**Piano wire demo (effect of tempering)**

**Requirements:** 3 lengths (~ 8 inches each) of piano wire, a bunsen burner, a beaker of ice water.

**Instructions:**

Take one length of piano wire and bend it to illustrate its hardness.

Take a length of piano wire, and heat it up (red hot) in the hottest (bluest) part of the flame of a bunsen burner. Once hot, quench cool it by dipping it immediately into a beaker of ice water. The wire will be quite brittle and will snap very easily.

Take another length of piano wire and heat it up (red hot). Then move the heated portion of the wire to a cooler (yellower) part of the flame for ~ 20 sec, then to the coolest region of the flame (yellowest) for another ~20 sec. Remove the wire from the flame and let cool to RT (this will only take a minute or so). The wire will now be quite hard, and difficult to bend.

**Discussion/Explanation:**

This demonstration provides a very quick illustration of the process of tempering, as is done in the fabrication of carbon steel. This can be presented in the context of solid state phase morphologies/microstructures and the importance of thermal history/processing in the determination of bulk physical properties or in a discussion of kinetic vs thermodynamic control of phase behavior. It’s also an opportunity to talk about the idea that different physical properties might be desirable for different applications.

Carbon steel is an alloy of carbon in iron, and the process of tempering involves manipulation of the transition between two particular phases, the ferritic (also known as a-Fe, a bcc phase) and the austenitic (also known as g Fe, an fcc phase.) C is more soluble in the fcc phase (~ 2 % by weight forms an interstitial alloy) than in the bcc form (a-Fe) iron (which can only reach a concentration of ~0.02%). [This may not be obvious as the bcc structure is overall more open than the fcc phase, but some of the interstitial spaces in the fcc structure are actually bigger than those in the bcc, so it can actually dissolve more C.]

http://www.roymech.co.uk/Useful\_Tables/Matter/Phase\_diagram.html

The fcc alloy, upon cooling will phase separate into a two phase mixture of ferrite and cementite (Fe3C). If the cooling is carried out slowly enough, this transformation is possible because diffusion is fast relative to the cooling rate. But depending on the rate of cooling, because the transformation is from a liquid to a solid phase, a variety of kinetically controlled (but thermodynamically disfavored states) can be achieved. The actual temperature (rate of cooling) of the transformation will dictate the length scale of the resulting microstructure. If the material is only slightly supercooled, nucleation occurs infrequently and we get a coarse structure in which few nuclei form and grow. If the material is significantly supercooled, the nucleation rate is higher, yielding many nuclei and a finer structure.

In the case where the fcc alloy is cooled **very** **rapidly** (quenched), then diffusion can’t occur at all, and the transformation to the thermodynamically favored two-phase mixture of ferrite and cementite is not possible. At this point, the structure consists of clumps of Fe3C (no longer in really in solution) which can’t migrate (because you’re in a solid phase) to form the preferred structure. This phase (known as a martensitic phase) - is kinetically controlled but thermodynamically disfavored (and therefore doesn’t show up on the phase diagram). Steel prepared in this manner will be much harder than pure iron, but also quite brittle, because there’s a lot of strain in the material, and therefore will shatter/fracture easily. But if we heat the martensitic phase very gently (though not hot enough to remelt it), the C can diffuse short distances, allowing atoms to relax into less strained arrangement (still not the thermodynamically favored arrangement, but much less strained than the quench-cooled material.) This method of processing is known as tempering (or annealing), and leads to a very strong material used in making knives, swords...

**Some additional thoughts**

The explanation given above may be a bit more than others might want to introduce, depending on the level or focus of a given course. But I think that even introductory level students can understand the idea of a supercooled phase (if they’ve seen the supersaturated ammonium acetate demo for instance, or superheated water in a microwave.) So this is just an example of a supercooled phase which, because it’s a solid, gets kinetically trapped. The gentle heating (not all the way to melting) allows for relaxation of the strained martensitic phase into something that’s can’t get all the way to the thermodynamically preferred arrangement, but is also not as brittle as the quench cooled sample.

Another parallel can be drawn to the tempering of glass – in glass blowing, you work the material into the molten state, then cool it relatively quickly, trapping in the desired macroscopic shape of the object. But this object will contain a lot of strain at the molecular level (which can be observed through cross-polarizers for instance – there are a lot of effective images of strained glass available on the web). The glass object is then tempered/annealed (heated gently, to some temperature at which individual atoms/molecules can move about a bit, but that’s not free-flowing) in order to allow the object to relax into a less strained (and therefore more durable) state.

Another example that they’ll be familiar with is chocolate. Working chocolate is also a matter of manipulating a complex phase diagram. If molten chocolate is cooled very quickly, the solid phase that results is metastable (kinetically trapped, thermodynamically disfavored), and will eventually begin to phase separate (since the phase transition temperatures are not so far from RT) resulting in “chocolate bloom” (the grayish, cloudy appearance that you sometimes see on cheap chocolate – completely edible, just not so attractive to us.) But tempered chocolate has been processed thermally to allow the more thermodynamically favored structure to predominate. Chocolate prepared this way will not phase separate with time (assuming appropriate storage temperature), and will remain glossy looking.

If desired, you can also talk a bit about cast iron samples as well: by adjusting the amount of C in the alloy, you can make a material that is still too brittle to be malleable, but because of the eutectic point (see the phase diagram above), can be melted (at reasonable temperatures) and cast into molds – this is how cast iron objects are made. These materials are hard, but brittle.