Edited by

Li Yanxiang, Shen Houfa Xu Qingyan, Han Zhiqiang

# Science and Processing of Cast Iron VIII



# **Science and Processing of Cast Iron VIII**

----Proceedings of the Eighth International Symposium on Science and Processing of Cast Iron

Beijing, China

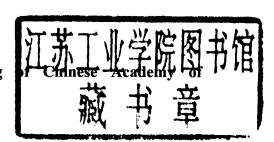
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#### Introduction

The International Symposium on Science and Processing of Cast Iron (SPCI), previously known as the Physical Metallurgy of Cast Iron, is one of the most famous conferences in cast iron. This proceeding includes 76 scientific papers presented in oral and poster in SPCI which was held in Beijing, China in 2006. These papers indicate the progress in the fundamental research on solidification and solid state transformation of cast iron, the computational modeling of cast iron transformation and processing, the methods of melting, casting, heat treatment and process control and the applications of cast iron.

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#### **Preface**

Cast irons are still the important engineering materials in modern human civilization and they are essential alloys for the future, because of their particular mechanical properties, high temperature resistance, etc.

This volume is a selection of the Eighth International Symposium on Science and Processing of Cast Iron (SPCI8), which will be held at Tsinghua University in Beijing of China from October 16 to 19, 2006. This international symposium belongs to the series of ever named Symposium on Physical Metallurgy of Cast Iron. The previous seven symposiums were held in Barcelona of Spain in 2002, Birmingham of USA in 1998, Nancy of France in 1994, Tokyo of Japan in 1989, Stockholm of Sweden in 1984, Geneva of Switzerland in 1974, and Detroit of USA in 1964, respectively.

In the recent decade, the iron casting industry has faced great challenges: the need to introduce and improve environmental protection ..., the need to attract and develop technology ... (cited from Carl R. Loper, Jr. in the 65<sup>th</sup> World Foundry Congress). Therefore, a deep investigation of physical metallurgy and a broad communication in science and processing will be significant for the cast iron industry. The main subjects of the SPCI8 emphasize the fundamental research on solidification and solid state transformation of cast iron, the computational modeling of cast iron transformation and processing, the innovation technologies of melting, casting, heat treatment and process control and the applications of cast iron as well. Seventy six scientific papers from 18 countries are selected in the proceedings.

Thanks are due to the authors in the proceedings and the delegates in the symposium. Thanks are also due to the International Scientific Committee, the Local Organizing Committee and the Secretariat of the Eighth International Symposium on Science and Processing of Cast Iron.

Special thanks are also given to National Natural Science Foundation of China, Beijing Mechanical Engineering Society, Division of Mechanical and Vehicle Engineering of Chinese Academy of Engineering, China Foundry Association, and Foundry Institute of Chinese Mechanical Engineering Society.

Liu, Baicheng

Professor and Chairman of the Organizing Committee of SPCI8

# **Contents**

### Keynote

C. R. Loper, Jr. 3 State of the Art of Processing Technology of Ductile Iron Casting 15 Factors Influencing Solidification Structure and Mechanical Properties T. Yashida, K. Yamamoto, of P-B Cast Iron for Marine Engine Cylinder Liner S. Higashi and K. Ogi Y. C. Zeng, K. R. L i 23 Development and Application of Austempered Ductile Iron in China and Z. C. Zhang State of the Art in Solidification Modeling of Cast Iron D. M. Stefanescu *32* 

