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PRODUCTION AND USE OF NOVEL (WTi)C MASTER ALLOYS IN FERROUS CASTINGS

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ABSTRACT

A novel method for the preparation of (WTi)C - containing master alloys suitable for addition to ferrous melts is described. Embodiments of the master alloy and methods of addition to different types of furnace melt are discussed.

The effects of the particulate addition on microstructure, mechanical properties and service performance of a range of cast products are presented. It is shown that the master alloy provides an effective route to introduce an even dispersion of fine, well-bonded carbides into castings. The reinforcement enhances key engineering properties of castings, particularly wear resistance, and offers opportunities for more cost effective use of cast and wrought ferrous products in heavy duty applications.

INTRODUCTION

A number of studies have concluded that the cost to an industrialised economy associated with wear of materials is 1-2% of GNP[1]. The driving force for improving wear resistance of materials is therefore clear. Ferrous castings find widespread application in aggressive environments where abrasive and adhesive wear are dominant failure modes [2]. Examples of such applications are Hadfield's manganese steel in mineral processing industries and alloy cast irons in steel rolling mills respectively.

It is known that the presence of hard particulates in a metal matrix can give rise to improvements in engineering design properties such as strength, stiffness, fatigue and wear resistance though often at the cost of lower toughness [3]. This approach is exemplified in the aluminium industry where carbide reinforcement has stimulated commercialisation of lightweight metal matrix composites. In ferrous systems, precipitation of carbides from the melt can not always be relied upon to deliver a desirable, uniform dispersion of the hard phase. Casting geometry, alloy constitution and solidification conditions often dictate that expensive post-casting homogenisation and heat treatment cycles are necessary to achieve the required microstructure. Powder metallurgy techniques can be employed to exercise better control over dispersion of hard phases[4] but with a large cost penalty compared with simpler casting techniques.

Attempts to add refractory carbides to ferrous melts directly are generally unsuccessful because of e.g. oxidation, poor wetting and segregation (settling or flotation). An alternative method of particle addition is via the Osprey process whereby particulates are injected into a molten metal stream and billets are formed from the atomised stream. This method has proven effective [5] but involves an extra process step which must be closely controlled to give a uniform product.

Today, there is renewed interest in Reaction Processing for introducing hard ceramic particles into metals[6]. LSM has developed a family of reaction processed products known generically as 'XTiC'. The reaction product, a porous mixture of fine carbides (borides, nitrides are also possible) in a metal matrix, can be crushed to a powder which can then be used as a master alloy melt additive, powder metallurgy additive, thermal spray powder or welding electrode consumable.

It is the purpose of this paper to describe production of the master alloy and melt addition practices and also to show how addition affects microstructure and properties of some key classes of ferrous castings. Validation of the property improvements identified in the laboratory is provided by results of practical field trials.

METHODS

Master Alloy Production

The 'XTiC' master alloy used in the current work was made by a patented, proprietary process based upon the exothermic reaction,

$$Ti_2Fe + C \rightarrow 2TiC + Fe \, . \qquad (1)$$

This is an example of a Self-propagating, High-temperature Synthesis (SHS) reaction. In practice, it involves blending powdered ingredients in a reaction vessel and igniting the mix locally with an intense heat source. The reaction front propagates throughout the charge with local melting occurring in the reaction zone. The transient combustion temperature has been measured at ca. 2500°C[7]. On completion of the reaction, the partially-fused block is allowed to cool to room temperature prior to being crushed and ground to size.

The reaction product is composed of a high volume fraction of fine, well dispersed and fully wetted carbides in an iron matrix. Choice of raw materials and control of thermal conditions are critical to achieve a uniform, fine carbide size[8]. The composition of the reaction mix can be controlled to produce specific combinations of alloy matrix and carbide type.

The master alloy used in this study has been designed for its intended use in the melting shop. To this end, tungsten has been incorporated into the mix to produce a mixed (WTi)C particulate whose density matches that of iron. Fig 1 shows a micrograph of granulated FeWTiC master alloy: the (WTi)C volume fraction is ca 75% and average carbide size is 5 - 10μm.

