

# The Aluminum (Al) - Copper (Cu) System

## What is It?

Advanced

Aluminum - copper alloys are just one member of the large aluminum alloy family. Or should that be aluminium - alloy? You may not be aware of the fact that different versions of the name for the [chemical element](#) 13 with the symbol Al exist: It's **aluminum** in the USA and **aluminium** in the rest of the world. [Why?](#)

Anyway, aluminum is probably the second most important metal after iron / steel. It comes in many modifications; here is a very superficial survey:

Major Aluminum Alloys		
Alloy / Metal	Typ. Comp. (wt%)	Properties / Typical Uses
Pure Al 1000 series	> 99 Al	Weak, very ductile, good conductor. Power transmission lines, "aluminum foil", capacitor electrode.
Cu alloyed 2000 series	4% Cu (+ Mg, Si, Mn, ...)	Strong, age-hardening. Aircraft skin, spars, forging, rivets.
Mn alloys 3000 series	1% Mn	Moderate strength, ductile, excellent corrosion resistance. Roofing sheet, cooking pans.
Mg alloys 5000 series	3 % Mg + 0.5 Mn	Strong, work-hardening, weldable. Pressur vessel, ship parts, beverage cans.
Mg+Si alloys 6000 series	0.5% Mg, 0.5% Si	Moderate strength, age-hardening, good for extrusion and anodisation. Window frames.
Zn+Mn alloys 7000 series	6% Zn + Mg (+Cu, Mg, ..)	Strong, age hardening, aircraft forging, spars, railway carriage.
Li	3% Li	Good strength, low density. Aircraft skins, spars

Source: [M. Ahsby's and D. Jones' invaluable book](#)

Age hardening is just another name for [precipitation hardening](#), work hardening is just another name for [strain hardening](#).

The [case study in the backbone](#) thus covers only a tiny bit of Al alloy science and technology. But its insights can be generalized to some extent to all alloys where age hardening is possible and important.

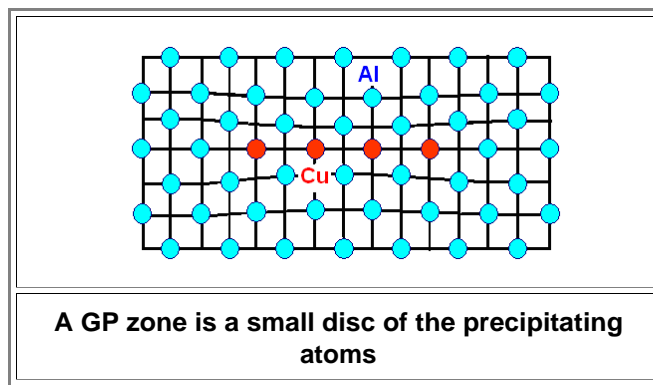
What I'm going to do here is to dig a bit deeper into the matter, showing how the theory behind what is happening is extremely helpful and saves a lot of work.

Most everything is based on the source given above.

## Formation of the precipitates

First, we quench the Al-4%Cu alloy from a solid solution to room temperature sufficiently fast to freeze in the 4 % solid solution. We will see below how "sufficiently fast" can be quantified by theory.

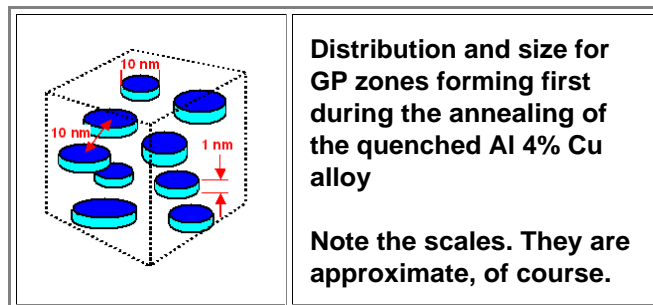
As a consequence, we have a large supersaturation of Cu at room temperature. The equilibrium mixture, according to the [phase diagram](#), would be 93 %  $\alpha$  + 7 %  $\text{CuAl}_2$ , and the  $\alpha$  phase contains at most 0.1 % Cu. The quenched solution thus contains 40 times more dissolved Cu than required for equilibrium. There is thus a large driving force for precipitation, and [nucleation](#) starts quickly, homogeneously, and in many places. The very first steps must be to get 2,3, 4, ... Cu atoms together in about the same place. Since you cannot produce a proper  $\text{CuAl}_2$  precipitate with just a few Cu atoms, the first precipitate formed under the circumstances is something special, called a **Gunnier-Preston zone**, always abbreviated as **GP zone**. This is what it looks like:



- We substituted some Al atoms in a small disc (max. diameters around 10 nm or so) by Cu atoms. The lattice then is somewhat distorted as shown, but the GP zone or precipitate is what we call fully **coherent** with the lattice, i.e. meshing perfectly at the "seams" or the interface. The **coherency strain**, needed to keep the fit to the Al lattice, is what obstructs the dislocation movement.

