Impurities in Engineering Materials

IMPURITIES IN ENGINEERING MATERIALS

IMPACT, RELIABILITY, AND CONTROL

edited by

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Preface

Over the past 4 decades, there has been a continual decrease in the impurity content of many engineering alloys. The driving force behind this improvement came about from large-scale engineering failures that could be attributed to the presence of impurities in the material. Initially, it was thought that the use of high purity material would be too expensive to be practical. However, the demand for such materials became so great that newer and less expensive methods were found to produce them, thereby making them much more readily available.

Because of the many advances that have been made in this field, the preparation of a book that reviews this entire area seems timely and appropriate. Other books on this topic have been published in the past, and many are referred to in the following chapters. To set this particular book in the proper perspective, it is interesting to consider how the contents of previous books have evolved and how this one is distinct. Early books on this topic focused on the problems that were caused by impurities in materials. In particular, temper embrittlement of steels, which occurs when impurities segregated to the grain boundaries of steel cause them to become paths for low energy brittle fracture, received significant attention. Yet even in the 1960s, the mechanism for this embrittlement could only be considered hypothetically because there was no way to detect the presence of impurities at grain boundaries. Engineers instead relied on correlations between bulk composition and performance. The availability of Auger electron spectroscopy in the 1970s allowed this segregation to be detected, and books published then often contained papers that incorporated data obtained with this new technique to explain the cause of specific problems. In addition to temper embrittlement, it was recognized that impurity segregation played a significant role in problems such as intergranular stress corrosion cracking and intergranular creep, and these topics were also the subject of significant discussion.

In more recent years, attention has been focused on ways to make materials with very low impurity concentrations. For instance, new casting practices that achieve this goal economically have become available. Furthermore, our ability to analyze materials for impurities has improved. Thus, this book comprises detailed chapters on the need for clean materials, ways to make clean materials, ways to analyze for impurities in clean materials, and, finally, the effect of impurities on the properties of materials. It is hoped that for the engineer and the researcher alike, such extensive information in a single volume will prove to be useful.

This book can be divided into four sections. The first section includes chapters by Briant and by Nutting. The chapter by Briant (Chap. 1) reviews the problems associated with the presence of impurities in materials, and the chapter by Nutting (Chap. 2) reviews the ways in which the impurity content in materials tends to increase with time. The next set of chapters (Benz and Cramb) reviews current methods for producing clean materials. Benz's chapter (Chap. 3) primarily considers nonferrous materials, whereas Cramb's chapter (Chap. 4) focuses on making clean steel. Benz also examines the origins of many of the specifications that currently exist for impurity limits in these materials. The next two chapters, by Skelly Frame and by Grabke, address methods of analyzing for these impurities. Skelly Frame's chapter (Chap. 5) considers current chemical methods for detecting impurities in the bulk composition. As impurities continue to decrease and the demand to analyze for them has increased, new methods have been developed to determine reliably the concentrations of these elements at lower and lower levels in the material. This chapter reviews these methods. Grabke's chapter (Chap. 6) reviews the detection of impurities at grain boundaries as well as theories that can describe the segregation of impurities to these locations. Finally, in the chapters by Briant (Chap. 7), George and Kennedy (Chap. 8), and Mohri and Suzuki (Chap. 9), the effects of impurities on the properties of materials are discussed. Briant describes embrittlement at low temperatures as well as stress corrosion cracking, George and Kennedy describe the role of impurities in creep, and Mohri and Suzuki discuss the interaction between impurities and dislocations.

Clyde L. Briant

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The Need for Clean Materials

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It has been recognized for many years that the mechanical performance of materials is affected by the presence of impurities. Papers dating from the first half of this century consider this problem and suggest that uncontrolled impurities could be detrimental [1–4]. However, during the 1950s and 1960s, as outlined below, concern about the cleanliness of materials became especially great because of the demands of the power generation industry. This interest led to significant research on ways to manufacture clean materials, methods to analyze for impurities, and documentation of the harmful effects of these impurities. This book attempts to summarize this progress and present a picture of where each of these areas of research stands today. The purpose of this introductory chapter is to provide a historical background for this work so that it can be set in the proper perspective.

The term "impurity" can be broadly defined as any unwanted or uncontrolled chemical element present in a material. However, in the examples that we consider below and in the chapters that follow, this definition can be refined. In most alloys that are based on transition metals, impurities will either be those elements from groups IVA–VIA in the periodic table, such as phosphorus, sulfur, tin, and antimony, or elements that are gases in their pure state at room temperature, such as hydrogen, oxygen, or nitrogen. Members of the former group usually come into the material through the raw materials or scrap that are used to make the alloy, and those of the latter group enter the material through the atmosphere. Even in a material that is termed a "dirty" alloy, the bulk concentrations of these elements may seem relatively small; often they are less than 0.1 wt%. However, these elements can combine with the host metal or with other alloying elements in the material to form precipitates that can affect mechanical properties. More importantly, they can segregate to grain boundaries in their elemental form, and at these boundaries their local concentration can become very high. It is these impurities concentrated at the grain boundaries that can lead to intergranular fracture and intergranular corrosion, and it was originally the concern about these two problems that provided the impetus for eliminating impurities from materials.

