

QUENCHING OF ALUMINIUM ALLOYS IN SODIUM SILICATE SOLUTIONS OF VARIOUS SILICATE CONCENTRATIONS

P. Krug, T.Tenostendarp, W. Stips

Precipitation hardening is a common process in heat treatment of automotive components, e.g. chassis parts, cylinder heads and others. Due to distortions after water quenching subsequent levelling operations or machining is necessary, which causes additional cost. Avoiding or minimizing such distortions is desirable and can be achieved by applying alternative quenching media. The use of aqueous solutions of sodium silicate enables one to adjust the quench severity in between pure water and high concentrated polymer solutions. Since critical cooling velocity is low among the 6xxx alloys in comparison to 2xxx or 7xxx alloys, a smaller cooling rate can be acceptable. Sodium silicate solutions are non-toxic and will cause no environmental hazards. This is an overview about the use of silicate media, the mechanical properties and the hardness of aluminium alloys quenched in sodium silicate solutions of various concentrations and the possibility of compensating the reduced cooling velocity by modifying the ageing parameters.

KEYWORDS: QUENCHANT – ALUMINIUM – HEAT TREATMENT – SODIUM SILICATE – DISTORTION.

INTRODUCTION

Distortion of aluminium components is often a result of quenching due to thermal gradients occurring during rapid cooling. Different quenching media with various quenching intensities are available, e.g. polymer solutions, oil, hot water, pressurized air or other gases, to adjust cooling velocity. Especially the 6xxx series aluminium alloys allow moderate critical quench rates in the range of 1 to 50 K/s [1]. A quenchant with adjustable quench intensity and - of course non-toxic - would be of competitive advantage in combination with easy handling, low cost and with reduced or even no efforts of cleaning necessary. Therefore it should be water based and available in appropriate amounts. Polymer quenchants will fulfil the boundary condition of thermal gradient reduction and will lead to a more uniform heat transfer but their cooling mechanisms are not fully understood yet and a sticky film will remain on the component's surface which has to be removed prior to ageing.

In water quenching usually four phases of heat transfer mechanisms can be found [2]: Immediately after immersion of the component a vapor film is formed on the component's surface. Due to its poor heat conductivity and good insulating properties, heat transfer coefficients are very small in

this phase. After reaching a distinct temperature (Leidenfrost point) turbulent boiling starts, which raises the heat transfer coefficient significantly up to several thousand W/m^2K . This is followed by the phase of nucleate boiling and finally to convective cooling. These phases can be controlled by the surface condition of the component [3-7] the flow velocity, the composition as well as tap water hardness [8], the viscosity and the boiling point of the quenchant [9].

**Peter Krug, Thomas Tenostendarp, Walde-
mar Stips**

Cologne Technical University of Applied Sciences - Department
of Automotive Engineering - Betzdorfer Strasse 2,
50679 Cologne - Germany

An aqueous sodium silicate solution may fulfil the before mentioned requirements. It is water based with a pH value between 9 to 11 which is slightly alkaline. It exhibits a viscosity higher than that of water, is non-toxic and - since it is used in several applications like silicate paintings and inorganic binders in sand casting industry – is therefore available in huge amounts at low cost.

Sodium silicate solutions are colloidal, mostly clear or slightly opaque solutions, consisting of small particles homogeneously distributed in water, causing light to be scattered (Tyndall effect). These particles exist as single nanometer sized spheres (colloidal solution) or as small polymerized networks (gel). By controlling pH value and/or the content of other ionic compounds one can influence the solution in on of both directions. Usually it is available along with different viscosity grades, which are still given in the non-SI unit Baumé (°Bé).

