

# Metals

## I.1

### Principal Characteristics of Metals

Of the 92 naturally occurring elements, 80 are metals. Only about a third have practical applications, as defined by these parameters: a useful metal must be present in nature in reasonable quantities and able to be removed from the earth with sufficient economy, it must be able to be formed using standard metalworking methods, and it must have characteristics such as strength or conductivity that contribute to a practical use.

Even with modern refining methods it is impossible to yield a totally pure metal: one that contains a single kind of atom. There are always some foreign atoms included, but whenever possible it is best to use alloys that have fixed degrees of purity, as established by government or industry standards. Metals are formable by chip removal or other methods. They are also opaque, reflect light when polished, and conduct heat and electricity.

Many characteristics of metals can be explained by similarities in their atomic structure. For instance, most metals have only a few electrons on the outer shell of the atomic structure, (usually only one or two) that are easily given up as valence electrons. The remaining atomic bodies form the crystal structure of the metal while the valence electrons move relatively freely between them. In chemical compounds, metals give up the valence electron when forming molecules with non-metal atoms; the non-metals turn into anions by incorporating these electrons.

Despite the similarity in principle between metals, there are considerable differences between the characteristics of density, hardness, tensile strength, melting temperature, and chemical activity.

Group	Metal										Nonmetal									
	I											II	III	IV	V	VI	VII	VIII		
	1 H																	1 H	2 He	
1. Short Period	3 Li											4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne		
2. Short Period	11 Na											12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
1. Long Period	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr		
2. Long Period	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
3. Long Period	55 Cs	56 Ba	57 La 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi					
	Non-noble metals			Metals of the first kind								Metals of the second kind								

Figure 1.1  
The Periodic Table of Elements.  
above: entire table  
below: important groups of elements.

11 Na	<i>Basic elements of the most important</i>		
19 K	20 Ca		

<i>Basic elements of the most important acids.</i>				
5 B	6 C	7 N	8 O	9 F
	14 Si	15 P	16 S	17 Cl

12 Mg	13 Al	14 Si	<i>Aluminum alloys.</i>
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22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni
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*Steel*

50 Sn	51 Sb	<i>Lead alloys, soft solders.</i>
82 Pb	83 Bi	

*Non-ferrous alloys.*

			13 Al
28 Ni	29 Cu	30 Zn	

		28 Ni	29 Cu	30 Zn	<i>Noble metals and their alloy additives.</i>
44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	
76 Os	77 Ir	78 Pt	79 Au	80 Hg	

50 Sn
82 Pb

## 1.2 Metals in the Periodic System

The connection between atomic structure and the characteristics of elements can be made clear by looking at the periodic chart (figure 1.1).

The elements are organized in Mendeleev's Periodic Table according to the sequence of their atomic charges; that is, the number of positively charged protons contained in their nucleus. As a rule, the number of protons is the same as the number of electrons that orbit the body of the atom.

Imagine the structure of the atom as a series of concentric spheres. Electrons (which are negatively charged) are distributed on individual shells or spheres, each of which can hold only a specific number of electrons. The inner shell (or first sphere) has to be filled to its capacity before electrons can be deposited on the next layer. Reading horizontally, the top tier of the chart contains hydrogen (H) with one electron and helium (He) with two. This fills up the first sphere, which is called the K shell. Another shell is indicated on the chart by moving down to the next horizontal row, starting at the left with lithium (Li) which has 3 electrons, beryllium (Be) which has 4 and so on, across the chart to neon (Ne), which has all 8 of the available spaces of the second sphere occupied.

This system works well until reaching lanthanum (La, No. 57) where things become more complicated, because electrons are deposited on the next shell before the previous one is fully occupied. The periodic chart accommodates this anomaly by skipping from 57 to 72 in the main grid and setting down elsewhere the two groups numbered 58–71 and 90–103.

As an example, let's look at the element gold (Au, No. 79). Here the K, L, M and N shells are fully occupied. The next shell, (O) is left with its 14 places unoccupied while one electron is deposited on the P shell. It is this lone electron that is given up as a valence electron when forming ions (figure 1.2).

Even this peculiarity of empty shells occurs with enough regularity to form a system, as becomes increasingly clear by examining the physical char-

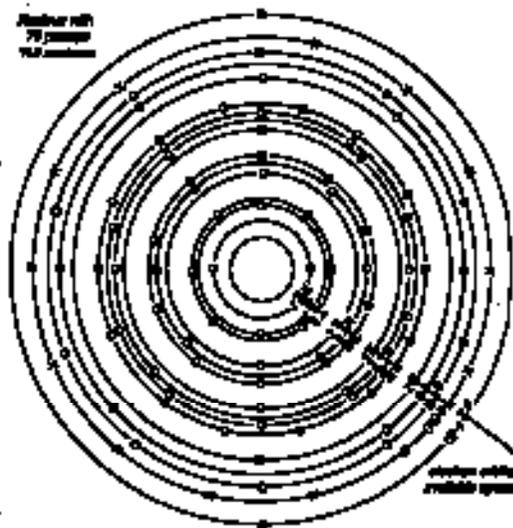


Figure 1.2  
Electron disposition in the gold atom.

acteristics of metals. These similarities allow the elements to be set one above the next in the chart to form a vertical column called a family.

The purpose of all this is to understand fundamental characteristics of metals and their relationships to each other. Some very interesting conclusions can be drawn from the periodic chart for the metals used by goldsmiths.

- It is apparent that those metals that are placed closely together usually alloy themselves with each other, while those that stand further apart are often incompatible. An example of the former is seen in copper and zinc, numbers 29 and 30, that combine easily to make brass. By contrast, vanadium (23) will not join easily with zinc (30).
- It is noteworthy that the components of the metals most familiar to goldsmiths – gold, silver and copper – stand over each other in a unified family. Neighboring them are the platinum group metals, the lightest next to silver, the densest next to gold.
- On the other side, positioned next to the precious metals, are the amalgam-forming mercury (Hg)

and the additives cadmium (Cd) and zinc (Zn) that are used in making solders.

- Next to copper are the addition metals for brass and nickel silver, zinc (Zn) and nickel (Ni).
- The components of soft solders, tin (Sn) and lead (Pb), are placed above one another as related metals in the IV main group; they are so far removed from the precious metals gold (Au) and silver (Ag) that we can surmise (correctly) that there are not useful alloys.
- Even though copper (Cu) and tin (Sn) are just as widely separated, they form the bronze alloys; this apparent contradiction can be explained in that copper can absorb only a small proportion of tin. Alloys with more than 15% tin are unworkably brittle.
- The most important metals for improving steel are in the same Period (or horizontal row) as iron (Fe), and therefore have a certain relationship to each other. Molybdenum (Mo) and tungsten (W) take their place in the same family with chromium (Cr), and show certain similarities to it.
- On the left side of the Periodic Table with the “non-noble metals” are found the elements of bases, while the acid forming non-metals are on the right.

### 1.3 Internal Structures

#### 1.3.1 ATOMIC AND CRYSTAL LATTICES

As many metalsmiths have seen firsthand, when the button on a casting is broken, a texture that is significantly different from the surface of the metal is revealed. While the cast piece is smooth and flat on the outside, the fracture surface is matte white, rough and grainy. This is a glimpse into the crystal-line structure of which all metals are made.

Molecules of a metallic element are bound into structures called “crystals” or “grains” (figure 1.3). These are established along an ordered crystal structure, though they assemble into clusters that show an

irregular outer shape. As metal cools and converts from liquid to solid, countless crystals form simultaneously. They interfere with each other, in the same way that the ripples caused by throwing a handful of pebbles into a pond soon collide with each other. In the case of metals, the internal structure of a sample retains the accidental shape that this gives them. If we could look inside this kind of crystal, we would see a world measured in ten millionths of a millimeter, thousands of atoms ordered in regular rows, the rows stacked one on the other to form flat planes. These planes are in turn layered tightly upon each other to produce an orderly lattice structure.

Cohesion within the lattice is created by the fact that the metal atoms have given up the valence electrons of their outer shells. Technically this makes them ions, so we would properly refer to this as an ionic lattice structure. After giving up the valence electron, the positive charge of the protons predominate. The freed valence electrons of course stay in balance with the entire number of ions, but they no longer belong to a specific atom and instead move about as an “electron gas.” The interaction of the negative charge of the electron and the positive charge of the proton ensures the cohesion of the entire structure. This is the principle of “metallic cohesion.”

As metal solidifies from a molten state, crystals are formed independently of each other in random orientations. This means that although the geometry of the lattice is the same throughout the metal, the planes of the lattice structure in the individual crystals are positioned in completely different directions in individual crystals relative to each other.

The concept is relatively easy to picture on a two dimensional surface, but remember that this restructuring is happening “up” as well as “out.” Because of the complexity of rendering this image, it is typical to simplify the crystal to a drawing such as figure 1.4, in which the unit cell is removed from its lattice. Ions are represented as spheres and the forces of cohesion are depicted as connecting lines.

