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Titanium in the Rapidly Cooled Hypereutectic Gray Iron

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The effect of titanium on the structure and properties of a rapidly cooled hypereutectic cast gray iron has been studied on the example of permanent mold (PM) casting. A microstructure study showed that titanium is a relatively strong element in controlling solidification structure by increasing undercooling and thus promoting type D graphite. The effectiveness of titanium additions depends on the base iron carbon equivalent (CE) with more pronounced changes in iron with a lower CE. The undercooling ability of the titanium decreases after exceeding a certain level. Increasing titanium from 0.09-0.12% slightly increases undercooling in iron with lower CE, but this effect was reduced in a more strongly hypereutectic iron. Alloying with titanium generally improves tensile strength, but the effectiveness of titanium additions also depends on the base iron CE range. Scanning electon microscope (SEM) studies revealed that most of the titanium-containing compounds were located in the metallic matrix: titanium carbides have been found in pearlite, while titanium nitrides and carbonitrides were located in ferrite. The presence of large amounts of extremely hard titanium-containing compounds, which often appear with steadite in a relatively high phosphorous content PM gray iron, amplifies the negative effect of titanium on machinability. This study suggests that for optimal combination of tensile strength/microstructure with good machinability, the titanium content in PM gray iron should not exceed 0.075%.

Keywords hypereutectic cast gray, machinability, solidification structure, titanium-containing compounds, type D graphite, undercooling

1. Introduction

Permanent mold (PM) and horizontal continuous casting (HCC) are casting methods that use rapid cooling to produce a large variety of gray iron cast parts.[1,2] These methods use mostly hypereutectic gray iron containing titanium additions to promote type D graphite.

In HCC of gray iron, titanium is added to produce Type D graphite, size 6-8, in a predominantly ferritic matrix with approximately 15-25% pearlite. According to Ref. 3, this iron was originally developed for the glass industry where dimensional growth and superior machining finish were needed.

In PM casting of gray iron,[4] titanium is routinely added to provide the undercooling required to meet ASTM specification A823-84, which calls for predominantly Type D graphite, size 5-8, with some Type A graphite, size 4-6, associated with the center of the casting or any sand cores, in a fully ferritic or ferritic-pearlitic (≥30% pearlite) metallic matrix. This has been found as a most desirable microstructure, ensuring relatively high tensile strength, good pressure tightness, and excellent machinability. Tensile strength, for example, is proportional to section size: 30 000 psi is the minimum for a separately cast standard 22.4 mm (0.88″) diameter test bar A, and 25 000 psi is the minimum for a separately cast standard 30.5 mm (1.2″) diameter test bar B; hardness ranges from 143-229 HB depending on heat treatment: annealing or normalizing.

As a promoter of undercooled Type D graphite, titanium significantly reduces graphite flake size and the eutectic cell count.[5] These effects of titanium are attributed to its ability to nucleate austenite and increase eutectic undercooling.[6]

From the foundry practice, it is well known that the titanium is also a nitrogen scavenger that eliminates gas porosity, and reduces hardness and tensile strength in sand mold gray iron castings.[7-9]

Addition of titanium to the cast iron chemistry results in the presence of titanium-containing compounds such as titanium carbide (TiC), titanium nitride (TiN), or titanium carbonitride Ti (CN) in the microstructure of the iron.[10,11] Very rarely, when the manganese content is inadequate to balance the sulfur, titanium may be present as a titanium sulfide (TiS).[11]

Researchers[12] have found that at certain titanium contents, nitride/carbonitride precipitated particles act as substrates for graphite nucleation. The resulting finer graphite flake structure contributes to increased tensile strength and improved thermal shock resistance of gray cast iron for ingot molds.

Authors[13] studying the effect of up to 0.11% titanium in ferritic ductile iron observed numerous titanium-containing inclusions (≥300-400/mm^2) of various sizes, roughly from 3-30 μm, and deteriorated graphite shape and tensile properties.

Authors[14] have reported the positive effect of titanium-containing compounds on the wear resistance of brake part castings, while another study[15] found that the machinability of cast parts was significantly reduced by the presence of titanium-containing compounds.