Only scarce information can be gained from literature about the application of sodium silicate solutions as a quenchant. First trials has been conducted in 1931 by Thomas Hamill, from the US. Bureau of Standards [10]. Different concentrations of sodium silicate solutions has been used in steel hardening experiments, showing the ability to modify the cooling intensity somehow in between water and oil. As an advantage he found that there was no corrosive action in contact with steel which is rather rational since plain steels are in passive state at those pH-values. As disadvantage he mentioned the instability of some diluted concentrations in terms of flocculent precipitation, which can be fixed by adding a certain amount of sodium hydroxide. A transcript from the Russian author Yu. G. Krotov and co-workers is available in [9]. They used sodium silicate with a concentration of 50% quenchant as an admixture together with K- and Na- spruce wood tannins in comparison to sulphite-alcohol malt concentrate with different additives for quenching the aluminium alloy D16 (AlCu4Mg1) and V95 (AlZn5.5MgCu). Only limited information is given about the effect on cooling velocity, distortion and the resulting mechanical properties but film formation is mentioned although it remains unclear from which substance these films have originated.

Effect of nanoparticle size and coating with ceramic layer of various thickness was reported in [11-13]. They found, that a certain content of nanoparticles may enhance cooling but care has to be taken, since altering of the boiling behaviour will occur.

Taking all the information together, one could claim that the higher viscosity may lead to a retarded boiling, but nanosizes particles in a colloidal solution may improve cooling intensity. In addition, one may expect that a solid silicate film will form on the surface after immersion due to the calcifying effect of the hot component. Film formation can shift the Leidenfrost temperature to higher values, but this depends on the resulting film thickness and the growth velocity of the silicate film in comparison to heat transfer into the surrounding liquid.

Delivery state was semi-hard for the plates and T6 peak aged for the rods. The chemical composition is given in Table 1.

EXPERIMENTAL

For quenching trials rolled sheets (thickness 25 mm) and extruded rods (31 mm in diameter) made of aluminium alloy EN AW 6082high strength were used (see also Figure 1 and 2).

Delivery state was semi-hard for the plates and T6 peak aged for the rods. The chemical composition is given in Table 1.

Tab. 1 - Nominal chemical composition

Chemical Composition of EN AW 6082 in wt.-%										
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	other	Al
Min.	0.7			0.4	0.6					
Max.	1.3	0.5	0.1	1.0	1.2	0.25	0.2	0.1	0.05	Bal.

Rods were machined down to a diameter of 25 mm and with two 3 mm holes drilled parallel to the axis of the rods, one in the centre and one near the surface, for placing two thermocouples (Type K, class 1, Sensortherm GmbH) 50 mm from the upper end of the rod. A drawing is given in figure 1 showing the relevant geometrical features. The surface was wet grinded with 4000 emerald paper to an average roughness of 5.5 +/- 0.7 µm. Temperatures were sampled by a TC-08 AD/DA data logger (Omega Engineering GmbH) with sampling

rates of 0.01 per second. For optimization the ageing time and temperature, small cylinders of 30 mm diameter and 30 mm height were machined and heat treated, too.

Heat treatment

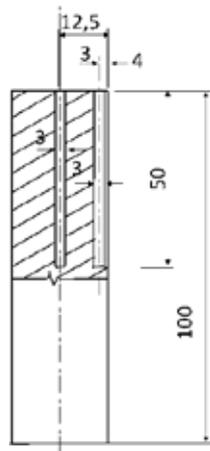


Fig. 1 - Rods with holes for thermocouples for recording cooling rate

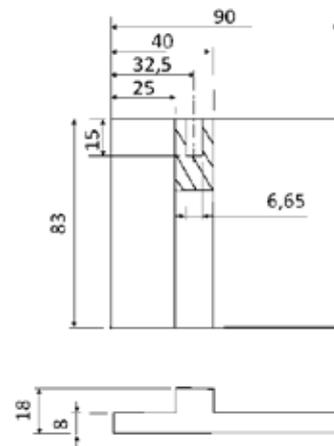


Fig. 2 - Plates with fillet for characterization of distortion behavior.

