Aluminium Alloys – A Century of Age Hardening

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Abstract

A century has elapsed since Alfred Wilm made the accidental discovery of age hardening in an aluminium alloy that became known as Duralumin. His work, and the gradual realization that hardening arose because of the presence of fine precipitates which provided barriers to the motion of dislocations, is a good example of the transition of metallurgy from an art to a science. A brief account is given of the development of age hardenable aluminium alloys and the way that modern experimental techniques allow precipitation processes to be understood on an atomic scale. Some contemporary issues in age hardening are then discussed.

1. Discovery of Age Hardening

If a poll was taken to decide the most important metallurgical development during the 20th century, it would be surprising if the discovery of age hardening by Alfred Wilm 100 years ago was not the popular choice. Although this phenomenon has been associated particularly with aluminium alloys, it is now realized that far more types of alloys may be strengthened by this method of heat treatment than through the traditional martensitic transformation in ferrous alloys.

Alfred Wilm was born on a farm in 1869 in Silesia, which was then in South Eastern Germany. While a student at an agricultural school, he became interested in chemistry and later, in 1901, he was appointed metallurgist at the Neubabelsberg Scientific and Technical Analysis Centre near to Berlin. For two years he investigated the possible strengthening of Al-Cu alloys by heat treatment, no doubt being frustrated to find that, contrary to carbon steels, these alloys were soft rather than hard after quenching from a high temperature. Then, in 1903, his Centre was commissioned by the German War Munitions factory of Berlin to find an aluminium alloy with the characteristics of brass that could be used for the manufacture of ammunition [1]. By experimenting with an Al-Cu-Mn alloy in 1906, Wilm almost achieved the required strength but the hardness remained too low. He then added 0.5% Mg and prepared some sheet which he heated in a salt bath at 520°C and quenched. This was on a Saturday morning just before closing at noon and Wilm's assistant, Jablonski, only had time to make a quick hardness measurement before leaving. Wilm himself is said to have spent the remainder of a sunny weekend sailing nearby on the Havel River [2].

On the following Monday, Jablonski completed his measurements and both men were astounded to find that the hardness was significantly higher than previously recorded.

The calibration of the hardness machine was checked and the experiment repeated confirming that the hardness increased for four days, after which it remained constant (Fig.1). A patent was obtained for an alloy with 3.5-5.5%Cu, plus less than 1% Mg and Mn [3], and by 1908 experimental work had advanced to a stage that it was considered ready to be released for commercial production. Wilm was allowed to acquire all patent rights and agreed to licence the invention to Durener Metalwerke in Duren, north western Germany. Presumably contractions of the words "Durener" and "aluminium" led to the name "Duralumin" for the alloy, which was copyrighted in 1909, and is still recognized today. Wilm eventually published papers in 1911 describing his work [4] and soon after abandoned metallurgy to return to farming, perhaps financed by the proceeds of the licence. As noted by Hornbogen [2], he died in 1937 unaware that he had invented the first nano-technology.
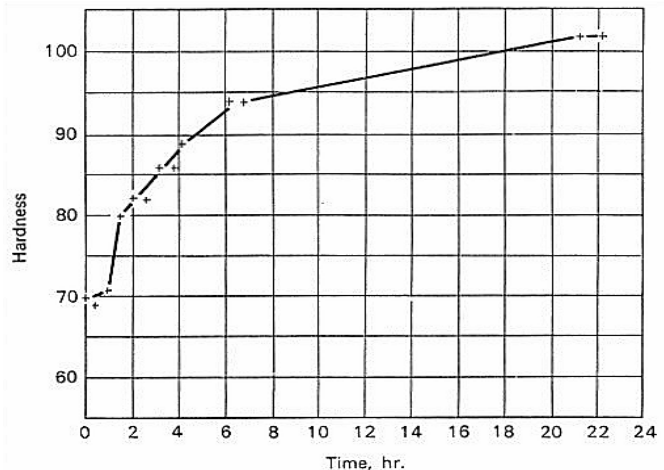

Figure 1: The first age hardening curve published by Alfred Wilm (courtesy of J.W. Martin, Precipitation Hardening, Pergamon Press, Oxford, 1968, p.104).

While Wilm was the first person to recognize the process of age hardening, this phenomenon inadvertently had been the cause of strengthening in some earlier alloys. Two examples are silver base coins used by the Greeks around 300BC [5] and an Au-Pt-Cu-Ag dental alloy marketed in America in 1906 [6]. Another possibility is the casting alloy Al-8Cu, known as P12, which was used for the crank-case of the 12HP engine that powered the Wright brothers flying machine [7].