Currently, the titanium range in PM cast gray iron varies from 0.06-0.14%, and limited data are available on the optimum titanium level in these castings.

The objectives of this study were:

- to evaluate the titanium effect on the solidification structure, tensile strength, and nitrogen content;
- to identify titanium-containing inclusions produced with different titanium levels; and
- to determine, ultimately, the optimum titanium content.

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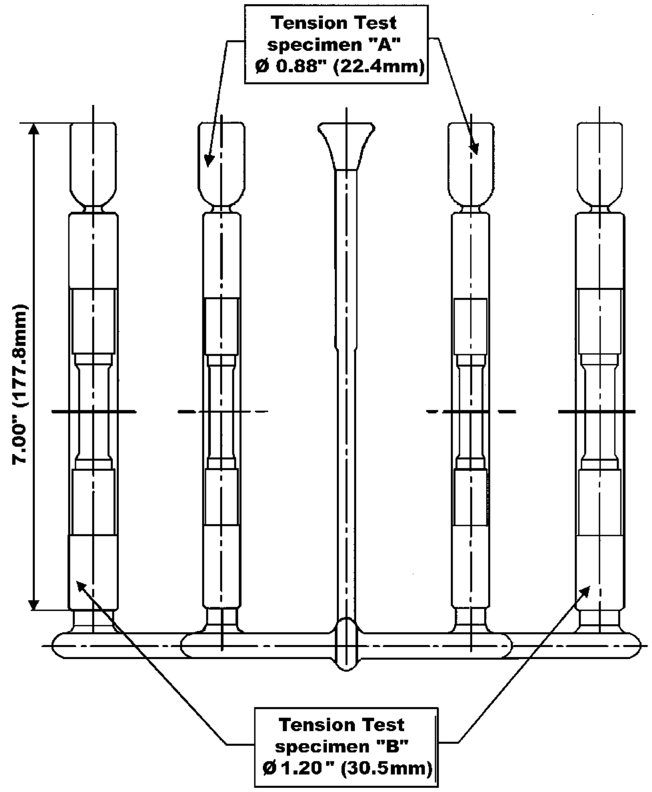

Fig. 1 Permanent mold cast gray iron tension test bars with the gating system

2. Experimental Procedures

Experimental castings and tensile test bars were made in an operating permanent mold iron foundry. The base iron was melted in a hot blast cupola from a charge mix consisting of pig iron, steel, and returns. To obtain the desired titanium level in the base iron, an ilmenite ore (30% TiO2) was used in the charge mix as a briquette containing 90% ore and 10% binder. Other appropriate ferroalloy additions were made to produce hypereutectic gray iron with the following chemical composition (wt.%): 3.55-3.65 carbon; 2.45-2.55 silicon; 0.45-0.55 manganese; 0.2-0.3 phosphorous, and 0.06-0.075 titanium. Iron from the cupola was tapped into a channel induction holder, which was periodically tapped at 1420-1440 °C (2588-2624 °F) into 364 kg (800 lb) transfer ladles, transferred into 100 kg (220 lb) pouring ladles, and then poured into vertically parted permanent molds mounted on a 12-station carousel.

Three chemical compositions of hypereutectic gray iron with different CE levels from approximately 4.44-4.58% were tested, while the titanium content was varied from 0.065-0.12%.

Standard ASTM A-823-84 test bars A, 22.4 mm (0.88″) diameter; test bars B, 30.5 mm (1.2″) diameter; and experimental castings were poured at 1330-1350 °C (2420-2460 °F) into soot coated air-cooled permanent molds. Figure 1 shows the permanent mold cast gray iron tension test bars A and B with the gating system.

After knockout, the test bars were annealed, while the castings were either annealed or normalized, depending on the specification requirement. The typical annealing cycle consisted of austenitization at 843-927 °C (1550-1700 °F) for at least 1 h and furnace cooling to obtain a fully ferritic metallic matrix. Normalizing consisted of austenitization at 843-927 °C (1550-1700 °F) for at least 1 h and then air quenching. The microstructure of normalized PM castings was predominantly ferritic and contained not more than 30% pearlite.