For distortion characterization, plates with an asymmetrical fillet were machined out of the rolled plates (see figure 2). Dimensions were measured by using an ATOS II Scanner und ATOS Professional Software (GOM GmbH). The rods were solution annealed for 40 min. at 540 °C in a vertical resistance furnace (Gero Carbolite HTRV 40/500-16) and plates in a resistance furnace (Carbolite, Typ: ELF 11/14B) for the same time at same temperature. Ageing was done in a Memmert UF55 circulating air furnace. All furnace temperatures were recorded and controlled by the same type of thermocouples as above. For quenching commercially available sodium silicate solutions (WHC GmbH) was applied with a viscosity of

37/40 °Bé and various concentrations from 0 to 35,5 wt.-% sodium silicate content were adjusted by using simple tap water. The concentrations used and data of sodium silicate solutions are given in table 2. The quenching procedure was recorded by using a Sony RX100 Mark 4 camera with up to 960 fps and a high speed camera Photron FASTCAM Mini AX200 (Model 900K-M-16GB) with frame rates up to 30.000 fps. Tensile tests were performed with a 100 kN tensile test unit (Z100 TEW) from company Zwick Roell GmbH using short proportional tensile rods with a diameter of 10 mm and hardness testing was performed at a Wolpert hardness tester DIATESTOR 2Rc using Brinell hardness HB2.5/125.

Tab. 2 - Data of sodium silicate solutions

Concentrations used in quenching experiments and data of the 35.5 wt.-% solution					
0 (= pure water) 2.5 / 5.0 / 7.0 / 10.0 / 12.0 / 18.0 / 20.0 / 30.0 / 35.5 in wt.-%					
Baumé (°Bé)	Density (g/cm ³)	Na ₂ O (wt.-%)	SiO ₂ (wt.-%)	H ₂ O(wt.-%)	Viscosity (cP)
37-40	1.34-1.38	8.2	27.3	64.5	70-150

RESULTS

Boiling behaviour

The boiling behavior of pure tap water and 35.5 wt.-% sodium silicate solution is completely different. As shown in figure 3 a) to c) on can distinct clearly the phases of boiling during the first seconds. In contrast, there is no evidence for any boiling action with sodium silicate solution (figure 3 d) to f)). From high speed recordings it cannot be revealed if there is a vapor blanket around the rod or not. Nevertheless, no turbulent bubble formation can be observed. There are some areas where small clusters adhere at the surface and move very slowly upward. From visual assessment, this cooling behavior is similar to the quenching in ionic liquids.

At the lower right picture beginning silicate film formation can be seen, but it will not grow immediately fast over the complete surface. During further cooling more and more silicate "islands" occur and grow slowly together while some small bubbles appear from time to time at and separating of the surface (see picture on the lower left).



Fig. 3 - a) Quenching in pure water 1 second after immersion.



Fig. 3 - b) Quenching in pure water 1.75 seconds after immersion.



Fig. 3 - c) Quenching in pure water 3 seconds after immersion.



Fig. 3 - d) Quenching in silicate solution (35.5 wt.-%) 1 second after immersion.



Fig. 3 - e) Quenching in silicate solution 1.75 seconds after immersion.



Fig. 3 - f) Quenching in silicate solution 3 seconds after immersion.

If the concentration is lowered to 20 wt.-% film formation will appear instantaneously during immersion with a growth speed of approximately 0.5 m/s (!). Even lowering the concentration down to 2.5 wt.-% will lead to the same result but with decreasing film thicknesses.

Heat treatment



Cooling rate

Comparing the cooling curves of both samples reveal for the high silicate concentration a period of about 20 seconds the existence of an insulating vapor film with subsequent slow

cooling but nearly no difference in the temperatures of the two thermocouples near the surface and at the center of the rod (see figure 4a) and b)).