#### P

Part	Part I: Fundamental Research on Solidification and Solid State Transformation of Cast Iron						
45	Searching for a Unified Explanation of the Solidification of Cast Irons	G. L. Rivera, R. E. Boeri					
		and J. A. Sikora					
51	Partition Coefficient of Si and Mn in Multi-component	H. Rivera-Garza,					
	Fe-C-Si based Alloys	M. Castro-Román,					
		M. Herrera-Trejo					
		and J. López-Cuevas					
56	Chilling Tendency and Chill of Cast Iron	E. Fras, M. Górny,					
		W. Kapturkiewicz and H. Lopez					
62	Eutectic Cell and Nodule Count in Cast Irons	E. Fras, M. Górny,					
		W. Kapturkiewicz and H. Lopez					
68	Nucleation of Pearlite in Grey Cast Iron	A.A. Nofal and M.M. Mourad					
74	Inoculation of Primary Austenite in Grey Cast Iron	A. Diószegi, K. Z. Liu					
		and I. L. Svensson					
80	Effects of Carbon Content and Solidification Rate on the Thermal	D. Holmgren, A. Diószegi					
	Conductivity of Grey Cast Iron	and I. L. Svensson					
86	Characterization of Titanium-containing Compounds in Gray Iron	D. X. Zeng, Y. H. Zhang, J. Y.					
		Liu, H. J. He and X. X. Hong					
92	The Mechanisms of Metal Expansion Penetration in Grey Cast Iron	A. Diószegi and I. Dugic					
98	Eutectic Solidification Mode of Spheroidal Graphite Cast Iron and	H. Nakae, S. Jung					
	Graphitization	and T. Kitazawa					
104	Effect of Bismuth on Refinement of Graphite Nodule in Spheroidal	H. Takeda, K. Asano					
	Graphite Cast Iron	and H. Yoneda					
110	Factors Influencing the Surface Graphite Degeneration in Ductile Iron	I. Riposan, M. Chisamera,					
	Castings in Resin Mold Technology	S. Stan and T. Skaland					
116	Shrinkage Evaluation in Ductile Iron as Influenced by Mold Media	M. Chisamera, I. Riposan,					
	and Inoculant Type	S. Stan, P. Toboc, T. Skaland					
		and D. White					
122	Gradient Structure and Chilling Tendency of Thin Wall Ductile Iron	E. Fras, M. Gorny and H. Lopez					
128	Influencing Factors on the As-cast and Heat Treated 400-18 Ductile	I. Riposan, M. Chisamera					
	Iron Grade Characteristics	and S. Stan					

134	Study on As-cast Austenite-Bainite Ductile Cast Iron	Z. L. Ning, S. Z. Ren, J. F. Sun
		and Y. Q. Feng
139	Austempered Ductile Iron with Duplex Matrix	M. J. Pérez L, M. M. Cisneros,
		H. F. López, S. Rodríguez and
		D. Vázquez
145	Crack Initiation in Austempered Ductile Iron Strained in Contact with	R. A. Martínez, S. N. Simison
	Different Liquids	and R. E. Boeri
151	Metallurgical Properties of Retained Austenite in ADI at Sub Zero	M. Tadayonsaidi,
	Temperatures	M. Hanumantha Rao, G. V. S.
		Nageswara Rao, N. Varahram,
		N. Baghersaee and Z. Moniri
157	Structure of Thin Wall Austempered Ductile Iron (TWADI)	E. Fras and M. Górny
163	Effect of Ferritic Grains Mixing in Matrix on Water Embrittlement	Y. Osafune
	Resistance of ADI	
169	Relationship Between Image Analysis Graphite Shape Factors,	C.A. Silva Ribeiro, C. Sá, L. F.
	Mechanical Properties and Thermal Analysis Solidification Behaviour	Malheiros, W. Baumgart, E.
	of Compact Cast Irons	Wüller, M. Donhauser
	•	and C. Henke
175	Effect of Si and Mg Contents on Microstructure and Mechanical	A. Motallebzadeh
	Properties of Compacted Graphite Iron	and A. Halvaee
181	The Microstructure and Metamorphic Regularity of Graphite in Cast Iron	K. M. Fang, G. C. Wang, X. J.
		Wang, L. Huang and G. F. Deng
188	Effects of the Fluctuation and Modification on the As-cast	X. H. Zhi, J. D. Xing, X. J. Wu
	Microstructure of the 20Cr% Hypereutectic White Cast Iron	and Y. M. Gao
194	The Use of Electron Microscopy for the Microstructural	J. T. H. Pearce, T. Chairuangsri,
	Characterisation of High Chromium Cast Irons	A. Wiengmoon, N. Poolthong
		and H. Nomura
200	Investigation of Improving the Toughness and Wear Resistance of	Z. F. Huang, J. D. Xing,
	Hypereutectic High Chromium White Cast Iron	A. F. Zhang and Y. M. Gao
206	Interfacial Characteristics and Wear Resistance of WC Particles	G. S. Zhang, Y. M. Gao
	Reinforced White Cast Iron Composites	and J. D. Xing
211	Study of Corrosion Resistance of Boron White Cast Iron in Zinc	J. H. Liu, G. L. Li, X. Y. Hao,
	Liquid	X. B. Zhao and X. Y. Xu
216	Mechanics of Chip Formation during the Machining of Compacted	R. C. Voigt, P. H. Cohen
	Graphite (CG) Cast Irons	and R. Mehendiratta
	•	

