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CHALLENGES FOR RESEARCH AND DEVELOPMENT OF NEW ALUMINUM ALLOYS

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Modern trends in research and development of new aluminum alloys are characterized in the present work. Although conventional wrought and casting Al-based alloys show good specific strength, as compared to steels or Ti-based alloys, there is still a potential for significant improvement of their performance. It consists in application of new alloying elements, mainly transition metals, and uncommon processing routes, for example powder metallurgy. By this way, qualitatively new materials with ultra high strength and excellent thermal stability can be developed. However, there are many questions to be answered before new alloys can be competitive to conventional Al-based materials.

Key words: aluminum, high-strength, thermal stability, powder metallurgy, nano-crystalline alloy

Izazovi u istraživanju i razvitku novih aluminijskih legura. Članak daje karakteristike modernih stremljenja u istraživanju i razvitku novih aluminijskih legura. Mada konvencionalno oblikovane deformiranjem i ljevanjem Al-temeljne legure daju dobru specifičnu čvrstoću u usporedbi sa čelikom ili Ti-legurama, još postoje mogućnosti značajnijeg optimiranja njihovih svojstava. To se sastoji u rabljenju novih legirajućih elemenata, glavnih prijelaznih kovina i neobičajenih procesa, npr. praškaste metalurgije. Na taj način mogu se usavršavati kvalitetno novi materijali sa visokom čvrstoćom i izvanrednom termičkom postojnošću. Unatoč tome, ima više pitanja na koje treba dati odgovore prije nego nove legure mogu biti kompetentne sa konvencionalnim Al-temeljnim materijalima.

Ključne riječi: aluminij, visoka čvrstoća, termička postojanost, raškasta metalurgija, nano-kristalične legure

INTRODUCTION

Aluminum alloys show a low weight, relatively high specific strength, good corrosion resistance in neutral environments and high electric and thermal conductivity. It makes them of interest for production of various functional components in aerospace and automotive industry. Wrought alloys generally have good formability and they are processed by common technologies, such as extrusion, forging, rolling, drawing etc. Complex shape components are also produced from casting alloys, mainly Al-Si-based, by various casting processes, like gravity casting, centrifugal casting, die casting etc. Industrial development of Al-based alloys is conservative, because it is mostly concentrated on modifications of common and well known alloy systems (Al-Cu, Al-Si, Al-Mg-Si, Al-Zn-Mg, Al-Li-Cu etc.) and processing routes. The reason is that there is a lack of experience in new alloy systems and production methods. However, standard systems stated above seem to approach their mechanical limits. By appropriate thermo-mechanical processing routes, i.e. combination of forming and age hardening, so-called high-strength alloys (Al-Zn-Mg or Al-Li) can reach a maximum tensile strength of about 700 MPa. To exceed this limit, qualitatively new alloys and processing routes should be developed. In addition, common high-strength alloys generally show low thermal stability, i.e. fast reduction of strength at temperatures above 200 °C. The poor thermal stability is a consequence of relatively high diffusion coefficients of the main strengthening elements (Cu, Mg, Zn) in solid aluminum. Therefore, for elevated temperature applications, new additives to Al should be used.

ULTRA HIGH-STRENGTH ALUMINUM ALLOYS

Strengthening mechanisms operating in aluminum alloys are well known; dislocation strengthening, solid solution strengthening, grain boundary strengthening, strengthening by particles and/or precipitates of intermetallic phases are the most important. If one wants to design an alloy having ultra high strength, such an alloy should consist of:

- extremely fine grains and
- high volume fraction of fine intermetallic phases.

Moreover, supersaturation of aluminum with alloying elements is also positive.

D. Vojtěch, Institute of Chemical Technology, Prague, Czech Republic

Classical Hall-Petch theory says that grain boundaries represent effective obstacles for dislocation movement. Therefore, dislocation slip becomes very difficult in fine-grained structures in which volume fractions of grain boundaries are high. As a result, strength of such alloys grows. In alloys having grain size under a certain critical value (generally tens nm) plastic deformation can not further occur by dislocation slip. In contrast, processes on grain boundaries, such as grain boundary diffusion or slip, control the plastic deformation. This behavior is inverse to the classical Hall-Petch theory, because extremely fine grains facilitate the deformation and reduce the strength. In literature, this attribute of some nano-crystalline alloys is termed as inverse Hall-Petch behavior [1-6].