The important metals for goldsmiths share a structure called the cubic face-centered lattice. The unit cell consists of a cube with three layered planes: the

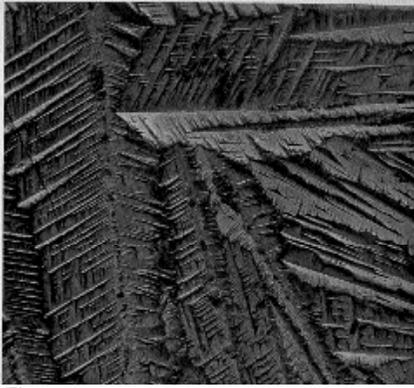


Figure 1.3  
Clearly formed crystals (dendrites) upon the surface  
of slowly cooled antimony.

Figure 1.4  
Basic unit cell.  
a) cubic face-centered lattice  
b) cubic body-centered lattice.

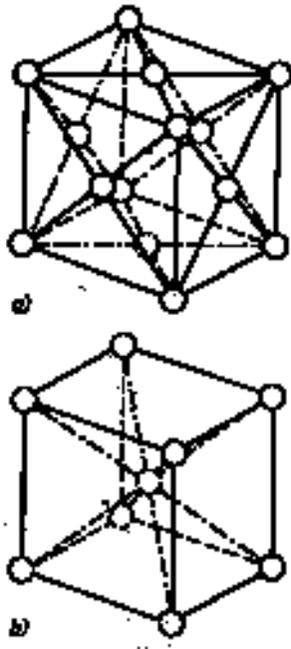


Figure 1.5  
Surface etching of grains in fine gold.

This surface is then treated with an etchant to reveal the edges of each crystal. Even though all crystals of a pure metal have the same composition, they are attacked differently by the etchant because of their different orientations in the block of metal; if they were all ordered in the same direction they would be dissolved with equal intensity and the surface would remain smooth. The result of this process is called an etched grain surface (figure 1.5).

In grain boundary etching the etchant is made in such a way that the crystals themselves remain undamaged and only the thin easily soluble layer of grain boundary material is attacked. When a light source is beamed at an angle across this surface, minor differences in height show up as a fine-lined, spider web picture of the grain contours (figure 1.6).

The prepared test piece is placed into a metallurgical microscope, where a strong light source floods the surface and makes it possible to observe the object using a conventional eyepiece and lens. In general an enlargement of up to about 500 times is sufficient. The important information that can be derived from these images is detailed in the examples given in the following sections.

#### 1.4 Divisions of Metals

There is no single encompassing way to group met-



Figure 1.6  
Grain boundary etching.

grouped according to the extent each is unaffected by the oxygen in the air, i.e. their ability to resist tarnish.

- On the basis of optical appearance the non-precious metals and their alloys can be categorized as:
  - a) red and yellow metals (copper and its alloys)
  - b) white metals (tin, zinc, bismuth, lead and their alloys)
  - c) black metals (iron, steel, and nickel)

Because the last category is subjective, it should not be taken as completely accurate or always consistent. For instance we know today that the precious metals are not as resistant to oxidation as previously thought; the colored gold alloys are usually thought of first as precious metals, though on the basis of color they could just as accurately be placed with the colored alloys such as brass.

It is customary and correct to speak of “precious metal jewelry,” but we should avoid the misleading term “real jewelry” as being complete nonsense. All metals can only be “real” metals and every piece of jewelry, regardless of the material of which it is made, can only be a “real” jewelry piece.

### 1.5

## General Characteristics of Important Metals

### GOLD

Gold has been known and valued since ancient times. It is the only elemental metal with a beautiful yellow color; it appears greenish translucent as gold leaf and can be polished to a highly reflective surface. Gold can be made so thin that a stack of 10,000 gold leaves is only 1 mm thick! The melting temperature is so high that it is only with some effort that pure gold can be melted by most jewelry torches. The ability of gold to conduct heat and electricity is lower than of silver and copper. Gold is almost completely resistant to air, water and acids, and can be dissolved only by a very strong acid called aqua regia. It is attacked by free chlorine, potassium and sodium cyanides, bromine and some other chemicals, though this has little meaning for the goldsmith. Gold forms chemical compounds only with difficulty.

Gold is almost always alloyed with other metals to reduce the cost of a given weight, to increase tensile strength and to lower the melting point. By altering the additive ingredients, gold alloys may also be made in several colors. The standard colored gold alloys consist of gold, silver and copper. Cadmium or zinc are added to create solder; white gold is bleached by adding palladium and nickel.

### PLATINUM

Platinum has been known since the middle of the 19th century but only since the beginning of the 20th century has it been used for making jewelry. It has a gray-white color similar to steel. Platinum is as soft and ductile as copper and takes a high polish. The melting point is so high that it can be melted only with an oxygen-fed flame or in an electric kiln. Like gold, platinum is essentially resistant to air, water and acids; like gold, it is only soluble in aqua regia. Platinum forms chemical compounds only with difficulty. Its ability to conduct heat and electricity is only half that of silver. Because platinum is very soft, it is typically alloyed with copper, palladium and sometimes iridium to increase hardness.

### PLATINUM GROUP METALS (PLATINOIDS)

The following five metals are found together with

Table 1.1  
Characteristics of the important metals.

Metal	Symbol	Number	Relative Atomic Mass	Valence	Density in g/cm <sup>3</sup>	Melting Point in °C	Boiling Point in °C	Specific Heat in kJ/(kg•K)	Specific Melting Heat in kJ/kg	Heat Expansion in 10 <sup>-6</sup> m/(m•K)	Heat Conductivity in W/(K•m)	Brinell Hardness in Bhn	Tensile Strength in N/mm <sup>2</sup>	Ductility in %
Gold	Au	79	196.97	1, 3	19.30	1063	2600	0.1310	67	14.30	311.5	18,5	131	40
Platinum	Pt	78	195.09	1, 2, 3, 4, 6	21.45	1774	4350	0.1331	113	8.99	73.7	56	132	41
Iridium	Ir	77	192.22	1, 2, 3, 4, 6	22.42	2454	4800	0.1294	117	6.80	59.3	179	491	6
Osmium	Os	76	190.20	2, 3, 4, 6, 8	22.48	2550	5500	0.1302	154	6.57	87.1	350	-	-
Palladium	Pd	46	106.40	2, 3, 4	12.03	1554	3387	0.2273	162	11.86	72.2	47	184	25
Rhodium	Rh	45	102.91	1, 2, 3, 4, 6	12.40	1960	4500	0.2474	217	8.3	149.9	127	410	9
Ruthenium	Ru	44	101.07	4	12.30	2450	2700	0.2315	193	9.1	105.1	220	378	5
Silver	Ag	47	107.87	1	10.53	960.5	2170	0.2332	104	19.17	418.7	26	137	60
Copper	Cu	29	63.54	1, 2, 3	8.96	1083	2350	0.3835	205	16.98	414.1	45	221	42
Mercury	Hg	80	200.59	1, 2	13.55	-38.84	357	0.1398	12	182	10.5	-	-	-
Zinc	Zn	30	65.37	2	7.13	419.5	907	0.3869	111	29.1	111.0	43	35	32
Cadmium	Cd	48	112.41	2	8.64	320.9	767	0.2315	57	30.0	92.1	16	63	55
Tin	Sn	50	118.69	2, 4	7.28	231.9	2360	0.2261	59	21.4	67.0	4	27	50
Lead	Pb	82	207.2	2, 4	11.34	327.4	1750	0.1251	24	29.1	35.1	4	13	31
Iron	Fe	26	55.85	2, 3, 6	7.86	1539	3000	0.4509	272	11.9	71.2	40	210	32
Titanium	Ti	22	47.90	2, 3, 4	4.49	1800	3262	0.5568	324	8.35	15.1	120	343	40
Aluminum	Al	13	26.98	3	2.70	660	2270	0.8959	385	23.86	230.3	17	45	40

platinum in Column VIII of the Periodic Table, and are similar in important chemical and physical characteristics. They are resistant to the effects of air, water and acid, and with the exception of palladium they are even resistant to aqua regia. Generally they are found together in nature. Palladium and rhodium were discovered in 1803, iridium and osmium in 1804; and ruthenium was first discovered in 1844.

*Iridium* is a silvery-white, brittle and very hard metal. Even when red hot, it can barely be deformed plastically. It may be worked in chip forming operations and it can be polished. It is rarely used in its pure form, but it is an important hardening agent in alloys; a small amount of iridium will significantly increase the hardness of platinum.

*Osmium* takes a special position in comparison to all the natural elements. It is very dense, and has extremely high melting and boiling temperatures. Osmium has such unusual hardness and brittleness that it cannot be worked in chip forming operations at all. Because of these unpleasant characteristics osmium is not used as a working material.

*Palladium* has a somewhat lighter color than platinum, takes a high polish, softens below the melting temperature and responds well to forging and welding. It is tougher than platinum but not quite as ductile or hard. Of all the platinum metals, palladium is the least noble, and therefore can be dissolved in sulfuric and nitric acids as well as aqua regia.

Because of its good workability, low melting point and relatively low price, palladium is the most com-

monly used of the platinum group metals. It plays an important role in electronic and dental applications. Palladium improves the characteristics of jewelers' platinum while brightening its color; palladium is also used to whiten white gold.

*Rhodium* is similar in color to platinum. It is normally completely resistant to attack by acids and acid mixtures but it can be dissolved in molten potassium hydrogen sulfate,  $\text{KHSO}_4$ , as well as in the alkaline cyanide solutions  $\text{KCN}$  and  $\text{NaCN}$ . It forges and rolls well at red heat. Because of its good optical characteristics and its high resistance to corrosion, it is used for electro-deposition (rhodium plating).

