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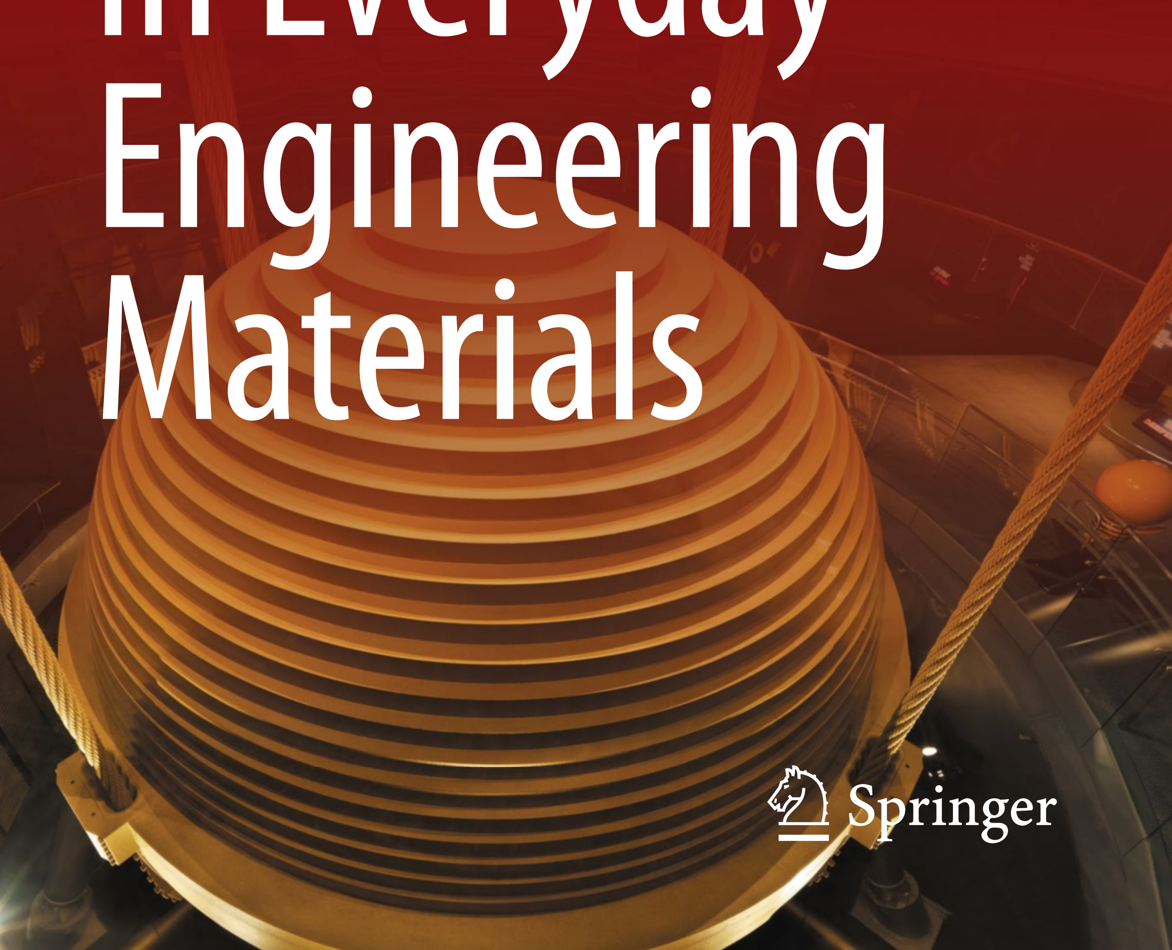
Innovations in Everyday Engineering Materials



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Preface

Many successful materials and processes are so good that people do not need to know of the tremendous ingenuity in their creation and application. Innovations made in artificial materials have been important in improving the quality of life. Many of the innovations originated from organised research although serendipity in creative settings has contributed to advancements.