# Part II: Computational Modeling of Cast Iron Transformation and Processing

229	Parameters Influencing the Temperature Distribution in Cast Iron	D. Holmgren, A. Diószegi
	Cylinder Heads Operating at Elevated Temperatures	and I. L. Svensson
235	Optimization of Casting Conditions for Heat and Abrasion Resistant	S. M. Yoo, Y. S. Cho, C. C. Lee,
	Large Gray Iron Castings	J. H. Kim, C. H. Kim
		and J. K. Choi
240	Simulation of Feeding Flow and Prediction of Macro Porosity of SGI	H. D. Zhao and B. C. Liu
	Casting Based on Microstructure Formation	

- 247 Numerical and Experimental Study on Thermal Stress of Gray Iron Casting
- 255 Modelling the Effect of Graphite Morphology on the Deformation Behaviour of Cast Irons
- 260 The Analysis of Thermal Stresses of Cylinder Block Casting by Coupling of Thermal and Mechanical Behaviors
- 266 Development of High Performance Casting Analysis Software by Coupled Parallel Computation
- 272 Selected Problems of Validation and Effective Prognosis Limitation of Ductile Iron Casting Quality, Using Computer Simulation Codes
- B. H. Choi, J. H. Nam, S. W. Lee, S. Y. Kwak and J. K. Choi T. Sjögren and I. L. Svensson
  - Y. Xu, J. W. Kang, T. Y. Huang and Y. Y. Hu
    - S. H. Cho and J. K. Choi
    - Z. Ignaszak, J. B. Prunier, J. Ciesiolka and B. Beszterda

#### Part III: Method of Melting, Casting, Heat Treatment and Process Control

- 281 Influence of Blast-induction Duplex Melting Process on the Melt Quality and Solidification of Gray Cast Iron
- 288 A Study on Veining, Burn on Sand and Distortion of Water Jacket Cores at the Ford Casting Plant
- 294 The New Method and Device for Monitoring the Quality of Vermicular Cast Iron in Front of Furnace
- 300 Producing High Quality Ductile Iron with Entire-steel-scrapMelting Process
- 303 Melt Quality Evaluation of Ductile Iron by Pattern Recognition of Thermal Analysis Cooling Curves
- 309 Homogenization of High Mn Heavy Section Ductile Iron Using Partial Melting Aided by Modeling
- 315 Effects of Casting Process Parameters on the Mechanical and Corrosion Behaviors of High-silicon Cast Irons
- 321 The Iron Casting's Riser Optimizing Design by Modulus Net Method
- 329 Study of the Formulas Used for Calculating the Least Cross Section of Ductile Iron Casting Gating System
- 336 Study for the Calculation Formula of Gray Cast Iron Effective Pouring Time
- 343 Study on the Preparation of Wear Resistant Surface Cast Iron by V-EPC
- 348 Semi-solid Processing of Cast Iron Under Low Convection Conditions
- 354 Effect of Slope Plate Variable and Reheating on the Semi-Solid Structure of Ductile Cast Iron
- 359 Influence of Semi-Solid Processing on Wear and Damping Properties of Gray Cast Iron
- 365 Investigation for Eliminating Austempering Heat Treatment Cycles in Ductile Iron through Structural Variations

