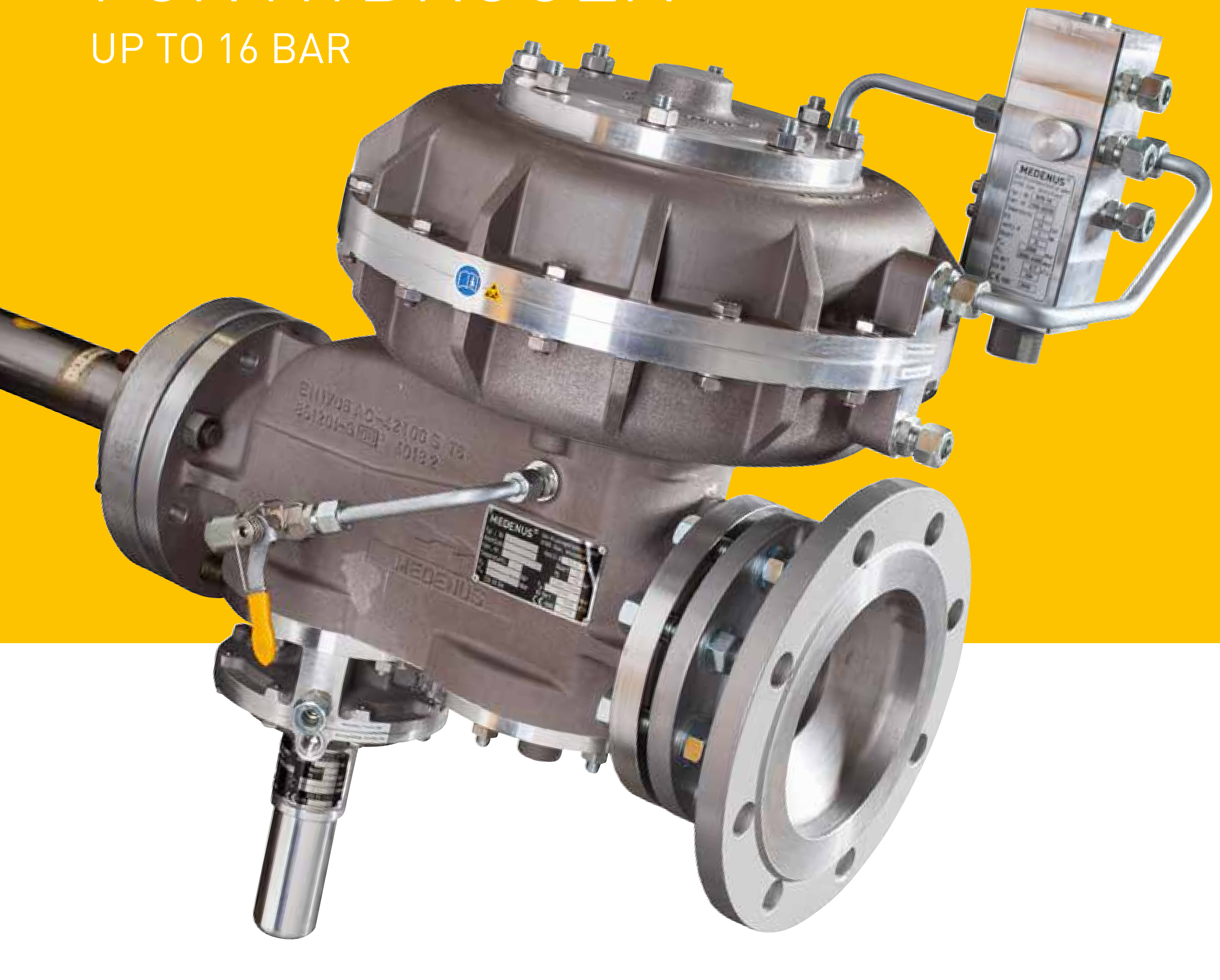
MEDENUS

Gas Pressure Regulation

GAS PRESSURE REGULATION FOR HYDROGEN

UP TO 16 BAR



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GAS PRESSURE REGULATION FOR HYDROGEN UP TO 16 BAR USING ALUMINUM MATERIALS