Our intention with this book is to introduce a few of the key innovations without which our quality of life would be dramatically different. But in addition, we selected a couple of cases where we felt that it is realistic to expect quite significant developments. One such case is low-density steels and the other, high-entropy alloys.

More than anything else, we tried hard to keep this book small. Our goal was to create a book that was not too onerous to read, accessible to a wide audience and illustrate the vitality of the field of engineered materials. The book can, we think, be read in a leisurely fashion within a couple of days and yet can provide a degree of learning.

We hope that the book brings some balance to the trend where research is publicised before it has delivered. The greatest achievements illustrated in the examples come from scientists and engineers who take pleasure in creating materials that make a difference, no matter how long it takes or how many barriers have to be surmounted.

We gratefully acknowledge the support of Professors Kwadwo Osseo-Asare, Thomas W. Eagar, Ronald M. Latanision, Chobi DebRoy and David G. C. Robertson for their knowledge, patience and many valuable comments. Drs John Elmer, Jared Blecher, James Zuback and Tuhin Mukherjee made valued comments.

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Chapter 1
A Remarkable Innovation in Stainless Steel Making

1.1 Engineered Materials

An engineered material is one that is not found occurring naturally anywhere on earth. The adjective also implies that the material has some use. Imagine a material that is strong and tough, has great looks, costs about the same as a cup of coffee on a weight comparison, which relies on an atomic surface that fends away the environment. This is steel that will not stain.

The lure of their attractive appearance, their excellent properties and right price have all contributed to their many uses in large iconic structures (Fig. 1.1), buildings, bridges, automobiles, sophisticated kitchen appliances, ordinary kitchen utensils and medical devices. The latest *Tesla* truck has a stainless steel body, rather like the *DeLorean* that featured in the movie "Back to the future". All of these rely on a thin layer of chromium oxide that forms spontaneously on the surface. It is coherent, adherent and regenerates when scratched. The film protects the underlying steel from corrosion, hence the designation "stainless". It was in 1913 that Harry Brearley invented the steel in Sheffield, UK. However, the story here is about a young engineer Krivsky [1], fresh from college, pursuing fundamental research in a large corporate laboratory in a town that most people visit for a different purpose—Niagara Falls. What started as an unusual research result did not end up in the usual equations, charts and research papers. After a long saga filled with many formidable difficulties and uncertainties, the payback was a new process so technologically advanced and profitable that it disrupted the contemporary method of manufacturing stainless steel which quickly became obsolete throughout the world [1].

Like most major inventions looked at with hindsight, the process modification is in essence simple. Oxygen must be blown through the molten metal to reduce and control the concentration of carbon, but chromium has a strong affinity for oxygen and is an expensive element to lose as an oxide. Instead, Krivsky used a mixture of argon and oxygen, distributed uniformly inside the melt, thereby dramatically limiting the loss of chromium.

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Fig. 1.1 (**a**) Cloud Gate, nicknamed the *bean*, designed by Sir Anish Kapoor, built using 168 stainless steel plates joined together. The concept was inspired by liquid mercury. (**b**) An aesthetically pleasing stainless steel street lamp in Busan, South Korea. (**c**) Double-walled cups and saucers made of stainless steel. (**d**) An island restaurant made using stainless steel, in the River Mur in Graz, Austria

1.2 Unexpected Results

A metallurgist by training, Krivsky, had just joined the Metals Research Laboratories of the Union Carbide Corporation in Niagara Falls, New York after his doctoral work. His first job was to examine the high temperature metallurgical reactions between oxygen and hot molten alloys containing iron, chromium and carbon from which stainless steels are made. Professor Richardson in England and Drs Hilty and Crafts in the USA were all established researchers in this field, but their thermodynamic data on the iron–chromium–carbon system were somewhat different. Dr Krivsky was trying to resolve these discrepancies. We shall see that working with hot liquid steels has its challenges in a laboratory, but even more so when scaling to industrial production.