By using traditional metallurgical routes, i.e. combination of ingot or continuous casting, forming and heat treatment, the grain size can be reduced to about micrometers. Further reduction is possible by using non-conventional processing routes, such as rapid solidification (RS) or intensive plastic deformation. By these routes, grain sizes may be reduced to hundreds and even tens of nanometers. During the rapid solidification of a melt, a deep undercooling of this melt under its melting point may be achieved. As a result, nucleation rate dramatically increases producing a high number of refined grains in a solidified structure. Intensive plastic deformation, on the other hand, is a solid state process. It can be realized by accumulative roll bonding (ARB), equal-channel angular processing (ECAP) and other techniques [7, 8]. Intensive plastic deformation generally performed at relatively low temperatures introduces a high amount of defects into aluminum lattice. It results in a high driving force for nucleation of new grains and recrystallization. By an appropriate combination of deformation and subsequent heat treatment, nano-crystalline structures with controlled grain size can be obtained.

High fraction of sufficiently refined intermetallic phases can be obtained by using high concentrations of alloying elements. However, in conventional metallurgy maximum concentrations are limited due to undesirable effects like segregations, formation of coarse primary intermetallic phases and other. These negative features can be in part or totally removed by using rapid solidification in preparation of alloys. As stated before, rapid solidification leads to a significant refinement of present phases. Moreover, only small volumes of melts can be rapidly solidified and it removes problems with segregations. Of course, rapidly solidified powders are further processed to obtain a desired shape.

Beside structural refinement, rapid solidification brings about another favorable structural feature – considerable supersaturation of Al-based solid solution with alloying elements. This supersaturation results from solute trapping at a rapidly moving solid/liquid interface [9]. The supersaturation enhances age hardening potential of an alloy and also hinders dislocation movement which supports strengthening.

In principle, both rapid solidification and intensive plastic deformation can be applied on conventional alloy systems, as well as on qualitatively new systems. In literature there are a number of reports containing both concepts. For example, by rapid solidification of an Al-Zn-Mg-Cu alloy combined with subsequent hot extrusion, a tensile strength of more than 800 MPa was achieved [10]. However, rapidly solidified alloys of non-conventional compositions recently attracted great interest, because they are able to achieve tensile strength exceeding 1000 MPa. In particular, RS Al-TM-based alloys (TM=transition metals, such as Fe, Ni, Cr, V, Zr, Ti, rare earth metals etc.) with amorphous or nanocrystalline structure are of importance. It was reported that ultra-high tensile strength levels of above 1200 MPa, more than double that of the commercial high-strength Al alloys, were achieved for some fully amorphous RS Al-based alloys.

The excellent mechanical properties have been measured on the rapidly solidified ribbons of the amorphous alloys. To obtain a compact product, these ribbons should be milled into powder and extruded. However, the amorphous phase is metastable, i.e. it transforms to a more stable crystalline phase at elevated temperatures. The crystallization of amorphous phase sometimes called devitrification limits the maximum extrusion temperatures which thus should be as low as possible. Nevertheless, it has been shown that a narrow temperature interval between the glass transition temperature and a temperature of the onset of crystallization of the amorphous phase can be sometimes used for extrusion. At these temperatures an alloy behaves like a supercooled liquid, which means that it may be capable of a slow viscous flow under a loading. Although small amounts of Al-based amorphous alloys have already been prepared [11-19], there are many problems which should be solved. If the amorphous RS Al-TM alloys crystallize under carefully controlled conditions, nanocrystalline alloys can be prepared. Presence of the nanocrystalline particles may further increase strength due to a high area of internal interfaces. It was reported that even 1500 MPa tensile strength was achieved for partially crystallized Al-9at. %Ni-1at. %Fe-2at. %Ce alloy ribbon [11]. Comparison of specific strength for various materials is illustrated in Figure 1.