One of the primary driving forces behind this type of work, as previously stated, came from the power generation industry. In the 1940s the power requirements in the United States and other countries were such that they could be met with the use of small turbines. The integrity of these turbines could be controlled through heat treatment and through extensive inspection programs [5,6]. However, during the 1950s and 1960s the demand for more and more power led manufacturers to design and build larger and larger turbines. These large turbines presented a number of challenges. The first was that their size meant that the mechanical stresses on the turbine were much greater than those that had existed in the past. The second problem was that the turbines were so large that they could not be rapidly quenched and thus have uniform mechanical properties throughout their thickness. The centers of the turbines inevitably cooled more slowly than the surface regions. This slow cooling also allowed time for the impurities to segregate to the grain boundaries and make regions of the material very brittle. Finally, in such a large casting it was impossible to provide uniform composition throughout the piece, and bands of varying chemical composition were observed [5].

The awareness of the embrittlement problem, which is referred to as temper embrittlement (see Chaps. 6 and 7), increased as the steels used to make the newer turbines were developed and tested. The fractures of the embrittled steels were clearly intergranular, but at that time it was not yet possible to obtain chemical analyses of the grain boundaries. Thus, the only recourse was to examine many different heats of materials in which different impurity levels were present [6–10]. The results that were obtained were similar to those shown in Figure 1. Here there is a clear correlation between the amount of embrittlement, which is measured as a change in the ductile to brittle transition temperature* and the amount of phosphorus present in the steel. Other results similar to those shown in

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*The ductile to brittle transition temperature is a measure of the degree of embrittlement. As this temperature increases, the temperature at which the steel continues to fail in a brittle manner, which is associated with a low fracture energy and therefore is undesirable, increases. Thus one can have a brittle material at temperatures well above room temperature when the steel is severely embrittled.

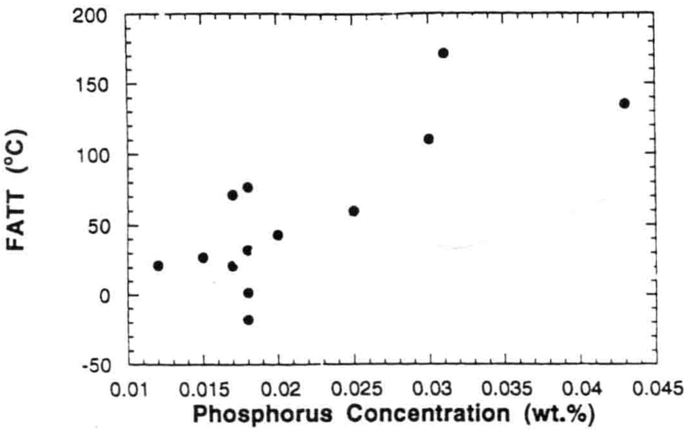

Figure 1 The change in the ductile to brittle transition temperature plotted as a function of the bulk phosphorus concentration in the steel. (From Ref. 9.)

Figure 1 provided convincing evidence that impurities did cause embrittlement, and therefore it was necessary to develop the technology to produce much cleaner materials.

One way in which the impurity level in these materials could be improved immediately was through the use of higher purity starting materials. This approach was taken, but it was primarily through the development and use of improved melting practices that real improvements were made. The early turbines were prepared with a basic electric furnace, but with the development of vacuum degassing and vacuum deoxidation, followed by electroslag refining and vacuum arc refining, the impurity level in steels decreased significantly. In addition to these general melting procedures, various ladle technologies and the change from single-slag to double-slag melting practices made significant improvement in the cleanliness of the steel [5,11,12]. Figure 2 shows the overall average decrease in phosphorus and sulfur in materials as a function of time as these various technologies were introduced. Figure 3 shows the general increase in fracture toughness that occurred as a result of changes in melting practice.

At the same time that efforts were being made to improve the cleanliness of steels, research was also being performed to improve the overall composition of steel. One of the goals of this work was to develop compositions that would provide adequate hardness throughout a thick section casting such as those required for large turbine applications. Figure 4 shows that the shift from NiMoV steels to NiCrMoV steels caused a significant improvement in the ductile to brittle transition temperature, as did other melting practices. At the same time these compositions proved to be more resistant to temper embrittlement. Figure 5 shows the change in the ductile to brittle transition temperature plotted as a function of ex-

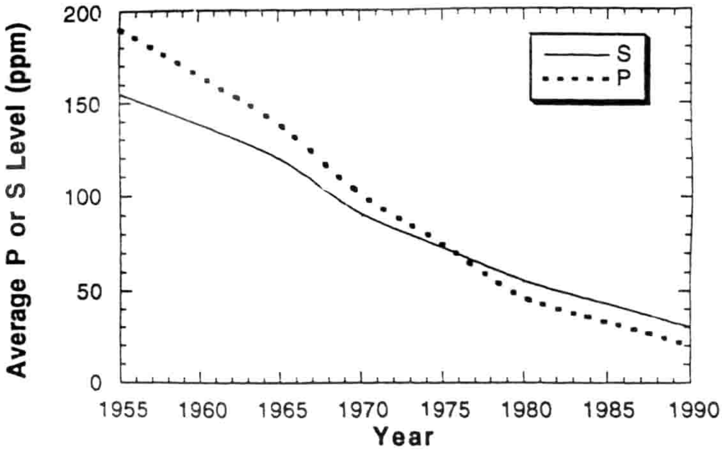

Figure 2 The average phosphorus and sulfur concentrations in heavy steel castings for the power generation industry plotted as a function of year. (From Ref. 5.)

