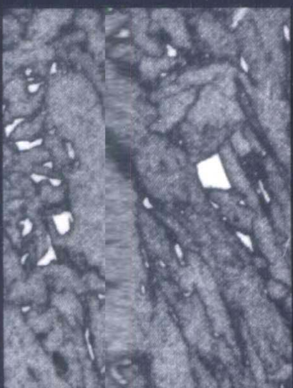
Residual and Unspecified Elements in Steel



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Overview

It has been generally accepted practice when writing material specifications to indicate limits or ranges, or both, of individual elements in the tables of chemical compositions. Normally, only those elements pertinent to a particular alloy designation or grade of material were listed with appropriate limitations.

There existed a general understanding among knowledgeable producers and users of steel products that there would always be present some minute levels of trace, residual, or unspecified elements orginating from the basic ores during melting and from additions during the subsequent metal refining processes. ASTM Methods, Practices, and Definitions for Chemical Analysis of Steel Products (A 751) addressed the permissive reporting analyses of these elements as well as the impracticality of establishing limits for all possible elements.

ASTM held its first symposium on the subject of residual elements in 1966. *Effects of Residual Elements on the Properties of Austenitic Stainless Steel* (Special Technical Publication [STP] 418) contains the papers presented at the symposium. There were a combination of influencing factors taking place in the steel industry resulting in an increasing interest in the subject of residual and unspecified elements at this time. First, there was the proliferation of steel alloys, grades and specifications. Not only were these new alloys being specified in standards writing bodies, but also, corporate and government specifications were equally being developed. Second, within these new specifications were narrower and more restrictive limitations on certain elements to satisfy the end product-oriented needs of the user. Third, steelmaking changes were taking place not only aimed at satisfying the new requirements but also aimed at improving efficiency of operations brought on by competitive pressures.

One of the first technical subcommittees of ASTM Committee A-1 on Steel, Stainless Steel, and Related Alloys to address the subject of residual and unspecified elements originating in 1968 was Steel Forgings. When it was brought to the attention of the subcommittee, certain ASTM standards have tables of chemical composition wherein not all the elements have limitations specified, it may be construed that those unspecified elements may be present in any amount or they are neither permitted nor prohibited. This was certainly not the intent since the specification addressed only those elements pertinent to the grade of steel. Other technical subcommittees soon initiated task groups to discuss residual and unspecified elements, for example, Steel Castings, Pressure Vessel Plates, Valves, Fittings and Bolting, Pipe and Tubular Products, Bar, Stainless Steel and Structural Steel.

Acknowledgment of the contribution by Mr. Vernon W. Butler, who deceased during the preparation of this volume, is particularly noted for his leadership on residual and unspecified elements as Subcommittee Chairman of Boiler and Pressure Vessel Steel Plates.

As the interest in residual and unspecified elements in steel grew among the various technical subcommittee, so did an interest in Committee A-1 to sponsor a symposium to address the concerns of those producing, specifying, designing, manufacturing, testing, examining, joining and evaluating the properties of steel products.

In this volume of the papers presented at the symposium, are technical examples of the broad range of interest in the subject of residual and unspecified elements in steel. Raw materials used in steelmaking were covered by the scrap metal industry indicating how that industry has taken steps to segregate raw materials for the steel producers to improve their chemical composition requirements. Steel producers presented papers detailing the progress that has been made in their internal manufacturing processes for controlling residual and unspecified elements not only to meet specification requirements but also for economic advantages. How the steelmaking industry has responded to the challenges of controlling residual and unspecified elements is well exemplified by these papers.

Not only were the controls for residual and unspecified elements covered, but also papers in this volume addressed very low, or ultra-low, levels of certain elements. Steel manufacturing technology, mechanical property effects, and metal joining characteristics of steels with extremely low levels of certain elements have been included.

Machinability of steels as affected by individual and combined effects of certain residual and unspecified elements was also addressed by authors in this volume. Microstructural constituents and inclusion morphology examples were presented.

There were quite a few papers presented by authors interested in the effects of residual and unspecified elements on specific material behavior characteristics. Covered in this volume are properties, such as temper embrittlement, corrosion resistance, elevated temperature creep-rupture strengths, fracture toughness, and room-temperature tensile strengths. Some of the papers dealt with steels in nuclear applications.

