination of high strength (as high as 1300 MPa and 1800 MPa yield and UTS respectively) and high ductility (elongation can be up to 18%) [13]. The strength-to-weight ratio of ADI is superior to that of aluminium. This unique combination of strength and ductility is attributed to a dual microstructure of stabilised austenite and ferrite, both of which are ductile phases. The high strength is due to martensite formed on the surface as a result of strain hardening of meta-stable austenite. ADI is used in wear-dominant applications such as farm machinery and construction equipment e.g. plough points, bucket and digger teeth and in automotive parts e.g. CV joints, control arms, wheel hubs, sprockets, shift forks and gears [14]. General Motors in 1978 installed differential gear sets made of ADI to light-weight truck-trailer wheel hubs as well as high performance automobile [15].

3. EXPERIMENTAL WORK

The materials under investigation were obtained from three different foundries in Johannesburg, South Africa. Hadfield steel and high chromium cast iron were procured from foundries that produce hammers and crushers mainly used in the mining industry. Ductile iron was obtained from a foundry specialising in automotive parts.

3.1. Chemical analysis

The chemical analysis on the three materials was conducted at the foundries of origin in conformity to respective chemical specifications namely grade ASTM128 Grade B2 for Hadfield steel [16], BS4844: 1986 Grade 3D for high chromium white cast iron [17] and ASTM536 for ductile iron to produce ADI conforming to **ASTM A897 [18]**. The samples were delivered to the physical metallurgy laboratory at the Department of Metallurgy, University of Johannesburg for metallographic investigation and mechanical testing.

3.2. Heat treatment

The bulk of the microstructure of Hadfield steel consists of austenite stabilised to room temperature by a combination the high carbon and high manganese contents. In as cast condition Hadfield steel contains gross carbide networks tend to line up along the austenite grain boundaries resulting in reduced toughness. Thus, necessitating heat treatment to dissolve carbides followed by rapid cooling to room temperature. The heat treatment involved soaking at 1050°C to dissolve grain boundary carbides and was subsequently quenched in agitated water to obtain an entirely austenitic microstructure. High chromium white cast iron was investigated in as-cast condition. Ductile iron was austenitised at 900°C for 2 hours and austempered in a salt bath at 290°C for 2½ hours then air cooled to room temperature.

3.3. Hardness Testing

For high chromium white cast iron, the typical hardness for in as-cast and annealed condition is 400 HB with a mandatory minimum of 600 HB after heat treatment according to the British Cast Iron Research Association (BCIRA). However, this paper discusses the behaviour of as-cast high chromium white cast iron often used in the ragged impact crushing conditions is compared with that of Hadfield steel and ADI, which have comparatively similar mechanical characteristics.

4. RESULTS AND DISCUSSION

The three materials exhibiting similar microstructural transformation during service are compared in terms of chemistry, microstructure, hardness, and mechanism of transformation austenite to martensite.

4.1. Chemical composition differences

Table 2 shows the different chemistries of the three materials. Different alloying elements are employed mainly to stabilise austenite at room temperature. In Hadfield steel the austenite stabilisers are carbon (1% min) and manganese (11% min), while in high chromium cast iron the austenite stabilising alloying elements are carbon (2% min) and chromium (22% min). In ADI a minimum of 3.5% carbon and 2.25% silicon are responsible for retaining austenite at room temperature. ADI is different from the two other alloys in that the austenite gets enriched in carbon during the austempering process. Since formation of carbides is inhibited by high silicon, the carbon is rejected from the ferrite that is formed to enrich the surrounding austenite, thus stabilizing it. Martensite will not be formed even at low temperatures, unless the material is subjected to stress and/or strain.

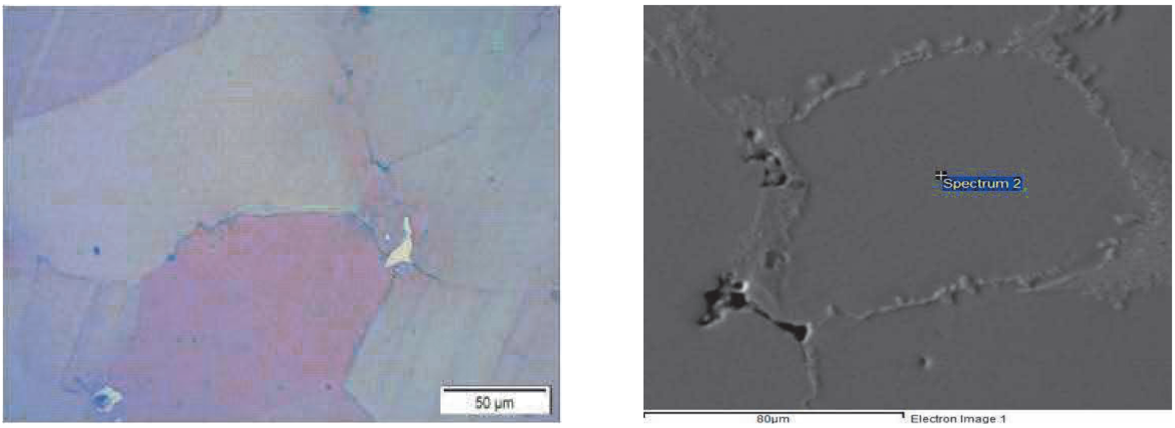
Table 2 Chemical specifications of Hadfield steel [16], high chromium white cast iron [17] and ADI [18]