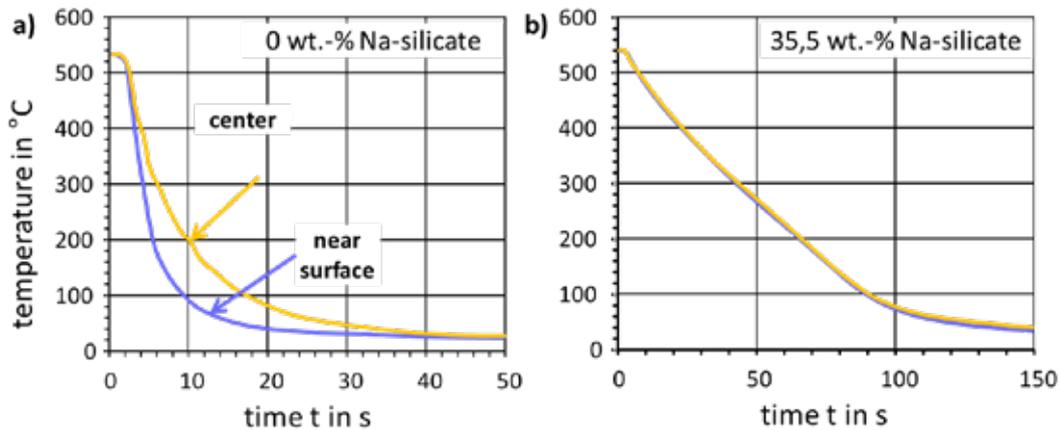


Fig. 4 - a) Cooling curves recorded during quenching of rods. Temperatures measured in the middle of the rod height.
b) Cooling curve for rods quenched in silicate solution (35.5 wt.-%). Please note the different time scale!

The sample quenched in pure water exhibits only a small time interval of film boiling (approx. 1 to 2 seconds) with subsequent nucleate boiling. Note that the time scale is different for both graphs by a factor of 3. This effect can be better

identified, when the calculated cooling velocity is shown as a function of temperature, as it is given in figure 5 a) and b). A difference of about 45 °C/s exists in the tap water quenched rod.

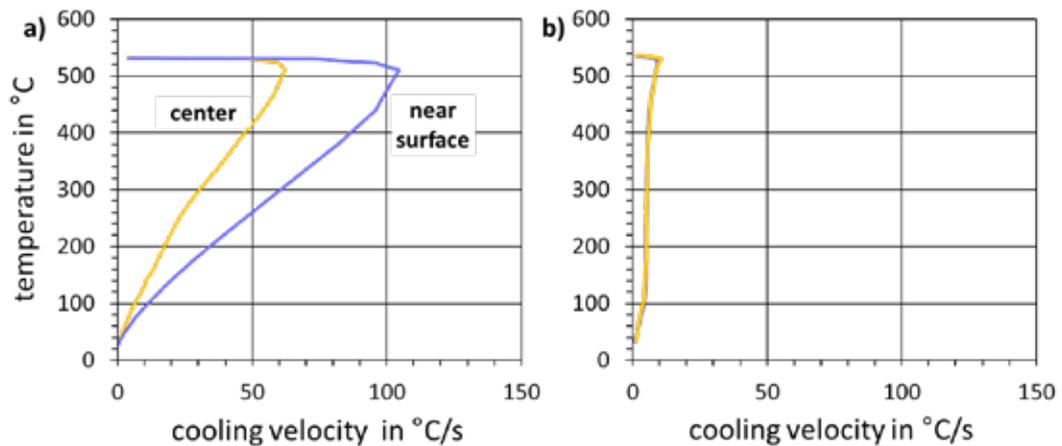


Fig. 5 - a) Cooling rates calculated from cooling curves recorded during quenching of rods in pure water.
b) Same as in a) but quenched in silicate solution (35.5 wt.-%). The cooling rates measured in the center and near the surface show only very slight differences.