*Ruthenium* is so hard and brittle that it only appears as a gray white powder. When heated in air it forms black ruthenium dioxide,  $\text{RuO}_2$ , but it is resistant to other chemicals. Because of its unfavorable working characteristics, ruthenium is not used in the pure form, but is sometimes seen as an alloying ingredient for other platinum metals.

#### SILVER

Silver, which has been known since ancient times, has a pleasant white color and exceeds all other metals in its ability to conduct heat and electricity and in its reflectivity, polishability and shine. The thin silver oxide coating that forms in clean air has no practical significance, but sulfur in air causes the formation of a black silver sulfide layer. Silver is practically insoluble in water, but bactericidal silver ions are given off by the oxide layer. Because of this ability to kill germs, food vessels are sometimes silver plated. A more romantic manifestation is the historical trivia that Alexander the Great drank only from his silver helmet while on the march. Silver is easily dissolved in nitric acid and is attacked by the alkaline cyanides.

Because pure silver is too soft for most applications, it is almost always used in alloyed form. Tradition and centuries of experimentation have determined that the most suitable alloys contain an addition of 7.5% to 20% copper. Zinc and cadmium are added to create solders.

#### MERCURY

Mercury has also been known since ancient times. It is unlike any other metal in that it is fluid and gives off poisonous fumes at normal temperatures and must therefore be stored in a sealed container. Because mercury expands proportionally to temperature increases, it is used for thermometers. It is silvery-white and highly reflective; because of the high surface tension it rolls upon a solid surface as droplets. In the solid state, mercury is soft and ductile. It is easily dissolved in nitric acid and in aqua regia.

Historically mercury was known as quicksilver, quick as in "living." It forms amalgams with gold and silver and in this form it was important to the process of fire gilding. Though the process is not widely used today, in the past base metals were "quicked" with mercuric nitrate solution to reduce the electrochemical potential difference for subsequent electroplating.

#### COPPER

Copper, the only metal with a reddish color, was probably the first metal used by humankind. Copper can be easily polished, but gradually tarnishes in air. The first layer to form is a red oxide layer, followed by a black layer, created by the action of sulfur contained in air, and finally ending in the creation of a green patina caused by various sulfates and salts. Copper is soluble in nitric and hydrochloric acids and forms poisonous copper acetate with acetic acid. Only silver is a better conductor of heat and electricity than copper. The high melting point of copper makes it difficult to melt with a traditional natural gas flame. Copper is seldom used for jewelry but is often used for hollowware. It has great importance as an addition metal for precious metal alloys, for instance in sterling silver and karat golds.

#### TIN

Tin has a silver-white color and a high shine. It is very stable in air, but when heated it burns to form tin oxide, a white powder also known as "tin ash." It is attacked by acids. Tin is subject to a rather rare phenomenon called tin pest, which can cause old tin

objects to disintegrate. The reason for this is still unexplained but is probably related to structural changes of the tetragonal  $\beta$ -tin and the cubic-tin that occurs below 180°C. Tin is very ductile, has a low tensile strength and melts at a low temperature.

The combination of tin with copper forms bronze, a metal so important it gave its name to an entire prehistoric epoch. Tin is alloyed with lead to make soft solders that are used in plumbing, electronics and several craft applications. Small amounts of tin can be absorbed in precious metal alloys, but larger tin contents cause brittleness.

#### LEAD

Lead, also known since ancient times, has a bluish-white color. It quickly forms dull gray insoluble coatings in air, water, sulfuric and nitric acids, but can be dissolved by hydrochloric acid. Lead is very soft and can be easily cut with a knife; its density lies significantly over the values of most other familiar metals.

Lead is contained in tin solders as an addition metal, and effects the lowering of the melting zone in niello. Small traces of lead can cause such brittleness in precious metals that they are rendered unusable. Because traces of lead stuck to precious metal alloys “eat” holes into them if heated to soldering temperatures, it is critical that even minute amounts of lead be removed from gold or silver alloys before they are heated. This is achieved first by scraping off as much as possible. If the metal is resistant to nitric acid, for example gold alloys over 18k (Au 750), the piece is boiled in a solution of 20% nitric acid. Gold alloys under 18k and silver-copper alloys such as sterling are treated in the following solution at a temperature of 60°C.

1 part 30% hydrogen peroxide ( $H_2O_2$ )  
5 parts 20% acetic acid ( $CH_3-COOH$ )

#### ZINC

When zinc was first isolated in the 16th century, its primary use was as an addition to copper to make brass. Its bluish-white color does not last long because in air it is covered by a dull gray oxide. When heated

in air, zinc forms a white powder called zinc oxide. Zinc is readily soluble in hydrochloric acid and is attacked by sodium hydroxide and liquid ammonia.

Zinc has a noticeably high coefficient of expansion. At normal temperatures zinc is fairly brittle. Between 100°C - 150°C zinc can be plastically deformed, but at temperatures over 200°C it becomes so brittle it can be easily pulverized. Zinc is added to precious metal alloys to lower their melting points and to improve castability. In brass alloys, a greater proportion of zinc increases tensile strength and lightens the color of the metal.

#### CADMIUM

Cadmium, which was first discovered in 1817, has a silvery-white color but develops a dense gray oxide film in air and for this reason polish and luster do not last. It is similar in its chemical characteristics to zinc, but its combustion product, cadmium oxide, has a brown color in contrast to the white zinc oxide. Cadmium is soft and ductile.

Cadmium is used industrially as a corrosion-prevention coating for iron and steel. In colored gold alloys it improves the color of green gold. Cadmium can be used to lower the melting point of precious metal solders, but this is not recommended because of the serious health risk involved. Breathing fumes from melting cadmium can cause damage to the brain, nervous system, lungs and kidneys.

#### ALUMINUM

Aluminum was isolated in pure form in 1825, but it was not until the development of electric furnaces that mass production of aluminum became possible. Aluminum is silvery white, polishes well, and is air and water resistant because of an invisible, dense oxide layer that forms naturally. Aluminum dissolves easily in hydrochloric acid and sodium hydroxide. After silver and copper, it is the third most conductive metal of heat and electricity. It is sufficiently ductile to allow the creation of leaf; the foil version can be found in most kitchens. When a colored product is desired, the natural oxide layer is electrolytically thickened by anodizing to create a tough porous surface that can be dyed and sealed. This process not

only opens the surface for coloring but also renders it more wear-resistant and nonconductive.

#### TITANIUM

Titanium, first isolated in 1825, has a flat gray color similar to steel. It takes a good polish and is resistant to air and water but has a high affinity for oxygen, hydrogen and nitrogen. The best means of dissolving it is in hydrofluoric acid, but titanium is also attacked by diluted hot hydrochloric acid; in nitric acid it covers itself with insoluble titanic acid,  $\text{TiO}_2 \cdot \text{H}_2\text{O}$ . In a very pure state it may be cold worked; otherwise it must be worked red hot.

Titanium is distinguished by an interesting combination of its metallic characteristics: high melting temperature and great tensile strength with relatively low density. In other words, it's tough and light, and has therefore found many applications in aircraft and rocket technology.

Titanium is used for jewelry because of the lovely effects that are produced by the clearly developed interference colors that can be achieved by exposing the metal to specific voltages of electricity. Another method, metal vapor deposition with titanium nitride and titanium carbide, is becoming more important. In the jewelry industry this interest is spurred by the gold or black coatings and the resistance to abrasion that can be developed.

#### *Working titanium*

Because titanium behaves somewhat differently than the standard metals in the goldsmith's workshop some special attention to its working is in order here. When sawing, begin the cut with a very light stroke, and increase the pressure only when the blade has securely caught. The sawblade can be protected with a lubricating grease, but even with this precaution it will dull quickly. Titanium can be worked with standard files, but a light pressure is recommended. The file has a tendency to clog, loading itself with particles of titanium that will "smear" the workpiece. Because of this, the file must be cleaned frequently. When drilling, use sharp bits and a lubricant. You will notice that even quality bits will dull after a few holes are made. If a drill bit is broken off in the metal,

it can be etched out with nitric acid. When using a rotating bur, cool the action with oil and work at a slow rotational speed (RPM). Titanium responds well to diamond and ceramic abrasive points.

Titanium can be plastically deformed, but it must be annealed often because it becomes hard quickly. When rolling, considerable pressure is required. To draw wire, anneal it first; the lubricant sticks better to the oxide layer. Instead of the usual drawing wax, oil or soap are recommended as lubricants. The metal toughens quickly so you can expect to anneal after about three passes through the drawplate. It's possible to hot forge titanium at temperatures between  $650^{\circ}$ – $950^{\circ}\text{C}$ , but the metal can also be worked cold. You will find that it is more amenable to stretching than compressing. Titanium cannot be soldered with either soft or hard solders; welding can only be done under a protective gas. SAFETY NOTE: there is a hazard of spontaneous combustion when titanium is heated at its surface, as for instance, when turning a sample on a lathe.

Because of the difficulty of welding, titanium is frequently joined with mechanical methods such as riveting or setting. Relatively low-cost spot welders (one brand is called Sparkie®) have made heat joins possible, particularly for attaching findings. It is generally impractical for the goldsmith to create a seam in the conventional sense. Titanium can be glued like any other metal if the connecting surface is large enough.