Owing to the increasing importance of the topic regarding gas pressure regulation of hydrogen and contradictory statements regarding the use of aluminum alloys for these applications up to 16 bar, we, as MEDENUS Gas-Druckregeltechnik GmbH, have ordered from the RWTH Aachen a comprehensive investigation and literature search into this problem. The objective was to examine, first and foremost, the aluminum alloys used by MEDENUS Gas-Druckregeltechnik, with the aim to approach the open questions scientifically and to find answers.
The results of these investigations have shown that the alloys used by us can be used without restrictions for dry hydrogen up to an inlet pressure of 16 bar and represent an attractive alternative to conventional steel/cast iron and copper materials. Additional advantages are their substantially reduced weight, thus giving better handling and a higher corrosion class (C5-I) even without painting. This investigation focused specifically on the alloys used by MEDENUS and has no validity for other aluminum materials.

The specific T6 heat treatment of the alloy mentioned in the report is also in use for MEDENUS devices and is implemented by one of Europe´s most advanced aluminum foundries, Ohm and Häner in Olpe, Germany. The owners of the foundry are simultaneously also the owners of MEDENUS, thus giving rise to further positive synergies.

The alloys that were examined are used at MEDENUS not only for spring-loaded (R and RS series) but also for pilot-controlled gas pressure regulators (RSP series), cellular gas filters (DF series), and safety relief valves (SL series) in all nominal widths up to DN200.

The specific pressure and tightness test for hydrogen applications is done at MEDENUS with helium as the test medium.

THE ANALYSIS BY RWTH AACHEN (DUE TO THE VOLUME OF THE ANALYSIS, IT HAS BEEN ABBREVIATED TO INCLUDE ONLY THE MOST RELEVANT SECTIONS):

QUESTION

The hypoeutectic aluminum cast alloy AlSi7Mg0.3 (EN-AC 42100) is being used widely in the automotive industry or aviation and aerospace technologies and is also being used for safety-relevant structural components. This range of applications is due to the favorable properties of the material, such as low density, good casting properties, good mechanical properties in the heat-treated state, and generally good corrosion resistance.

Previously, especially steel casting, cast iron, and brass materials have been used as material for gas pressure regulation fittings for hydrogen. However, due to the attractive properties of AlSiMg0.3 and based on the literature of the last 20 years, the suitability of the material for such an application shall now be investigated focusing especially on the risk caused by hydrogen embrittlement.

STARTING POSITION AND LITERATURE SEARCH

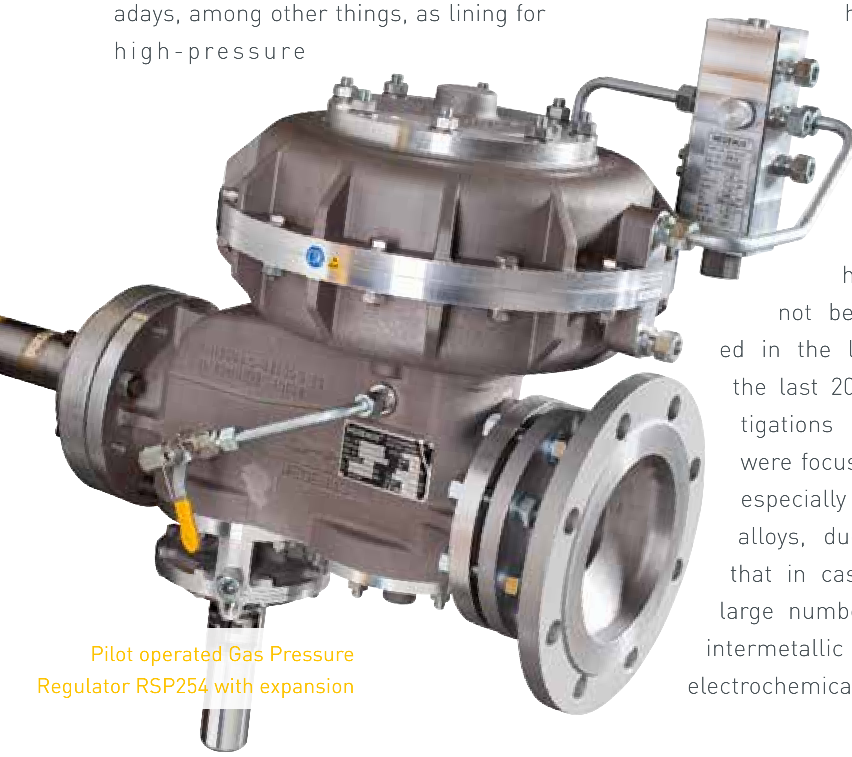
The fact that hydrogen has a high solubility in liquid aluminum, which, due to the simultaneously low solubility in the solid, may lead to the formation of gas bubbles during solidification, is generally known. The resulting porosity in the material may result in a dramatic deterioration of the mechanical properties, which, however, can be largely avoided by a degasification treatment. However, the reaction of gaseous hydrogen with the solidified cast material has not been investigated in the literature until now.