Tensile strength tests were performed on specimens machined from the test bars and on test specimens cut from experimental castings with different section sizes. Metallographic samples from the test bars and experimental castings were first examined by light microscopy in the unetched and etched (1% nital) conditions and then via scanning electron microscope (SEM), the latter being used to identify titanium-containing particles. The amount and morphology of Type D graphite in the cross section of metallographic samples have been used as a method for evaluating the effect of titanium undercooling.

Samples for gas analysis were taken at various steps of the casting process: from the cupola, from the holding furnace, and then from castings with varying titanium content. A series of experiments has been conducted to evaluate the feasibility of 70% ferrotitanium (FeTi 70) ladle additions to increase the titanium content in the base iron from 0.06-0.075% up to 0.12%. A standard grade of FeTi 70 (8 Mesh × Down) was added into the stream of iron during tapping from the transfer ladle into the pouring ladle. Major slag build-up in the pouring ladle has been observed after the first 4-6 h of operations, resulting in a low and erratic recovery of titanium.

Experiments with different lining materials (silica and alumina) and ladle coatings (magnesia) were unsuccessful in solving the build-up and related low titanium recovery problems. Only additions of about 0.03% of a proprietary calcium-bearing flux have solved the problem: slag build-up was eliminated, and titanium recovery was significantly increased from approximately 26-30% to 45-50%. These experiments have confirmed recommendations[11] that the introduction of the calcium, an element with higher affinity for oxygen than titanium, together with ferrotitanium, may prevent titanium oxidation and loss, and subsequently improve recovery of titanium.

3. Results and Discussion

3.1 Microstructure and SEM Evaluation

These studies have shown that titanium additions to the PM cast gray iron increase undercooling and promote Type D graphite formation. Figure 2(a) shows the microstructure of annealed PM cast gray iron casting containing 0.12% Ti (4.44%CE), and Fig. 2(b) illustrates the typical titanium compounds observed in this iron in the ferrite and near the ferrite/graphite regions. The quantity of these compounds significantly increased when the titanium content was increased from approximately 0.08-0.12%. It was found that the effectiveness of titanium additions on the degree of undercooling depends on the carbon equivalent, with more pronounced changes in irons with a lower CE of about 4.44%. It also appears that the undercooling ability of the titanium decreases after exceeding a

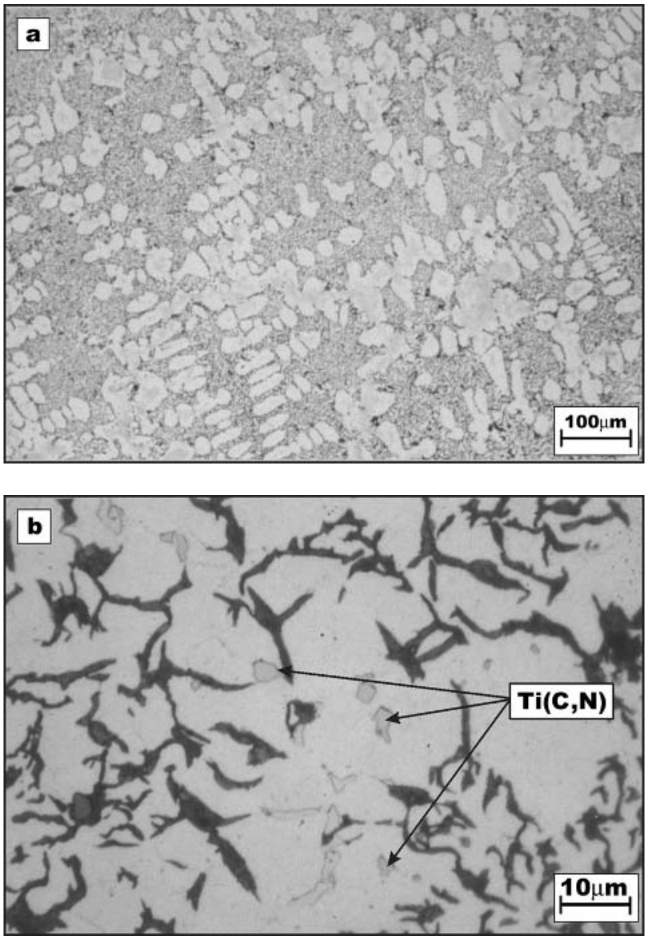

Fig. 2 **(a)** Microstructure of permanent mold cast gray iron casting containing 0.12% Ti (100X); **(b)** titanium containing particles observed in this casting in ferrite and near ferrite/graphite region (1000×), nital etched