Titanium has established itself as a jewelry metal because of the beautiful colors that can be predictably achieved. When the metal is heated it shows the same colors associated with the tempering of steel, plus a few others. Unlike the fleeting effects on steel however, titanium colors are completely stable. When created by heat they are difficult to locate, but when the colors are achieved through the use of electricity, both the location and color can be precisely controlled.

The color phenomenon is caused by the development of an oxide layer, in which a certain part of the light is absorbed and only the remainder is reflected to be perceived by a viewer. As the temperature increases, the oxide layer becomes thicker and absorbs more light. There is a clear series of these

colors, beginning with a bright yellow, which has a thin oxide layer (meaning that only a small amount of light is absorbed) and running through green, violet, bright blues to a dark blue. At this point, all colors except blue are being absorbed by the oxide film. If heat is continued, a second yellow color will be created at about 320° C.

#### *Surface preparation*

As mentioned, titanium is a tough, wear-resistant metal. To clean the surface in preparation for coloring, it is first sanded with various grits of abrasive paper. Standard abrasive compounds cannot be used for polishing on the machine. The best shine seems to come with nickel oxide paste or with compounds intended for polishing steel.

To prepare the surface for color treatment, lightly etch the surface to create a matte texture. SAFETY NOTE: It is imperative to use great care when dealing with hydrofluoric acid. Because the skin will be attacked instantly upon exposure, rubber gloves and air-tight goggles are an absolute must.

#### METHOD 1

To prepare the surface, dip the object in a 2% hydrofluoric acid solution, then rinse it well in running water. A commercially available proprietary enamel or glass etching paste will also achieve the desired matte surface and, because of its consistency, it is safer. To prevent spotting while the piece is waiting to be colored, leave it submerged in a standard pickle such as Sparex®.

#### METHOD 2

While wearing rubber gloves, splashproof goggles, a rubber apron, and using extremely effective ventilation, combine these ingredients:

- 20 parts concentrated nitric acid
- 20 parts concentrated hydrofluoric acid
- 20 parts lactic acid
- 40 parts distilled water

Only a plastic container may be used, and care should

be taken that the environment is not too warm because hydrofluoric acid evaporates at 16°C (room temperature).

Dip the object into the solution with plastic tweezers, then immediately dip it, without rinsing, into concentrated nitric acid. To avoid grease spots, from this point on the titanium is no longer touched with the fingers.

#### *Coloring process*

A welding torch is particularly suited to achieving color effects on titanium because of its high temperature and focused flame. The torch can also be used to melt into the metal, throwing the surface up into relief, thickening the edges and generally developing organic textures like those associated with reticulation. The opportunity for contrasting smooth and textured areas offers immediate and intriguing design possibilities. Only generalized colors and effects can be created with a torch. Because titanium is a poor conductor of heat, colors crawl slowly and it is difficult to achieve a specific uniform color on a large surface.

Because of the exactly defined relationship between the applied current and the thickness of the oxide layer that is created, titanium coloring is most precise with a process called electrolytic anodizing. In this technique, household electrical current is passed through a rectifier to reduce its voltage. An anodizing unit with a voltmeter can then be used to control the specific amounts of electrical current that are relayed to the titanium. This current will create the growth of a layer of oxidation of a specific thickness, which in turn translates to the perception of a specific color.

SAFETY NOTE: All connections and contacts outside the bath must be well insulated because a dangerously high current is used. Always wear rubber gloves and, because hydrogen gas is emitted in the process, ensure sufficient ventilation.

The piece being colored is submerged in a bath to evenly conduct the electrical current. This bath is called the electrolyte, and may be made of a wide range of liquids. A 10% solution of sodium sulfide is used commercially, but solutions as disparate as

a weak liver of sulfur solution, sodium carbonate, ammonium sulfate, cyanide salt baths and Sparex® (sodium bisulfate) have also been used.

The workpiece is held with stainless steel clamps and attached to stainless steel cathodes with an insulated copper wire. Use a current density of 5 A/dm<sup>2</sup>. As the current in the bath increases, thicker layers of oxide are formed. These in turn create the various color tones:

- 16v - yellow
- 22v - dark blue
- 27v - bright blue
- 58v - violet
- 70v - bluish-green

To create several colors on the same piece, the plate is first treated with the lowest voltage. The area on which this color is to be retained is then covered up (insulated) and the piece is taken to the next voltage. It is also possible to proceed in the reverse manner: first the highest voltage is used, then this region is covered up and all the remaining color everywhere else is removed by sandblasting. A lower voltage is applied to the metallic surface and a thinner oxide layer is formed, creating another color. To make specific areas metallically blank (white) use resists with sandblasting or cover the colored areas and etch selectively with hydrofluoric acid.

#### *Special effects*

The fact that colors are considerably more pronounced on an etched surface opens the possibility for a special effect. If the unprepared metal is covered with a resist and a pattern is scraped away then etched, the exposed metal will take the color in a vibrant hue, which will contrast with a duller color in the adjacent area. Use hydrofluoric acid to achieve this, and again, only when proper safety precautions have been followed meticulously. Another interesting effect is created by leaving the resist in place while the metal is electrolytically colored. In this way it is possible to decorate the colored surface with a gray design.

#### IRON

Iron, known since ancient times, has a bluish-white

color, and can be polished to a reflective silvery surface. A characteristic indication of iron is its strong magnetism. Pure iron remains magnetic only temporarily, while carbon-containing iron (i.e. steel) retains magnetism permanently.

Iron rusts in moist air, and when heated forms a black layer of scale. It is more soluble in diluted acids than in concentrated solutions. Hardness and tensile strength of technically pure iron are similar to those of copper; chemically pure iron has even less strength. For these reasons it is very rare to find iron used in its pure form. Two examples are the iron cores of transformers and electromagnets.

Iron is the most widely used metallic material in the world, perhaps because of its alloying characteristics. Iron can absorb a wide variety of addition agents during the smelting process and responds well to a range of improvement agents. Such addition agents are silicon, manganese, chromium, molybdenum, vanadium, tungsten, cobalt and nickel. By far the most important additive to iron is carbon. Up to 6.67% carbon can be chemically bonded as iron carbide, Fe<sub>3</sub>C; the carbon can also be dissolved in the structure as graphite.

Further information about the iron alloys are given later in this chapter in section 1.8.

#### 1.6

#### **Behavior of Various Metals in Air and Water**

*Gold*, the most familiar precious metal, remains unchanged even when heated in air; in water it is just as passive.

*Platinum and platinum group metals* behave like gold in air and water. Platinum develops a blue-violet oxide film between 400°C (752°F) and 850°C (1562°F) which dissolves upon further heating.

*Silver* reacts in the solid state with oxygen, forming a coating of silver oxide (Ag<sub>2</sub>O) on the surface. Because this coating is only one molecule thick and therefore of no practical importance, we generally say that pure silver is resistant to oxygen in air. On the

other hand, when there is hydrogen sulfide ( $\text{H}_2\text{S}$ ) in the air, silver develops a dark coating of silver sulfide ( $\text{Ag}_2\text{S}$ ). Silver is usually unaffected by water.

*Mercury* remains unchanged in dry air. When heated to  $300^\circ\text{C}$  it forms mercuric oxide (II)  $\text{HgO}$ , but it dissolves again at temperatures over  $400^\circ\text{C}$ . Because mercury is fluid at room temperature, it is markedly volatile and gives off highly toxic mercury vapor. It must be stored in sealed containers. Mercury is passive in water.

*Copper* is fairly stable in water and dry air; generally it develops a film of red copper (I) oxide  $\text{Cu}_2\text{O}$  that can be easily mistaken for the color of the metal itself. A dark deposit of copper (II) sulfide  $\text{CuS}$  is formed through the action of hydrogen sulfide in the air. Upon heating, black copper (II) oxide  $\text{CuO}$  develops which, together with the copper (I) oxide  $\text{Cu}_2\text{O}$ , forms a brittle, flaking scale on copper. In moist air, copper develops a dense coating of green patina of various copper salts. In earlier times patina was formed of

basic copper (II) carbonate  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

In our present atmosphere, we are also likely to find

basic copper (II) chloride  $\text{CuCl}_2 \cdot 3 \text{Cu}(\text{OH})_2$

basic copper (II) sulfate  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2$

Under the influence of weathering, dirt and dust particles are also incorporated into the patina. This explains why a beautiful green patina might be found on the top of a church tower while a copper monument at the ground level develops a black-brown patina.

*Tin*, for all practical purposes, is not attacked by air and water. If it is burnt in a stream of air it produces a white powder, tin (IV) oxide  $\text{SnO}_2$  (also known as tin ash) that is difficult to dissolve.

*Lead* develops a grayish-blue protective film of lead

(I) oxide  $\text{PbO}$  quickly in air. This lead oxide also forms on the molten metal as so-called litharge (lead monoxide). In water, the metal will develop a thick coating of lead hydrogen carbonate  $\text{Pb}(\text{HCO}_3)_2$  and lead sulfate  $\text{PbSO}_4$ .

*Zinc* is barely attacked by pure water. In air it forms a gray protective layer of basic zinc carbonate  $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ . When heated, zinc combusts to form zinc oxide (zinc ash)  $\text{ZnO}$ , a white powder that burns with a greenish light.