Despite the fact that the cause of age-hardening was unknown, Duralumin was quickly adopted by Count von Zeppelin for constructing rigid airships at his factory in Freidrichhafen in Germany. Almost 100 of these vessels were produced during World War 1 and as much as 750 tonnes of this new alloy was produced in one year in that country during this period [8]. Duralumin was also embraced by Professor Junkers at his Dessau works in Germany where he produced the first all-metal passenger aircraft, the Junkers F13, that first flew in 1919 [1]. A feature was the use of corrugated sheeting for the fuselage to increase stiffness. The Vickers company in England became a licensee for Duralumin and produced a small commercial quantity in 1911. Alcoa in the USA made some laboratory heats in the same year and commercialized its own version known then as 17S (Al-4Cu-0.6Mg-0.5Si-0.6Mn) that is still available under the designation 2017.

2. Precipitation Processes

Examination of the microstructure of Duralumin by optical microscopy failed to reveal any change that could account for the response to age hardening, and it was not until 1919 that this phenomenon was associated with the decreasing solid solubility of alloying elements with lowering temperature.

Osmond first reported this feature in Ag-Cu alloys in 1897 [9] but it remained for Merica, Waltenburg and Scott [10,11] in the USA to propose that quenching from a high "solution treatment" temperature could suppress the equilibrium separation of a second phase and result in the formation of an unstable supersaturated solid solution (SSSS). These workers suggested that hardening was the result of the precipitation of this second phase when the quenched alloy was "aged" for sufficient time to allow a "submicroscopic dispersion" to form. Thus, the first description of the decomposition of an Al-Cu alloy was SSSS→saturated $\alpha+\theta$ (Al$_2$Cu). Another seminal paper was published in America in 1921 by Jeffries and Archer [12] who proposed that age hardening in Al-Cu may arise because small particles of these invisible precipitates acted as "keys" that blocked crystallographic slip, thereby increasing the resistance of the alloy to deformation. They also concluded that maximizing hardening would occur when this dispersion of particles was the smallest size consistent with retaining the crystalline characteristics of the θ phase.

Rosenhain in England first made the suggestion that maximum hardening in Al-Cu alloys need not be associated with the presence of particles of the equilibrium phase in 1924 [13]. He reasoned that the formation of discrete particles of this phase would reduce the concentration of solute in solid solution and should actually result in softening rather than hardening. Instead he suggested age hardening to be an increase in disorder in the parent lattice at an earlier stage in the ageing process. In 1932, Merica [14] largely rejected his earlier theory and proposed that age hardening may be caused by aggregates or "knots" of Cu atoms needed to form the equilibrium precipitate. Then Wasserman and Weerts [15] in Germany in 1935 confirmed that the ageing process in Al-Cu did involve more than one stage when they detected, by X-ray diffraction, a phase they called θ' which they claimed had the same composition as equilibrium θ, but different lattice constants.

It remained for Guinier in France [16] and Preston in England [17], working independently in 1937, to produce the first direct experimental evidence of pre-precipitation phenomena in an aged Al-4Cu alloy. Both concluded that characteristic streaks in x-ray diffraction patterns indicated the presence of two-dimensional, copper rich groups of atoms coherent with the {100}α planes of the aluminium matrix. These aggregates became known as GP zones, much to the surprise of Preston, who had changed to a quite different area of physics and only heard of this nomenclature many years later! Now it is recognized that GP zones form during an early stage of the decomposition of a SSSS in most age hardenable alloys.

The concept of pre-precipitates was disputed. Fink and Smith [18] in 1938 and Geisler [19]in 1949 in the USA continued to support the simpler idea that hardening was caused by coherent, submicroscopic nuclei of the equilibrium phase. A much more radical theory was put forward in 1947 by Röhner in Switzerland in which he dismissed both pre-precipitates and precipitates as having any significant influence on hardening [20]. Instead, he proposed that the first stage in the decomposition of a SSSS was the migration of solute atoms into interstitial spaces in the parent lattice, leading to the creation of vacant lattice sites that then interfered with the process of slip. Röhner's theory was published by the Institute of Metals, London, at a time when it was the practice to discuss selected papers at its Annual Meeting. The subsequent report of robust comments about Röhner's paper [21] makes interesting reading now at a time when public criticisms of this sort are usually so muted.

For example, one contributor said that "It is always interesting to find contrary theories put forward--- but I regret to say that I disagree most heartily with the theory. The author has started on premises which I think are quite wrong. He has neglected data which are of fundamental importance. My point is that the author has not made his theory fit the facts, but has taken the facts which fit his theory, which is not scientific".

It is now recognized that vacant lattice sites retained in the quenching operation play other roles that are vital to precipitation processes, one being the assistance they give to solute diffusion. For example, it has been estimated by extrapolation from high temperature diffusion data that GP zone formation in Al-Cu alloys aged at room temperature occurs at 10^7 times the expected rate due to the presence of vacancies [22]. Discs of vacancies may also condense and collapse to form dislocation loops [23] or vacancies can diffuse to screw dislocations causing them to climb into helices [24]. Both configurations provide sites at which heterogeneous nucleation of precipitates can occur during ageing.