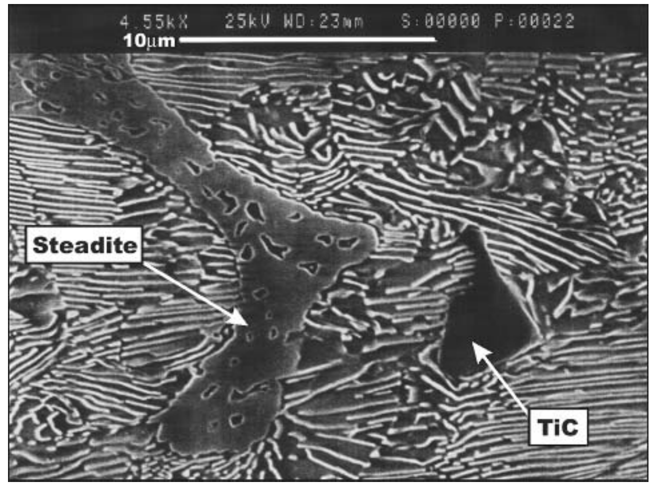

Fig. 3 SEM micrograph of iron containing 0.07% Ti taken from cupola showing TiC (right) and steadite (left) in pearlite. Nital etched, 4550×

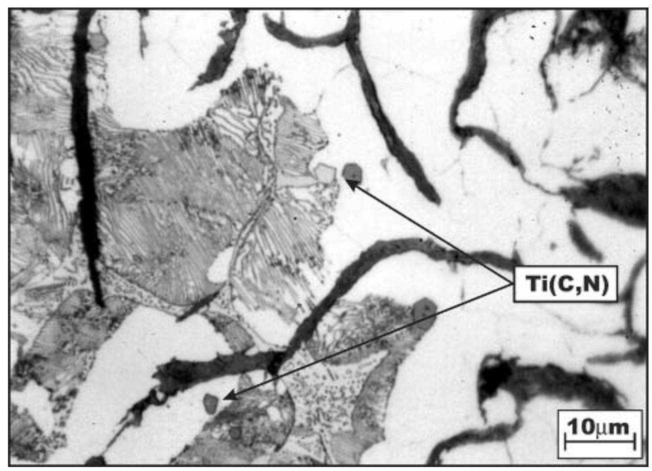

Fig. 4 Microstructure of iron containing 0.068% Ti showing Ti-bearing compounds associated with pearlite and ferrite. Sample was taken from the holding furnace. Nital etched, 1000×

certain level. Increasing titanium from 0.09-0.12% slightly increases undercooling in iron with a lower CE (4.44%) and has little effect on iron with a greater CE (4.58%).

SEM evaluation of gray iron samples taken at various steps of the casting process has been done to identify titanium-containing compounds. In the microstructure of iron taken from the cupola containing 0.07% Ti, titanium carbides were found in pearlite, often appearing in conjunction with the lighter steadite particles (Fig. 3). Titanium nitride particles that appeared in the ferrite areas also contained some complex particles that consisted of an Al/Mg/O core, which was surrounded by titanium nitride. It appeared that this core precipitated the TiN particles.

In the microstructure of iron taken from the holding furnace containing 0.068% Ti, titanium-containing particles have been found associated with pearlite and ferrite as shown in Fig. 4. Titanium carbides were also found in pearlitic regions. More angular-shaped particles containing titanium, carbon, and nitrogen were seen at or near pearlite/ferrite interfaces. In the microstructure of castings containing 0.068% Ti, titanium carbides along with MnS were found in pearlite areas such as shown in Fig. 5. In ferrite or ferrite/graphite areas, the particles were mainly TiN. As in the other samples, the TiN particles were more angular than the TiC particles.

