Phase Diagrams—Understanding the Basics F.C. Campbell, editor

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CHAPTER 14

Phase Diagram Applications

ALLOY PHASE DIAGRAMS are useful to metallurgists, materials engineers, and materials scientists in four major areas: (1) development of new alloys for specific applications, (2) fabrication of these alloys into useful configurations, (3) design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical, and chemical properties, and (4) solving problems that arise with specific alloys in their performance in commercial applications, thus improving product predictability. In all these areas, the use of phase diagrams allows research, development, and production to be done more efficiently and cost effectively.

In the area of alloy development, phase diagrams have proved invaluable for tailoring existing alloys to avoid over design in current applications, designing improved alloys for existing and new applications, designing special alloys for special applications, and developing alternative alloys or alloys with substitute alloying elements to replace those containing scarce, expensive, hazardous, or "critical" alloying elements. Application of alloy phase diagrams in processing includes their use to select proper parameters for working ingots, blooms, and billets, finding causes and cures for microporosity and cracks in castings and welds, controlling solution heat treating to prevent damage caused by incipient melting, and developing new processing technology.

In the area of performance, phase diagrams give an indication of which phases are thermodynamically stable in an alloy and can be expected to be present over a long time when the part is subjected to a particular temperature (e.g., in an automotive exhaust system). Phase diagrams also are consulted when attacking service problems such as pitting and intergranular corrosion, hydrogen damage, and hot corrosion.

In a majority of the more widely used commercial alloys, the allowable composition range encompasses only a small portion of the relevant phase diagram. The nonequilibrium conditions that are usually encountered in practice, however, necessitate the knowledge of a much greater portion of the diagram. Therefore, a thorough understanding of alloy phase diagrams in general and their practical use will prove to be of great help to a metallurgist expected to solve problems in any of the areas mentioned.

While some of these uses have previously been discussed, phase diagrams are used to:

- Predict the temperature at which freezing or melting begins or ends for any specific alloy composition in an alloy system. A vertical line represents the composition of a specific alloy, for example, point X in Fig. 14.1. Its intersections with the solidus (T_2) and liquidus (T_1) indicate, respectively, the temperature below which, at equilibrium, the alloy is completely solid, and above which it is completely liquid. On heating, melting begins at T_2 , and the alloy is completely liquid above temperature T_1 . If an alloy is to be cast, then the temperature of the molten alloy has to be higher than T_1 . In order to fill the mold completely before freezing blocks of any thin section, the alloy should be at least 50 °C (28 °F) higher than its liquidus temperature, T_1 .
- Predict the safe temperature for hot working or heat treatments. The temperature of hot working, or heat treatment, should be at least 30 °C (17 °F) lower than its solidus temperature to allow for any impurities present and for furnace temperature fluctuations. Heating the alloy above temperature T_2 causes partial melting, called burning of the alloy. The "sweat out" molten metal leaves behind voids whose interior surfaces become oxidized at elevated temperature. Because a burnt



Fig. 14.1 Eutectic phase diagram with partial solid solubility

alloy cannot be repaired by welding during hot working, a burnt alloy is essentially scrap. If the alloy contains coring, then a homogenizing temperature above T_3 will also cause "burning" of the alloy. A safer temperature is T_4 . During precipitation hardening, if the solutionizing temperature T_5 is chosen instead of T_6 , grain growth of α phase will occur at the higher temperature.

• Determine the number of phases, type of phases, and composition of phases present in any given alloy at a specific temperature. One of the primary functions of an equilibrium phase diagram is to graphically show the extent and boundaries of composition-temperature regions within which an alloy exists as a single phase or as two phases. Thus, the fields of the diagram are labeled so that the number and the general nature of the phases present are indicated at a specific temperature.

If the point with coordinates at a specific composition and a particular temperature lies in a single-phase field, then the alloy is either an unsaturated homogeneous liquid or a solid solution with the composition of the alloy. A point in a two-phase field indicates that both the phases are saturated solutions, which could be liquids, solids, or a liquid and a solid. If the composition of the alloy is changed at the same temperature but still lying within the two-phase field, the number, type, and composition of the phases do not change, but their relative amounts change.

A horizontal line in a binary phase diagram indicates a particular temperature and a range of alloy compositions at which three phases can coexist at equilibrium. The horizontal line separates either a twophase field from some other two-phase field that has only one phase in common with it, or a two-phase field from a one-phase field that is different from both of these two phases.