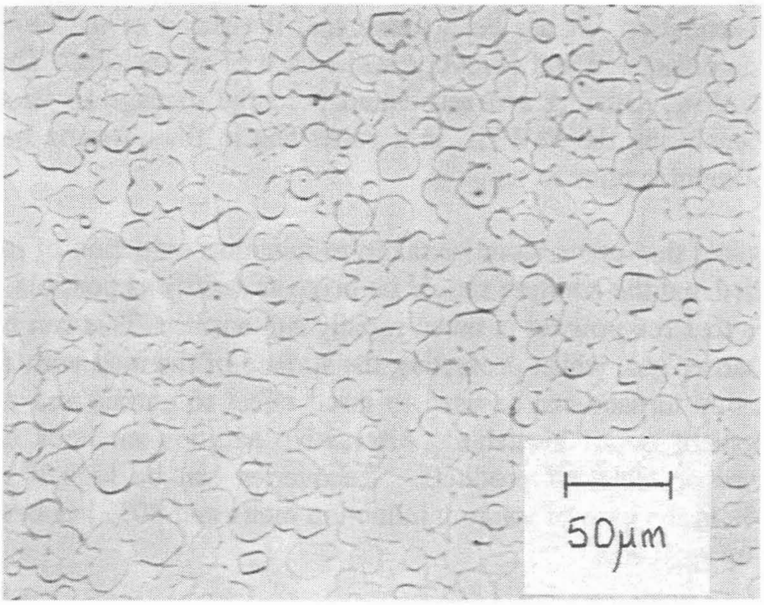

FIG 1 Microstructure of master alloy granule. Darker phase is (WTi)C.

Melt Addition

Table 1 summarises the alloy systems, furnace types and means of FeWTiC addition referred to in the current work.

Alloy System	Additive	Furnace Type	Form of Addition
Hadfield manganese steel	FeWTiC	Vacuum Induction	Bagged powder
0.4%C steel	FeWTiC	Vacuum Induction	Bagged powder
Indefinite chill Cast Iron	NiFeWTiC	Air Induction	Injection
CrMo Steel	FeWTiC	Vacuum Induction	Bagged Powder

TABLE 1 Melt addition routes

To date, work has concentrated on XTiC addition levels up to a maximum of 17%. Beyond this, difficulties are experienced because of excessive melt viscosity. A 5 - 10% addition has been found to yield most attractive property enhancements. At this level, a significant melt chilling effect is experienced which means that ladle additions cannot be made satisfactorily. Instead it has been found necessary to make additions directly to the furnace. For many alloy melt systems, FeWTiC represents the most reactive additive and should be added to a killed bath as late as possible, just before tapping.

Vacuum induction melt additions are straightforward and FeWTiC can be added without problems associated with oxidation. It has been found that the sizing of the FeWTiC has a strong influence on carbide dispersion and recovery in the case of air-melting. The preferred size range is -500μm granules. Dusting and associated potential damage to vacuum pump equipment is avoided by enclosing the FeWTiC in a paper bag in the charging basket. The addition is made about 10 minutes prior to tapping.

Air induction melting requires that precautions be taken to minimise oxidation of the additive. The bath must be fully killed and the addition should be made as swiftly as possible. Measures should be taken to ensure that the powder is taken rapidly sub-surface. This can be achieved by injection using argon carrier gas, whilst protecting the surface of the melt with argon. The powerful stir of the induction furnace can be used to good effect to entrain and disperse the additive if injection equipment is not available. Alternative addition methods can also be considered e.g. cored wire or tabletted products. Recoveries can be high if appropriate measures are taken: 100% in the case of vacuum induction melts and 80% has been reported for air induction melts of up to 4t size.