X. J Sun and Y. X. Li

- S. Ighaniyan, W. Hall, J. Long and P. Hodgson
- D. Y. Li, D. Q. Shi, L. H. Wang and Y. T. Zhang
- T. G. Fu, G. Q. Huang, Z. L. Huang, P. X. Lan and H. C. Chen
- Z. H. Li, Y. X. Li and R. Zhou
  - S. Feghahati
- and M. Nili-Ahmadabadi
- B. H. Kim, J. S. Shin, S. M. Lee and B. M. Moon
  - R. Li, H. W. Liu, J. X. Ma, Y. C. Ju and J. L. Liu
- W. C. Liu, H. Wen, X. P. Peng
- and H. M. Zhou
- W. C. Liu, X. P. Peng, Z. F. Li and H. M. Zhou
  - H. X. Gao, J. X. Liu, Q. Y.
  - Shang, J. Ding and L. P. Mi
    - S. S. Kanta, D. B. Kumar
      - and G. Sukomal
- M. Nili-Ahmadabadi, F.
- Pahlevani and P. Babaghorbani
  - M. Ramadan, M. Takita and H. Nomura
    - M. Tadayonsaidi,
    - w. Taaayonsatat,
  - M. Hanumantha Rao, G. V. S. Nageswara Rao, N. Varahram
    - and N. Baghersaee

371 The Effect of Sub-Zero Cooling on Microstructure and Mechanical S. Yazdani and M. Ardestani Properties of a Low Alloyed Austempered Ductile Iron Effect of Tempering on Properties of High-Cr Cast White Iron D. Li, Y. L. Su and X. K. Zhang 376 The Precise Control of Heat Treatment in High Chromium White Cast Iron Y. L. Su, D. Li and X. K. Zhang 381 Nonconventional Nitriding of Austempered Ductile Iron D. Myszka 387 J. J. Hao, Y. J. Ma Study on Bond Ability of Arc-Spraying Coatings with Different 393 and Y. Z. Shen Surface Pretreatment on Cast-Iron A. A. Nofa, H. N. El-din 397 Thermomechanical Treatment of Austempered Ductile Iron and M. M. Ibrahim D. L. Wang, T. Jin, S. Q. Yang, 403 Surface Recrystallization of DZ4 Alloy J. B. Li, Z. Wei and Z. Q. Hu A. Basso, R. Martínez 408 Development of Dual Phase ADI and J. Sikora

#### Part IV: Applications of Cast Iron

417 The Studying of Riserless Foundry Technology for Large Cylinder R. Li, Y. C. Liner of Marine Engine	Ju, H. W. Liu and J. L. Liu
424 Study About the Optimisation of Chemical Composition of Cast Irons  A. Crisan, S.	I. I. Munteanu,
	and I. Riposan
430 Using SPC to Remedy Some Surface Defects of Gray Iron Cylinder B. F. L. Blocks and Heads	Li and J. J. Wu
434 Development and Industrial Application of a Novel Coated X. W. Gao, Q.	. G. Xue, Z. D.
Mg-cored Wire Zhao, Q.	Li, J. S. Wang
an	nd H. L. Zhang
440 Research and Application of Wear-resistance Bainite Ductile Iron Y. Xu, J. Y. I	Liu, J. M. Jian,
Y. K. Huang o	and S. K. Zhou
446 The Implementation of the Taguchi Method to Improve Foundry S. Ighan	niyan, W. Hall,
Scraps in Hot Box Core Production Process at Ford Casting Plant  J. Long at	nd P. Hodgson
452 Environmental Embrittlement of Ductile Iron M. Gagné and k	K. L. Hayrynen
458 An Overview of the Development of Austempered	I. Mehrara, M.
Cast Irons for Railway Brake Shoe  Nili-Ahmada	badi and H. R.
	Ghasemi
464 Experimental Study of Machinable ADI Z. K. Zhao, Q. Z.	Sun, H. L. Ma
	and J. X. Zhu
468 Unique Microstructure and Excellent Mechanical Properties of ADI	J. C. Liu
474 Developments in the Technology and Engineering Application of	J. R. Keough
Austempered Ductile Iron (ADI) and I	K. L. Hayrynen