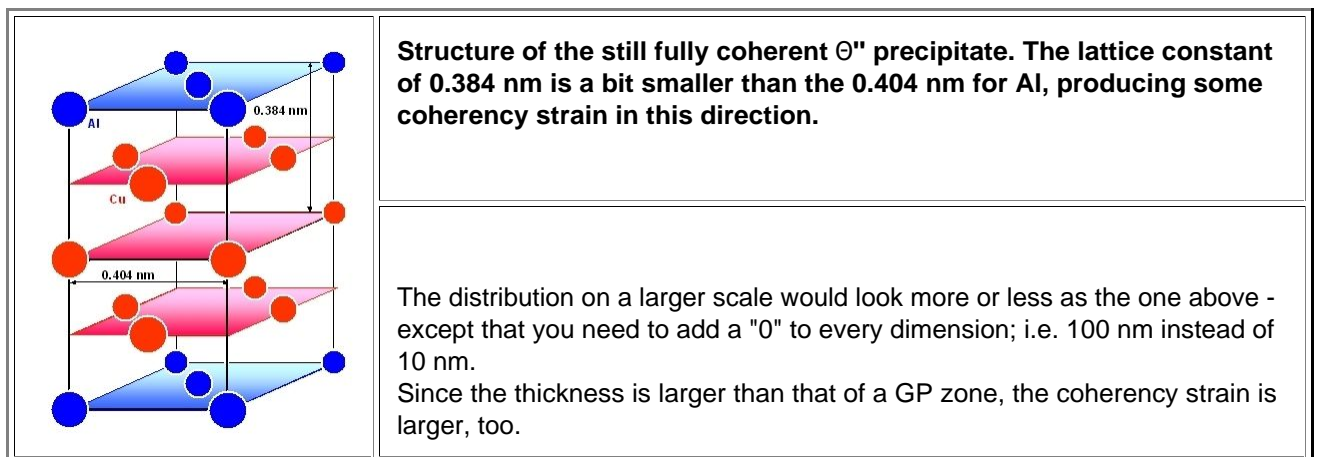
The formation of GP zones simply happens when Cu atoms meet accidentally while diffusing around. They settle down and become immobile as soon as there are enough (2 might already be sufficient) and form a disc as lowest energy configuration by slight rearrangements of some of the atoms.

On a larger scale the arrangement it looks like this:



- Growth is only possible in one dimension. The strain, and thus also the strain energy, increase with the circumference or square root of the diameter. This limits growth and thus also the removal of supersaturated Cu. Eventually *some* of the GP zones will also grow perpendicular to the disc, and a more three-dimensional precipitate is formed. It is not yet proper  $\Theta$  or the  $\Theta$  phase but a compromise between the need to "be"  $\Theta$  and to still be coherent and to fit it into the lattice. Otherwise a large prize would have to be paid in terms of interface energy since the surface to volume ratio is bad for small precipitates.
- That's why these early and small precipitates are called  $\Theta''$  precipitates. They catch migrant Cu atoms more efficiently than the GP zones, which thus will shrink and release their Cu atoms which now feed the growing ones.

That's what the  $\Theta''$  precipitates look like:

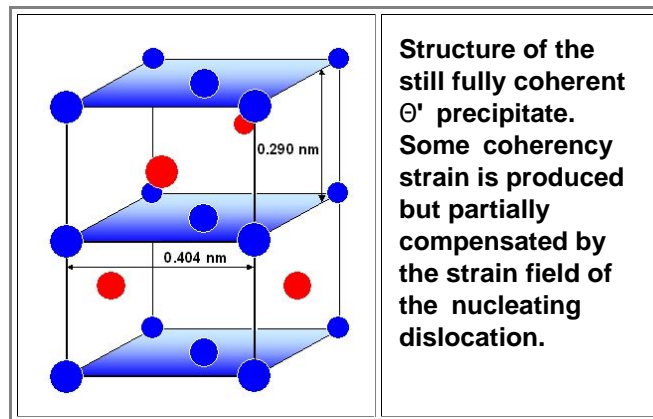


- In a way, you just add more Cu planes keeping the basic fcc structure. However, with increasing thickness the coherency stress and thus also the strain energy increases, and that is rather unwelcome. This limits the growth of the  $\Theta''$  precipitates.