- *Calculate the relative amounts of the phases present in a two-phase alloy.* The lever rule can be used to calculate the amounts of the two phases present in a two-phase field.
- Describe the freezing or melting of an alloy. Cooling of an alloy from the molten state to room temperature can be observed with the help of an equilibrium diagram. During slow heating of the alloy, the changes would be exactly reversed.
- Predict the microstructure of an alloy at a given temperature. A major advantage of phase diagrams is to make fairly accurate predictions of the microstructure developed in an alloy at a specific temperature or after an actual or proposed heat treatment. This is important because the microstructure controls the properties of an alloy. For example, the structure of the pure element that is freezing is quite important. Zinc has hexagonal close-packed crystal structure and is strongly anisotropic. When zinc crystals are growing in liquid zinc, growth tends to be more along one or another of its close-packed directions. Acicular (needle-shaped) crystals develop. However, when zinc is part of a

eutectic reaction, it freezes as a finely distributed phase with the other phase in the eutectic mixture.

- *Predict possible heat treatments.* The presence of a solvus line in a phase diagram, which shows decrease of solid solubility (line OD in Fig. 14.1) with the decrease of temperature, indicates the chance of using a precipitation-hardening heat treatment. The presence of a eutectoid reaction in a phase diagram helps to predict possible heat treatments such as annealing, normalizing, or hardening. It is also possible to predict what heat treatments are likely to be harmful and must be avoided. For example, if an alloy is not going to be cold worked, and if no phase transformation occurs during heating (or cooling), then heating such an alloy to high temperatures can result in grain growth and inferior properties.
- Choose the alloy composition to develop the best properties. The composition of the alloy that gives the best properties can be chosen. An alloy having maximum solute content indicated by the solubility limit by the solvus line may develop maximum strength by precipitation hardening if it develops a coherent precipitate. If the solute content is more (or less) than optimal, then the maximum strength will be less. The castability of an alloy system is usually best at the eutectic composition.

14.1 Industrial Applications of Phase Diagrams

The following are but a few of the many instances where phase diagrams and phase relationships have proved invaluable in the efficient solving of practical metallurgical problems. The areas covered include alloy design, processing, and performance.

14.1.1 Alloy Design

Four examples of the application of phase diagrams to alloy design are given: the development of a basis for age-hardening aluminum alloys, material substitution in two types of wrought stainless steel alloys to reduce costs, and an improvement in the manufacturing process for Fe-Nd-B-base magnets.

Age-Hardening Alloys. One of the earliest uses of phase diagrams in alloy development was at the suggestion in 1919 by the U.S. Bureau of Standards that precipitation of a second phase from solid solution would harden an alloy. The age hardening of certain aluminum-copper alloys (then called "Duralumin" alloys) had been accidentally discovered in 1904, but this process was thought to be a unique and curious phenomenon. The work at the Bureau, however, showed the scientific basis of this process. This work led to the development of several families of commercial "age-hardening" alloys covering different base metals.

Austenitic Stainless Steel. In connection with a research project aimed at the conservation of always expensive, sometimes scarce, materials, the question arose: Can manganese and aluminum be substituted for nickel and chromium in stainless steels? In other words, can standard chromiumnickel stainless steels be replaced with an austenitic alloy system? The answer came in two stages—in both instances with the help of phase diagrams. It was first determined that manganese should be capable of replacing nickel because it stabilizes the γ -iron phase (austenite), and aluminum may substitute for chromium because it stabilizes the α -iron phase (ferrite), leaving only a small γ loop (see Fig. 14.2 and 14.3).

Aluminum is known to impart good high-temperature oxidation resistance to iron. Next, the literature on phase diagrams of the Al-Fe-Mn system was reviewed, which suggested that a range of compositions exists where the alloy would be austenitic at room temperature. A nonmagnetic alloy with austenitic structure containing 44% Fe, 45% Mn, and 11% Al was prepared. However, it proved to be very brittle, presumably because of the precipitation of a phase based on β -manganese. By examining the phase diagram for C-Fe-Mn (Fig. 14.4), as well as the diagram for Al-C-Fe, the researcher determined that the problem could be solved through the addition of carbon to the Al-Fe-Mn system, which would move the composition away from the β -manganese phase field. The carbon addition also would further stabilize the austenite phase, permitting reduced manganese content. With this information, the composition of the alloy was modified to 7 to 10% A1, 30 to 35% Mn, and 0.75 to 1% C, with the balance iron. It had good mechanical properties, oxidation resistance, and moderate stainlessness.