#### **Authors Index**

# Keynote



## State of the Art of Processing Technology of Ductile Iron Casting

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#### **ABSTRACT**

The development of the technology required to produce commercial ductile iron castings from the inception of its discovery to the present date will be reviewed and analyzed. This presentation will include a review of the events leading resulting in the announcement of ductile iron, as well as a discussion of the inter-relationship of the multiple processing variables involved to the metallurgical and mechanical property requirements of these alloys as specified and as commercially produced. Advancements developed through engineering research as well as through commercial practice will be considered both in the light of their development as well as their impact on today's state of the art.

**Keywords:** BCIRA, charge material, discovery, INCO, melting and melt handling, Millis, Morrogh, nodularity and nodule count

#### INTRODUCTION

Since we first heard of the development of a technique to reproducibly convert the shape of the graphite phase in cast irons to one which is spheroidal, that new cast iron alloy (known as spheroidal graphite cast iron, nodular iron or ductile iron) has seen significant growth and will soon be the principle member of the ferrous family of cast alloys in most countries of the world. Not only has the procedure for producing SGI resulted in the production of quality castings over a range of casting geometries and section thicknesses, the mechanical properties attainable have been greatly expanded through control of solidification and graphite morphology and of rigorous matrix structure development. This discussion will review the steps involved in the initial discovery of the procedure to manufacture SGI, and will address near future developments.

The production of ferrous alloys reaches back into ancient times and for thousands of years advances in the art and science of ferrous casting developed slowly, even though many prior achievements were lost during the course of that development. Some of those achievements came about by accident; some were the result of serious development programs. While iron was found as an extraterrestrial object, and converted into objects that were held dear or could be used in weaponry, it is generally accepted that the Hitites, in about 2000 BC, re the first peoples to discover a method to convert reddish iron ore into metallic iron. That procedure was essentially solid state, with end products produced through extensive forging techniques which were kept rigidly secret. However, with time that technology spread, the Hitite Empire faded away about 1200 BC, and ferrous metallurgy spread throughout Asia and Europe. Having been highly successful in developing the technology of producing bronze castings, the Chinese invented furnace technology capable of melting iron and producing iron casting dating to 512 BC.

Typically, iron casting was associated directly with the reduction of iron ore with charcoal or coal used to generate sufficient heat. It was only in about 1700 AD that Simon Sturtevant, a German, invented a procedure to manufacture coke that enabled iron to be re-melted to produce a more refined ferrous alloy. For the most part these cast ferrous alloys were produced with lamellar, or flake, graphite from molten irons which were satisfactory, but not well

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controlled. Thin section castings were often white cast iron, free of graphite. The result was extreme sensitivity to solidification cooling rate, or casting section size, variable microstructures and mechanical properties.

Then in about 1722 the French physicist, Rene Antoine Ferchault de Reamur, one of the foremost scientists of the 18<sup>th</sup> century, developed white heart malleable iron enabling some ferrous castings to exhibit higher strengths with appreciable toughness. Reamur found that if a thin white iron casting was heated in a suitable atmosphere the casting could be completely decarburized at the surface without scaling (surface oxides). As a result, the surface was converted to a high ductility, ferritic, low carbon content steel while the center of the casting, the "white heart", retained some as cast carbide and pearlite (which was far less ductile). White heart malleable iron was used to produce thin section castings which were tough and could withstand some bending.

