Materials • Mechanics • Physiology • Engineering • Aerodynamics

# BIKE TECH

August 1982 Bicycling Magazine's Newsletter for the Technical Enthusiast

## MATERIALS

## The Metallurgy of Brazing, Part 1

Mario Emiliani

Have you ever wondered what you're doing when you braze two metals together? What makes them stick? Why is a wellbrazed joint so strong when the filler metal is so weak? What factors affect the strength of the joint, and how sensitive are they?

Brazing isn't a difficult skill to learn, and it's not even really necessary to know much about it to produce a well-brazed frame. But knowing a few details of the process can only help you produce more consistently sound joints, and satisfy your curiosities. "The Metallurgy of Brazing" is a series intended to thoroughly explain brazing. The above questions are but a few that will be answered in this series.

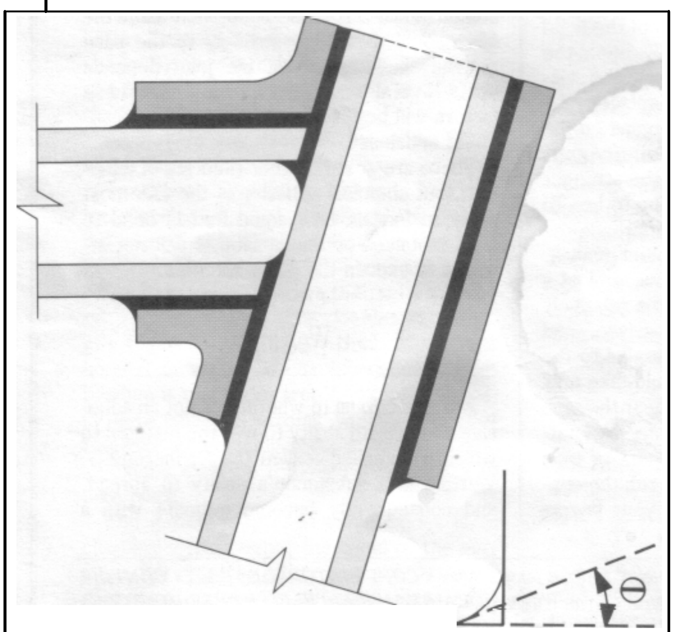
### History of Brazing

It's difficult to say when brazing was invented, let alone who invented it. Brazing, like most other manual arts, was something handed down from generation to generation. Apparently nobody thought enough of brazing to document it, or perhaps documentation would have led to a loss of one of the world's first trade secrets. In any event, its origins are a mystery.

The earliest examples of brazing are found in jewelry and other types of adornment from about 2,500 years ago. Pieces of pure gold were joined together using lower-melting alloys of gold and silver.

About 900 years ago, when it was discovered that zinc was a separate metal, brazing with brass filler metals became popular. It was through the use of these filler metals that the term "brazing" came about. Originally, the process of joining metals using lower-melting brass filler metals was called "brassing." Through the centuries, this term evolved to the word "brazing."

### Definitions



Effect of wetting on brazing alloy penetration.
A: good wetting; low contact angle; full penetration.

Before we continue, we must go over a few definitions. Brazing is a process which joins metals by heating them to a suitable temperature, then introducing a non-ferrous filler metal. The filler metal must have a liquidus* *above* 840°F (450°C), but below the solidus of the base metals. The filler metal is distributed through the joint by capillary attraction.

Soldering is the same as brazing, except the non-ferrous filler metal has a liquidus *below* 840°F (450°C). Because a few silver brazing alloys melt at very low temperatures, and because silver brazing was originally termed hard soldering, silver brazing is usually referred to as silver soldering. The difference in

liquidus between a brazing alloy and a soldering alloy has so crucial an effect on the nature of the joint that the term silver soldering should never be used when referring to silver brazing.

(There are several factors that contribute to this difference; most of them are too complex for a brief description. One major factor, though, is simply that soldering alloys are generally much weaker than brazing alloys, and this difference is reflected in the strength of the joint.)