Modern experimental techniques have established that the ageing processes in most aluminium alloys are complex and may involve several stages. Typically coherent GP zones and a semi-coherent intermediate precipitate may precede formation of the equilibrium phase. In some alloys, two types of GP zones have been identified; in others there are more than one intermediate precipitate. As will be shown later, atomic clustering during and immediately after quenching from the solution treatment temperature, may also influence the precipitation processes that follow.

3. Alloy Development

Wilm's discovery led to searches for other aluminium alloy systems that would age harden. As noted by Staley [8], all approaches were essentially empirical. Alloying elements were added or subtracted, and the user evaluated the product. When trying the various elements, the dictum was said to be "if a little is good, add more until something bad happens". Three series of cast and wrought alloys emerged that are based on the Al-Cu-(Mg), Al-Mg-Si and Al-Zn-Mg-(Cu) systems. More recently, a major effort has been made to exploit the age hardening potential of alloys containing the light element lithium (s.g 0.54).

Duralumin (2017) had a yield strength of 280MPa, and the historical development of alloys with progressively increasing strength levels, that have been used for upper wing skins of commercial aircraft, is depicted in Fig. 2 [25]. These improvements have come from the development of new alloy systems, modifications to compositions within particular systems, and from the use of a range of multi-stage ageing treatments (tempers).
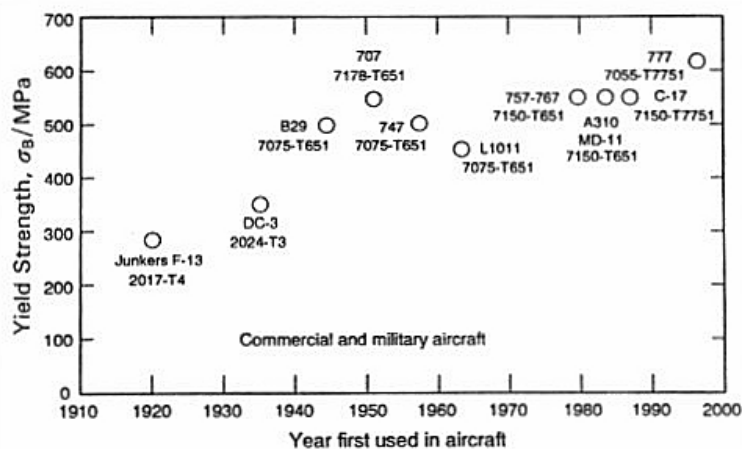

Figure 2: Wing upper skin alloys and tempers for passenger aircraft 1919 to 1994 [25].

3.1. Al-Cu-(Mg) Alloys

Stimulated largely by early demands from the aircraft industry, stronger Al-Cu-Mg alloys were developed including the wrought alloy 2024 (Al-4.3Cu-1.5Mg-0.6Mn) which, in the T3 temper (solution treated, quenched, cold worked and naturally aged), had a yield strength 20% higher than Duralumin and a high ratio of tensile to yield strength, which promotes damage tolerance. In the alclad condition, it was used for the famous DC-3 aircraft and has been used for the fuselage of most passenger aircraft built since that era [8]. Another early alloy was 2014 (Al-4.4Cu-0.5Mg-0.9Si-0.8Mn) which, in the artificially aged (T6) condition, has a yield strength some 50% higher than Duralumin. Further increases in strength were possible by cold working these alloys prior to artificial ageing (T8 temper).

Alloys based on the Al-Cu system have the advantage of superior creep strength at elevated temperatures [26]. One example is the alloy 2618 (Al-2.2Cu-1.5Mg-1.1Fe-1Ni-0.2Si) that was used for the skin and much of the structure of the Concorde aircraft. Another is the alloy 2219 (6.3Cu-0.3Mn-0.1V-0.18Zr), which is weldable and has been used for fuel tanks in several space vehicles. Developed from this alloy are several experimental compositions [27-29] containing minor additions of Ag and Mg which promote nucleation of a relatively stable precipitate known as the Ω phase that forms as finely dispersed thin plates on the $\{111\}_\alpha$ matrix planes [e.g.30-33]. This stability is attributed to the segregation of these elements to the precipitate/matrix interface, which restricts plate coarsening at temperatures up to around 200°C [34-36]. Tests indicate that Al-Cu-Mg-Ag alloys have creep properties superior to those of commercial 2000 series alloys [27,29,37]. In the underaged condition, one alloy, (Al-5.6Cu-0.45Mg-0.4Ag-0.3Mn-0.18Zr) has shown zero secondary creep after exposure at 130°C for 20000h at a stress of 200MPa [38].