Mechanical Properties

Since cooling velocity is rather slow in the 35.5 wt.-% silicate solution it is of interest how mechanical properties are influenced by the cooling rate. Tensile test specimens were heat treated and quenched in silicate solutions of various concentrations and tested after an ageing procedure comprising 4 hours at 180 °C. The results of the tensile tests are

shown in figure 6. By increasing the silicate concentration to 10 wt.-% a decrease in strength of approximately 20 MPa will occur. Nevertheless, elongation seem to be unaffected by the reduced quench rate. From 10 to 30 wt.-% silicate concentration the mechanical properties remain unchanged at the same level. Only when the concentration exceeds 30 wt.-% a further decrease of 20 MPa will occur, while elonga-

tion remains further constant. Since strength (and elongation) can be altered by adjusting ageing time and temperature, small cylinders of the same aluminium alloy were solution heat treated, quenched in different media and aged at different times at 180 °C. Water quenched specimens will reach a

Brinell hardness of about 100 HBW2,5/125 after 4 hours. By prolongation of ageing time to 12 hours at 160 °C for the silicate solution quenched specimens, the same hardness value can be reached. Due to the lower ageing temperature one can expect that elongation values will be improved.

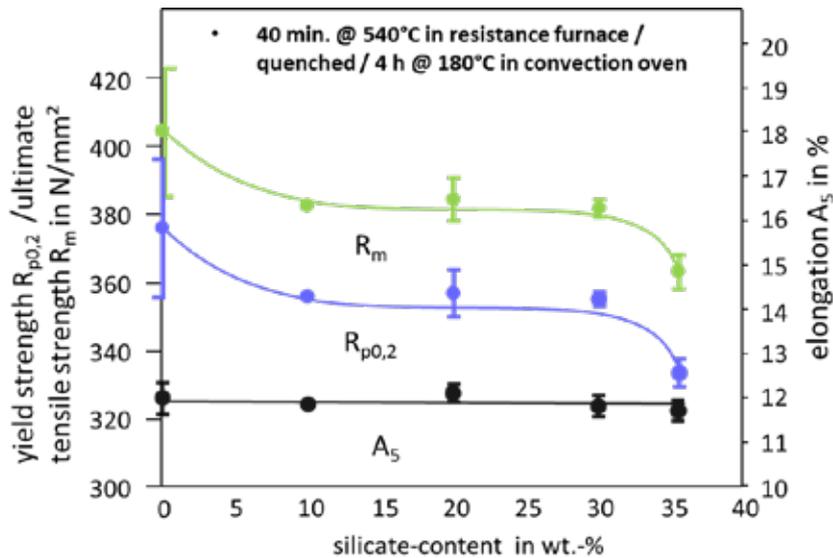


Fig 6 - Mechanical properties after complete heat treatment (solution annealed, quenched and tempered) as a function of silicate content of the quench bath.

Distortion

In figure 7 the results of the distortion measurement is shown for different silicate concentrations and with/without stirring during quenching. With increasing silicate content in the quench bath the quenching velocity decreases which transfers into reduced geometrical deviations.

At about 18 wt.-% the distortions are diminishing. Stirring itself has a positive influence but is not sufficient enough to avoid distortions alone.

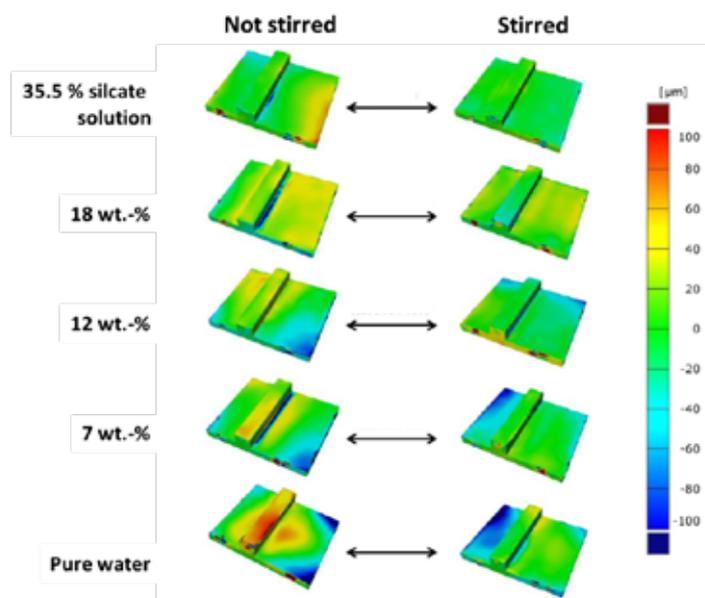


Fig. 7 - Distortion of fillet plate quenched in sodium silicate of varying concentrations.