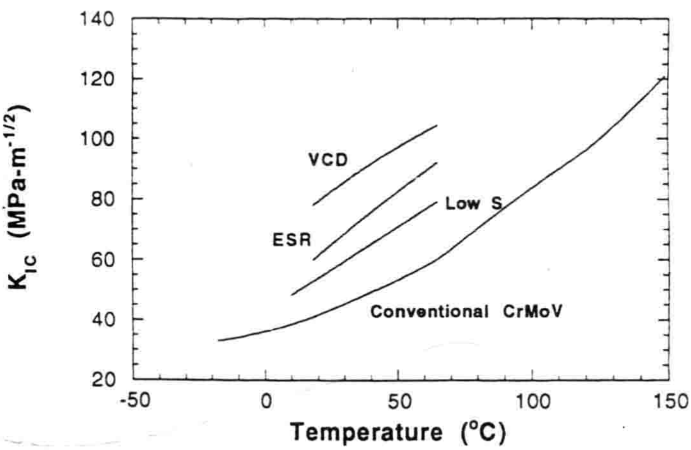

Figure 3 Variation in the critical stress intensity factor, K_{IC}, plotted as a function of testing temperature. All steels had a CrMoV base. The conventional steel had higher sulfur than the other two. VCD-vacuum carbon deoxidation melting practice; ESR-electroslag remelt melting practice. (From Ref. 6.)

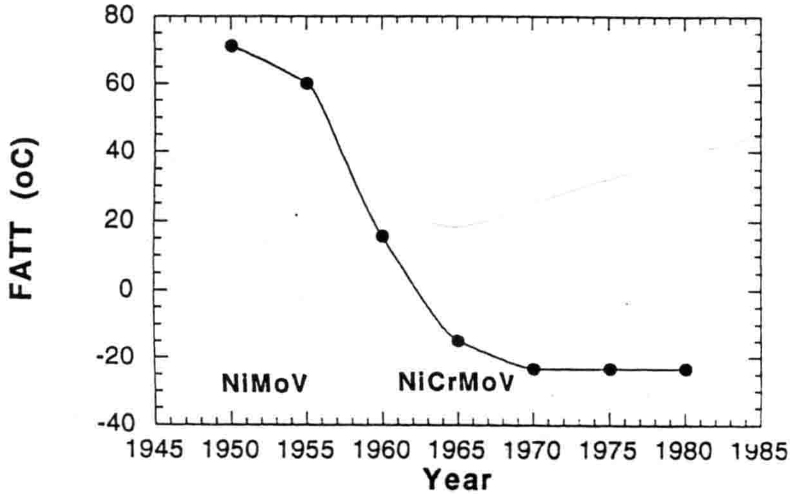

Figure 4 Trends in the impact toughness of steam turbine rotors. During the 1858–1961 time frame the following changes were made: vacuum pouring, electric furnace melting, the introduction of NiCrMoV steels, water quenching of rotors, and general use of vacuum carbon deoxidation melt practices. (From Ref. 6.)

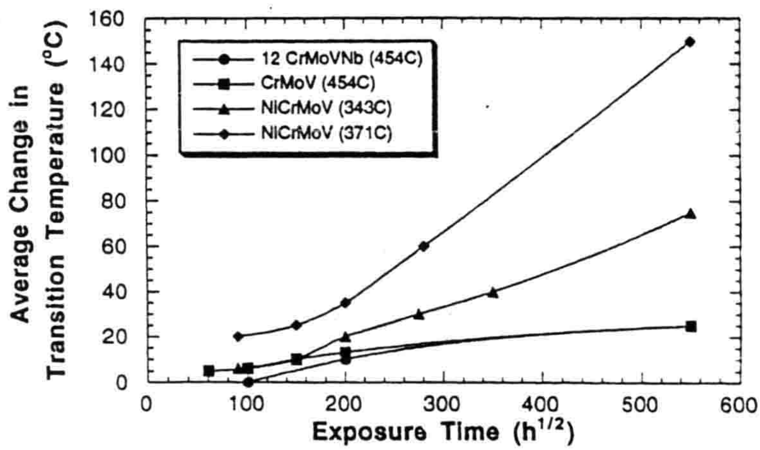

Figure 5 The change in the ductile to brittle transition temperature plotted as a function of exposure time for different steel compositions and temperatures. (From Ref. 5.)

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