3.2. Al-Mg-Si Alloys

Although early experiments failed to achieve an age hardening response with binary Al-Mg and Al-Si alloys, attempts to heat treat ternary Al-Mg-Si alloys were successful. The first alloy was 6051 (Al-0.5Mg-1Si), which was introduced in the USA in 1921 [8]. Alloy 6051, although not as strong as 2017, was easier to fabricate and had a much higher corrosion resistance. Many wrought Al-Mg-Si alloys have since been developed and they have become the most widely used general-purpose alloys for extruded sections. As it has turned out, the ageing processes in these simple alloys have proved the most perplexing.

The additions of Mg and Si are made either in balanced amounts such that quasi-binary Al-Mg_2Si alloys would form (Mg:Si, 1.73:1) or with excess Si above that needed to form Mg_2Si (as with 6051). More recently, Al-Mg-Si alloys have been developed with higher levels of Cu, one example being 6013 (Al-1Mg-0.8Si-0.85Cu) that has a yield strength of 330MPa. Several 6xxx series alloys are attracting interest for automotive body sheet partly because the paint-bake cycle, which is usually carried out at 160-190°C after fabrication, may also be used to promote age hardening.

Al-Mg-Si alloys with high levels of Si also have important applications as castings. One example, commonly known as 356 (Al-7Si-0.3Mg) has a hypoeutectic microstructure in which the α- aluminium phase is hardened by Mg_2Si precipitates. The alloy is widely used for automotive wheels and various engine components.

3.3. Al-Zn-Mg-(Cu) alloys

In 1923, Sander and Meissner in Germany [39] found that some ternary Al-Zn-Mg alloys showed a greater response to age hardening than any other compositions investigated at that time. The potential of these alloys for aircraft materials was recognized in several countries but their adoption was delayed because they proved very susceptible to stress corrosion cracking (SCC). In Japan, an alloy known as ESD (Extra Super Duralumin) was developed that was successfully introduced to lower the weight of the Zero fighter aircraft in 1938 [40]. When this innovation was revealed to the Allies through chemical analysis of a crashed aircraft during World War 2, similar alloys were quickly used for the manufacture of military aircraft in the USA and England. The best known was 75S (later 7075: Al-5.6Zn-2.5Mg-1.6Cu-0.23Cr), which was used for the skin and stringers of the American B-29 "Super Fortress" bomber aircraft, and provided an immediate weight saving of 180kg [41]. The SCC resistance was improved due primarily to the inclusion of Cu as an alloying element [41] and the production of extrusions, forgings and plate soon followed.

The alloy 7075 was widely adopted for post-war passenger and military aircraft including the widely used Boeing 707 and the ill-fated Comet. Since then, continued demands for materials with higher and higher strength:weight ratios has led to the development of a family of alloys based on the Al-Zn-Mg-Cu system and this progressive trend is shown in Fig.2. A recent alloy, 7055 (Al-8Zn-2.05Mg-2.3Cu-0.16Zr), has a yield strength that may exceed 620MPa and the estimated weight saving attributed to its use for components in the Boeing aircraft 777 is 635kg [42]. Crucial to the introduction of these more highly alloyed compositions has been the parallel development of complex multi-stage ageing tempers, some incorporating cold or warm working, that allow adequate ductility, fracture toughness and a satisfactory resistance to SCC to be maintained.

3.4. Alloys Based on the Al-Li System

Reducing the density of materials is, in fact, the most effective way of lowering the structural weight of aircraft and space vehicles. As it happens, Li (density 0.54g/cm^3) is one of the few elements that has a high solubility in aluminium. This is significant because, for each 1% added, the density of an aluminium alloy is reduced by 3%. Lithium is also unique amongst the more soluble alloying elements in that it causes a marked increase in the elastic modulus (6% for each 1%Li added). Moreover, binary and more complex aluminium alloys containing Li respond to age hardening. Because of all of these features, the largest single aluminium alloy program of all time commenced in several countries between 1970 and 1980 to develop these alloys as a new generation of lower density, higher stiffness materials for use in aircraft.

Attempts to use Li as an alloying addition in aluminium date back to 1924 when an alloy having a higher yield strength than Duralumin called "Scleron" (Al-12Zn-3Cu-0.6Mn-0.1Li) was produced in Germany and used mainly for castings [43]. Alcoa released an alloy 2020 (Al-4.5Cu-1.3Li-0.5Mn-0.2Cd) in the late 1950's that had a high response to artificial ageing and developed a yield strength exceeding 520MPa [44]. This was successfully adopted for the wingskins and horizontal stabilizer of the US supersonic Vigilante military aircraft [45]. However, the alloy was later withdrawn because it was recognized that its fracture toughness was inadequate in some situations. Another alloy designated 1420 (Al-5Mg-2Li-0.1Zr) which had a particularly low density (2.47g/cm^3), was introduced into military aircraft in the former Soviet Union in the early 1970's [46].

