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Introduction to Carburizing and Carbonitriding

History

The origins of carburization have been lost to history, but it is believed that the first carburized tools were produced unintentionally as a result of making tools out of nonhomogeneous bloom iron. Archaeologists have found carburized implements dating over 3000 years old in western Turkey. It seems likely that early iron workers discovered that when they heated iron in hot coals for an extended period of time, the iron would become stronger than usual, even to the point of being competitive with the then state-of-the-art bronze tools being manufactured by their competitors. As iron workers sought to soften iron in forges in preparation for forming, they unknowingly heated the iron above its critical temperature (Ac_1). This resulted in two important conditions being satisfied simultaneously: 1) The iron was transformed from ferrite (α-iron) to austenite (γ-iron); 2) the combustion gases of the charcoal fuel in the forge shifted from CO_2 to CO as a result of the Boudouard reaction. The solubility of carbon in austenite is much higher than that of ferrite, and the carbon monoxide gas provided plenty of carbon for diffusion by means of the following reaction:

$$2CO \leftrightarrow C_{Fe} + CO_2$$

The elevated temperature necessary to transform the ferritic iron into austenite also increases the rate of diffusion, such that carbon diffuses into the iron at a significant rate, creating a new and extremely important material—steel. Under the proper conditions, the carbon content can increase to the point that the steel becomes hardenable. The discovery of cementation in the production of steel and tools is credited by some historians for helping to advance the Iron Age.

Carburization became an important process and found widespread use throughout the 1800s. During this period, carburization was performed by surrounding the part to be carburized with a carbonaceous material, such as charred leather, ground animal bones, or wood charcoal. These materials were then sealed in an iron box that was heated to a temperature above the Ac_1 temperature and held for sufficient time to achieve the desired case, typically 2 to 6 h. The box would then be cooled and the part removed and hardened in a separate heat treatment. This technique became known as pack carburization.

Scientists began to understand that it was the decomposition of the carbonaceous materials into carbon monoxide, and not direct contact with the solid carbon, that made carburization possible. This realization presented the possibility of developing gaseous ng atmospheres that could replace solid carbon sources altogether. In the early 1900s, experiments with gaseous atmospheres for carburization were being conducted. Gas carburizing was found to show great promise, but the furnace technology at that time was not yet sufficiently advanced to permit the use of gas carburizing on a commercial scale. Because of these limitations, pack carburization would remain the leading method of production until World War II. During this period, the heat treater remained limited to establishing the process by trial and error at that time because there was little available in terms of predictive calculations.

During World War II—undoubtedly in response to the increased demand for armaments and bolstered by advancements in furnace design and manufacture—gas carburizing began to take over as the dominant method of manufacture.

In 1943, F.E. Harris published equations that revolutionized how the industry understood the process of carburization. His approach provided a powerful quantitative tool for predicting the outcome when carburizing at saturation levels in austenite. Harris demonstrated that the (total) case depth could be calculated by the following relationship:

$$D = 802.6 \frac{\sqrt{t}}{10^{(3720/T)}}$$

where D is the total case depth (millimeters), t is time at temperature (hours), and T is the absolute temperature (Kelvin).

Harris' work formed the foundation for continued advances in quantitative carburizing that has greatly improved the understanding of this commercially important process. Although the Harris equation applies to carburizing at saturation levels in austenite (which applies in the case of the pack carburizing), it also provides an important conceptual foundation in understanding the control of carburization at conditions below saturation (as in gas carburizing).