*Cadmium* is similar in its behavior to zinc. It covers itself with an oxide film in air, and when heated it burns to form brown cadmium oxide,  $\text{CdO}$ .

*Aluminum* forms a thick protective film of aluminum oxide  $\text{Al}_2\text{O}_3$  that renders it resistant to air and water.

*Iron* remains as a rule unchanged in dry air. Through the combined effects of moisture and oxygen in the air or in air-containing water (i.e. in normal environmental conditions) iron decomposes to create the well known crusty reddish brown rust whose chemical composition changes according to the conditions of formation. It is described more or less by the formula  $x \text{FeO} \cdot y \text{Fe}_2\text{O}_3 \cdot z \text{H}_2\text{O}$ . The porous structure of this coating promotes the continuation of the process until the entire block has decomposed into rust. When heated, iron forms a brittle black layer of iron (II, III) oxide is formed. This is iron oxide,  $\text{Fe}_3\text{O}_4$  commonly called scale.

## 1.7

### Behavior of Various Metals in Acid

*Gold* is impervious to even strong acids, but can be etched in aqua regia, a mixture of 3 parts hydrochloric acid and 1 part nitric acid. In this solution the gold is dissolved and forms tetrachlorogold (III) acid  $\text{H}(\text{AuCl}_4)$ .

Metal	Acids and Their Salts							
	Nitric Acid HNO <sub>3</sub>		Hydrochloric Acid HCl		Sulfuric Acid H <sub>2</sub> SO <sub>4</sub>		Aqua Regia 3 vol.-parts HCl 1 vol.-part HNO <sub>3</sub>	
	salt	state	salt	state	salt	state	salt	state
Gold	-	-	-	-	-	-	H[AuCl <sub>4</sub> ]	-
Platinum	-	-	-	-	-	-	H <sub>2</sub> [PtCl <sub>6</sub> ]	h
Palladium	Pd(NO <sub>3</sub> ) <sub>2</sub>	h, c, v	-	-	PdSO <sub>4</sub>	c, k	H <sub>2</sub> [PdCl <sub>6</sub> ]	-
Silver	AgNO <sub>3</sub>	-	-	-	Ag <sub>2</sub> SO <sub>4</sub>	h	-	-
Mercury	Hg(NO <sub>3</sub> ) <sub>2</sub>	-	-	-	HgSO <sub>4</sub>	h, c	HgCl <sub>2</sub>	-
Copper	Cu(NO <sub>3</sub> ) <sub>2</sub>	-	-	-	CuSO <sub>4</sub>	h, c	-	-
Tin	H <sub>2</sub> SnO <sub>3</sub>	-	SnCl <sub>2</sub>	-	-	-	-	-
Lead	Pb(NO <sub>3</sub> ) <sub>2</sub>	v	-	-	PbSO <sub>4</sub>	v	-	-
Zinc	-	-	ZnCl <sub>2</sub>	v	ZnSO <sub>4</sub>	v	-	-
Cadmium	Cd(NO <sub>3</sub> ) <sub>2</sub>	-	CdCl <sub>2</sub>	-	CdSO <sub>4</sub>	-	-	-
Aluminum	Al(NO <sub>3</sub> ) <sub>3</sub>	h	AlCl <sub>3</sub>	-	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-	-	-
Iron	Fe(NO <sub>3</sub> ) <sub>3</sub>	h,v	FeCl <sub>2</sub>	v	FeSO <sub>4</sub>	-	-	-

Table 1.2

Solubility in acid of the metals. Codes refer to solubility only in h = hot acid, c = concentrated acid, k = boiling acid, v = dilute acid.

*Platinum* is resistant to acids, but like gold it can be dissolved in aqua regia. In a hot mixture of acids, platinum dissolves to form hexachloroplatinic (IV) acid H<sub>2</sub>PtCl<sub>6</sub>.

*Palladium* dissolves well in aqua regia, forming hexachloropalladium (IV) acid H<sub>2</sub>PdCl<sub>6</sub>, which decomposes by evaporation to form palladium (II) chloride PdCl<sub>2</sub>.

*Mercury* is easily dissolved in diluted nitric acid to form mercuric (II) nitrate Hg(NO<sub>3</sub>)<sub>2</sub> and in hot concentrated sulfuric acid to form mercuric (II) sulfate HgSO<sub>4</sub>. It is insoluble in hydrochloric acid but is easily dissolved in aqua regia to form mercuric (II) chloride HgCl<sub>2</sub>.

*Silver* is resistant to non-oxidizing acids such as hydrochloric and organic acids. It will dissolve in concentrated sulfuric acid to form silver sulfate Ag<sub>2</sub>SO<sub>4</sub>. Nitric acid is highly corrosive to silver (silver nitrate AgNO<sub>3</sub>). Because of the resistance of gold to nitric acid, the two metals can be separated from each

other with this “refining water.”

*Copper* is not attacked by hydrochloric acid, but in nitric acid it is dissolved to form copper (II) nitrate Cu(NO<sub>3</sub>)<sub>2</sub> accompanied by the formation of poisonous nitrous gases. In hot concentrated sulfuric acid, copper dissolves to form copper (II) sulfate CuSO<sub>4</sub>. In acetic acid, copper forms verdigris, a mixture of copper acetates, such as Cu(CH<sub>3</sub>COO)<sub>2</sub> · H<sub>2</sub>O and Cu(CH<sub>3</sub>COO)<sub>2</sub> · 5H<sub>2</sub>O.

*Tin* is transformed only slowly to tin (II) chloride SnCl<sub>2</sub> with hydrochloric acid; in sulfuric acid the transformation product is tin (II) sulfate SnSO<sub>4</sub>. In boiling nitric acid, tin is oxidized to an insoluble white powder called stannous acid, H<sub>2</sub>SnO<sub>3</sub>.

*Lead* dissolves in diluted nitric acid to form lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>. It is dissolved only slowly by diluted sulfuric acid, where it forms lead sulfate, PbSO<sub>4</sub>. In hydrochloric acid only the lead (II) oxide PbO is attacked and transformed to lead (II) chloride, PbCl<sub>2</sub>, which forms the highly toxic lead (II)

acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

*Zinc* dissolves easily in diluted hydrochloric acid to form zinc chloride,  $\text{ZnCl}_2$ . In diluted sulfuric acid it forms zinc sulfate,  $\text{ZnSO}_4$ .

*Cadmium* is easily dissolved in nitric acid to form  $\text{Cd}(\text{NO}_3)_2$ , but it is only slowly dissolved in sulfuric acid to form cadmium sulfate,  $\text{CdSO}_4$ . In hydrochloric acid it is transformed into  $\text{CdCl}_2$ .

*Aluminum* forms aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$  in sulfuric acid; in hydrochloric acid it forms aluminum chloride,  $\text{AlCl}_3$  and in hot nitric acid it forms aluminum nitrate,  $\text{Al}(\text{NO}_3)_3$ .

*Iron* forms passive protective coatings in concentrated acids, but is easily soluble in diluted acids; in hydrochloric acid, iron forms iron chloride (II)  $\text{FeCl}_2$ . Iron in sulfuric acid will form iron (II) sulfate,  $\text{FeSO}_4$  and in hot diluted nitric acid the transformation product is iron (III) nitrate,  $\text{Fe}(\text{NO}_3)_3$ .

### 1.8

#### Hardness of Various Metals

The science of materials testing creates quantifiable values for properties that determine the appropriateness of a metal to a specific task. The results of hardness and tensile strength testing are particularly useful because they offer comparisons between plastic deformability and the quality of the material when in use.

Hardness is generally understood as the resistance of a body to the pressure of another harder body that is pushed into it. In the Brinell DIN 50351 system, for instance, a hardened steel ball of diameter  $D$  is pressed into a test piece with a known pressure,  $F$ . The force continually climbs within 15 seconds and then is stabilized for 30 seconds at the maximum value. The result of this is an impression (or dimple) that has a measurable diameter,  $d$  (figures 1.8 and 1.9).

The size of the testing force is compared with the

impression surface that is formed in the material. Note that it is not the depth that is measured but the diameter of the hemispherical depression. This yields the following formula:

$F$  – testing force in N \*

$D$  – diameter of ball in mm

$d$  – hemispherical depression diameter in mm

Bhn – Brinell hardness number

\* Newton, a unit used to measure force.

To ensure the comparability of the measuring values, the impression size should be between .2 and .7 times the diameter of the sphere. In other words, if the material is so soft that a crater much larger than the sphere is created, the test results are no longer valid.

Precious and base metals are tested with a 5 mm ball. Two testing pressures are recommended:  $F = 2450\text{N}$  for harder materials and  $1225\text{N}$  for softer test pieces. (figure 1.10).

By comparing the Brinell values, we can see how individual alloys behave when a tool intrudes into the workpiece, such as is the case in chiseling, forging, pressing and so on.