Welding processes and post-weld heat treatments affected by residual and unspecified elements were discussed by several authors. Not only were the base materials of concern but also the welding consumables.

In summary, this volume treats the broad spectrum of residual and unspecified elements in steel from the raw materials used for steelmaking through machining and welding to the long-term effects on properties. Very specific technical data are included for future reference by those concerned from all phases of the steel industry.

ASTM Committee A-1 has already reflected many of the issues presented in this volume through its published books of standards. Residual and unspecified elements in steel is a dynamic subject and will continue to be evaluated by the ASTM technical committees as the need arises.

Albert S. Melilli

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Keynote Address

George J. Schnabel[1]

Service Experience Related to Unspecified Elements

REFERENCE: Schnabel, G. J., "**Service Experience Related to Unspecified Elements,**" *Residual and Unspecified Elements in Steel, ASTM STP 1042*, A. S. Melilli and E. G. Nisbett, Eds., American Society for Testing and Materials, Philadelphia, 1989, pp. 5-25.

ABSTRACT: Over the past 50 years the anomalous behavior of steels has not always been consistent. Part of the inconsistency can be attributed to transient or other conditions that exceeded design conditions. Another part can be attributed to unspecified elements. Conversely, some steels have proven exceptionally capable to withstand their service conditions. Some of the more generic problems were serious enough to generate cooperative group actions to resolve them. Graphitization, weldability, low creep resistance, stress corrosion, caustic embrittlement, poor fracture toughness, shifting nil-ductility transition temperatures, and low upper shelf impact resistance have been some of the more notorious problems.

Until recently there was little attention given to the buildup of residuals (or unspecified elements) in steels where scrap steels were recycled into new product forms. Copper, chromium, cobalt, zinc, tin, nickel, and nitrogen have all influenced the behavior of steels. In some cases they could be beneficial. However, without a clear understanding of their synergistic behavior, it is difficult to predict their service behavior. If our industry potential is to remain strong in its world position, it will be necessary to develop more specific information on materials. We look forward to the successful implementation of the National Materials Properties Data Network (NMPD) to provide the data base from which the generation of new or more specific data will provide more confidence for the least cost.

KEY WORDS: steels, unspecified elements, graphitization, weldability stress corrosion, caustic embrittlement

Over the past 50 years the anomalous behavior of materials used in Power Plant operation has been inconsistent. Since all failures are directly related to materials, it is imperative that an understanding, or at least an appreciation, of the causes of anomalous behavior be pursued. It can be generalized that there are three major contributors to failures. These are best represented by a Venn type diagram, more recognizable as the Ballentine logo, in which three intersecting circles depict the three conditions for failure. One circle represents force, which we term as stress, a second represents the environment to which the material is subjected, and a third represents the condition of the material. The area of intersection portrays the severity or the probability of failure.

It is natural for the control responsibility for one of these factors, that is, stress, environment, or material condition, to be more dominant than the other two. However, it has been well documented that all three usually have a part in the failure mode.

Time will not permit disclosure of the myriad of isolated failures that have occurred, but there are sufficient generic problems to illustrate that unspecified elements can and do contribute significantly to anomalous behavior in service. Some of the more serious problems have generated group actions to resolve or mitigate future faults. Typical of these are caustic embrittle-

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ment, hydrogen embrittlement, graphitization, sigmatization, poor weldability, low creep resistance, low fatigue resistance, corrosion, stress corrosion, inadequate fracture toughness, high nil ductility transition temperatures, and low upper shelf impact resistance.

As noted before, failures are usually caused by a combination of conditions and most post mortem analyses are hampered by difficulty in ascertaining the initiating condition leading to eventual failure. Furthermore, the multitudinous activities between production, forming, fabrication, erection, and operation of these materials can all be suspect. We are suspicious that the buildup of residuals or unspecified elements are becoming more influential in their effect on materials when recycled into new product forms via the scrap route.

Many years ago caustic embrittlement was a real concern for the drum steels in low-pressure boilers. Initially it was found that variable sensitivity appeared to be associated with an unspecified copper content in carbon steels, that is, the higher the copper content the less serious the attack. This caustic cracking problem was eventually mitigated by establishing a more specific feedwater chemistry control. Similarly, when graphitization of carbon and carbon molybdenum piping was a serious problem with the weld heat affected zones and cold bends of piping, it was found that materials with up to 0.25% chromium exhibited a significant resistance to graphitization. This problem was subsequently mitigated by establishing proper heat treatments after bending or welding.