Results of Krivsky's initial studies on blowing oxygen through the melt were complicated by the heat of reaction when carbon and chromium combined with oxygen and this must have dogged the earlier experiments; to have confidence in the scientific data, it is necessary to control the temperature. Krivsky decided to use oxygen diluted with an inert gas, argon, in order to slow down the rate of oxidation and hence to better control the temperature. This appeared to be a rock solid strategy, because argon, as an inert gas should not interfere with any reaction and only slow down the exothermic reactions by limiting the concentration of oxygen in the gas phase. He was examining how much carbon and chromium got oxidised. As expected, the carbon continued to combine with the oxygen, thereby decarburising the melt.

But, for some strange reason, the use of a mixed gas essentially stopped the oxidation of chromium. This should not have happened, because argon is inert. And Krivsky's results were not a fluke, they proved to be reproducible. But unexpected results are not uncommon in research, which by definition ventures into the unknown. It takes vision to realise their significance, beyond the ordinary method of scientific publishing. There also is some serendipity involved. Something in Krivsky's experiments attracted an intense interest from the highest echelons of Union Carbide. This is because the results were not ordinary. The loss of expensive chromium due to oxidation was a well-known cost in the manufacture of stainless steel. Krivsky's experiments eliminated chromium oxidation although that was not the original intent of his experiments. If these results could be reproduced on a larger scale, there was a potential to reshape the stainless steelmaking industry. The original mission of resolving the conflicting published data in metallurgical thermodynamics remained temporarily unresolved, replaced by an opportunity so much bigger in scope and impact.

1.3 Hope for a Big Change

The making of steel includes a process in which the carbon concentration of the liquid is controlled to the desired level by reaction with gaseous oxygen. When the melt contains chromium which is essential to render the steel stainless, it too will tend to oxidise. Traditionally, this was grudgingly accepted with the chromium concentration later adjusted to the required level by adding an alloy of iron that is rich in chromium (low-carbon ferrochrome); the entire process was implemented in the electric arc furnace responsible for melting the components in the first place. The special ferrochrome with its low-carbon concentration is about twice as expensive per kg of chromium as the commonly available, inexpensive variety which has too much carbon to be tolerated in stainless steel manufacture. If only a way could be found to use the high carbon variety of ferrochrome, the cost savings would be very significant! One hundred tons of stainless steel typically contains about 18 tons of chromium. The order of magnitude of cost savings for a 100 ton heat of stainless steel by switching from the low to the high carbon varieties of ferrochrome would be about $18,000 in the cost of chromium alone. Apart from the lower material cost, the productivity of the electric arc furnace could be enhanced if the oxygen treatment could be carried out in a separate vessel, the converter. But all these benefits were out of reach in the traditional electric furnace stainless steel making with low-carbon ferrochrome as the source of chromium. There was no known method of using low cost, high carbon variety of ferrochrome as the chromium source, because the added carbon had to be removed by oxidation and that meant that the chromium would also get oxidised. Krivsky's experiments indicated a solution although the underlying scientific principle remained a mystery. What had happened was unexpected, if reproducible on a large scale, the idea would be a no-brainer for all involved in the production of stainless steel.

1.4 From Experiment to Practice

Union Carbide was not a stainless steel producer, but there were powerful incentives to exploit Krivsky's experiments. First, there was the possibility of huge cost savings from the use of the cheaper high carbon variety of ferrochrome and achieving significantly higher productivity in a converter process that is inherently more rapid. Second, there was a growing demand for the particularly low-carbon variety of stainless steels because during welding, the carbon can cause local depletions in the chromium concentration by forming compounds. The depletion destroys the stainless character, leading to a pernicious decay in the properties. It was expensive to produce these low-carbon varieties using the conventional process because the greater temperatures necessarily degrade the refractories that line the furnaces.