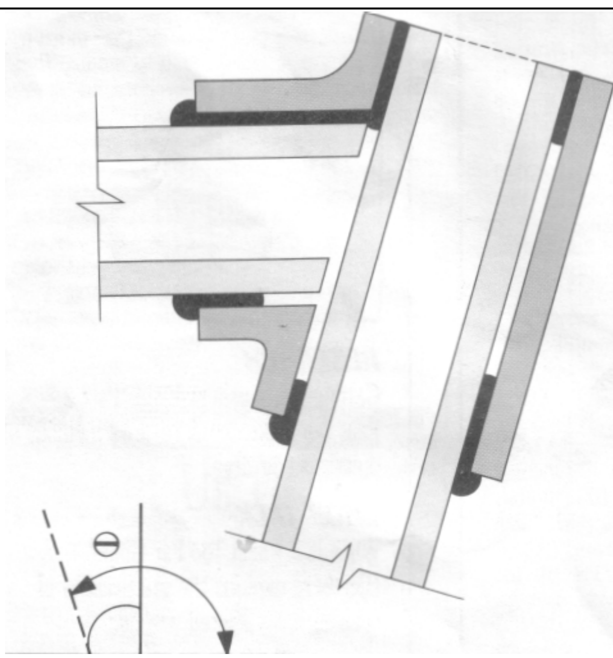
Welding differs from brazing and soldering in that the base metals are melted, and capillary attraction isn't a factor. Welding may or may not use a filler metal, depending on the p ess.

raze welding, as the name implies, is akin to both brazing and welding. The similarities are (to brazing) that the base metals aren't melted, and (to welding) that the filler metal (which may be ferrous or non-ferrous) isn't distributed by capillary attraction. An example of braze welding is two pieces of steel which are joined by simply building up a brass fillet betwen them as in a lugless frame joint. Thus, the strength of the joint depends upon the strength of the fillet.

I'm sure you are all well acquainted with

**See* Bike Tech, *June 1982 for definitions of liquidus, solidus, etc.*

the definition of brazing, but I bothered to define soldering, welding, and braze welding, with hopes of giving you a better understanding of what brazing is by comparing it with other joining processes. The differences should help clarify the important factors in brazing.



B:

angle; incomplete penetration.

## Adhesion Theory

What makes one substance stick to an other? Nobody really knows. It's not even known why ordinary Scotch® Tape sticks to paper, plastics, glass, or anything else it sticks to. The whole science of adhesives is very complex. Chemists and chemical engi neers spend a great deal of time experiment ing with thousands of substances, to see if any of them have uses as adhesives. It's very time-consuming trial-and-error work, but the payoff can be enormous - just look at all the adhesives in the hardware store.

Since nobody knows how adhesives work, there are a number of theories around to ex plain it. The trick in making things stick to gether is to develop very intimate contact between mating surfaces. The sticky stuff on Scotchs Tape is a very viscous liquid which bonds readily to a cellophane backing. When the tape is pressed onto a favorable surface, the air is squeezed out and the viscous liquid fills up all the microscopic gaps on the surface. This creates such intimate con tact that atomic forces be tween the viscous liquid and the surface (and be tween the liquid and the cellophane) can form a "mechanical bond." This bond accounts for most of the tape's holding ability. The strength of the bond depends largely upon the degree to which the vis cous liquid displaces air, and fills up the gaps on the surface. The more gaps that are filled, the stronger the bond is going to be. To illustrate the difference the amount of contact makes, lightly attach one end of a piece of tape to a relatively smooth, flat surface, and pull the tape parallel to the surface. It should take only a light tug to shear the tape from the surface. Now at tach another piece of tape to the surface, rub the con tact area with your finger ail, and pull. You'll agree, it akes a much larger force to hear the tape off. **In** fact. if ou do the experiment on a igid surface (ike a desk top), he tape will fail, not the joint. This is an example of mechanical bonding.

In mechanical bonding, secondary atomic forces called Van der Waals bonds are what give a joint its strength. These bonds are due to the electrostatic attraction between the nuclei of one molecule and the electrons of another. The forces generated by Van der Waals bonds vary according to the distance between **molecules** and the type of molecules. So **depending on these facmcs, any**thing from extremely weak **joints to rela**tively strong joints can be made.

Another type of **bonding is ri-rai band-**ing. In this case, much **stronger pcimars**-atomic forces form the **bonds,** enabling joints of very high strength to be made. Brazing. soldering, and welding are joining operations which form primary bonds of a type called metallic bonds.

Metallic bonds, as the **name** implies, are characteristic of metals. These are the bonds which hold metals together and give them their unique properties; i.e.. high electrical and thermal conductivity, ductility, shiny appearance when polished, etc. These bonds form when atoms with easily detachable electrons come so close together that their electrons can circulate freely between the atoms. Thus the negatively charged "sea" of electrons in a metal crystal holds the positively charged metal ions securely in place.

During brazing, metallic bonds are formed due to extremely intimate contact between the filler metal and base metals. In addition, there is always some degree of alloying between constituents of the base metals and filler metal. This action also forms metallic bonds. While it is these bonds that allow the filler metal to adhere strongly to the base metals, the strength of the joint depends upon several other factors as well. These factors will be discussed here and in subsequent articles.