A different but similar testing procedure is called the Vickers test DIN 50133, in which a pyramid-shaped point with a tip angle of angle of  $136^\circ$  is used as the testing body and the testing force is compared with that from the measurement of the diagonal surface impression:

$F$  – testing force in N

$d$  – diagonal of the impression in mm

VH – Vickers hardness unit

The usual testing force is 294 N with a load time of 10-15 seconds.

$$\text{Bhn} = \frac{\text{testing force}}{\text{impression surface area}} = \frac{0.102 \cdot 2F}{\pi D (D - \sqrt{D^2 - d^2})}$$



Figure 1.8  
Hardness testing machine. (Werkstoffprüfmaschinen, Leipzig)

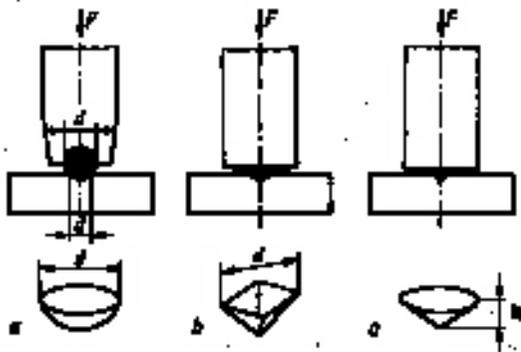


Figure 1.9  
Hardness testing procedures.  
a) Brinell hardness, b) Vickers hardness, c) Rockwell hardness.

The Vickers test is especially useful for thin or unusually hard surfaces, such as electrolytic coatings.

A third method, the Rockwell hardness test, uses as a testing body a steel ball with a diameter of  $\frac{1}{16}$ th of an inch, or a diamond cone with a point angle of  $120^\circ$ . A measurement of the depth of penetration is taken, and from this the Rockwell hardness is directly determined:  $1 \text{ RH} = 2 \mu\text{m}$ .

Because it is simple and quick, this method is particularly well-suited to testing in a production situation.

### 1.9 Tensile Strength of Various Metals

$$\text{HV} = \frac{\text{testing pressure}}{\text{surface impression}} = \frac{0.189 \text{ F}}{d^2}$$

Material to be used for making a setting must have as much ductility as possible so it can be pressed easily against a stone. Of course the hardness – the resistance to abrasion – can't be too low or the setting will wear away quickly. The material selected for a chain must have high tensile strength and considerable hardness to reduce wearing at the point where one link crosses another. At the same time, the links should be easy to bend while fabricating.

We could continue the list of examples in this manner. The results of tensile strength testing are helpful in clarifying the specific properties of materials. The values of hardness, ductility and tensile strength of the most important precious metal alloys are therefore plotted as curves and can be read from the diagrams.

If a metal has great tensile strength and a high elastic limit, it will be difficult to form the material permanently. Conversely (and positively in the case of jewelry) the piece will be difficult to bend out of shape or dent in use. If ductility is limited, the metal can only be stressed a little during rolling, drawing,

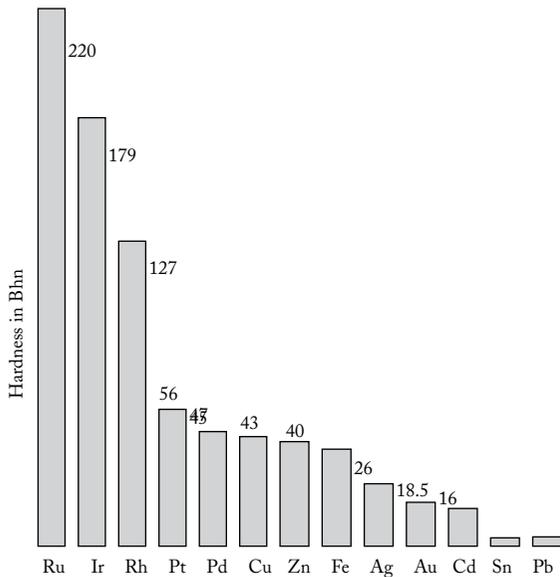


Figure 1.10

Brinell hardness of the most important metals.

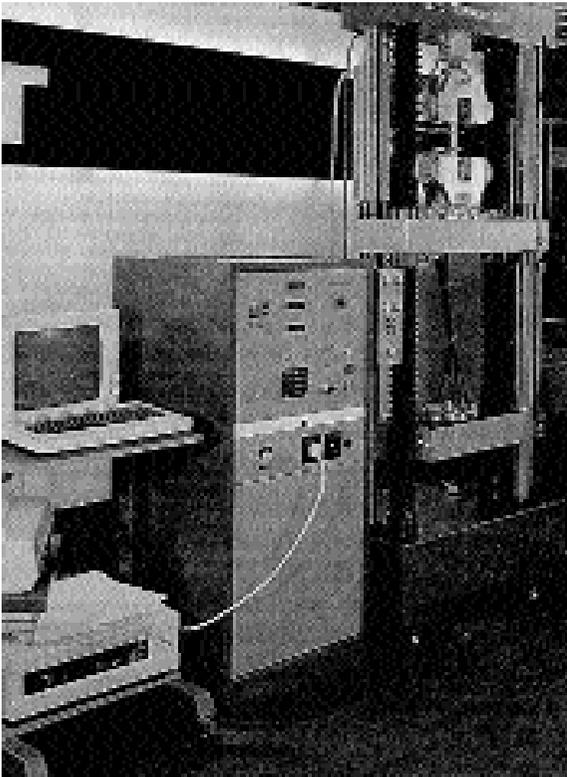


Figure 1.11

Universal testing machine TIRA test 2300 for draw, press and bending testing up to 100 kN testing load.

The starting cross section of the rod is inserted into an equation, along with the load used. From this, the important concept of tension or stress can be derived.

The ductility is ascertained from the relationship between the elongation and the original length of the rod.

#### *Stress-ductility diagram*

The elastic test proceeds with increasing stress and the diagram is usually drawn up by the machine itself (figure 1.14). The load first affects the elastic elongation of the test rod; both values are in this elastic zone of the plastic deformation and are proportional in the sense of Hooke's law and the curve climbs in a straight line. When the load is released, the elongation goes back to the initial values on the same straight line.

This is related to the fact that individual crystals (grains) oriented in the original direction are still permanently deformed; while the entire block is only elastically deformed.

If the load values exceed  $\sigma(0.01)$  the actual plastic deformation of the test rod begins. The transition from the elastic to the plastic portion of the curve in practice follows smoothly, therefore the stress  $\sigma(0.02)$  is taken as the practical yield point, which effects a 0.2% elongation, during the plastic deformation the elongation increases faster than the load; the curve then runs flatter than in the elastic zone.

If the load is removed after plastic deformation has occurred, the plastic elongation is retained when the stress is removed.

If for example  $\sigma_2$  is deloaded at a desired point; the curve does not fall vertically but instead returns to a line parallel to the straight line of the elastic deformation, so that at  $\epsilon_2$  the actual remaining elongation can be read off. If the elongation then is below the load  $\epsilon_1$  it goes back to  $\epsilon_2$  upon removal of the load.

If the same rod is then loaded again, the curve climbs on the straight line that it had descended on; that is from  $\epsilon_2$  to  $\sigma_2$ . This indicates that deformation of the elastic portion becomes even greater upon several repetitions.

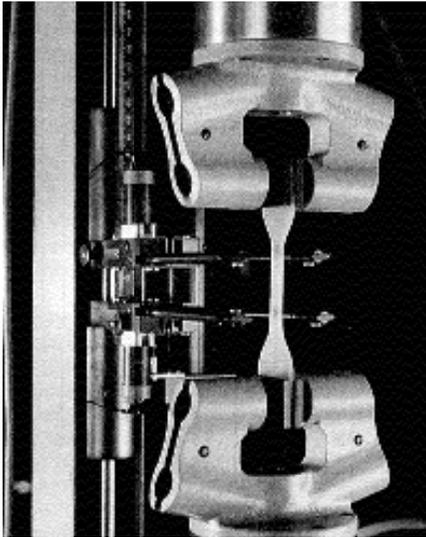


Figure 1.12  
Testing rod  
clamped in place  
on ductility  
measuring tool.

constructive calculations of strength, but it also gives a useful picture of the ability of a material to

$$\sigma = \frac{F}{A_0}$$

$\sigma$  – stress in N/mm<sup>2</sup> or MPa  
 $F$  – testing force in N  
 $A_0$  – initial cross section in mm<sup>2</sup>

withstand stress, shown as a comparative number; enlarged upon by the values of  $\delta$  (figure 1.15). In the precious and base metals there is an approximate relationship between tensile strength and Brinell hardness.

$$\sigma_B \approx 4 \dots 5 \text{ Bhn}$$

$$\varepsilon = \frac{\Delta L \cdot 100}{L_0}$$

$\varepsilon$  – ductility in %  
 $\Delta L$  – elongation in mm  
 $L_0$  – initial length in mm

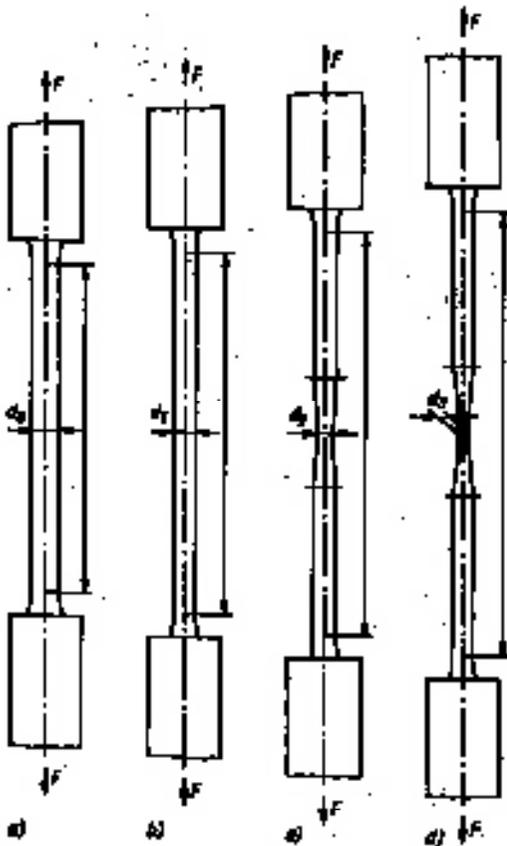


Figure 1.13  
Ductility of a test rod.  
a) original shape, b) uniform lengthening, c) the beginnings of necking-in, d) necking-in and fracture.