HIGH-THERMAL STABILITY ALLOYS

The term high thermal stability is related to the mechanical properties. Alloys are generally referred to as thermally stable, if they reduce strength and hardness only very slowly at increased temperatures. In practice, such alloys can be successfully exposed to elevated oper-

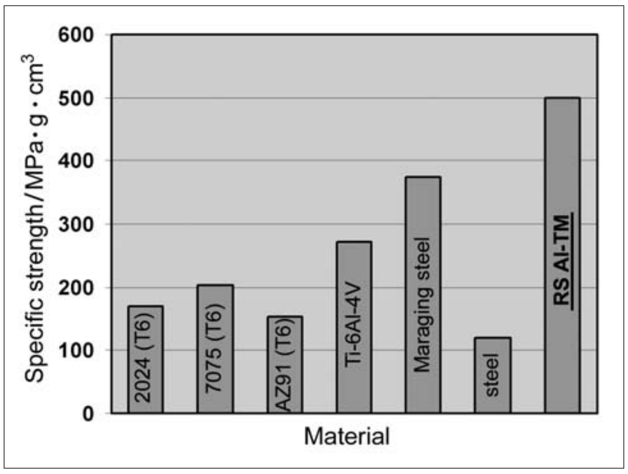

Figure 1 Comparison of specific strength (ratio of tensile strength to density) of various functional materials (2024 and 7075 – wrought Al-based alloys, AZ91 – Mg-9Al-1Zn alloy).

ation temperatures. The thermal stability of commercial age hardenable aluminum alloys is generally low. Structural changes which lead to reduction of their mechanical properties proceed rapidly already at above 200 °C.

The thermal stability of conventional wrought alloys can be significantly improved by alloying with small amounts of scandium and zirconium. These additives form nano-scale dispersoids, such as Al_3Sc and Al_3Zr, which effectively hinder recrystallization and grain growth at elevated temperatures. However, mass production of Sc-containing alloys is unlikely due to a very high cost of scandium metal.

Another approach in improving thermal stability of Al-base alloys is alloying with transition metals (TM) having low diffusion coefficients in solid aluminum [20-25]. The slow diffusivity of elements retards structure transformations at elevated temperatures, such as grain growth, coarsening of intermetallic phases etc., which are reasons for the strength and hardness reduction. Diffusion coefficients of various elements in solid Al are illustrated in Table 1. It can be seen that transition metals like Fe, Cr, Zr, Mn show significantly slower diffusivity in Al than copper, magnesium, zinc and silicon.

The alloys containing high concentrations of TMs can not be produced by conventional casting or ingot metallurgy, due to large volume fractions of hard and brittle intermetallics detrimental to mechanical properties. On the other hand, rapid solidification can remove these problems, because it produces finely dispersed phases and, in addition, alloying elements can be in part present in the supersaturated solid solution.

Table 1 **Diffusion coefficients D of elements in Al at 600 °C [26].**

element	D / cm^2 / s at 600 °C	element	D / cm^2 / s at 600°C
Cu	$4{,}8{\cdot}10^{-9}$	Fe	$3{,}8{\cdot}10^{-10}$
Mg	$2{,}1{\cdot}10^{-8}$	Mn	$2{,}5{\cdot}10^{-11}$
Zn	$1{,}6{\cdot}10^{-8}$	Co	$8{,}4{\cdot}10^{-9}$
Si	$1{,}6{\cdot}10^{-8}$	Ni	$8{,}1{\cdot}10^{-9}$
Cr	$1{,}3{\cdot}10^{-12}$	Zr	$2{,}4{\cdot}10^{-12}$

Among rapidly solidified Al-TM alloys with increased thermal stability, two systems have focused the greatest interest: Al-Fe and Al-Cr. Both alloying elements are easily available and inexpensive. The Al-Fe-based alloys in which Fe concentration can achieve 10 wt. % generally contain others additives like e.g. V, Si, Ce, Mo or Ti. Alloys developed by Alcoa (e.g. Al-8wt. %Fe-4wt. %Ce) or Allied-Signal (e.g. Al-8wt. %Fe-1wt. %V-2wt. %Si) show excellent thermal stability. They retain sufficient tensile strength of above 300 MPa up to 350 °C [11], whereas tensile strength of conventional 2XXX Al-Cu alloys at 350 °C is below 100 MPa. Strength of Al-Fe-V-Si alloys exceeds commercial age hardenable Al-based alloys already above approx. 150 °C.