Since then a number of commercial alloy compositions have been registered that are based mainly on the Al-Cu-Li and Al-Cu-Li-Mg systems, the properties of which have been exhaustively evaluated. It has been estimated that their use as direct substitutes for conventional aircraft alloys may give a structural weight saving of at least 10%. One alloy 8090 (Al-2.4Li-1.3Cu-0.9Mg-0.1Zr) has been adopted for much of the fuselage and main lift frame of the European Westland/Augusta military helicopter [47], but aeronautical applications have otherwise been limited due mainly to the high material cost penalty involved.

A more spectacular application has been the adoption of an Al-Cu-Li alloy containing minor additions of Mg and Ag for the huge welded "Super Light Weight" external launch tank for the US Space Shuttle [48]. This alloy system has the highest response to age hardening of all aluminium alloys and compositions have shown yield strengths exceeding 700MPa [49]. The use of the alloy has led to an estimated weight saving of some 3400kg [48] and has the potential to save many millions of dollars by reducing the number of launches needed to construct the International Space Station [50]. The exceptional strength arises because of the ability of minor additions of Mg and Ag to stimulate the nucleation of a fine dispersion of thin, high aspect ratio plates of the T_1 phase (Fig.3) that forms on the $\{111\}\alpha$ planes [51]. The T_1 phase co-exists with both the S' and θ' phases and all three precipitates form on different crystal planes.

4. Optimising Age Hardening

As understanding of the submicroscopic processes of precipitation in alloys developed, the equally invisible concept of dislocations was proposed in 1934 to explain plastic deformation [52,53]. Mott and Nabarro first suggested an explanation of age hardening in terms of dislocations in 1940 [54] well before these defects could be imaged. These workers considered precipitates with respect to their localized stress fields and reasoned that, for dislocations to pass through such regions, the applied stress must exceed the average internal stress. They also recognized that the inherent line tension of a dislocation placed limitations on its flexibility and therefore its capacity to curve between precipitates. Their theory predicted that a critical particle spacing for maximum hardening would be approximately 10nm.

In 1948, Orowan [55] proposed that, if the spacing between precipitates was large, dislocations could expand into the region between them, rejoin and move on.
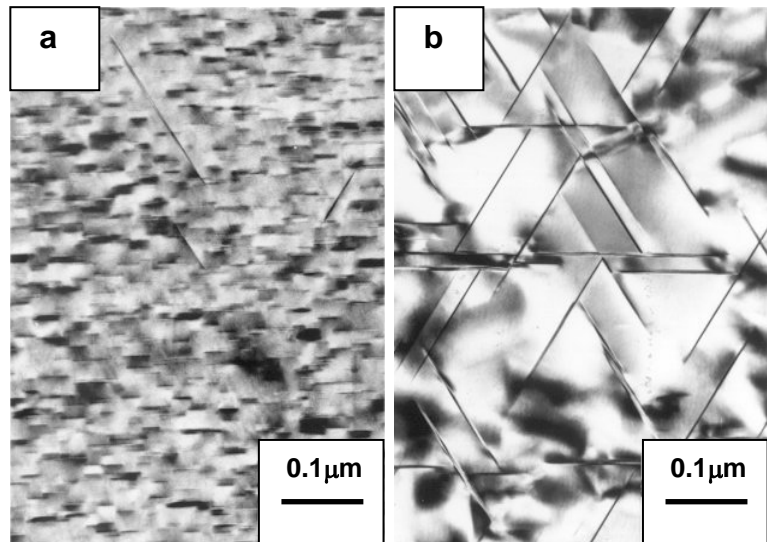

Figure 3: Electron micrographs of the alloy Al-5.3Cu-1.3Li-0.4Mg-0.4Ag-0.16Zr (a) quenched and aged 8h at 160°C (hardness 146 DPN) showing GP zones and occasional plates of T_1 phase (Al_2CuLi) and (b) quenched, cold worked 6% and aged 8h at 160°C (hardness 200 DPN) showing a uniform dispersion of T_1 plates having high aspect ratios (courtesy S.P. Ringer).

Providing the particles themselves could withstand the applied stress, Orowan postulated that the flow stress for the alloy would be governed entirely by their spacing. It was also recognized that smaller precipitates could be sheared by moving dislocations [56]. Each of these predictions has since been confirmed with the advent of transmission electron microscopy. It is now agreed that the greatest impedance to dislocation motion and hence the maximum potential for strengthening by age hardening will occur when an alloy contains precipitates that are large enough to resist shearing by dislocations and yet are too finely spaced to be by-passed. This is illustrated in Fig.3 for an Al-Cu-Li-Mg-Ag alloy containing (a) shearable GP zones and occasional plates of the T_1 precipitate (hardness 146DPN) and (b) a uniform dispersion of T_1 plates (hardness 200DPN) that strongly resist dislocation motion (see Fig.5 below).