In castings with 0.090% Ti, all of the titanium containing particles were TiN and Ti (CN), and they were found in ferrite or ferrite/graphite areas (Fig. 6 and 7). In castings with 0.12% Ti, TiC particles were observed at ferrite/pearlite interfaces, titanium carbonitride particles were seen in the ferrite and near the graphite (Fig. 2b and 8).

The results of this study suggest that titanium in a rapidly cooled hypereutectic gray iron produces different titanium-containing compounds depending on its content. Titanium carbide particles were found preferentially in pearlitic areas; titanium nitrides and carbonitrides were located in ferritic areas. Increasing the titanium content resulted in the formation of larger quantities of extremely hard titanium carbides and/or titanium carbonitrides that usually appeared in conjunction with steadite in a relatively high phosphorous content PM iron.

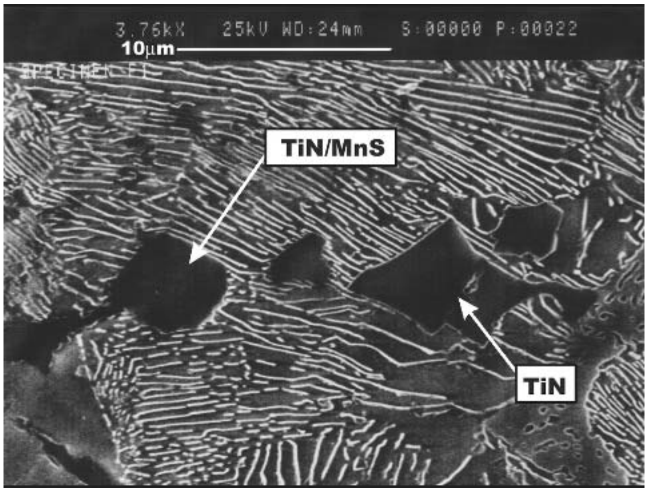

Fig. 5 SEM micrograph of permanent mold cast gray iron containing 0.068% Ti showing Ti N/MnS (left) and TiN (right) in pearlite. Nital etched, 3760×

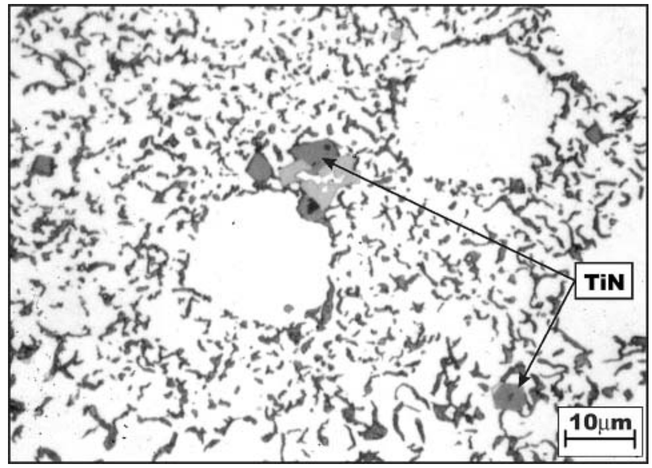

Fig. 7 Microstructure of permanent mold cast gray iron containing 0.09% Ti showing TiN in ferrite/graphite interface. Nital etched, 1000×

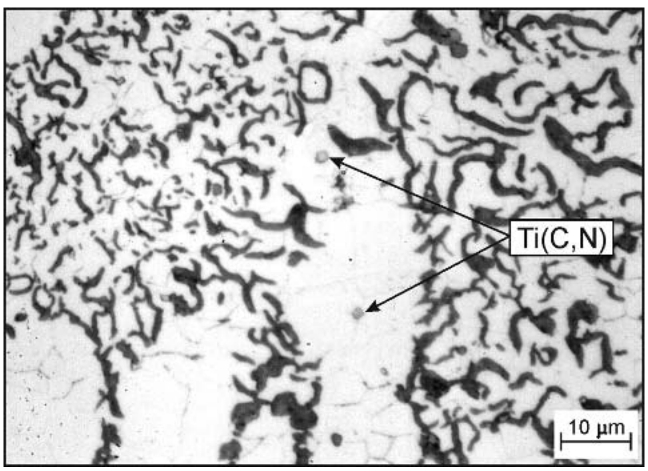

Fig. 6 Microstructure of permanent mold cast gray iron containing 0.090% Ti showing Ti (CN) in ferrite. Nital etched, 1000×