Heat treatment

DISCUSSION AND OUTLOOK

The results confirm that sodium silicate solutions are appropriate to quench aluminium alloys. By performing quench tests with high strength type EN AW6082, upper critical cooling velocity (UCCR) is too high to avoid the precipitation of zones during the quench process completely, as it is shown

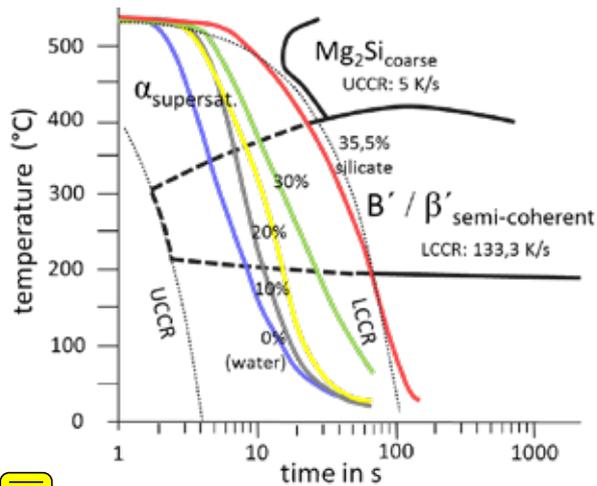


Fig 8 - a) Achieved cooling curves drawn into the underlying time-temperature-precipitation-diagram, taken from [1].

By choosing different silicate concentrations, it is possible to adjust quenching velocity from pure water to those which can be achieved by polymer, oil or ionic liquids (refer to figure 8 b)). No evidence could have been found so far, that the nano sized colloidal particles will enhance heat transfer. The loss of strength can be counteracted by modifying time/temperature regime in the subsequent annealing process. Although silicate solutions do not cause corrosion among the 6xxx aluminium alloys, the calcified coating which remains on the surface has to be removed prior to ageing since residual moisture will cause a significant volume increase of the silicate. This removal can easily be done by using a water jet and warm water. Nevertheless one has to take into account that some amount

in Figure 8 a) even when quenched in pure water at ambient temperature [1]. But is worth to mention that with silicate admixtures up to 35.5 wt.-% high temperature reaction, i.e. formation of coarse Mg_2Si , could be suppressed due to its lower critical cooling rate (LCCR).

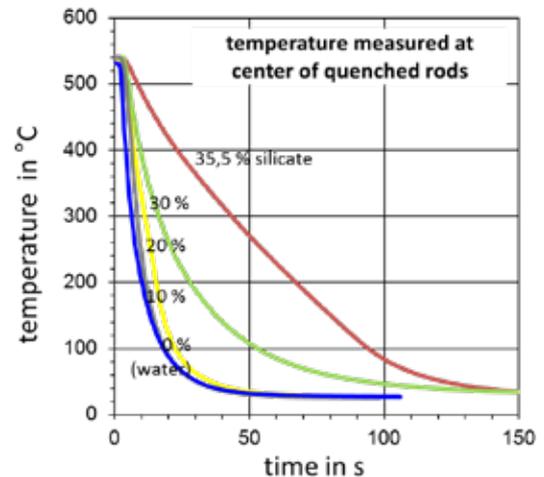


Fig. 8 - b) Cooling behavior can be adjusted by mixing silicate solutions continuously with water.

of silicate will be taken out of the quenching bath. Therefore monitoring of the bath quality by controlling the pH-value and the viscosity is mandatory.

Further investigations will be made to elaborate the film formation mechanism by adding inorganic compounds to the water silicate solution. Different surface structures will be tested, too, because controlling silicate film thickness at certain locations on the component may lead to a "designable" cooling velocity within one component. These experiments will also include higher concentrations to gain more information about the boiling suppressing mechanism of silicate solutions with high viscosities.

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