When austenitic Type 347 stainless steel became popular for high temperature steam service, it was necessary to add or maintain some ferrite to perform hot working or welding to minimize fissuring. Too much ferrite accelerated the formation of the Sigma phase, which increased hardness and reduced ductility. This challenged the ductility desired to accommodate thermal and pressure shocks. Close compositional control of ferrite and austenite formers reduced this tendency, but control was difficult to maintain. Another problem with the austenitic Type 347 and 321 stainless steels was the variability in hot shortness, which made sound casting and welding nearly impossible to predict. Efforts to establish proper ratios of specified elements did not produce consistent results. Reduction of unspecified elements, such as boron, tantalum, copper, tin, and so forth, as well as reducing phosphorus, silicon, and sulfur did not produce the desired results either.

A concerted effort was made to provide suitable specifications for heavy walled piping by introducing ASTM A376 and A430 for Central Station high temperature steam piping. Included in these specifications was a supplementary test called The Hot Ductility Test to predetermine the materials behavior during a welding cycle. Unfortunately, it could only be used for informational purposes and was never pursued to determine how to assure weldability with good hot ductility. Subsequently, heavy walled Type 347 and 321 stainless steels were outlawed for high-temperature service use because of unpredictable weldability. Recently both the German and Japanese steel producers have indicated a willingness to supply these materials with warranted hot ductility properties.

Type 316 was used to replace 321 and 347. As more service experience accrued, this material also exhibited poor weldability but not as serious as the previous grades. It was also found that the unstabilized Type 316 suffered a loss in ductility and structural stability by a carbide precipitation mechanism which occurred at the 1100°F (593°C) operating temperatures.

For operating temperatures at 1000 to 1050°F (538 to 566°C) the use of Type 304 for heavy wall main steam piping was made possible by the increased American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code allowable stresses for this material. There was no real change in the specifications, which supported the higher allowable stresses for Type 304, other than more recent test data that indicated that it was justified. This disturbed the utilities since the premature creep-rupture failures in the fine grained type 321 superheater tubes had been costly to rectify. Subsequent laboratory investigations of new and old heats of Type 304 uncovered a marked increase in nitrogen (unspecified) content, which was a result of the notable increase in manganese content from less than 1.00% to an average of about 1.30% thereby increasing the affinity for nitrogen during the melting process.

Efforts to establish a nitrogen requirement for the "H" grades in the ASTM standards were not successful, and the utilities had to write this requirement into their own specifications.

During production of materials with specific nitrogen additions, remarkable improvements in strength were noted with no other apparent problems. Hence, the introduction of a new "N" Grade of Austenitic materials. This grade has been used for nuclear grade piping in lightwater reactors that operate at temperatures below 600°F (565°C). This has been a particularly important consideration because of sensitization of austenitic stainless steels at the weld-heat affected zones promoting the onset of intergranular stress corrosion cracking. Hence the introduction of another new nitrogen enhanced extra-low carbon grade (ELC) grade with nitrogen added to maintain the desired strengths. However, strict control is needed to avoid fissuring and nitriding.

Pursuit of successful operation necessitates control of the environment to which the material will be subjected. Consequently a significant effort has been exerted to provide a rigorous water chemistry control as well as matching materials to the service conditions. This includes an in-depth understanding of the specified and the unspecified elements.

Successful operation of pressurized water reactors mandates strict control of materials and water chemistry. Corrosion and wastage of tubes and supports in steam generators has made it necessary to reduce the ionic form of copper and nickel as much as possible. Both the boiling water reactor (BWR) and pressurized water reactor (PWR) operation requires the lowest achievable oxygen to inhibit corrosion. The elimination of copper alloys and the introduction of hydrogen to scavenge oxygen in the feedwater circuit are corrective actions that have been instituted to accommodate material behavior in existing nuclear power plants. Eventually it will be necessary to develop alloys that will be more tolerant of the nuclear system environment.

Fracture toughness has now become much more important to assure safety and reliability of nuclear power plant operation. Copper in carbon and low alloy steels has a marked effect on the fracture toughness of reactor pressure vessel steels when subjected to a high neutron fluence. The upward shift of the nil-ductility transition temperature and the lowering of the upper shelf Charpy impact values have been associated with increasing copper contents in reactor pressure vessel steels and their weldments. This is of particular concern for pressurized thermal shock. It is also of concern for water hammer.