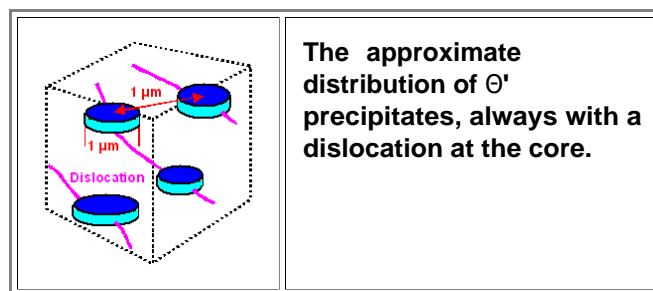
While the  $\Theta''$  precipitates form and grow, we still have some supersaturation of Cu albeit much reduced compared to the starting value.

Bear in mind that during the formation of GP zones and  $\Theta''$  precipitates there is still some nucleation going on - all processes always occur in parallel, just with different rate. Heterogeneous nucleation at defects, especially dislocations, is now the favored mode. You just have to get far more Cu atoms together in comparison to what is described above. That is more cumbersome and takes longer, but eventually it will win.

These precipitates start out three-dimensionally right away - but are still not yet the proper  $\Theta$  phase. That's why we call them  $\Theta'$  precipitate. Here is their structure:



The distribution on a larger scale now looks like this:



And we aren't done yet! As time goes on, the final  $\text{CuAl}_2$  or  $\Theta$  precipitate will nucleate at grain boundaries and at the  $\Theta'$  precipitates. These precipitates are fully three-dimensional and *incoherent*. There is no match of the lattices at the interface, in other words. That makes the interface energy much larger in comparison to the coherent precipitates but so what! As the precipitates grow to larger and large sizes, the interface energy increases more slowly with size  $r$  (with the *square* of  $r$ ) than the energy associated with coherency strain (increases with the *cube* of  $r$ ). Coherent precipitates thus carry the day as long as they are small but loose against incoherent ones at large sizes. I won't give a picture  $\Theta$  precipitates because I'm getting tired of drawing all these crystal models. It's also a more complex structure, not so easy to draw.

So the  $\Theta$  precipitates always win in the end. The  $\Theta'$  precipitates will duly shrink and disappear, and eventually only  $\Theta$  precipitates are left behind, which then commence to increase in size while decreasing in density by regular Ostwald ripening.

Why oh why? Easy. Making proper  $\Theta$  precipitates right away is too difficult. Or, in other words, the nucleation takes a lot of energy and time. So the crystal does what is easiest to start, the "realizes" that it can't finish this way and switches to then next process. Some people, I hear, have switched to different life styles and spouses (repeatedly) for essentially the same reason.

You can compare that to two guys doing a long distance race. The one who starts out very fast but gets slower and slower as time drags on will eventually be overtaken by the one who starts slower but keeps his speed constant.

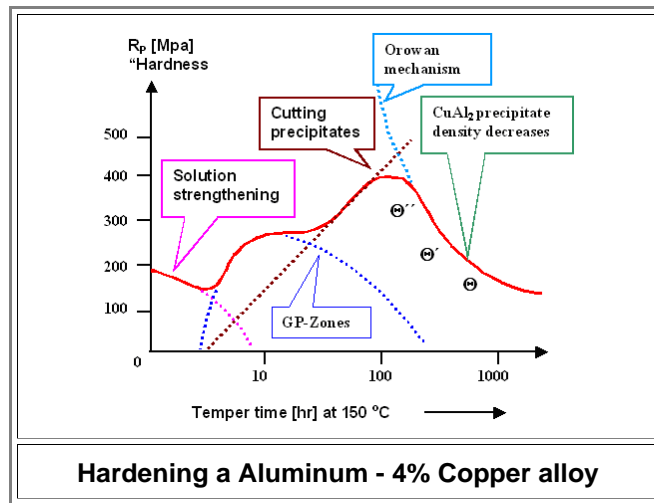
You did similar things yourself. You didn't learn to read and write fluently right away, you started with spelling and writing out every letter by itself. It's easier but it won't get you very far. Eventually you switch to the more difficult to ~~nucleate~~ learn cursive script, and you stop to spell out words because you learned to recognize whole words at a glance. Same thing with playing the piano or another demanding musical instrument. You typically start with a recorder, getting quick results. It just won't get you very far. Then you start again with a more complex instrument, and playing the recorder fades into the background.