There are several other theories of adhesion, but chemical adhesion is the one most likely to explain how liquid metals bond to solid metals. For this reason, I will not attempt to explain the other theories.

## Wetting

A factor critical to whether or not an adhesive sticks is its ability to wet the material to which it's applied (called the "adherend"). Wetting is a substance's ability to spread, and consequently become intimate with a

*BIKE TECH: EXECUTIVE EDITOR Crispin Mount Miller • EDITOR John Schubert • EDITOR-AT-LARGE John S. Allen -COPY EDITOR Kathy Fones • CONTRIBUTING EDITORS Frank Berto, Fred DeLong, Mario Emiliani, Richard Jow, Gary Klein, Dr. David Gordon Wilson • CHAIRMAN Robert Rodale • PRESIDENT Robert Teufel • PUBLISHER James C. McCullagh • ART DIRECTOR John Lenaas • CIRCULATION MANAGER Pat Griffith • BIKE TECH is published bimonthly by Rodale Press, Inc., 33 E. Minor St., Emmaus, PA 18049. Subscription rates: $11.97 yearly, $13.97 Canada, $15.97 other foreign. Single copy $2. Inquire about bulk rates.* 

*BIKE TECH application to mail at second-class postage rates is pending at Emmaus, PA 18049.*

sold

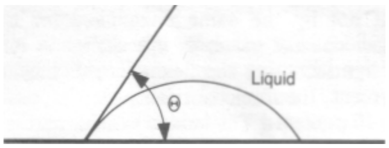



Figure 1: The angle (3 is one way of measuring how well a liquid wets a solid surface. As the angle decreases, wetting increases.

surface. Wetting ability depends on the relative magnitude of two variables: the adhesion between the liquid and the surface (due to attraction between molecules of the liquid and molecules of the solid); and the cohesion of the liquid (due to its molecules' attraction for each other). In other words, wetting depends on whether a liquid sticks more tightly to itself or to something else.

A measure of how well a liquid wets a solid is the contact angle 8. Figure 1 shows a drop of liquid that has come to rest on a surface. The angle formed between the surface and a line tangent to the drop is high, which means the liquid isn't wetting the surface very well. The lower the contact angle, the better the wetting. For example, if Figure 1 shows how a water drop acts on the surface of a newly waxed car, then the wax is a barrier to wetting.

All metals are covered by oxide films, which form when a metal is exposed to an environment containing oxygen. You can clean oxides off, mechanically or chemically, but immediately a new oxide layer will start to form. The thickness and tenacity of the oxide layer depends upon the metal and the environmental conditions. Oxides are barriers to wetting because their atoms are bonded ionically. A characteristic of ionic bonding is that there aren't any free (or easily detachable) electrons, which are a prerequisite for forming metallic bonds. Thus, all oxides must be removed if wetting is to take place.

The easiest way to remove oxides is to chemically treat either the liquid or the surface. For brazing either mineral fluxes or gaseous atmospheres are used. Since most bicycle frames are brazed with mineral fluxes, I will forego discussion of protective gaseous atmospheres (although the principle is the same).

It was once believed that molten fluxes increased the wetting ability of brazing alloys (and therefore the bonding) by reducing the alloys' surface tension. All liquids have a surface tension, measured as the force per unit length on a surface, which opposes expansion of the surface area. Surface tension results from the cohesive forces between adjacent molecules of the liquid. Its origin can be visualized in the following way: Imagine a molecule in the middle of a stationary drop of water. This molecule's relation to its nearest neighbors is symmetrical in all directions, and therefore the forces acting on the molecule are the same on all sides. Now imagine a molecule at the free surface of the drop. This molecule isn't being pulled equally from all sides; there's a force pulling it inward that isn't opposed by any force pulling it outward. This means that every molecule on the surface is under a constant force tending to pull it inside the drop (Figure 2). As a result the surface exhibits a tension, and will contract at any opportunity.

But to affect the alloy's surface tension, the flux would have to change the cohesion, and to do this it must dissolve in the brazing alloy. Experiments were done to verify this, and it turned out that fluxes were virtually insoluble in molten brazing alloys. So how does flux enable the brazing alloy to flow better?

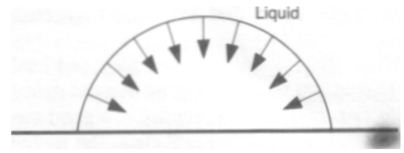
Flux is a chemical consisting mostly of fluorides, chlorides, and borates. When applied to a metal in paste form and heated, the water boils off leaving the flux crystals attached to the metal's surface. Upon further heating, the flux melts, wets the metal, and becomes chemically active. During this "active" period, the flux dissolves and absorbs contaminants (primarily oxides) on the metal's surface, and prevents further oxidation of the metal by coating it.