The following influences can alter the tensile strength.

- Tensile strength usually increases with alloy formation.
- In deformed metal the tensile strength climbs at first, but then sinks sharply with the increasing degree of deformation when the limit of ductility is reached.
- Fine-grained structures offer higher tensile strength than coarse-grained ones.
- Tensile strength decreases with increasing temperature.

#### 1.10

### The Effect of Heat on Various Metals

The heat of a material is determined by the disordered individual movement of the unit cells within it. The most important measure for this internal energy is the temperature of the metal. If an amount of heat energy is added to metal, the temperature increases

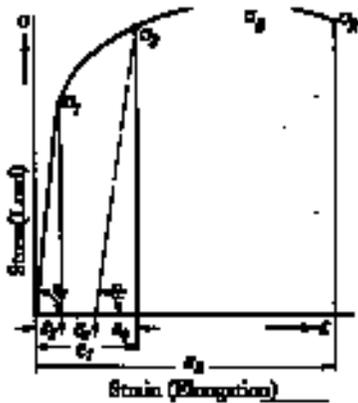


Figure 1.14  
Stress strain diagram.

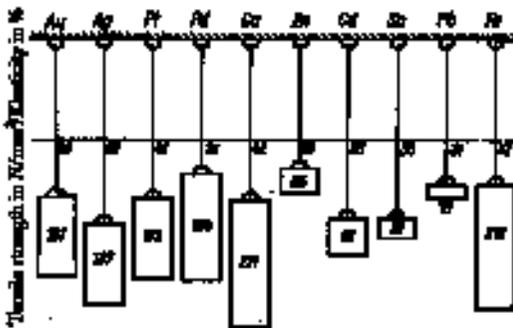


Figure 1.15  
Elasticity and tensile strength of the most important metals.

and the energy of the disordered movement of the atoms increases.

Increased movement causes thermal expansion in metals – as a metal heats up, it increases in size. The heat energy that is added to a metal is transferred from hotter to cooler regions because of the metal’s heat conductivity, until a state of balance is achieved in the entire piece of metal.

Temperature is measured in °C; when the temperature changes the difference is expressed in K. For example, if a metal is heated from 10°C to 650°C when annealing, the difference is 640K. To determine the amount of heat required to raise the temperature of a sample a specific amount, use this formula.

$$Q = m \cdot c \cdot \Delta t$$

$Q$  - amount of heat in kJ  
 $m$  - mass in kg

$c$  - specific heat in kJ/(kg · K)

$\Delta t$  - temperature change in K

*Example*

What amount of heat is necessary to heat 25 grams of gold from 20°C to 1063°C?

$$Q_1 = 0.025 \text{ kg} \cdot 0.1310 \text{ kJ}/(\text{kg} \cdot \text{K}) \cdot 1043 \text{ K} = 3.42 \text{ kJ}$$

In order to liquefy the metal sample after reaching the melting temperature, (that is to dissolve the cohesion of the lattice structure), the additional energy of the melting heat is required. To continue with the previous example:

$$\sigma_B = \frac{F_{\max}}{A_0} \quad Q_2 = m \cdot q = \delta = \frac{L_B - L_0}{L_0} \cdot 100$$

$$0.025 \text{ kg} \cdot 67 \text{ kJ/kg} = 1.68 \text{ kJ}$$

$$\text{kJ/kg} = 1.68 \text{ kJ}$$

$q$  - specific melting heat in kJ/kg

According to this calculation, to heat 25 grams of gold from room temperature to its melting point and then to liquefy it, it is necessary to have:

$$Q_1 = 3.42 \text{ kJ}$$

$$Q_2 = 1.68 \text{ kJ}$$

$$Q_{\text{total}} = 5.10 \text{ kJ}$$

The heat required for melting is transferred to the metal from a torch or the elements of a kiln. Because it is impossible to direct all of this heat exclusively into the metal sample, a great part of the heat energy is inevitably lost. In practice this means that soldering surfaces, crucibles and the space around the operation is heated up along with the object. This means that more heat must be used to raise the temperature of the metal than is calculated in the formula.

The comparative values assembled in figure 1.16 give a good opportunity for comparison and show that significant differences can exist between metals. For example, melting copper requires about

three times as much heat as is needed to melt gold, though both metals have almost the same melting temperature.

*Heat expansion*

All metals expand in all directions uniformly when heated, and shrink upon cooling. Because this phenomenon is particularly evident with wires and rods, measuring systems use linear expansion to describe the effect. The length-temperature coefficient is used to express how much a rod of 1 meter lengthens if it is heated by 1K. The measured values are assembled for comparison in figure 1.17.

If we were to heat identical rods of zinc and platinum, and carefully measure their size, we would find that expansion in the zinc rod is more than three times that of the platinum rod. The remarkably low thermal expansion of platinum that this reveals can be useful information. For instance if you were to clad normal colored gold with white gold or platinum, the gold alloy will be elongated during soldering, while the thin sheet of platinum will remain almost unchanged. After both metals have been soldered together, the normal contraction of the colored gold will be prevented by the stability of the platinum, resulting in a warped object. A similar problem can occur when a silver object is bound with steel or iron binding wire. The binding wire indents the object during soldering and will distort the shape because the steel wire expands far less than the silver.

The thermal expansion of glass is minimal ( $\alpha = 8.6 \cdot 10^{-6} \text{ m}/(\text{m} \cdot \text{K})$ ), as with platinum, so it is necessary to mix additional materials with enamel to raise its thermal expansion. By increasing the rate of expansion the enamel is better able to fuse with metals that are similarly expanded.

*Heat conductivity*

As shown in figure 1.18, the ability of a material to conduct heat is compared with the help of the coefficient of heat conductivity in  $\text{W}/(\text{m} \cdot \text{K})$ .

Any goldsmith who has used bare hands to hold a silver wire while drawing a bead has been convinced of the high heat conductivity of silver. If equal lengths

of silver and platinum wire are tested, you will find that the silver wire conducts six times as much heat as the platinum. Or to say it another way, to conduct equal amounts of heat, the silver wire would have to be 6 times as long as the platinum.

If a ring with a stone sensitive to heat has to be repaired, soldering must be so rapid that the stone can't heat up. Though such a soldering might be possible on a gold or platinum ring, it might prove impossible on an identical silver ring. So much heat will be conducted away that the joint is slow to reach soldering temperature. The ring as a whole will heat up to the point where the stone is threatened.

**I.II  
Reflectivity of Various Metals**

All metals are understood to be opaque bodies that absorb a portion of the light that falls on their surface and reflect the rest. This is what determines their individual color, luster and brightness. The portion of the rays of various wavelengths that is reflected from various precious metals is diagrammed in figure 1.19. This chart assumes that the light falling on them is 100% of the visible spectrum.

Gold, the only colored precious metal, reflects less

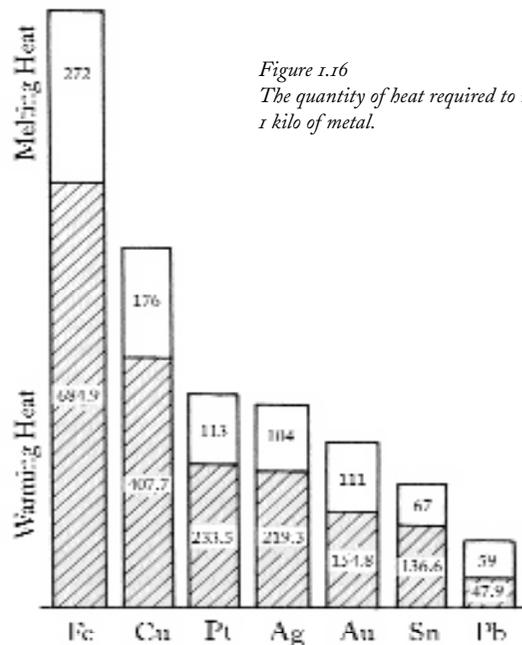


Figure 1.16  
The quantity of heat required to melt 1 kilo of metal.

a silver object that has been patinated with liver of sulfur.

Sometimes a silver object is plated with rhodium to protect it from tarnishing. In this case the transient but high reflectivity of silver is replaced by the somewhat lower but more stable reflectivity of rhodium.

### 1.12 Precious Metal Alloys

A mixture of two or more metals is called an alloy. These are usually made by melting together the component ingredients, but alloys can occur in exceptional circumstances through diffusion of solid, fluid or gaseous materials. These mixtures themselves in turn possess metallic characteristics.

Through careful selection of alloying components, characteristics of a pure metal can be significantly influenced and entirely new characteristics created. In the case of precious metals, the desire for creating new characteristics is combined with the intention of lowering their cost.