Another group of thermally stable alloys is based on the Al-Cr system. Chromium shows one of the lowest diffusion coefficients in solid Al, see Table 1 [26]. In addition, in rapidly solidified alloys, chromium is able to achieve high supersaturation in Al solid solution. It has been shown that mechanical properties, as well as thermal stability, of the Al-Cr alloys can be considerably improved by alloying with additional elements, such as Zr, Fe, Ti etc. Particularly, the Al-Cr-Fe-Ti system has been extensively studied. It was shown that room temperature mechanical properties of these alloys are retained almost constant even after long-term annealing at 400 °C [27, 28], see Figure 2.

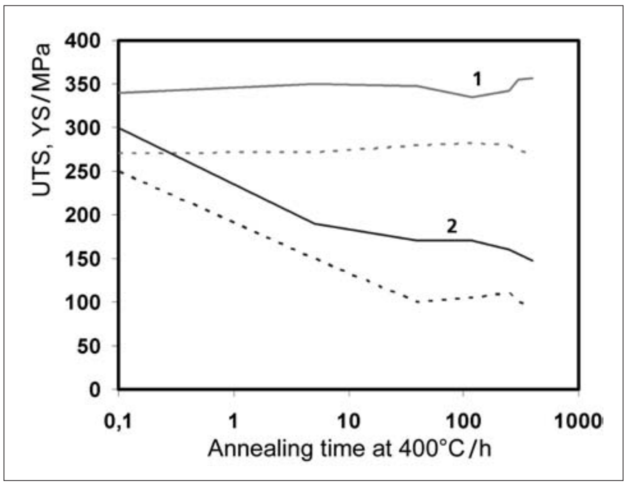

Figure 2 Room temperature tensile properties of Al-6wt. %Cr-2wt. %Fe-0,5wt. %Ti alloy (red lines) prepared by rapid solidification and hot extrusion versus annealing time at 400 °C. Conventional thermally stable Al-12wt. %Si-1,2wt. %Cu-1,2wt. %Mg-1wt.% Ni casting alloy (blue lines) commonly used for production of thermally loaded parts like pistons is shown for comparison (solid lines – UTS – ultimate tensile strength, dashed lines – YS – yields strength).

PROCESSING OF ULTRA HIGH-STRENGTH AND HIGH-THERMAL STABILITY AL-BASED ALLOYS

As stated in previous paragraphs, conventional metallurgical routes can be hardly used to prepare alloys containing high concentrations of non-conventional alloying elements, mainly transition metals. Among processes utilized for preparation of Al-TM alloys, rapid solidification appears to be most suitable. The common feature of all rapid solidification techniques is that rapid cooling is achieved only in a relatively small volume of melt. This means that processing of rapidly solidified alloys should involve their subsequent compaction into a desirable shape, e.g. hot extrusion, forging etc. Nowadays, several techniques of rapid solidification are used for research purposes, for example melt atomization, spraying of melt onto a substrate, melt spinning, remelting of thin surface layers and others. However, only melt atomization and melt spraying may be potentially utilized for mass production.

Melt atomization is the most viable route for production of rapidly solidified powders of Al-based alloys. An alloy to be powdered is first melted in an induction furnace. The melt is then introduced to a chamber in which either pressure gas, such as nitrogen (gas atomization), or a rapidly rotating disc (centrifugal atomization) atomize it into fine droplets which immediately solidify. The processes and resulting powders are shown in Figure 3. Morphology of gas atomized powder particles is almost spherical, whereas centrifugal atomization produces flake-like particles. Rapidly solidified powders commonly contain various particle dimensions depending on melt viscosity, surface tension and on the type of RS method used. High pressure of the atomizing gas or high rate of atomizing disc generally produce powders dominated by fine particles and vice versa. The smaller the powder particle, the higher the cooling rate of this particle. This is the reason for which fine powder fractions consisting of the most metastable structures are sometimes separated for further processing.