For aluminum wrought alloys, the reaction with hydrogen in the solid state has been investigated much better and comprises the phenomena of stress corrosion in which, under a mechanical load and the effect of a corrosive medium, a simultaneous anodic dissolution reaction and cathodic embrittlement can take place and of „Environmentally Assisted Cracking" (EAC) which describes pure hydrogen embrittlement in moist air without dissolution of the material. The effect of dry hydrogen gas on the mechanical properties of aluminum and its alloys has also been already examined by several groups and been classified as being negligible. It is assumed that the reason for this is the protective action of the thin oxide layer on aluminum at which the energetically unfavorable cleavage and addition reaction of hydrogen molecules is inhibited.

The degradation of the mechanical properties of aluminum materials due to hydrogen is in most cases attributed to the absorption of hydrogen at „traps" such as grain boundaries, precipitations, dislocations, and voids, leading to a local decrease in ductility. Known mechanisms include hydrogen-enhanced localized plasticity (HELP), hydrogen-enhanced decohesion (HEDE) and absorption-induced dislocation emission (AIDE). Especially the secondary phases MgZn2, Mg2Si, Al-Fe-Si and Al7Cu2Fe have been identified as hydrogen traps. Accordingly, the susceptibility to hydrogen embrittlement can be correlated, among other things, to the existing microstructure.

For Al-Zn-Mg(-Cu) wrought alloys of the 7xxx series, susceptibility not only to stress corrosion but also to EAC has already been observed. Whereas the prevalence of hydrogen embrittlement in stress corrosion has not yet been clearly elucidated, the investigation of EAC has shown a clear correlation between the crack propagation rate and relative moisture which determines the introduction of hydrogen. However, in a dry hydrogen atmosphere, no embrittlement of the 7xxx alloys has been observed. The microstructure of 7xxx alloys exhibits, in addition to the finely divided strength-increasing MgZn2 phases, also phases high in Cu, such as Al2Cu/Fe and, depending on the composition, also Mg2Si and Al-Fe-Si.

Al-Mg-Si(-Cu) alloys of the 6xxx series are known for being insusceptible to stress corrosion, while nothing is known in the literature about EAC of 6 xxx alloys. Despite the lack of proof for the susceptibility of 6xxx alloys to hydrogen embrittlement, this possibility is still being discussed by a few groups. However, in the examination of 6061-T6 in dry hydrogen gas, no adverse effect on the mechanical properties has been observed, which is why this material is used nowadays, among other things, as lining for high-pressure hydrogen tanks. The microstructure of 6xxx alloys is distinguished in particular by Mg2Si phases, in addition to which typically Al-Fe-Si phases are also present. However, this microstructure is devoid of the zinc-containing phases of the 7xxx alloys, thus generally providing fewer hydrogen traps. Upon comparing 6061-T6 with 7075-T6, a lower distribution density of precipitations in the 6xxx alloy was also observed, resulting additionally in a smaller amount of absorbed hydrogen in the material.