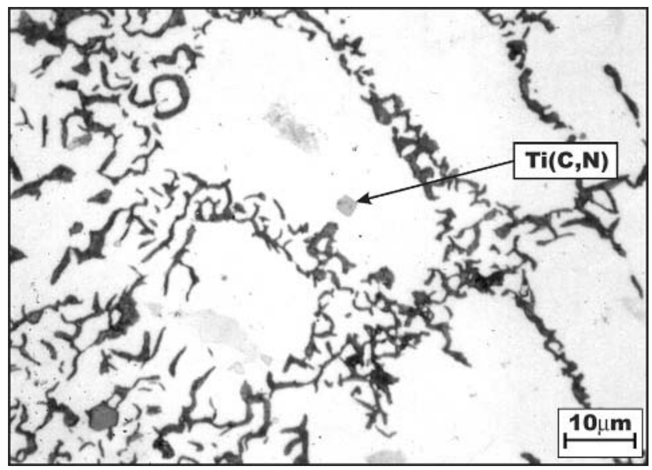

Fig. 8 Microstructure of gray iron permanent mold cast iron containing 0.12% Ti showing Ti (C,N) in ferrite near graphite. Nital etched, 1000×

Some authors[16] observed titanium compounds as carbides or carbonitrides in conjunction with graphite. Other authors[10] also found titanium carbonitrides embedded in eutectic compacted graphite. In our study, some of the titanium nitrides and/or carbonitrides were found in ferrite/graphite regions, but most of the titanium compounds were located in the metallic matrix.

3.2 Gas Analysis

The results of gas analysis of samples taken at various steps of the casting process are given in Table 1. These data represent total nitrogen, which includes soluble and insoluble (combined) nitrogen. The latter is the nitrogen, which is present in the titanium-nitrogen compounds, resulting from the reaction of titanium and nitrogen. As can be seen, the nitrogen content in the base cupola iron is very low due to titanium-bearing additions to the charge mix. The nitrogen content in the base iron slightly decreased in the holding furnace, where the holding time was about 4 h, and then remained relatively constant throughout the pouring period. This coincides with a slight titanium loss occurring because titanium nitride/carbonitride compounds floated to the slag blanket and because of titanium oxidation (oxygen content is also reduced).

Authors[17] studied the influence of titanium additions to a gray iron containing 3.5%C and 2%Si on the soluble and insoluble nitrogen contents. According to this study, the soluble nitrogen content remarkably decreased from about 0.003% to about 0.0009% as the titanium content increased from nil to 0.10%, and remained nearly unchanged when more titanium was added. Accordingly, the insoluble nitrogen increased due to the formation of Ti (CN) compounds. Comparison of these data with our results of microstructure and SEM study confirmed that in low soluble nitrogen base iron, as titanium content increases from about 0.09-0.12%, the excess of titanium produces mostly titanium (CN) compounds.

Table 1 Nitrogen and Oxygen Content in Hypereutectic Gray Irons Taken at Various Steps of the Casting Process and From Castings With Varied Titanium Content (a)

No.	Sample	Titanium Content, %	Nitrogen, %	Oxygen, %
1	Cupola iron	0.070	0.0036	0.0055
2	Holding furnace iron	0.068	0.0032	0.0051
3	Permanent mold iron	0.068	0.0032	0.0050
4	Permanent mold iron	0.090	0.0030	0.0051
5	Permanent mold iron	0.120	0.0033	0.0052

(a) Average of 6 tests

3.3 Tensile Strength Testing

Figure 9 illustrates the tensile strength of annealed test bars A as a function of titanium content in base irons with 4.44 and 4.50% CE; each point represents 25-30 tests. These data demonstrate that titanium additions increase the tensile strength at both CE levels. As can be seen, the tensile strength increases fairly rapidly from 0.05-0.075% Ti in the 4.50% CE iron and up to about 0.085% Ti in the 4.44% CE iron, then relatively slowly at higher titanium levels in both irons.