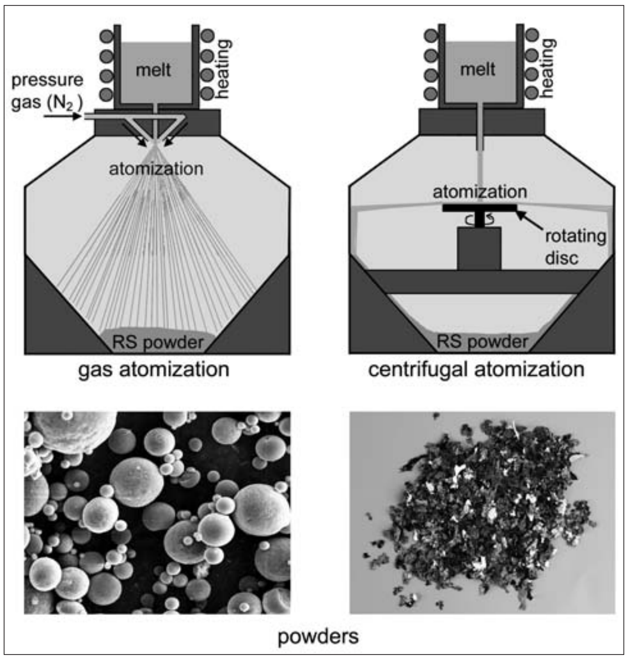

Figure 3 Schematic simplified drawings of gas and centrifugal atomization with scanning electron and optical micrographs of resulting particles.

The compaction of powders can be in principle performed by various techniques. For aluminum alloys, hot extrusion is mostly utilized, involving encapsulation of a powder into an aluminum or copper container, followed by its evacuation and sealing. Extrusion temperatures of Al-TM alloys lie between 300-600 °C and depend on chemical composition of a powder, its deformability and on properties required. If one wants to obtain a product with high strength and hardness (but with lower ductility), lower extrusion temperatures are used. However, the reduced extrusion temperatures require increased pressing forces during extrusion, so that we may be limited by extrusion press used. Extrusion temperature is often a compromise between required mechanical properties and maximum achieved pressing force. Advantage of the hot extrusion is a relatively low cost and that it produces semi-products with high density and optimum mechanical properties in one step. Oxide layers which are always present on Al-based powder particles, due to oxygen traces in atomizing gas or in atomizing chamber, are broken during extrusion by intensive friction between particles. This ensures sufficient contacts between particles and their strong diffusion bonding.

Melt spraying onto an appropriate substrate produces semi-products which are subsequently forged or extruded to desired shapes, see Figure 4. Due to rapid solidification of a melt, resulting structure is uniform and refined. When hard particles are continuously supplied into the melt flow, aluminum matrix composites can be formed which well resist to high mechanical and temperature loadings. At present, this technology is em-

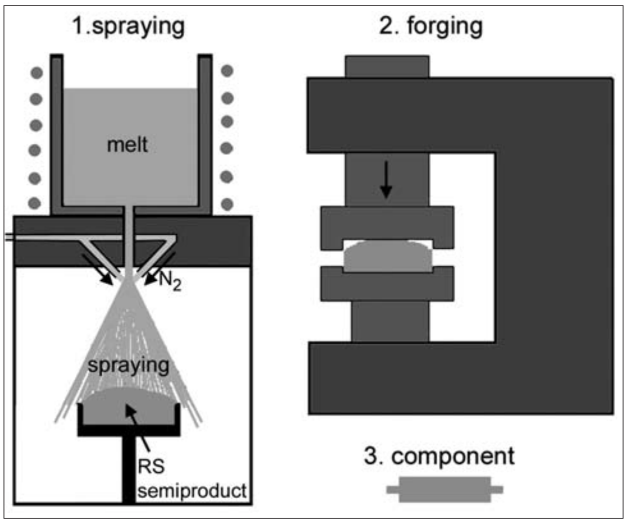

Figure 4 Schematic simplified drawing of melt spraying and subsequent forging.

ployed in automotive industry for production of components or their parts for combustion or diesel engines (pistons, cylinder liners etc.).

CONCLUSIONS

It is demonstrated is the present review paper that aluminum alloys still have a great potential for further considerable improvement of properties and performance. However, much research and development work is still needed before new alloys can be produced in industrial scale for an acceptable cost which is competitive to conventional Al-based alloys. Although powder metallurgy is well established today and Al-TM-based alloys have been known for three decades, there is a certain skepticism towards the mass utilization of this technology and materials in aluminum industry. This situation is given by a lack of practical experience and industrial standards connected with properties, handling and processing of aluminum-based powders. Moreover, high reactivity and even explosiveness of improperly treated Al powders, which led to several dangerous accidents in the past, support conservatism of the industry. Historically, powder metallurgy parts have a bad reputation, because they are commonly regarded as porous, brittle and low-strength. However, this is not true when using a proper processing route of rapidly solidified powders.

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