So now the surface of the base metal is essentially free of all oxides, and the brazing alloy has no difficulty in wetting it when introduced. After a while, the flux becomes saturated with oxides from the base metals, brazing rod, oxygen in the air, and torch flame (if an oxidizing flame is used), and is no longer effective. One should complete the brazing operation before this happens (or add more flux).

So the flux doesn't reduce the surface tension or cohesion of the molten brazing alloy; instead it enables good adhesion by cleaning the metal's surface.

Wetting agents can be added to improve wetting, but they must be soluble in the liquid. About 28 years ago, a program was undertaken to develop brazing alloys that didn't require flux, either mineral or gaseous. The brazing alloys were to be made self-fluxing and airproof by alloying them with small amounts of powerful deoxidizers. In addition, it was hoped that the deoxidizers would reduce the surface tension of the brazing alloy.

The results were that the brazing alloys




solid

Figure 2: The arrows indicate the direction of surface tension forces. These forces tend to make the droplet contract, thus assuming a spherical shape.

containing the strongest deoxidizers (lithium, magnesium, aluminum, etc.) exhibited improved wetting on steel, but diffusion of atmospheric oxygen through the molten brazing alloy was fast enough to oxidize the base metal. Thus the molten brazing alloy wet the base metal well, but only if the brazing time was very short. Some elements, such as copper, actually increased the diffusion rate of oxygen.

It was also discovered that small additions of nickel or tin might make the molten brazing alloy impervious to diffusion of atmospheric oxygen. As it turns out, this endeavor found use, but only in specialty applications such as jet engine components. Bicycle builders still have to use fluxes.

In view of all this, the importance of using the proper mineral flux is obvious. A good mineral flux should have the following properties:

1. Melt at temperatures below the melting point of the brazing alloy.
2. Completely wet the base and filler metals.
3. Reduce, dissolve, and absorb oxides. 4. Protect the base metal from oxidation during heating.
5. Be displaced by the molten brazing alloy when liquid.
6. It must not run off the base metal, leaving areas open to oxidation.

All six points are important, but the fifth one has special significance. Molten brazing alloy pushes flux out of its way as it's sucked into the joint. If the flux is too viscous, flow of the molten brazing alloy will be impeded. Thus, there will be many areas where the

brazing alloy didn't wet the base metals, and the joint strength will be reduced significantly. Fortunately, most, if not all, commercial fluxes meet the six requirements.

It's commonly believed that the criterion for a liquid metal to wet a solid metal free of oxides is that the two metals must be soluble and form an alloy at their interface. This isn't true; wettmg will occur if the surface tensions are favorable. Specifically, the surface tension of the solid must be greater than the sum of the liquid and solid/liquid interface surface tensions.

While alloying between the filler and base metals occurs to some degree in most cases, it isn't essential to the forming of a good metallic bond. A good flux will clean the metals so well that metallic bonds are easily formed (provided the surface tensions are favorable). Alloying at the interface usually occurs because at brazing temperatures, it's easy for filler metal atoms to diffuse into the base metal (and vice versa). (Alloying is different from the phenomenon called "brass inclusion" sometimes found in bicycle frames, which is generally harmful, as will be discussed in a subsequent part of this series.)

The degree of alloying at the interface depends upon the brazing temperature, brazing time, composition of the base and filler metals, and how well the flux removes oxides. Sometimes it's possible to have alloying at the interface which has a deleterious effect on the joint strength. For example, when steels are brazed with silicon-bearing brazing alloys, the iron and silicon form FeSi (iron silicide). This is a strong but brittle compound called an "intermetallic." If sufficient silicon is present in the brazing alloy (greater than about 0.2%), the FeSi formed at the interface will greatly reduce the strength of the joint.

Other alloy combinations can also produce similar reductions in joint strength. Fortunately it's been determined, by experimentation and/or trial and error, which combinations of metals produce efficient bonding without extensive formation of intermetallics. These favorable combinations are what eventually end up on the market. But re
member, not all brazing alloys are compatible with all base metals. I'll say more about that in Part 2.

V

*Topics of succeeding installments will include:*

*Compatibility of fluxes and filler metals with bicycle tubing and lugs - capillarity; formation of intermetallic compounds; brass inclusion.*

*Strength of joints (tensile, yield, impact, fatigue); the role of defects in joints.*

*Strength of steel tubes after brazing - annealing and hardening; temperature gradients versus length of butt in tube.*

*Proper framebuilding procedures.*