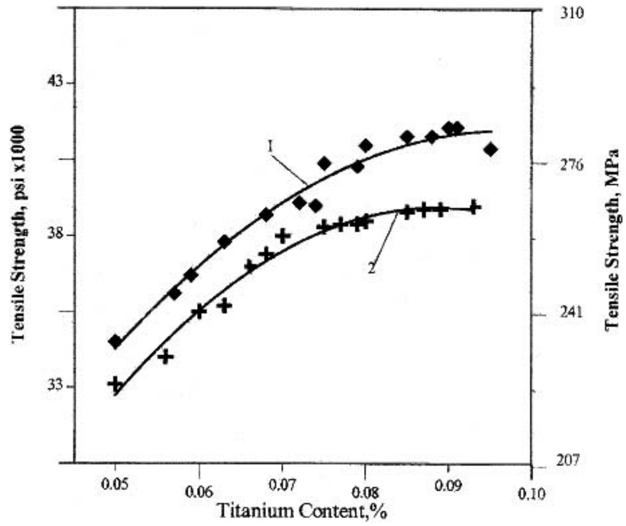

Fig. 9 Tensile strength of 22.4 mm (0.88″) diameter annealed gray iron test bars cast in air-cooled permanent molds: 1-4.44% CE; 2-4.5% CE

3.4 Machinability

The presence of extremely hard titanium compounds substantially reduced machinability and decreased tool life in all machining operations of PM castings, even in grinding. For instance, raising the titanium content from 0.065-0.087% halved feed at a given speed in grinding finish stock of 0.06 in. from each side of normalized 0.5 in. thick plates using aluminum oxide-silicon carbide grinding wheels. Thermal cracks have been experienced during turning of 16 in. diameter sheaves made of PM gray iron containing 0.096% Ti. It was found that these cracks resulted from excessive heat developed at the thin rim area.

In PM gray iron containing a relatively high phosphorous content (0.2-0.3%), titanium carbides often appear in conjunction with steadite. This combination amplifies the adverse effect of titanium on machinability.

Note that the data presented reflect the given melting process parameters and may vary when using another charge material, particularly pig irons with different heredity, or changes of degree of superheating and holding time. Other factors affecting the degree of undercooling are PM process parameters such as mold temperature, soot coating thickness, and iron pouring temperature. The combination of the above-mentioned factors affects primary solidification conditions and austenite/graphite morphology, and controls final mechanical properties of PM mold castings.

4. Conclusions

1) Titanium is a relatively potent element in controlling the solidification structure of PM gray iron castings, increasing undercooling, and thus promoting Type D graphite. The undercooling effect of titanium decreases above a certain level and also depends on the base iron CE with more pronounced changes in iron with lower CE.
2) Changes in structure produced by titanium additions resulted in significant variations in tensile strength, improving tensile strength, but the effect depended on base iron CE. In 4.44% CE iron, tensile strength was maximized at about 0.075% titanium, while the maximum tensile strength in 4.5% CE iron occurred at about 0.085% titanium.
3) Titanium produces different compounds in rapidly cooled hypereutectic gray iron: titanium carbides, which are located in pearlitic areas, and titanium nitrides and carbonitrides, which are in ferritic areas. Some of the titanium nitrides and/or carbonitrides were found in ferrite/graphite regions, but most of the titanium compounds were located in the metallic matrix.
4) In a low soluble nitrogen level base iron, increasing the titanium content up to 0.12% provides no added benefit in producing Type D graphite and increasing tensile strength. The excess of titanium produced large amounts of extremely hard titanium-containing compounds in the metallic matrix that are detrimental to machinability. To obtain the optimal combination of required microstructure/tensile strength with good machinability, the titanium content in PM cast gray iron should not exceed 0.075%.

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