Few changes in cast iron technology occurred until about 1820 when the American, Seth Boyden, unsuccessfully attempted to reproduce Reamur's procedure resulting in the discovery of conventional, or "black heart", malleable iron. Instead of controlling the heat treat furnace atmosphere to decarburize the casting, Boyden observed the development of temper carbon nodules throughout the casting, and slow cooling resulted in a soft, ferritic matrix structure. The castability, strength and toughness of Boyden's malleable iron proved to be a boon to engineering development during a critical growth period in manufacturing.

The invention of the steam engine in 1765, combined with the new fuel, coke, enabled the invention of the blast furnace by John Wilkinson of England in 1790 AD. This greatly facilitated the production of gray irons and of white irons, which were often re-melted in another furnace to reduce their carbon content. Cast irons could now be produced to a controlled microstructure, determined by the nature of the surface of a fractured casting or specimen. The ability to produce an iron with controlled mechanical properties enabled the application of these ferrous alloys to engineered structures.

The development of steel processing was largely a solid state procedure until methods to achieve higher melting temperatures were developed (e.g., the Bessemer converter, the open hearth furnace, the electric arc furnace, etc.) in the late 1800's and early 1900's when steel casting technology was developed and expanded. The development of metallurgical technology during this period of time greatly enabled the success of both malleable iron and steel casting production, but it was not until the 1940's that a major breakthrough in ferrous casting occurred – the discovery of spheroidal graphite cast iron.

This discovery took place independently in two locations – in the laboratories of the British Cast Iron Research Foundation (BCIRA) in Birmingham, England and in the laboratories of the International Nickel Company (INCO) in New Jersey, USA. While the results of these studies were somewhat similar, the motivation and scientific and engineering aims were far from being similar.

#### **DEVELOPMENTS AT BCIRA**

The BCIRA was organized to improve the reliability and quality of iron casting production, serving as a center of science and engineering technology for the cast iron industry. Early in the 1940's a young laboratory assistant who specialized in preparing and examining metallurgical specimens of cast iron, Henton Morrogh, became interested in the fact that on rare occasions certain cast iron artifacts exhibited some graphite that was more compact, sometimes spheroidal, in irons where lamellar graphite was expected. This led to studies, carried out with a BCIRA engineer, W. J. Williams, concerning graphite formation in cast irons as well as in more "sophisticated alloys" of Ni-C and Co-C recognizing that a wide variety of graphite structures might be attainable in cast irons without heat treatment.

The results of these studies was announced in a several papers such as that submitted to the Iron and Steel Institute on May 4, 1946 by Morrogh and Williams [1] where it was concluded that:

"The addition of calcium (and also probably barium and strontium) or magnesium can cause the formation of spherulitic nodular structures in nickel-carbon and cobalt-carbon alloys, provided that the sulfur content of the alloys is sufficiently low. The calcium and magnesium may be added to the alloys in a wide variety of forms in combination with other elements if necessary. These structures are produced with greater ease in nickel-carbon alloys than in cobalt-carbon alloys."

É

The authors further reported that nodules are produced "only with great difficulty in iron-carbon-silicon alloys."

Continued studies [2] demonstrated that cerium, in the form of mischmetal, added to a low sulfur content hypereutectic melt produced on solidification spheroidal graphite and that the nodule count could be increased by the addition of a graphitizing inoculant after the cerium addition. Only partial success was reported for hypo-eutectic melt compositions. This material was referred to as "nodular cast iron" and was capable of developing improved strength and ductility as illustrated by the data contained in Tables I and II.