Material	C%	Cr%	Mn%	Mo%	Si%	Ni%	Cu%	S%	P%
Hadfield steel	1.05-1.25	0.5*	11-14	-	0.6-1.0	-	-	0.06*	0.07*
HCWCI	2.0-2.8	22-28	0.5-1.5	1.5*	1.0*	2*	2*	0.1*	0.1*
ADI	3.5-3.9	-	0.15-0.35	-	2.25-2.75	-	-	0.01-0.025	0.05*

*Maximum content of element in alloy

4.2. Microstructural similarities

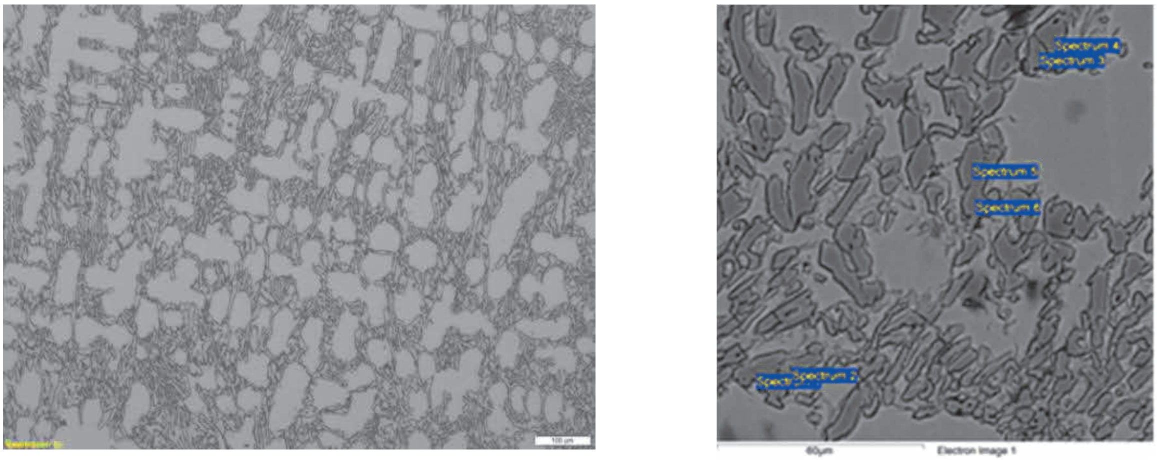
Figure 1 shows heat treated Hadfield steel consisting predominantly of austenite in the microstructure. Some residual carbides indicate that soaking at 1050°C could not fully dissolve the carbides forms during solidification. Either the soaking time was insufficient or the carbides were too coarse to dissolve completely. Such gross carbides are typical in large castings where solidification is prolonged resulting in nucleation and growth of carbides type $(Fe,Mn)_3C$. The undissolved carbides line up at grain boundary of stabilised austenite resulting in reduced impact strength since brittle cracking starts at these carbides [19].



(a) (b)