Seen in another way, it's all about probabilities. In the beginning it's just more likely that a few Cu atoms stick together in disc form to make a GP zones than a number of them in a complicated arrangement for a  $\Theta$  precipitate.

## Understanding what Determines Hardness

We have seen that during tempering several kinds of precipitates form while the concentration of dissolved Cu atoms goes down. Solute atoms and precipitates influence dislocation movement in some ways that depends on their nature, size and density.

- We can actually calculate most of that. The result can be drawn into the hardness-time curve given before. Somewhat simplified, it looks like this



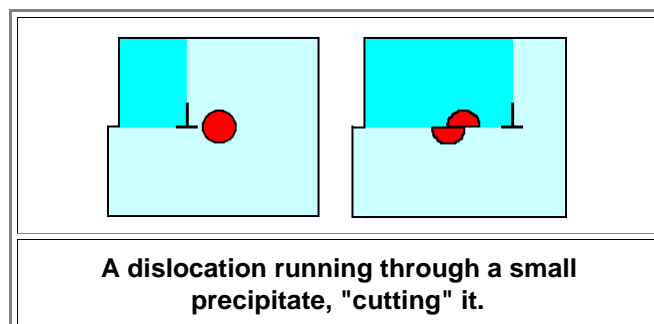
Let's look at what is happening bit by bit.

- At the beginning of time there is **only solution hardening**. This gives the red curve followed by the red dots, and hardness decreases because the concentration of dissolved copper atoms goes down. Solution hardening is well understood, the general relation between hardness or (better) the critical shear stress  $\tau_{sol}$  needed to move dislocations and the concentration of the solute atoms  $c_{sol}$  is

$$\tau_{sol} = k_{sol} \cdot c_{sol}^{1/2}$$

and  $k_{sol}$  is some constant describing the effect of the particular solute atom chosen.

- The concentration of the dissolved Cu atoms goes down because GP zones are formed. The way they influence dislocation movement is not much different from that of single solute atoms. At the beginning we only have a few small ones that are less effective than the remaining dissolved Cu atoms. But as time goes on, more and more GP zones are nucleated, their density increases, and their influence on hardness is felt. The influence of the GP zones on hardness is shown by the blue dotted line. After reaching a maximum, the curve goes down again because we now form  $\Theta''$  precipitates,
- Precipitation hardening** is well understood. In essence, dislocations can deal with precipitates in two ways. Small and coherent precipitates (including  $\Theta''$  precipitates) are simply "cut" like this:

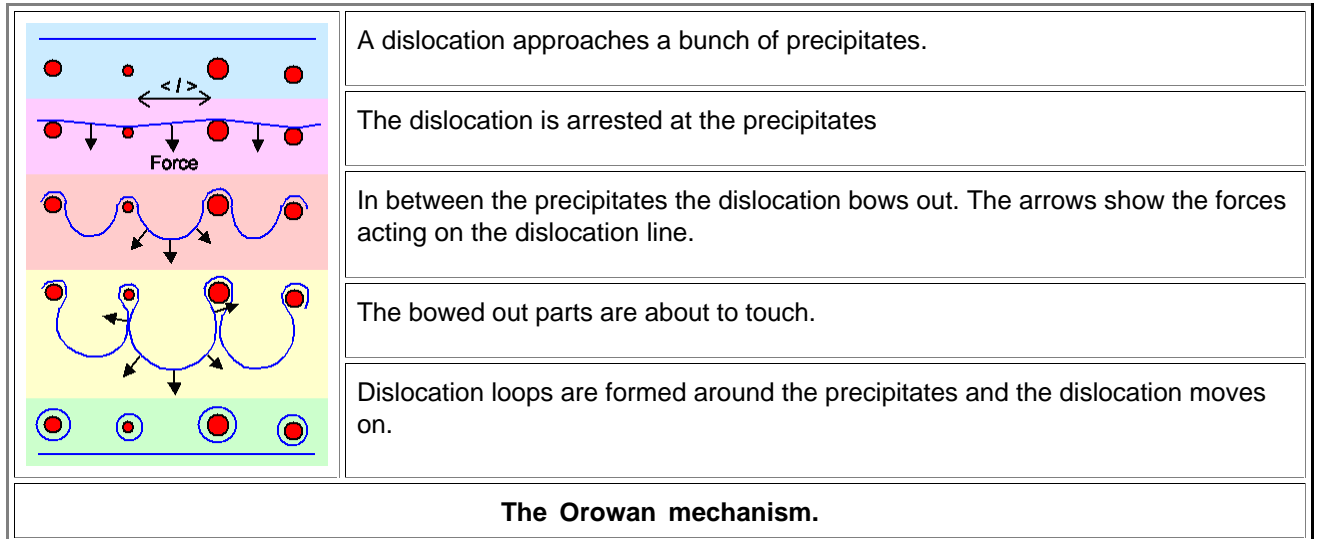


The stress needed for cutting increases with the size of the precipitate. If "cutting" would be the only mechanism, the hardness would go up about linearly with time since the precipitates get bigger and bigger. This is shown by the dotted black line above.

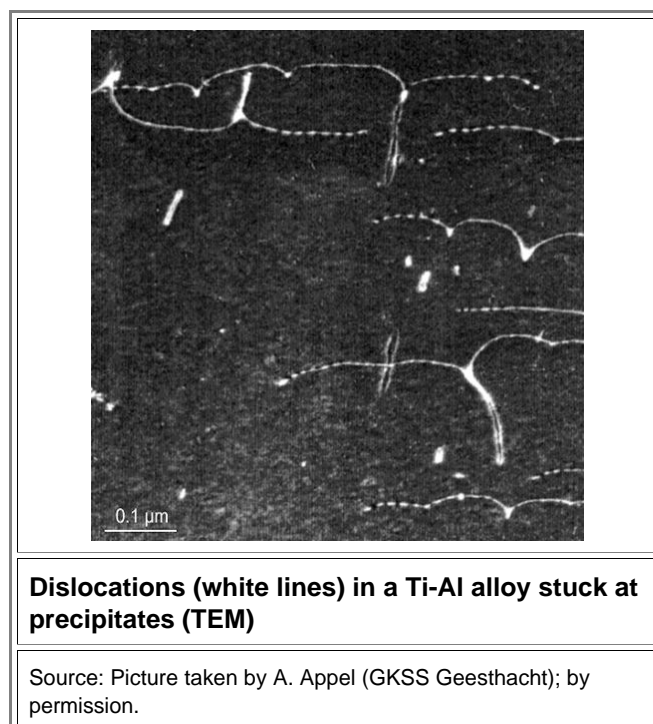
- However, for *big* precipitates the second mechanism called "**Orowan mechanism**" becomes operative as shown below. The effect of "big" precipitates does not depend on its size, only the average distance  $\langle l \rangle$  between the precipitates is important. It is related to the density  $\rho_{\text{prec}}$  via  $\langle l \rangle \propto (\rho_{\text{prec}})^{1/3}$ . We have

$$\tau_{\text{prec}} = \frac{2Gb}{\langle l \rangle}$$

and  $G$  is the [shear modulus](#),  $b$  the [Burgers vector](#) of the dislocation in Al. The way the Orowan mechanism works is shown here:



- The stress to produce small "bows" is larger than for large ones. It's like blowing up a balloon. It takes more effort to make its radius a little bigger when it is small. That's the reason why only the average distance between the precipitates is important since it governs the amount of bowing necessary before a loop can be formed. In real life this looks like this:



- The precipitates are not visible at the relatively low magnification. Some dislocations are majorly stuck, pulling out long trails.  
It is not so easy to see "stuck" and bowed dislocations in a [transmission electron microscope](#) (TEM) image because they usually become unstuck during stress release and specimen preparation, and all you see are straight lines.  
The white dots are dislocation loops surrounding precipitates that were left back
- After the crystal has gone through all the early stages of precipitation formation, only the Orowan mechanism is left to obstruct the dislocation movement. It doesn't matter what kind of precipitates we have, and the hardness now comes down with time as shown since the density decreases due to Ostwald ripening, leading to an increase in the average distance and thus to a decrease in hardness.
- ▶ The total hardness vs. time curve then is just the superposition of all the individual mechanisms working in parallel. Obviously, the best one can achieve is to have early  $\Theta''$  precipitates plus a few GP zones that are still around.
- ▶ It is clear that the major task is to calculate the development of the structure. What kind of mix of solute atoms, GP, zones,  $\Theta$  precipitates of all kinds do we have at some specific time  $t$ , with all the concentrations and average sizes? It is not an easy task because everything is coupled to everything else:
  - The density  $\rho_{\text{prec}}$  and the average spacing  $\langle l \rangle$  of one kind of precipitate is directly related; average size and density determines how many atoms are involved; the degree of supersaturation gives you the maximum number of atoms you can precipitate, and the difference between the actual number of atoms in precipitates to the total number tells you what can go on besides the precipitation you are looking at. The value of the temperature tells you how fast atoms can move by diffusion and thus how *fast* things can happen. In addition it gives you an idea about the magnitude of the driving forces that tell you how *urgently* things should happen.
  - If we have the basic data (in particular about the relation between matrix and alloy atoms and diffusivities) we can come up with a system of coupled differential equation and solve them. That's not all that easy with pencil and paper but no problem with computers. I gave you an example about something similar (though far easier) [before](#).
  - In essence, we need to calculate the *rate of nucleation*, how many nuclei form per second, and how fast they *grow*. The two processes involved are opposed: At low temperatures you form a lot of nuclei per second, but they grow very sluggishly due to slow diffusion. At high temperatures it is the other way around. This gives us already a hint that you want to go for some special medium temperature if you want things to happen fast.  
I look at this in detail in [another module](#) and won't discuss it here anymore. The catch word is "*time-temperature-transformation*" or **TTT** diagram

### The Aluminium - Aluminum Controversy

- ▶ The metal was named by the English chemist Sir Humphry Davy in 1808 when he was trying (unsuccessfully) to isolate it from the mineral **alumina**, a name given by the English chemist Joseph Black in 1790 to what french called alum, the German Alaun, and the old Romans alumen and modern chemists  $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$ . It's a white mineral that had been used since ancient times for dyeing and tanning, among other things.  
Sir Humphry knew that some not yet discovered element was hiding in there: "Had I been so fortunate as to have obtained more certain evidences on this subject, and to have procured the metallic substances I was in search of, I should have proposed for them the names of silicium, *aluminium*, zirconium, and glucium", he wrote in the Philosophical Transactions of the Royal Society of London in 1808.  
Note that he used yet another version in this first try. He changed his mind, however, and went from **aluminium** (in 1807) to **aluminum** and finally, influenced by learned colleagues, to **aluminium** in 1812. The -ium ending just was more musical and went well with the -ium endings of other elements like potassium (K; from German "Kalium"), sodium (Na, from German natrium), magnesium (Mg), calcium (Ca) or strontium (Sr).  
The Danish physicist and chemist Hans Christian Ørsted might first have produced Al in 1825 in an impure form. This seems not be absolutely certain, however, so Friedrich Wöhler, a German guy who definitely produced aluminium in 1827, is also credited with the discovery.
- In the USA, some dictionaries stuck to "aluminium" but nobody gave a damn as long as Al was extremely rare and more expensive than Gold (Au). Shortly before the 1900 millennium the metal began to be widely available and the word started to be needed in popular writing. The USA eventually settled on aluminum, the rest of the world mostly went for aluminium  
The American Chemical Society only adopted "aluminum" in 1925, in response to the popular shift that had already taken place.  
The International Union of Pure and Applied Chemistry (IUPAC), the top authority on this, officially standardized on aluminium in 1990. The people in the US, of course, have totally ignored that decision. So in 1993 IUPAC grudgingly also accepted "aluminum" and that's where we stand today.
- ▶ Aluminium is the third most abundant element after oxygen and silicon. That makes it the most abundant metal in the Earth's crust. It makes up about 8% by weight of the Earth's solid surface.  
But Aluminium, like silicon, is very reactive and therefore never found in an elemental stage. It is not easily induced to give up its partners and belongs to what I have termed the [electro-smelting of very difficult metals age](#).