Table 1. Composition of BCIRA Heats with Ce Additions

Alloy	% C	% Si	% Mn	% S	% P	% Cu	% Ce
1	3.90	2.96	0.51	0.006	0.024		0.016
2	3.76	3.09	-	0.008	~		0.021
3	3.90	3.10	-	0.007	~		0.031
4	3.91	3.08	_	0.003	~		0.036
5	3.75	3.11	-	0.004	~		0.063
6	3.80	2.17	0.92	0.015	0.052	2.17	0.054

Table 2. Properties Developed from BCIRA Heats

Alloy	Section	Tensile	Deflection	Hardness	Impact
•	Dia., in.	Str., ksi	In	HB	Str. ft.lb.
1	1.6	54.9	0.51	179	32
	1.2	60.5	0.68	189	46
	0.875	62.9	0.39	213	76
	0.6	75.9	0.35	239	
2	1.6	58.9	0.55	187	37
	1.2	69.9	0.85	191	64
	0.875	72.1	0.52	224	111
	0.6	80.9	0.28	255	
3	1.6	73.5	0.90	193	89
	1.2	73.9	1.02	199	120
	0.875	77.3	0.66	231	120
	0.6	98.1	0.43	252	
4	1.6	73.7	0.55	194	120
	1.2	73.9	1.05	209	120
	0.875	77.3	0.64	236	120
	0.6	79.1	0.45	257	
5	1.6	69.2	0.55	204	53
	1.2	65.4	0.90	225	60
	0.875	80.0	0.50	236	58
	0.6	87.4	0.35	237	
6	1.6	89.2	0.30	260	88
	1.2	79.3	0.40	288	92
	0.875	96.5	0.30	302	94
	0.6	103.9	0.27	333	

While tensile strength was determined from transverse test bars, and yield strength and elongation were undetermined, an understanding of the nodularity and matrix structure may bed educed from these properties. A considerable variation in ferrite and pearlite content of the matrix is readily apparent, and nodularity varies considerably but is generally good, but borderline by usual standards. It would be expected that many of these castings exhibited graphite flotation, but this would not be encountered in the transverse test samples. A low nodule count was obtained in alloy 5 with the high cerium content, and a significant increase in nodule count was realized in alloy 6 which was post inoculated with ferrosilicon.

The ability to produce a cast iron with spheroidal graphite was widely acknowledged, as now components could be produced as iron castings having mechanical properties approaching those of steel.

#### **DEVELOPMENTS AT INCO**

Meanwhile, experiments at INCO developed in a significantly different manner. Back in the late 1920's or early 1930's INCO, having somewhat limited markets for nickel, realized that a potential sale outlet for the sale of nickel was possible in foundry products, particularly in gray cast irons. As a result, the INCO research laboratories directed considerable effort to examining the effects of nickel on the graphitization, carbide formation, matrix structure development and properties of gray cast irons as well as white cast irons. Research concerning the role of alloying elements in cast irons was in its earliest stages so that the effects of composition changes and control, heat treatments and alloying elements in broadening the range of properties for any cast irons was just being appreciated.

**Improvements in White Cast Irons.** One alloy developed during this period was a nickel alloyed white cast iron which INCO named Ni Hard. It was an abrasion resistant alloy with high hardness generated from a carbidic structure and a martensitic matrix resulting from alloying white cast iron with about 4.5% Ni and about 1.5% Cr. Its outstanding wear resistance led to applications such as grinding mill balls, plates, rolls, etc. and the use of Ni Hard expanded rapidly throughout the 1930's and into the 1940's.

However, in the early 1940's certain allying elements became critically short in supply and programs were entered into to seek alternative solutions to the use of many alloys [3-5] (the oncoming World War II hampered the importation of many critical materials, including Cr which was primarily obtained in Africa). Since it was essential that Cr be used to achieve a carbidic solidification structure, and to aid matrix hardenability, an effective substitute for Cr had to be located, and that the new element be plentiful and available and used in only relatively small amounts. Keith A. Delonge, an INCO development engineer, wrote a memo on January 9, 1942 to the laboratory outlining this concern and requested that the laboratory seek a substitute for Cr. The head of the laboratory. N. B. Pilling, accepted the challenge and assigned the task to Keith D. Millis, a young engineer who joined the company year before having graduated from the Rensselaer Polytechnic Institute in New York and who had just been transferred to the ferrous metals section.