The increase in yield stress due to the presence of small, hard precipitate particles can be described by a modified Orowan equation [57]:

$$\sigma_p \approx \frac{Gb}{S_p} \approx \frac{Gb}{d}\sqrt{f}$$

Where G= shear modulus of the particles, b=Burgers vector of a dislocation, S_p=spacing between particle centers, f=volume fraction of particles and d=diameter of particles. Hornbogen and Starke [58] have depicted the theoretical relationships between hardening (σ_p) and both the volume fraction and diameter of the particles. This is shown in Fig.4. Another common feature with high strength aluminium alloys is the presence of plate-shaped, shear resistant precipitates that form on the $\{111\}_\alpha$ and $\{100\}_\alpha$ planes of the aluminium matrix, or rod shaped precipitates that form in the $<100>_\alpha$ directions. However, comparatively little attention has been given to a quantitative analysis of the effects of shape, orientation and distribution of such precipitates on strengthening because of the lack of appropriate versions of the original Orowan equation which was developed for alloys containing spherical particles.
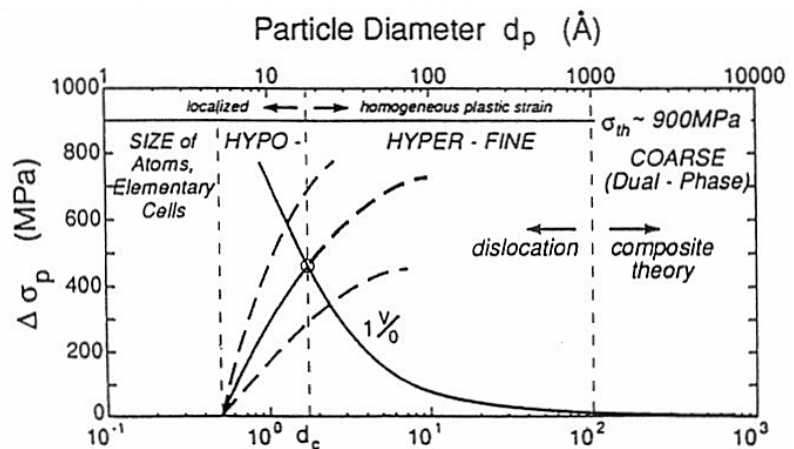

Figure 4: Calculated upper limit of hardening by different volume fractions of dispersed particles in aluminium alloys [57].

The accepted version of this equation is [58]:

$$\Delta\tau = 2\left\{\frac{Gb}{4\pi\sqrt{1-v}}\right\}\left\{\frac{1}{\lambda}\right\}\left\{\ln\frac{D_p}{r_0}\right\}$$

where $\Delta\tau$ = increment in critical resolved shear stress due to dispersion hardening, v = Poissons ratio, r_0 = core radius of the dislocations, λ = effective planar precipitate spacing and D_p = planar spacing of precipitates.

Within this equation, it is λ that varies with shape, orientation and distribution of the particles, and derivation of appropriate versions of the Orowan equation requires calculation of this spacing for various particle arrays.

Earlier determinations of λ were made for defined precipitate distributions by Kelly [59], Merle et al. [60], and Huang and Ardell [61]. More recently Nie and colleagues [62,63] have sought to calculate λ for a wider range of precipitate distributions and this analysis has shown, quantitatively, that plate shaped precipitates do provide a much more effective barrier to gliding dislocations than either rod-shaped or spherical precipitates. Furthermore, the increment of strengthening produced by $\{111\}_\alpha$ plates is invariably larger than for $\{100\}\alpha$ plates and, for both orientations, this increment becomes progressively larger as the aspect ratio of the plates increases. All these features are demonstrated in Fig.5, which models the ratio of Δτ (plates) to Δτ (spheres) plotted as a

Figure 5: Variation in ratio of critical resolved shear stress Δτ (plate, rod) / Δτ (sphere) with aspect ratio for Orowan strengthening attributable to $\{111\}_\alpha$ and $\{100\}_\alpha$ precipitate plates and $<100>_\alpha$ precipitate rods [62]. Volume fraction of precipitates f=0.05).