Once FeWTiC is added, the iron matrix melts liberating (WTi)C, which has a density equivalent to steel, into the melt. The composition of the XTiC matrix can be tailored as necessary to match its melting point with that of the operating furnace temperature. It can, for example, be desirable to use a lower melting point NiFeWTiC variant for addition to cast irons where melt temperatures are lower than for alloy steels.

Some degree of carbide dissolution and reprecipitation is believed to occur on melt addition [9] since the mean carbide size after addition is somewhat smaller than in the master alloy. Fig 2 shows that a very good dispersion of fine particulates is achieved. This is the case for all of the trial melts listed in Table 2 which covers key classes of ferrous alloys - cast irons, Hadfield manganese steel, low alloy steels. The next section describes the impact of the added reinforcements on alloy properties.

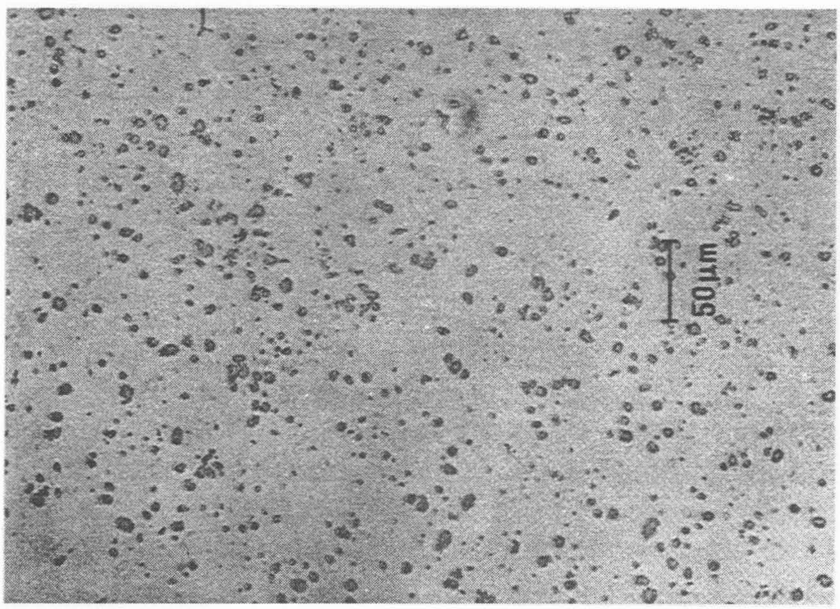

FIG 2 Microstructure of cast, ferrous alloy after 5%(WTi)C addition (Unetched)

Element	Austenitic Manganese Steel	0.4%C Steel
C	0.45	0.38
Si	0.65	0.23
Mn	10.61	0.53
P	0.03	0.01
Cr	1.81	0.15
Mo	0.17	0.03
Ni	0.21	0.15
Al	0.02	0.05
Ti	0.04	-
W	0.04	-

TABLE 2 Composition of steels

RESULTS

Addition of FeWTiC to 0.4%C Steel

50kg batches of 0.4%C steel, composition shown in Table 2, were vacuum induction melted and 7-20% FeWTiC granules added, corresponding to 5-17%(WTi)C. The composition of the FeWTiC master alloy is: 35.5W - 30Ti - 10C-bal Fe. The cast ingots were hot rolled to plate to facilitate extraction of test blanks. Fabricability of the composites was good, with edge cracking occurring only at higher volume fractions (≥ 10% (WTi)C).

The following heat treatments were applied to test blanks: austenitise at 850°C + AC or OQ/temper at 550°C. Table 3 shows mechanical property data for the unreinforced and selected reinforced 0.4%C steels. It is clear that addition of (WTi)C substantially increases the yield and tensile strength of the base steel at the expense of some ductility. Examination of sub-fracture surface microstructures indicates that failure is initiated by particle cracking whilst the particle/matrix interface remains intact[10].