Figure 1 Microstructure of Hadfield steel (a) Optical (b) SEM

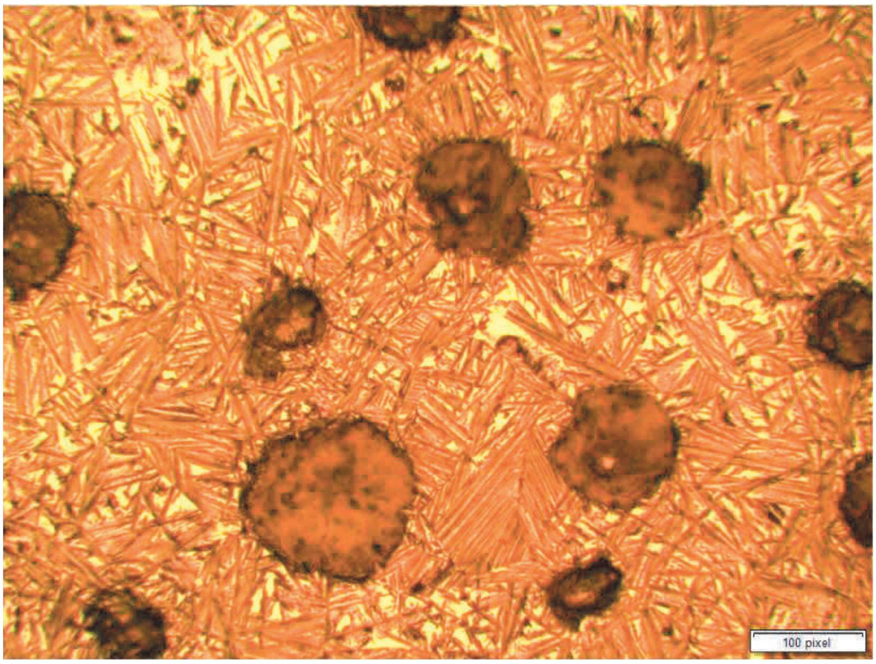
Figure 2 shows the microstructure of as-cast of high chromium white cast iron showing the primary dendrites (light) of austenite and the matrix of eutectic of austenite and carbide (dark). The eutectic carbides of type $(Cr,Fe)_7C_3$ are the most preferable because they are typically fine, discrete and do not compromise on toughness. Type $(Cr,Fe)_7C_3$ carbides tend to predominate in the matrix when the Cr to C ratio is maintained below 10. Undesirable gross carbides such as Cr_3C and $Cr_{23}C_7$ start to emerge at higher Cr to C ratio of 11:1 and above. Thus a practical maximum limit for ensuring $(Cr,Fe)_7C_3$ is set at Cr to C ratio of approximately 10.5:1.



(a) (b)

Figure 2 Microstructure of as-cast high Cr cast iron (a) Optical (b) SEM

Figure 3 shows the microstructure of austempered ductile iron with graphite modules sporadically distributed in an intricate mixture of austenite and ferrite commonly referred to as “ausferrite”. The composition of ausferrite matrix shows considerably larger volume fraction of austenite than ferrite. The relative proportions of austenite and ferrite in the final matrix is determined by the temperature and time of both austenitising and austempering processes. The higher the austenitising temperature and the longer the exposure, the more the carbon dissolves in austenite, thus effecting austenite stabilisation. Similarly, the lower the austempering temperature, the lower will be the austenite volume fraction in ausferrite. The resultant properties of ADI are also dependent on the proportion of austenite, which in turn is governed by the temperature and time of austenitising and austempering. High volume fraction of austenite resulting from high isothermal transformation temperature leads to high ductility, while low austempering temperatures are more favourable for high strength and low ductility.



100μm

Figure 3 Optical micrograph of ADI etched in 2% Nital

The microstructure of Hadfield steel consists of 100 percent austenite stabilised by carbon and manganese. In high chromium white cast iron the microstructure is made up of primary austenite and eutectic of carbides and secondary austenite. In ADI sporadic graphite are widely distributed in a matrix of the dual phase ausferrite. The common feature in all three materials; heat treated Hadfield steel, as cast high chromium cast iron and austempered ductile iron is austenite in the microstructure. This is responsible for the closely similar properties of hardness and toughness exhibited by the materials.

4.3. Microstructural transformation and evolution of mechanical properties

The incidence of high strength and ductility that is uncharacteristic of ferrous materials is attributed to work hardening behaviour attributed to dynamic strain aging of austenite grains. The transformation of austenite to martensite is subject to both tensile and shear effects on austenite grains. The dominant factor, whether tensile or shear; stress or strain will determine the transformation mode. Austenite has to be subjected to either abrasion or heavy impact loads, and stressed or strained sufficiently for martensitic transformation to occur. It should be noted that the transformation mode is due to the dominance of either stress or strain. In Hadfield steel and high chromium white cast iron transform is induced by heavy impact loads that are typical in hard rock crushing, thus strain initiates transformation. In austempered ductile iron on the other hand, austenite-martensite transformation is induced by abrasion, which is a predominant mechanism in earth engaging and working friable ores, thus the micro stresses are responsible for transformation. Stresses and strains induced in austenite at the worked surface cause microstructural transformation of austenite to martensite while the rest of the component remains tough.

According to Chih-Kuang and Yi-Lin [20] the strain-induced transformation of austenite to martensite takes place particularly in the sliding planes and the intersection points of twinning sites by two mechanisms of sliding and twinning that tend to lower the potential energy held in the area. Sliding planes and intersection of twinning sites in the parent austenite grains act as active sites for martensite. Micro-defects such as dislocations and shear bands introduced in the austenite as a result of applied stress are also idea nucleation sites for martensite. By this mechanism the worked surface presents a hard surface for the required wear resistance, while the bulk of the component remains tough as a result of untransformed retained austenite (and ferrite in the case of ADI) making the composite part less prone brittle failure.