function of plate aspect ratio for a precipitate volume fraction of 0.05. Nie et al. have also concluded that, when the aspect ratio of plates exceeds a critical value, they form an effectively continuous three-dimensional network, which increases strengthening by placing further severe constraints on the movement of dislocations (see Fig 3b). It is also found that the strongest alloys usually contain more than one type of precipitate.
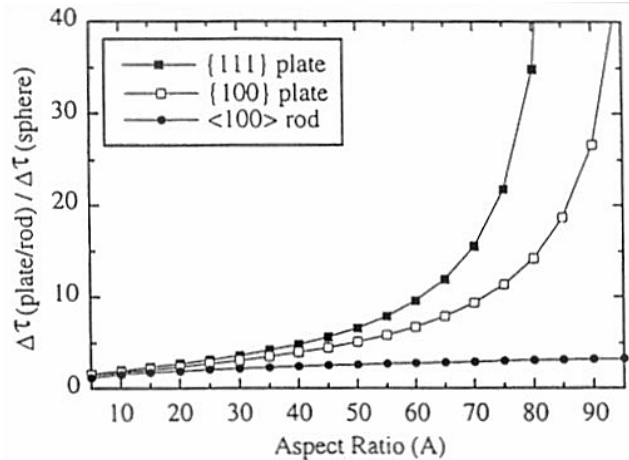
Optimal dispersions, shapes and orientations of precipitates are usually hard to achieve in practical alloys. For example, when ageing treatments that give maximum strengthening in 7000 series alloys produce microstructures containing only shearable GP zones, other properties such as ductility, toughness and resistance to stress corrosion cracking may be deficient. Frequently, the maximum response to hardening occurs when a microstructure contains a combination of GP zones and relatively widely dispersed, semi-coherent intermediate precipitates. Greater hardening is possible if more uniform dispersions of one or more of these latter phases can be encouraged to form and this has been one of the objectives of the multi-stage ageing treatments that have been developed. Microalloying may also stimulate nucleation and growth of specific intermediate precipitates.

5. Some Contemporary Issues in Precipitation Hardening

As mentioned earlier, after the origins of age hardening were established, there was a long period when it was generally accepted that these processes could involve GP zones, intermediate and equilibrium precipitates. Now the availability of more refined experimental techniques such as high-resolution electron microscopy (HRTEM), one and three-dimensional atom probe field ion microscopy (1DAP & 3DAP) and positron annihilation spectroscopy has disturbed this comfortable situation.

These techniques are revealing that some ageing processes are more complex than was realized, and these observations have both theoretical and practical implications, some of which are discussed below.

5.1 Clustering Phenomena

Although the clustering of solute atoms prior to precipitation in quenched and aged aluminium alloys was detected by small angle x-ray scattering many years ago [64,65], effects of this phenomenon on subsequent ageing processes have been little understood. Now there is evidence that clustering events may promote formation of existing precipitates, stimulate nucleation of new precipitates, and contribute to the actual hardening processes in certain alloys.

In the Al-Mg-Si system in which the ageing processes are particularly complex, 1DAP studies by Edwards et al. [66,67] and more detailed 3DAP studies by Murayama and Hono [68] have revealed that the formation of GP zones is preceded by the appearance of individual clusters of Mg and Si atoms, followed by co-clusters of these elements. These clusters will, for example, form during a delay at room temperature after quenching and before artificial ageing. In some compositions, this leads to the nucleation of a coarser dispersion of precipitates at elevated temperatures with the result that the response to hardening may be significantly less than expected for a T6 temper [69].

The techniques of 1DAP and 3DAP have shown that nucleation of the Ω phase in Al-Cu alloys containing small additions of Ag and Mg, is facilitated by clusters of Ag and Mg atoms that have been detected within seconds after commencing artificial ageing [70-72]. Moreover, strain energy considerations [73] then dictate that growth of Ω occurs along the preferred $\{111\}_\alpha$ planes rather than the cube planes on which the θ' phase forms in the absence of Ag and Mg.

It is well known that age-hardening of most other high-purity or commercial Al-Cu-Mg alloys over a wide temperature range (~100°C to 240°C) occurs in two distinct stages [74,75]. The first stage, which may account for 60-70% of the total age hardening, is characteristically rapid and may be complete within only 60s. This is then followed by what can be a prolonged period during which the hardness may remain effectively constant. Previously this early hardening has been attributed to the formation of GP (Cu,Mg) zones (also known as GPB zones) although the actual structure of these zones has been poorly defined [e.g. 76]. Recently HRTEM, 1DAP and 3DAP have all failed to detect any evidence of these zones until near the end of the hardness plateau [77]. Instead, what was observed after the rapid early hardening were small clusters containing ~3 to 20 atoms and the phenomenon has been termed "cluster hardening" to distinguish it form normal precipitation reactions. This behaviour has been attributed to solute/dislocation interactions [78] although the precise mechanism remains uncertain.

5.2 Chemistry of Intermediate Precipitates

There has been a general acceptance that semi-coherent intermediate precipitates formed in aged aluminium alloys have compositions and crystal structures that differ only slightly from those of the respective equilibrium phases. However, recent 1DAP and 3DAP structures of some alloys have revealed unexpected compositional variations between intermediate and equilibrium precipitates.