% WTiC	Heat Treatment	0.2% PS (MPa)	UTS (MPa)	Elongation (%)	TRS (MPa)
0*	Normalised	280	540	16	-
0*	Hardened + Tempered	465	690	16	-
5	850°C/AC	613	881	13	2080
5	850°C/OQ + 550°C/AC	1036	1075	9	2501
10	850°C/AC	863	1126	7	2303
10	850°C/OQ + 550°C/AC	1455	1488	6	2974

TABLE 3 Effect of FeWTiC on mechanical properties of 0.4%C steel (*from ref. 9)

Abrasive wear testing was performed on heat treated samples to ASTM-G65-85: a range of media (rounded quartz, sub-angular quartz, sinter and coke) in the size range 400-700μm were used. Fig 3 shows the impact of 5% (WTi)C treatment on wear resistance compared with a 0.15C reference steel (VHN ~190). Reductions in weight loss in the order of 20 - 800% are observed ranging from relatively hard sinter to softer coke abrasives.

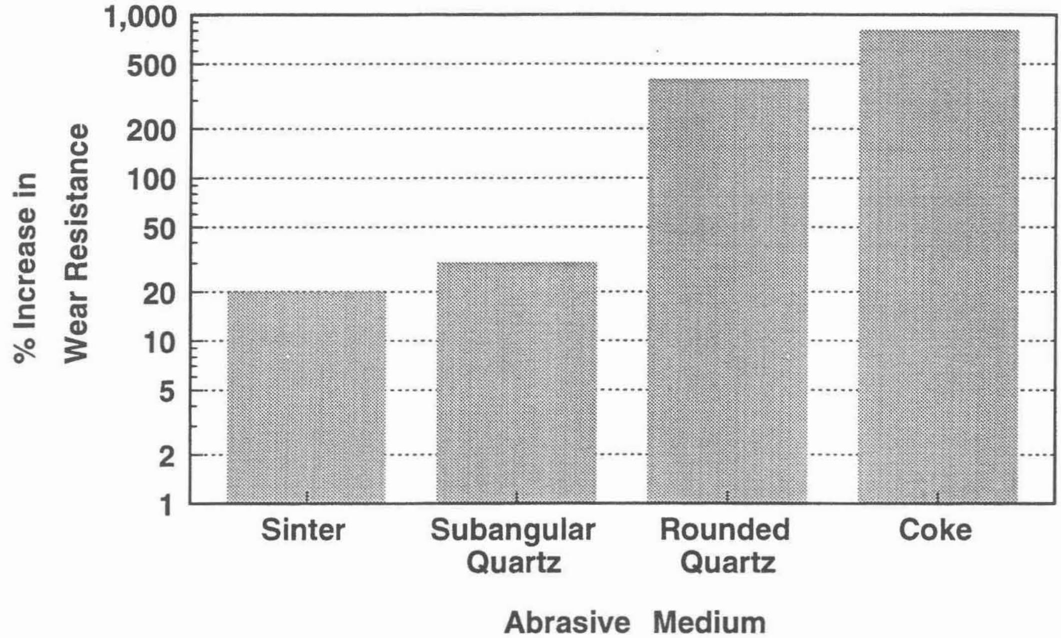

FIG 3 Abrasive wear resistance of (WTi)C reinforced 0.4%C steel compared with 0.15%C base steel

Addition of FeWTiC to Hadfield's Steel

50kg vacuum induction melts of austenitic manganese steel were prepared with and without 5% FeWTiC addition. The composition of the base steel is shown in Table 2. Test blanks were extracted from the heat treated ingots (1050°C/CWQ) for mechanical testing. Table 4 summarises mechanical test data including tensile test and Charpy impact toughness results. As in the wrought alloy system described above, strength levels are enhanced compared with the base steel at the expense of some ductility and impact toughness. The increase in hardness mirrors the trend in yield strength. Table 4 also provides evidence that tensile modulus increases significantly with particulate reinforcement.

Wear testing of these samples has been carried out under adhesive (pin-on-disc) and abrasive (wet sand) conditions. Fig 4 shows the effect of 5% FeWTiC adition on pin-on-disc wear of Hadfield's steel. Wear rate is reduced by ca 30% over a range of normal pin loads.