One factor in favour of Krivsky's idea was the ready availability of argon, because Industrial oxygen is distilled from liquified air that contains argon, which has a different boiling temperature and therefore can be extracted in the same process. The anticipation of a breakthrough was stimulating efforts in increasing the size of experiments. There were encouraging results when tests with 45 kg steel were scaled up in a 1000 kg electric furnace, albeit with procedural difficulties such as splashing of the molten-metal bath and refractory erosion, but the results confirmed the previous work so even larger scale tests were planned with some optimism [1]. The furnaces capable of handling 3000–5000 kg, were available at the Haynes Stellite Company, a separate division of Union Carbide. The results disappointed. Argon was found to be ineffective when blown above the surface of the melt as was previously done in a 1000 kg melt. A clear set-back given the scale of the experiments, but deep down, these results could not be a final verdict of failure. It was time for a fundamental change in the process design. In fact, encouraging results were obtained when argon was injected within the bath. Full commercial trials needed even larger furnaces not available at Union Carbide so an agreement for collaboration was reached with Joslyn Stainless Steel Company, which was much smaller than Union Carbide but courageous nevertheless. The tests demonstrated that when the furnace diameter was large, the selective oxidation of carbon did not work very well and it was necessary to inject the gas mixture deep into the liquid melt [1]. It took about 7 years before the first successful full scale heat in a 15,000 kg furnace was completed in a design that allowed both oxygen and argon to be injected within the melt. Krivsky's initial experiments started in 1954 and the first successful production melt was completed in 1967. The process is now known as the argon–oxygen decarburisation process or in short, the AOD process [1].

1.5 How It Works

The AOD process is illustrated in Fig. 1.2a and an operational furnace shown [2] in Fig. 1.2b. Oxygen and argon are blown into a steelmaking reactor through a gas injection port known as a tuyère placed on the side wall near the bottom of the vessel. At the high temperature of the melt, the oxygen quickly reacts with the alloying elements in front of the tuyère forming oxides of chromium and other solutes. This oxidation would mean the permanent loss of valuable alloying elements from the liquid iron melt, unless the oxides can be reduced within the furnace away from the tuyères to recover them into solution with the molten iron. The oxides are lighter than the iron melt so they tend to move upwards with the swarms of rising gas bubbles. During this journey, most of these oxides are reduced by carbon dissolved in liquid iron. For example, the chromium oxide (Cr_2O_3) can be reduced by carbon to produce chromium metal and carbon monoxide (CO) gas by a chemical reaction shown below.

$$Cr_2O_3 + 3\underline{C} = 2\underline{Cr} + 3CO \tag{1.1}$$

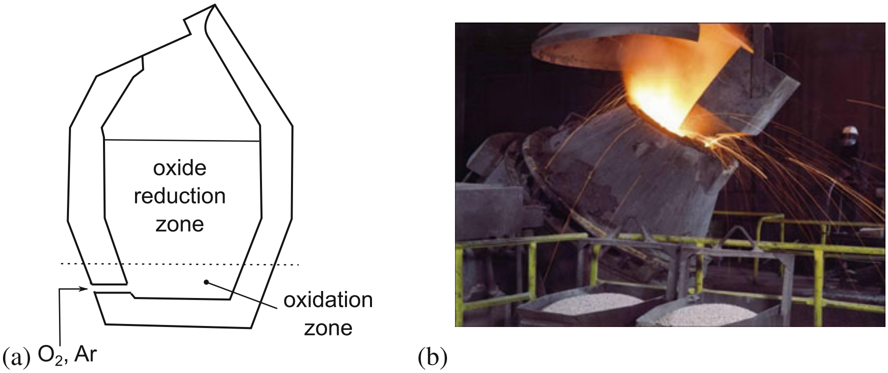

Fig. 1.2 (**a**) Schematic diagram of an AOD converter [3, 4]. (**b**) An AOD converter in action [2]