#### 1.12.1 SOLUBILITY OF METALS

The following possibilities can occur when melting metals together.

##### *Full insolubility*

If there is no mutual solubility of the components in the fluid state, the metals form distinct boundary layers in the melt. These will lie upon each other according to their density. In this case the component metals would separate out from each other in the mold when cast. As you might guess, in this situation there is no possibility of making a usable alloy.

##### *Complete solubility*

This term describes the situation created when metals form a homogeneous melt in all desired mixture proportions, in which the initial materials can no longer be differentiated from each other. This case is by far the most common and the most important.

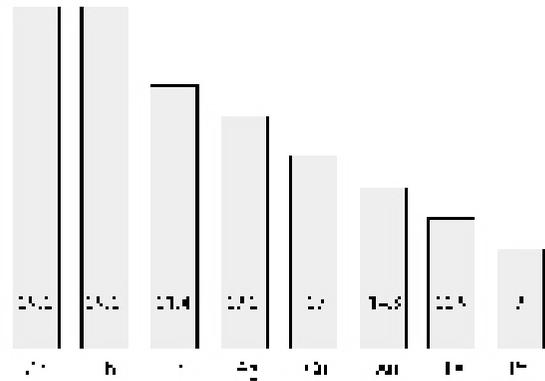


Figure 1.17  
Heat expansion of the most important metals.

homogeneous single phase melt is formed, in which

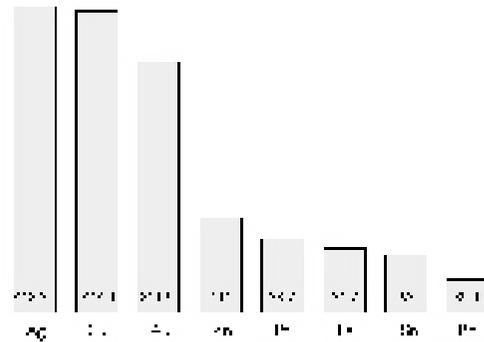


Figure 1.18  
Heat conductivity of the most important metals.

lization of the homogeneous melt (figure 1.20).

##### *Homogeneous mixed crystals*

If the component metals form the same lattice structure and have about the same atomic sizes, full solubility can be retained even in the solid state. The crystal lattice is formed by the atoms of the component metals together; in all grains the alloy metals are distributed in the same proportion as in the entire alloy. The micrograph of an alloy of Au-Ag or Au-Cu is similar to that of a pure metal.

##### *Heterogeneous mixed crystals*

If the components are different in their structural composition, the components separate out during

the solidification process and each lattice structure is only formed of one kind of atom. Individual grains will always consist of only one of the metals involved. This type of absolute insolubility in the solid state occurs only seldom in practice.

#### *Limited mixed crystal formation*

Although the components form a completely homogeneous melt in the fluid state, mixed crystals form during solidification in which one metal predominates. The crystal lattice of this metal incorporates a small number of the atoms of the other metals. The various kinds of grains may be easily seen on the micrograph. This type of alloy occurs fairly often and has great importance for goldsmiths. The Ag-Cu system is an example of this kind of alloy, and illustrates that characteristics of the alloy are significantly different from the pure metals.

#### *Intermetallic compounds (metallides)*

The atoms of the involved metals in the crystal lattice are incorporated in fixed proportional amounts, which are expressed with the aid of chemical symbols. Although these expressions, such as AuCu, Au<sub>2</sub>Cu<sub>3</sub> appear to be chemical molecule formulas, they are used only to express the proportion of amounts within metallic compounds. In a fixed proportion, the atoms of the lattice structure can be ordered in regular sequence so that, for example, the atoms of one metal occupy the cube's corners while the atoms of the other occupy the central positions.

Very complicated lattice structures can be formed which are significantly different from the pure metals, and whose components may be in such proportions as Cu<sub>5</sub>Zn<sub>8</sub>, and Cu<sub>31</sub>Sn<sub>8</sub>.

All metallides are hard and brittle and are barely or not at all plastically deformable.

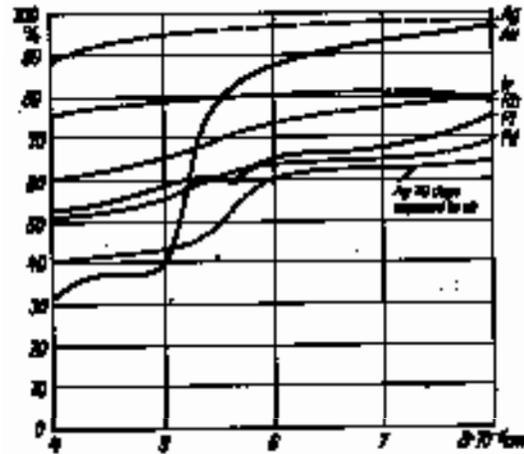


Figure 1.19  
Reflectivity of the most important precious metals in the region of visible light.

extremely useful in understanding important fundamentals of metallurgy. The gold-silver (Au-Ag) diagram has a particularly simple curve, which makes it a good example with which to explain the principles of a phase diagram (figure 1.21).

In the coordinate system (or grid), temperatures are given on the vertical axis of the diagram in °C and the alloy concentrations are listed in parts per thousand on the horizontal axis. Specific transformation temperatures are empirically determined for various alloys of the system being defined, and then entered into the diagram and connected to each other by a line. Tests are made in a laboratory, and the resulting temperatures are entered into the grid.

In the case of pure metals the change of the state (passing from solid to liquid) occurs at a single temperature. With alloys there is an interval between the beginning and end of the solidification, designated as the liquidus and solidus temperatures.

The liquidus curve defines the limit of the fluid and the solidus curve that of the solid state of the alloy; between both curves is the transition state; the slushy state, in which the melt and mixed crystals (the fluid and the solid phase) exist simultaneously. In the phase diagram the metals in Zone I are molten, Zone II designates the semi-solid transition state, and in

Zone III the alloy consists of solid mixed crystals.

The diagram is useful for understanding the process of solidification as well as for that of melting. The diagram illustrates:

- at what temperature a particular alloy solidifies
- the temperature necessary in order to liquefy it
- how it can be annealed
- whether it should be quenched

Following are some examples of information read from this.

1000 AU (0 AG)

In fine (pure) gold, the transition from solid to fluid occurs at  $1063^{\circ}\text{C}$ . At this temperature the metal stays in the slushy state only as long as is necessary to complete the transition from solid to fluid.

AU 900 (AG 100)

The diagram shows that this alloy of 10% silver displays an interval between the first sign of fluidness and the last bit of solid mass. The melting point has widened to a temperature interval, with a slushy transition state that lies between the solidus and liquidus values. At about  $1058^{\circ}\text{C}$  ( $1936^{\circ}\text{F}$ ) the first mixed crystals begin to precipitate out (the liquidus point). The mixed crystal formation is completed at  $1048^{\circ}\text{C}$  ( $1918^{\circ}\text{F}$ ), which is the solidus point.

AU 500 (AG 500)

In this alloy, in which both metals are mixed in equal proportions, the interval between the liquidus point of  $1020^{\circ}\text{C}$  ( $1868^{\circ}\text{F}$ ) and the solidus point of  $1000^{\circ}\text{C}$  ( $1832^{\circ}\text{F}$ ) is even greater.

AU 250 (AG 750)

With increasing silver content, the difference between the liquidus and solidus points is again reduced ( $988\text{--}975^{\circ}\text{C}$ ) ( $1810\text{--}1787^{\circ}\text{F}$ ).

AU 0 (AG 1000)

At the extreme right hand margin, the diagram indi-

cates that fine silver has a constant transformation temperature of  $961^{\circ}\text{C}$ , which is to say that it passes from a solid to a liquid without going through a slushy condition. As the phase diagram shows, all the possible liquidus points of the system lie on an arched convex curve while the solidus points form a curve that is arched toward the opposite, lower side. Both curves meet at the melting points of the original pure metals. Such a curve is typical for the formation of a homogeneous mixed crystal.

#### CHARACTERISTICS AND SIGNIFICANCE

Figure 1.21 graphs all the possible liquidus and solidus points between the melting points of pure gold and pure silver. The color changes with increasing silver content from the yellow of fine gold over to greenish and then to the white of silver. An especially clear green color develops between Au 600 and Au 700. The most intensive green-gold color is achieved with a 50% atomic proportion of Au and Ag, which occurs at Au 646.

Only those alloys whose gold content is somewhat under Au 523 can be destroyed by nitric acid. Alloys with a higher gold content are hardly attacked at all. They can be dissolved in aqua regia if the gold content is over Au 750, and the silver content is less than 25%. Alloys with a higher silver content become cloaked with an insoluble protective layer of silver chloride,  $\text{AgCl}$ , which prevents further attack. The tarnishing boundary lies at Au 377. Alloys with lower gold contents are blackened by sulfur and ammonia compounds contained in the atmosphere.

Alloys containing only gold and silver are rarely used in jewelry; there is usually some copper added. Even green gold, which contains little or no copper, contains other metals. The Au-Ag alloys are important as a boundary system of the ternary alloy Au-Ag-Cu, which will be described later.

#### *Au-Cu system*

The gold-copper system is similar to the gold-silver system just described in that it is made up of a homogeneous mix of two pure metals. The liquidus and solidus temperatures of all possible alloys lie under