Permanent Magnets. A problem with permanent magnets based on Fe-Nd-B is that they show high magnetization and coercivity at room temperature but unfavorable properties at higher temperatures. Because hard magnetic properties are limited by nucleation of severed magnetic domains, the surface and interfaces of grains in the sintered and heat treated material are the controlling factor. Therefore, the effects of alloying additives on the phase diagrams and microstructural development of the Fe-Nd-B alloy system plus additives were studied. These studies showed that the phase relationships and domain-nucleation difficulties were very unfavorable for the production of a magnet with good magnetic properties at elevated temperatures by the sintering method. However, such a magnet might be produced from Fe-Nd-C material by some other process, such as melt spinning or bonding.

14.1.2 Processing

Two examples of the application of phase diagrams to alloy design are discussed: alloy additions to a hacksaw blade steel to allow the production

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Fig. 14.2 Two binary iron phase diagrams, showing ferrite stabilization (iron-chromium) and austenite stabilization (iron-nickel). Source: Ref 14.1 as published in Ref 14.2



Fig. 14.3 The aluminum-iron and iron-manganese phase diagrams. Source: Ref 14.3 as published in Ref 14.2

of more cost-effective blades, and alloy additions to a hardfacing alloy that produced superior properties.

Hacksaw Blades. In the production of hacksaw blades, a strip of highspeed steel for the cutting edges is joined to a backing strip of low-alloy

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Fig. 14.4 The isothermal section at 1100 °C (2012 °F) of the Fe-Mn-C phase diagram. Source: Ref 14.4 as published in Ref 14.2

steel by laser or electron beam welding. As a result, a very hard martensitic structure forms in the weld area that must be softened by heat treatment before the composite strip can be further rolled or set. To avoid the cost of the heat treatment, an alternative technique was investigated. This technique involved alloy additions during welding to create a microstructure that would not require subsequent heat treatment. Instead of expensive experiments, several mathematical simulations were made based on additions of various steels or pure metals. In these simulations, the hardness of the weld was determined by combining calculations of the equilibrium phase diagrams and available information to calculate (assuming the average composition of the weld) the martensite transformation temperatures and amounts of retained austenite, untransformed ferrite, and carbides formed in the postweld microstructure. Of those alloy additions considered, chromium was found to be the most efficient.

Hardfacing. A phase diagram was used to design a nickel-base hardfacing alloy for corrosion and wear resistance. For corrosion resistance, a matrix of at least 15% Cr was desired; for abrasion resistance, a minimum amount of primary chromium-boride particles was desired. After consulting the B-Cr-Ni phase diagram, a series of samples having acceptable amounts of total chromium borides and chromium matrix were made and tested. Subsequent fine tuning of the composition to ensure fabricability of welding rods, weldability, and the desired combination of corrosion, abrasion, and impact resistance led to a patented alloy.

14.1.3 Performance

Four examples of the application of phase diagrams to performance are listed: the elimination of sulfur contamination from Nichrome heating elements, the elimination of lead and bismuth contaminants from extruded aluminum electric motor housings, a deficiency in the amount of carbon in sintered tungsten-carbide cutting tools, and a problem in which components were failing where the gold lead wires were fused to aluminized transistor and integrated circuits.

Heating elements made of Nichrome (a Ni-Cr-Fe alloy registered by Driver-Harris Company, Inc., Harrison, NJ) in a heat-treating furnace were failing prematurely. Reference to nickel-base phase diagrams suggested that low-melting eutectics can be produced by very small quantities of the chalcogens (sulfur, selenium, or tellurium), and it was thought that one of these eutectics could be causing the problem. Investigation of the furnace system resulted in the discovery that the tubes conveying protective atmosphere to the furnace were made of sulfur-cured rubber, which could result in liquid metal being formed at temperatures as low as 637 °C (1179 °F), as shown in Fig. 14.5. With this information, a metallurgist solved the problem by substituting neoprene for the rubber.