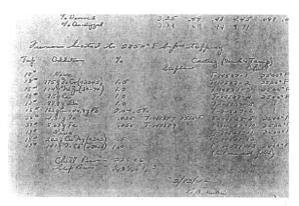


Figure 1. Page from the INCO laboratory notebook of Keith D. Millis setting up the experiment to study the effects of various carbide forming elements to substitute for chromium in a NiHard alloy.

Millis was new to the study of ferrous alloys, and to determine which elements were likely to form carbides he consulted a book on chemical com-pounds and came up with a listing of elements that would be added to molten cast iron: Cr, Zr, Ce, Bi, Cu and Pb, Te (two levels), Mg and Cb (Nb), Figure 1. Millis recalled [3], "I went over the plans with my superiors and was immediately told that I could make all the additions except magnesium, that was forbidden because it was dangerous." Some time previously the head of the laboratory had experimented with using Mg as a deoxidizer for Monel and high Ni-Fe alloys and found that in alloys in excess of 25% Fe the violence of the reaction became intolerable. Years later Pilling noted [3], "When Millis had prepared his program which involved making experimental melts of Ni-Fe containing a variety of elements which he thought might have an interest as carbide stabilizers, when I first saw the list and found on it Mg, I was first disposed to tell him to scratch it off and forget it. But perhaps a little charitable thought occurred. It seemed to me, "Well, we all have to learn, sometimes

the hard way. Let him go ahead and do it." When Pilling was asked, "Was he expendable?" he replied, "He was expendable, I was not!"

Millis had included Mg in the list of elements he wanted to try because his reference showed two carbides,  $Mg_2C_3$  and  $MgC_2$ . His review of the literature prior to this experiment was essentially nil, and he was unaware of the Meehan patent which taught that Mg would act similarly to Ca, promoting the breakdown of carbides and encouraging the formation of flake graphite. If he had known this, it is unlikely Millis would have included Mg in these tests.

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Figure 2. Results of the fracture appearance and hardness from the experiments to locate a substitute for chromium in NiHard as recorded in the INCO laboratory notebook of K. D. Millis. Extensive chill was found with the magnesium addition, which also noted toughness, "very tough to break", and surface appearance, "surface rather crappy".

On February 13, 1942 a 250 lb. melt was produced in a Detroit rocking furnace of the analysis shown in Table III. This was a normal base metal composition for Ni hard, but without Cr. The elemental additions to this base iron, Figure 2 and Table IV, were somewhat greater than would be expected based upon current under-standing of their effects. With the exception of the Te<sup>1</sup> containing heats where step bars were poured, the heats were divided into 18 lb. taps to which the additions were made prior to casting into 2x2x6 in. chill bars, chilled against the 2x6 in. face.

Table 3. Composition of INCO White Iron Base

	% C	% Si	% Mn	% S	% P	% Ni
Target	3.35	0.49	0.48	0.098	0.097	4.45
Actual	3.24	0.49	0.44	-	-	4.71

Table 4. Additions Made to INCO White Base Iron

Cr - Chromium	1.5%
Zr - Zirconium	1.0%
Ce – Cerium	1.0%
Cu - Copper +	2.0%
Pb - Lead	0.5%
Te - Tellurium	0.025%
Te - Tellurium	0.050%
Mg - Magnesium	0.5%
Nb - Niobium	1.0%

<sup>&</sup>lt;sup>1</sup> The taps to which Te was added were 38 lb., cast into the chill block as well as into a step block containing 0.25, 0.5, 1.0 and 2.0 in. sections.