Property	Austenitic Manganese Steel	+4.2% FeWTiC
Modulus (GPa)	159	178
UTS (MPa)	485	586
0.2% PS (MPa)	324	365
% Elongation	5	7
% RA	10	13
Charpy Impact Toughness (J)	50	38

TABLE 4 Effect of 4.2% FeWTiC addition on mechanical properties of austenitic manganese steel

Wet sand abrasive testing of Hadfield's steel of similar chemistry with and without 5% FeWTiC has been carried out according to a proprietary test procedure by a Japanese foundry group. Weight loss after testing is reported to be halved by addition of FeWTiC.

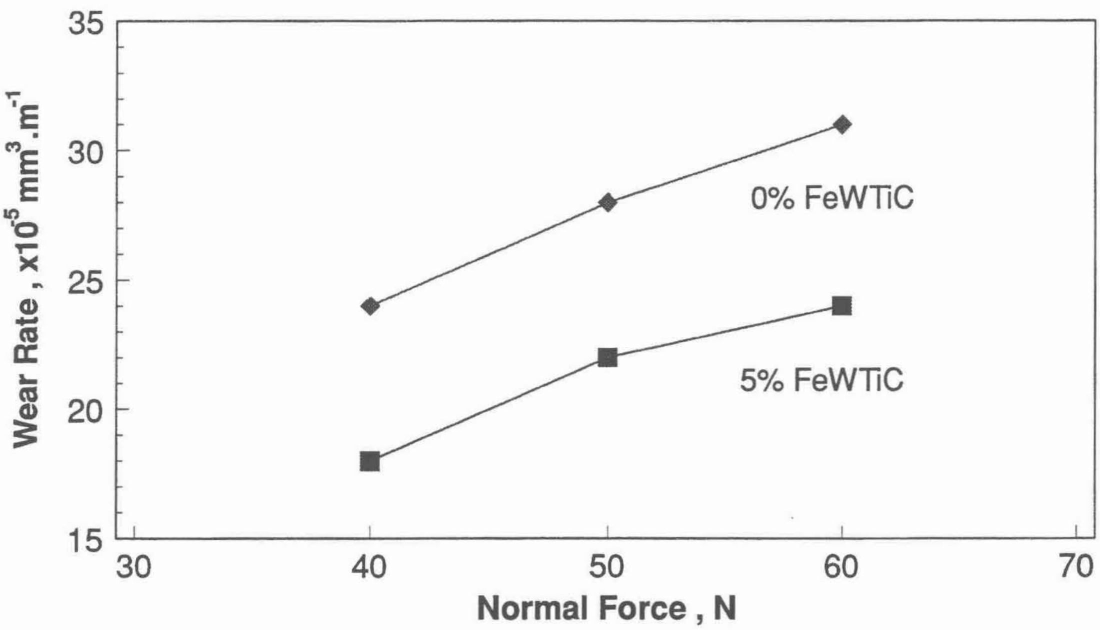

FIG 4 Pin-on-disc wear resistance of Hadfield's steel with and without 5% FeWTiC. Sliding speed 2ms^{-1} over total of 40km

Field trial experience with FeWTiC reinforced Hadfield's steel has come from two sources to date. The lifetime of an adjustable crusher comb casting for mineral processing was extended from 2 to 12 weeks following treatment with 5% FeWTiC. Jaw crushers with a similar reinforcement level have been evaluated against normal unreinforced castings in LSM's FeTi crushing plant. FeWTiC treatment enabled a 50% higher tonnage of FeTi to be processed before replacement became necessary.

DISCUSSION

Tensile Properties

Addition of (WTi)C has been shown to have a major effect on the properties of 0.4%C and austenitic manganese steel. In the latter case it should be noted that the base composition (Table 2) is not ideal and the data serve primarily for comparative purposes.