Not new but of increasing importance is the resistance of carbon steels to the erosion-corrosion of these materials in the feedwater, extraction steam, and main steam piping for power plants. Investigations have shown that small amounts of chromium, and to a lesser extent copper, have provided significant resistance to erosion-corrosion in feedwater and wet steam piping systems where high fluid velocities have reduced wall thicknesses to the point of failure. It has been well documented since 1948 that chromium can increase the resistance of carbon steels dramatically with additions of >0.25%.

Recently a relatively new problem called microbial corrosion has become a dominant factor in the service life of piping and pressure vessel components of cooling water systems for power plants. This appears to be associated with a reactivation of marine life and the lack of suitable chemical control of algae and marine organisms that attack the inner surfaces of these systems with subsequent failures. This will also demand corrective actions with more emphasis on the control of unspecified elements in materials.

Service experience cannot be related to static components only. There has been and continues to be a need to understand the high cycle fatigue characteristics and the recognition of what controls it. Rotating machinery, such as fans, motors, pumps, and turbines, have all been subject to sudden and complete failures because of crack initiation, growth, and eventual loss of mechanical stability. Efforts to produce improved steels for rotors, discs, retaining rings and blades must be increased as well as methods to inspect and categorize flaws. These flaws, occasioned by surface or subsurface separations can grow by creep-fatigue or pure fatigue because of cyclic stresses in operation. Here again the level of impurities or unspecified elements appear to be a dominant factor in the service behavior of these materials.

Improvements in inspection equipment and analytical capability have increased our knowledge and recognition of the condition of the faults. However, increased awareness must be generated to reduce the initiation of faults. Better steel production methods and more attention to unspecified elements in steel will be needed if we are to move forward.

Last but not least is the current activity of life extension for current power plants. Increasing the useful life of fossil fueled power plants from 25 to 50 years and from 30 to 60 years for nuclear power plants is an ambitious goal. It is necessary and has been economically justified because of the rapid increase in capital costs and the lack of environmentally suitable sites for new plants. However, investigations of the suitability for materials to be used safely and reliably must include careful considerations of the existing properties. Knowledge of unspecified elements will be an important part of these investigations.

There is no doubt that we have learned a lot about materials in the past 50 years. We have also found that we need to learn a lot more. As difficult as it is to account for all of the variables contributing to premature failures, we must apply our energy toward producing materials that will withstand the intended service conditions with the recognition and allowances for the dynamics that will occur during transients.

If our industrial potential is to remain strong in its world position, it will be necessary to develop more specific information on materials. This should also include the study of materials removed from service. Furthermore we must increase the accessibility to this information. The successful implementation of the National Materials Properties Data Network (MPDN) should provide the base from which the generation of new or more specific data will provide more confidence for the least cost.

Steel Melting

Daniel A. Pflaum[1]

Residual Problems and the Scrap Industry

REFERENCE: Pflaum, D. A., "**Residual Problems and the Scrap Industry,**" *Residual and Unspecified Elements in Steel, ASTM STP 1042,* A. S. Melilli and E. G. Nisbett, Eds., American Society for Testing and Materials, Philadelphia, 1989, pp. 11-25.

ABSTRACT: Purchased scrap is generally accepted as a major source of residual and unspecified elements in steel. Current trends in the steel industry will precipitate a more important role for scrap as a raw material. A principal factor in minimizing residual elements is the monitoring and control of this nonhomogeneous, nonmanufactured product by scrap processors and steel producers. By examining the variation in scrap grades through computer analysis and by integrating various techniques such as material segregation, inspection, and statistical process control procedures, more predictable and potentially lower residual levels can be achieved.

KEY WORDS: purchased scrap, nonhomogeneous, nonmanufactured, steel producers, scrap suppliers, examined variations, control procedures, more predictable, lower residuals

Trends in the Steel Industry

In 1970, 30 tons (27.23 metric tons) of scrap were purchased for every 100 tons (90.78 metric tons) of steel produced. In 1986, that ratio increased to 48 tons (43.57 metric tons) of scrap for every 100 tons (90.78 metric tons) of steel. Moreover, many factors currently affecting the steel industry indicate that the ratio of scrap melted to ton of steel produced should continue to increase in the future (Fig. 1).