Pilot operated Gas Pressure Regulator RSP254 with expansion

The susceptibility of AlSi7Mg0.3 to hydrogen has not been investigated in the literature over the last 20 years. Investigations on corrosion were focused in the past especially on wrought alloys, due to the fact that in cast materials a large number of complex intermetallic phases whose electrochemical properties are largely unknown are typically present. Nevertheless, some studies have shown a generally low rate of corrosion of AlSi7Mg0.3 in artificial seawater and a susceptibility to intercrystalline corrosion in the cast state, which, however, can be easily minimized by applying high cooling rates. However, the microstructure of the material is described in the literature in detail.

The cast structure of the subeutectic AlSi7Mg0.3 alloy exhibits α-aluminum dendrites in whose interstices an Al-Si eutectic has formed.

Al-Fe-Si phases are also present, with the preferred formation of the α-Al-Fe-Si phase at higher cooling rates and the β-Al5FeSi phase at lower cooling rates. Solution annealing can result in a clear increase in the Mg content dissolved in the matrix and thus in its strength. The increased strength also leads to improved fatigue properties, assisted further by crack deflection on the fibrous Si particles in the eutectic.

For further improvement of the mechanical properties, the material is often converted into the T6 state, achieved

SPRING LOADED GAS PRESSURE REGULATORS

SAFETY RELIEF VALVES

SAFETY SHUTT-OFF VALVES

CELLULAR GAS FILTERS

PILOT OPERATED GAS PRESSURE REGULATORS

by an aging treatment. This changes the microstructure from a dendritic to a homogeneous Al matrix, in which finely divided Mg2Si phases lead to an increase in strength. In contrast, the Si particles become coarser during the heat treatment and adopt a globulitic shape, which has an advantageous effect on the ductility of the material. The quality index which combines strength and ductility of cast materials in a single quantity is, for the T6 state, about 90 MPa higher than for the cast state. Investigations on the dynamic load have additionally shown that AlSi7Mg0.3 in the T6 state withstands non-proportional normal and shear stress better than ductile steels.

Due to the chemical composition of AlSi7Mg0.3 and the microstructure in the T6 state, in combination with the simultaneous presence of Mg2Si and AlFeSi phases in a homogeneous α-Al matrix, this material can be compared rather with the Al-Mg-Si(-Cu) wrought alloys of the 6xxx series than with the Al-Zn-Mg(-Cu) wrought alloys of the 7xxx series. Due to the missing zinc-containing phases, it must be assumed that at a comparable precipitation density, fewer hydrogen traps and thus probably less bound hydrogen is present in AlSi7Mg0.3-T6 and 6xxx alloys than in 7xxx alloys. In addition, the dislocation density compared with the wrought material is reduced due to the missing conversion, resulting once again in the presence of fewer hydrogen traps in the cast material. The role of primary Si phases in the hydrogen embrittlement of aluminum materials has not been investigated in the literature over the last 20 years. However, their globulitic shape in the T6 state decreases local stress concentrations due to a geometric notch effect, making it unlikely that the material will fail at these phases.

SUMMARY AND FORECAST

for the application of castings made of AlSi7Mg0.3 ST6 in gas pressure regulation fittings for dry hydrogen gas atmosphere

The cast alloy AlSi7Mg0.3 ST6 has a potentially lower number of hydrogen traps in the microstructure compared with 7xxx alloys that are susceptible to EAC and stress corrosion. In contrast, 6xxx alloys are being used as lining for high-pressure hydrogen tanks. Due to the proximity of the aluminum cast alloy mentioned to 6xxx wrought alloys in terms of microstructure and chemistry and on the basis of the extensive literature search performed, it must be assumed that AlSi7Mg0.3 ST6 will have similar resistance and be stable in a dry hydrogen atmosphere. Moreover, there is no evidence for any drawbacks compared with steel castings and spheroidal graphite cast iron.

Accordingly, the combination of favorable mechanical processing and corrosion properties of the alloy AlSi7Mg0.3-S/K-T6 makes this material an attractive alternative to conventional steel/cast iron and also copper materials in gas pressure regulation fittings for dry hydrogen gas, used for pressures of up to 16 bar.

AIX-LA-CHAPELLE, 09/04/19

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