4.4. Merits and demerits of materials in production and cost

Hadfield steel has the advantages of comparatively short heat treatment cycle to achieve an austenitic microstructure; however the down side of the material is high cost of manganese and poor machinability in as-cast condition. High chromium white cast iron is superior to Hadfield steel where heavy crushing of hard rock is involved. However the high cost of chromium and poor machinability in as cast condition makes it more expensive to procure that Hadfield steel. Austempered ductile iron has a number of comparative advantage that include: lower production costs due to lower raw-material, lower energy demand and good castability and machinability; higher noise damping properties makes it silent work during service and comparably attractive mechanical properties.

The demerits of ADI arise from limitation in size of casting that is determined by the capacity of austempering bath. The ruling section for full austempering of samples at the University of Johannesburg is 25mm, which means that specimens thicker than 25mm cannot be fully austempered. The microstructure at the core would be pearlite and not ausferrite. Therefore large cross-section gauges can hardly be made of ADI, unless hardenability is improved by alloying, preferably using copper (up to 1 %) or nickel (up to 3%), thus there size limit can be increased. However, for large sections such as jaw crushers, it may be even to an advantage if a core of a component remains pearlitic, similar to steel components where through-hardening is not always necessary.

The machinability is of practical importance in practice. In contrast to Hadfield and high-chrome steels, ADI components can be shaped before heat treatment, when the material is very easily machined. Chromium and more so, manganese are very undesirable in ADI, since apart from increasing cost, they cause segregation, leading to delay transformation zones (DTZ) and other problems.

4.5. Appropriate selection of the materials for application

The different modes of martensitic transformation dictate the application of the materials. For instance Hadfield steel and high chromium white cast iron where austenite-martensite transformation is induced by heavy impact loads, the materials do well in high impact application such as primary rock crushing in mining and quarrying and perform poorly in low impact with loose friable ores and secondary crushing. ADI is more amenable to transformation by surface abrasive wear, which is more predominant in friable ores and secondary crushing.

Factors such as hardness of rock ore, porosity and crack formation in ore have a bearing on the selection of materials to be used in rock crashing. The criteria to be considered for in material selection may include:

- Hardness and toughness of rock or ore
- Porosity, crack formation and friability of rock
- Rock type, whether igneous, metamorphic or sedimentary
- Size and texture of ore, whether run-of-mine or primary crushed
- Rugged percussive impact or static wear action

Some rocks were classified by Attewell and Farmer in 1976 [21] as weak with unconfined compressive strength (UCS) less than 40 MPa comprising uncompacted sedimentary rock. Some are of medium strength with UCS ranging between 40 and 80 MPa where compacted sedimentary rock and coarse-grained igneous belong. The strong to very strong rocks consisting of compacted fine grained metamorphic and igneous rock have an UCS of 80 to 320 MPa. The hardness and toughness of rock are also properties determining material selection. Haematite ore with Mohs hardness 5.5 to 6.5 is a tough ore that would require heavier impact crushing loads than gypsum that has a Mohs of 2 and has a low toughness. The choice of crushing is not arbitrary but very much dependent on these considerations.

Thus Hadfield steel and high chrome cast iron can be best applied in heavy crushing of hard and tough rock of dense, fine grained igneous rock such as the hard chromite and platinum ores of the Great Dyke of

Zimbabwe and may not be as good for the friable chromitite ores of the Merensky Bushveld Complex of South Africa. In the case of friable and secondary crushing, Hadfield steel and high chromium white cast iron the chemistries will have to be modified by addition of alloys such as titanium, vanadium and other elements and appropriately heat treated to precipitate carbides for improved wear resistance to the abrasive action of fine ore since there is no sufficient impact loading for strain induced transformation. Modifying the alloys with carbide forming elements also enhances abrasion resistance in percussive hard rock crushing.

ADI on the other hand is more suitable where wear action rather than heavy impact loading is prevalent. In application such as military tank track pads for instance, there is predominance of wear action rather than impact, hence ADI would be a more suitable material of choice than Hadfield steel. Earth-engaging applications such as diggers, excavators and agricultural implements, saw mill cutter blades, where the predominant mechanism is abrasion and wear rather than impact, ADI tends to outperform Hadfield steel and high chromium white cast iron.

5. CONCLUSION

The different chemistries were employed in the three alloys under investigation to bring about similar microstructures with stabilised austenite as the dominant phase. The transformation of austenite to martensite occurs in all the three alloys as the result of stresses and strains subjected to the working face of the component. While the mechanism of austenite to martensite transformation is the same, the mode in which the stresses and strains are induced is somewhat different. In Hadfield steel and high chromium white cast iron transformation is induced by impact strains while in austempered ductile iron transformation is by stresses caused by abrasive action on the working surface. The selection of material for rock crushing is thus determined by the type of forces that are at play on the surface of a component. Further investigation is required to evaluate the performance of ADI for application as hammers for crushing coal, which cleaves easily between layers but is an extremely abrasive material.

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