The enhancements in tensile properties probably arise from a combination of mechanisms. A number of references can be found to the inoculation effects of TiC in steels[11][12], and indeed evidence for grain refinement following FeWTiC addition to 0.4%C steel has been detected (5μm grain size with FeWTiC, 50-60μm without)[8]. Refinement of grain size will increase strength levels and this may be compounded by local matrix hardening around particles. This arises from residual stresses around carbides which have a large thermal expansivity mismatch with the surrounding matrix. Such local work hardening has been invoked to explain strengthening in aluminium particulate metal matrix composites[13]. For Hadfield's steel in particular both W[14] and Ti[12] additions have been found to be beneficial in raising strength levels and reducing the incidence of casting defects.

The increase in modulus seen in Hadfield's steel is expected to apply to other systems also and stems from the presence of a significant volume fraction of stiff reinforcing particles. The good matrix/particle bond strength, evident in failed tensile specimens, is instrumental in achieving improved tensile properties and confirms the value of the pre-wetted form of carbide in the master alloy. FeWTiC masteralloy therefore offers the design engineer a means of improving strength and stiffness of wrought components whilst retaining adequate fabricability and ductility.

Wear Properties

Japanese foundry data and the results shown in Fig 3 demonstrate that abrasive wear performance is enhanced by (WTi)C reinforcement of steels. Wear testing is notoriously complex involving physical and chemical processes and Fig 3 shows that the abrasive medium is particularly influential.

The field trial data with crusher combs and jaw-crushers represent particularly harsh conditions. In the first case, the mineral being processed contained significant amount of flint, and in the latter case occasional fragments of pure Ti in the FeTi alloy can be particularly aggressive. (WTi)C addition has therefore shown its potential for the most demanding of applications. Encouragingly there was no evidence of brittle fracture under the severe shock loading conditions imposed.

The pin-on-disc data shown in Fig 4 serve to illustrate a general point that (WTi)C reinforcement improves adhesive (metal-to-metal) wear resistance of steels. Other data have been obtained for a low alloy steel with and without 5% FeWTiC which shows a four-fold decrease in wear rate with (WTi)C present[10]. In this connection, the fine, rounded nature of the reinforcement may be advantageous and the increase in yield strength may raise the stress level required for onset of contact fatigue damage[3].

Trials are currently progressing in a steel strip mill with NiFeWTiC-reinforced indefinite chill cast iron rolls (subject to international patent application). Preliminary performance data suggest that wear rate is some 30% lower than with conventional untreated rolls. This validates the improvements in adhesive wear characteristics observed in laboratory trials, albeit the operating conditions are very different.

Work is continuing to address the possibilities offered by SHS processes. Alternative master alloy matrices have been developed including Ni and Co base variants - possibly suited to superalloys and stellites respectively. The hard particulate composition can also be varied as desired to produce e.g. nitrides and borides or indeed mixtures of these.

Methods of addition are also receiving attention and there appears to be no reason why e.g. tabletted and cored wire methods should not be feasible if required.

CONCLUSIONS

1. A novel (WTi)C-containing master alloy has been produced via SHS reaction. This is available in granular form with a high volume fraction of fine carbides, fully wetted in an iron matrix.

2. The master alloy has been added successfully to air and vacuum induction furnace melts representing a wide range of ferrous alloys including cast irons, low alloy steels and Hadfield steel.

3. Castings have been prepared, up to 4t in size, containing a good dispersion of fine carbides. Castings can be fabricated without significant problems up to 10% reinforcement.

4. (WTi)C reinforcement results in much improved tensile strength and stiffness properties at the expense of some ductility. Adhesive and abrasive wear performance is also enhanced in laboratory test situations. There is also evidence that (WTi)C addition yields a finer grain size in cast and wrought products.

5. Field trial experience demonstrates that addition of 5% FeWTiC can significantly improve service lives of engineering components - Hadfield steel crusher combs and jaws and indefinite chill cast iron rolls.

6. Alternative master alloy compositions have been prepared which are appropriate for addition of carbides to e.g. Ni-base superalloys and Co-base stellites. Nitride, boride and carbo-nitride master alloys have also been synthesised.

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