Some of the key technological shifts contributing to scrap's expanded role in steelmaking are as follows.

Electric Furnace Steel Production

In the United States, the percentage of steel produced by electric furnaces grew from approximately 6% of total production in 1954 to roughly 15% in 1970. A steeper growth curve followed with electric furnaces supplying 36.4% in 1986 (Fig. 2).

Continuous Casting

The growth of continuous casting in the U.S. steel industry has been astronomical. Continuous casting has risen from less than 7% of steel produced during the industry's record production year, 1973, to 54% in 1986 and has increased to more than 60% in 1987. According to estimates, three-quarters of the steel made in this country will be continuous cast by 1990 (Fig. 3).

A direct result of the conversion to continuous casting has been a sharp reduction in internally generated scrap, which, in turn, has decreased the amount of home scrap available for melting (Fig. 4).

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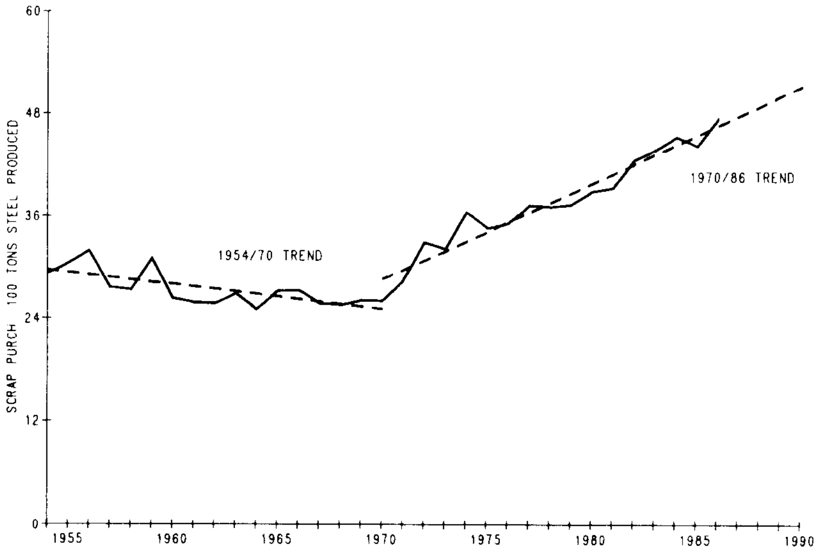

FIG. 1—*Ratio of scrap purchased to steel produced.*

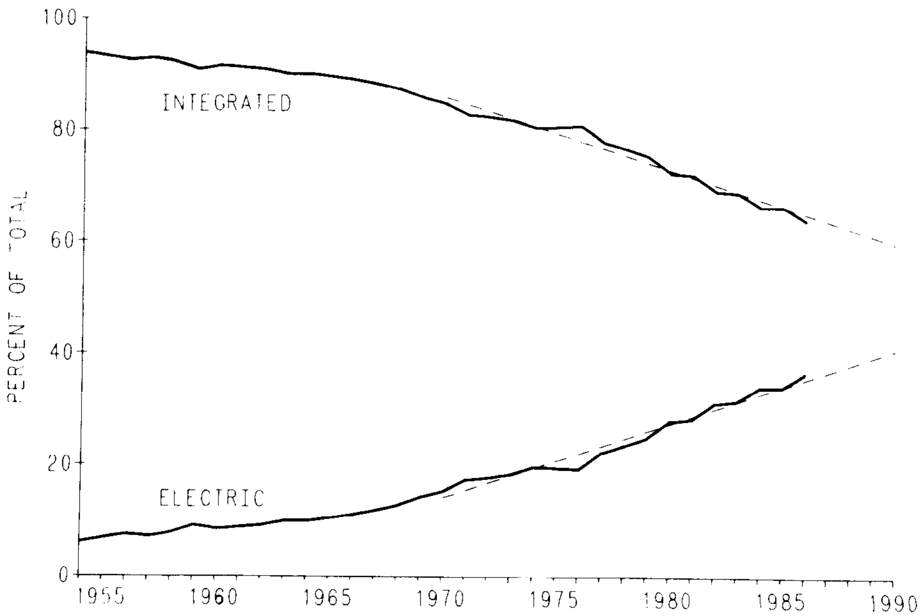

FIG. 2—*U.S. steelmaking mix, 1954–1990.*