Electric Motor Housings. At moderately high service temperatures, cracks developed in electric motor housings that had been extruded from aluminum produced from a combination of recycled and virgin metal. Extensive studies revealed that the cracking was caused by small amounts



Fig. 14.5 The nickel-sulfur phase diagram. Source: Ref 14.1 as published in Ref 14.2

of lead and bismuth in the recycled metal reacting to form bismuth-lead eutectic at the grain boundaries at 327 and ~270 °C (621 and ~518 °F), respectively, much below the melting point of pure aluminum (660.45 °C, or 1220.81 °F) (Fig. 14.6). The question became: How much lead and bismuth can be tolerated in this instance? The phase diagrams showed that



Fig. 14.6 The aluminum-bismuth and aluminum-lead phase diagrams. Source: Ref 14.1 as published in Ref 14.2

aluminum alloys containing either lead or bismuth in amounts exceeding their respective solubility limits (<0.05% and $\sim 0.2\%$) can lead to hot cracking of the aluminum.

Carbide Cutting Tools. A manufacturer of carbide cutting tools once experienced serious trouble with brittleness of the sintered carbide. No impurities were found. The range of compositions for cobalt-bonded sintered carbides is shown in the shaded area of the ternary phase diagram in Fig. 14.7, along the dashed line connecting pure tungsten carbide (WC) on the right and pure cobalt at the lower left. At 1400 °C (2552 °F), materials with these compositions consist of particles of tungsten carbide suspended in liquid metal. However, when there is a deficiency of carbon, compositions drop into the region labeled WC + η + liquid, or the region labeled WC + η where tungsten carbide particles are surrounded by a matrix of η phase. The η phase is known to be brittle. The upward adjustment of the carbon content by only a few hundredths of a weight percent eliminated this problem.

Solid-State Electronics. In the early stages of the solid-state industry, a phenomenon known as the "purple plague" nearly destroyed the fledgling industry. Components were failing where the gold lead wires were fused to aluminized transistor and integrated circuits. A purple residue was formed, which was thought to be a product of corrosion. Actually, what was happening was the formation of an intermetallic compound, an aluminum-gold precipitate (Al₂Au) that is purple in color and very brittle. Millions of actual and opportunity dollars were lost in identifying the



Fig. 14.7 The isothermal section at 1400 °C (2552 °F) of the Co-W-C phase diagram. Source: Ref 14.5 as published in Ref 14.2

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Fig. 14.8 The aluminum-gold phase diagram. Source: Ref 14.6 as published in Ref 14.2

problem and its solution, which could have been avoided had the proper phase diagram been examined (Fig. 14.8).

A question concerning purple plague problems, however, has remained unresolved: whether or not the presence of silicon near the gold-aluminum interface has an influence on the stability and rate of formation of the damaging intermetallic phase. An examination of the phase relationships in the Al-Al₂Au-Si subternary system showed no stable ternary Al-Au-Si phases. It was suggested instead that the reported effect of silicon may be due to a reaction between silicon and alumina (Al₂O₃) at the aluminum-gold interface that becomes thermodynamically feasible in the presence of gold.

14.2 Limitations of Phase Diagrams

Phase diagrams play an extremely useful role in the interpretation of the microstructures developed in alloys, but they have several limitations:

- Phase diagrams only show the equilibrium state of alloys (i.e., under very slow cooling rates); however, in normal industrial processes, alloys are rarely cooled slowly enough to approach equilibrium.
- Phase diagrams do not indicate whether a high-temperature phase can be retained at room temperature by rapid cooling.
- Phase diagrams do not indicate whether a particular transformation (e.g., a eutectoid transformation) can be suppressed, and what should be the rate of cooling of the alloy to avoid the transformation.
- Phase diagrams do not indicate the phases produced by fast cooling rates. For example, the formation of martensite is not shown in the

Fe-Fe₃C phase diagram. Thus, they do not indicate the temperature of the start of such transformations (e.g., the M_s temperature) and their kinetics of formation.

- Even under equilibrium conditions, phase diagrams do not indicate the character of the transformations. They do not indicate the rate at which the equilibrium will be attained.
- Phase diagrams only give information on the constitution of alloys, such as the number of phases present at a point, but do not give information about the structural distribution of the phases; that is, they do not indicate the size, shape, or distribution of the phases, which affects final mechanical properties. The structural distribution of phases are affected by the surface energy between phases and the strain energy produced by the transformation. For example, if the β phase, in a mixture of α and β, is present in small amounts and is totally distributed with the α grains, the mechanical properties will largely be governed by the strength and ductility of the alloy is largely dictated by properties of the β phase.

Additional examples of applications of phase diagrams developed by thermodynamics modeling and computer simulation are given in Chapter 13, "Computer Simulation of Phase Diagrams," in this book.

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