One example has been the Al-Mg-Si system in which the composition of the intermediate precipitates β" and β' were assumed to be the same as the equilibrium precipitate β (Mg_2Si). As mentioned earlier, some commercial alloys have been deliberately designed to have a balanced (2:1) ratio of Mg and Si with the aim of maximizing precipitation of these intermediate phases during ageing. Now there is strong experimental evidence that the actual Mg:Si ratios of these precipitates is close to 1:1, as has been observed for the pre-precipitate clusters [66,67]. This discovery has opened the prospect of producing new extruded Al-Mg-Si alloys in which the "unnecessary" Mg is deliberately removed so that they are easier to hot work [79]. Al-Zn-Mg-(Cu) alloys are others in which the composition of the intermediate precipitate η' has been shown to differ substantially from that of the equilibrium precipitate η ($MgZn_2$). In this case, the Mg:Zn ratio for η' has been measured to be in the range 1:1 to 1:1.5 rather than the expected 1:2 [80-82]. These results have indicated that the composition of η' is also linked more to that of the pre-existing GP zones than to the equilibrium precipitate η. These new observations that the compositions of the intermediate precipitates differ so much from those of the equilibrium precipitates means that a substantial number of lattice positions must still be occupied by Al atoms rather than the respective solute atoms.

5.3 Secondary Precipitation

For many years there was an implicit acceptance that, once an alloy had been hardened by ageing at an elevated temperature, its mechanical properties remained stable on exposure for an indefinite time at a significantly lower temperature. However, Bartuska et al. [83] showed that highly saturated Al-Zn alloys aged at 180°C will undergo secondary precipitation if then held at room temperature. More recently, similar behaviour has also been observed in certain lithium-containing aluminium alloys such as 2090 (Al-2.6Cu-2.2Li-0.12Zr), which is also highly saturated. If this alloy is first aged at 170°C and then exposed for long times at temperatures in the range of 60 to 130°C, there is a progressive increase in hardness and mechanical strength accompanied by an unacceptable decrease in ductility and toughness [84]. This deterioration in properties has been attributed to secondary precipitation of a finely dispersed δ' phase (Al_3Li) throughout the matrix [85,86]. Recent observations on a wide range of aged aluminium alloys with much lower solute contents have suggested that secondary precipitation is, in fact, a more general phenomenon [87]. This conclusion has been supported by results obtained using the technique of positron annihilation spectroscopy, which have indicated that vacancies may remain mobile at room temperature after aged aluminium alloys are cooled from a higher temperature [88].

Recent work has been directed at determining if secondary ageing could be exploited to improve rather than degrade mechanical properties.
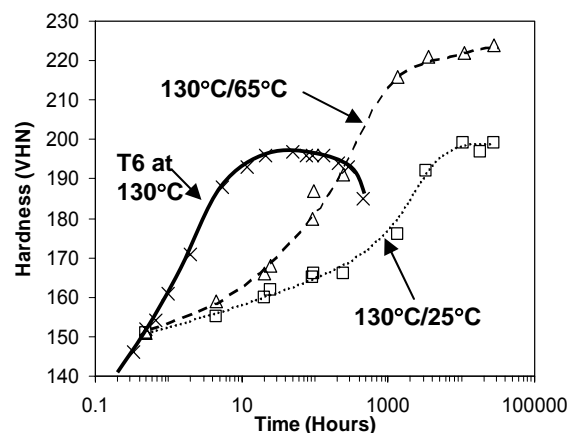

Figure 6: Age hardening response of alloy 7075 underaged 0.5h at 130°C prior to exposure at 25 or 65°C [89].

In this regard it has been found that, if the elevated temperature ageing of a wide range of aluminium alloys is interrupted by a dwell period at low temperature (25-65°C), then secondary precipitation of GP zones will occur which stimulates formation of more finely dispersed precipitates in the final microstructures [87]. Tensile properties may be increased by an average of 10% above those arising from a single stage T6 temper combined with significant improvements in fracture toughness [87,89]. With some alloys, continued secondary ageing at the lower temperature may also result in a greater total response to age hardening than obtained for a T6 temper, as is shown for the alloy 7075 in Fig.6.

5.4 Amorphous Alloys

Figure 4 shows that the theoretical strength of conventional aluminium alloys is approximately 900MPa. However, values exceeding 1000 MPa have been achieved with certain rapidly solidified alloys containing rare earth and transition metal elements that have amorphous structures [90,91]. Furthermore, if partial decomposition is encouraged at 250-350°C, then crystalline particles with sizes as small as 3-4nm may be formed in the amorphous matrix, further increasing strength and hardness. These alloys can be considered to be hardened by the presence of precipitates, although these phases have not been produced by a conventional ageing process. One such alloy, Al-9Ni-2Y-1Fe (at%) has recorded a tensile strength above 1500MPa. Small bulk specimens produced by extruding pressed atomized powders have shown some ductility but the alloys are costly to produce.

6. Concluding Remarks

As commented by Martin [92], the gradual realization that age hardening has its origin in complex precipitation processes provides a good example of the transition of metallurgy from an art to a science. Processes that were formerly invisible in an optical microscope can now be resolved at an atomic level. This intimate knowledge combined with advanced modeling procedures is assisting in the design of new alloys and ageing treatments to meet specific engineering requirements.

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