Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 74-81

Aluminium Alloy and Technology Developments for Advanced Gas Containment Applications

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Aluminium alloys have been successfully used in a variety of high pressure gas storage applications since the early part of the last century. This paper will outline the key requirements for candidate high pressure cylinder materials; describe the development and exploitation of high strength 7xxx series Al-Mg-Zn-Cu alloys for efficient lightweight storage solutions; and highlight ways in which novel manufacturing technologies and experimental methodologies are being explored to meet changing market requirements. In particular, technology options for large onboard vehicular alternate fuel gas storage systems will be considered. Finally, a number of strategic challenges facing cylinder manufacturers, the extended gas containment supply chain, and the broader aluminium industry will be discussed.

Keywords: *7xxx series, alloy design, gas containment, thermomechanical processing, modeling.*

1. Introduction

The dramatic advances in aluminium alloy science and technology during the last hundred years, accompanied by successful and rapid exploitation into a multitude of commercially and societally important end-user applications, must surely be considered one of the greatest innovation stories of the previous century. Indeed, it is difficult to imagine a world without aluminium's presence in commercial airline travel, road and rail transport, hygienic packaging for food and beverages and the construction industry. The growth in the aluminium industry is particularly remarkable when considering that extraction was only developed in the late 19th century and the discovery of age-hardening followed at the beginning of the 20th century, as described by Polmear [1]. A century later, in 2008, the level of global primary aluminium production was reported at 25.6 million metric tonnes, or approximately 70,000 tonnes per day [2]. A major challenge facing today's aluminium industry is the requirement for sustainability and efficiency in order to both ensure profitability and, importantly, to reduce the impact on the environment. Considerable efforts are thus directed toward deploying aluminium alloys in applications where their inherent light weight and recyclability can deliver real benefits. In parallel, it is desirable to increase the use of recycled rather than primary aluminium, since this greatly reduces the energy required for material production by a factor of around 20. In 2008, it was reported that approximately 2.7 million metric tonnes of aluminium was recovered from purchased or tolled scrap [2], i.e. around 10% of the primary production. New approaches to processing scrap, to improve the performance and properties, are being explored as a means to increasing the use of secondary material in some of the more demanding or high integrity applications [3]. The major market sectors for the aluminium industry are undoubtedly still transportation, packaging and civil engineering. It is interesting to note, however, that among the many other applications of aluminium alloys, high pressure gas cylinders have been described as a significant end use, with the potential to benefit from earlier industry developments in high strength aerospace alloys [4].

2. The Use of Aluminium Alloys in High Pressure Gas Cylinders

Large scale production of seamless aluminium alloy high pressure gas cylinders commenced around 1960, with the advent of cold impact (or backward) extrusion technology. Prior to this time, limited numbers of aluminium pressure containers had been manufactured in Europe but using multi-stage fabrication processes that were somewhat complex and inefficient, thus rendering aluminium cylinders rather expensive compared to the more established steel products. The first volume produced cylinders were based upon the 6xxx series Al-Mg-Si alloy system, and were used to store CO_2 for the beverage industry. An excellent account of early cylinder development and manufacture was given by Woodward and Bates [5].

Although 6xxx series cylinders are still in widespread use today, applications have become more widespread and technologically more demanding in recent years. In many markets such as health care, life support and alternative fuel vehicle applications, end-users require lighter weight solutions for increased portability and storage efficiency. One aspect remains constant irrespective of the end use however; all high pressure gas cylinder applications are highly safety critical. As a consequence, extreme caution and robust quality management principles must be exercised throughout product design and manufacture, and indeed must continue throughout the service life of the cylinder. Alloy selection is of great importance as suitable materials must exhibit a particularly demanding balance of mechanical strength, toughness and resistance to environmentally-induced degradation mechanisms. Some applications, such as specialty gas storage, may also require certain surface characteristics. One of the newest and most exciting opportunities for lightweight cylinders is in the storage of high pressure gases for alternative fuel (AF) vehicles. While there is considerable focus on developing an infrastructure for a hydrogen-based economy in the medium-to-long term, significant 'here and now' demand exists for compressed natural gas (CNG) vehicles. Aluminium alloys can provide an advantage over steel for traditional structural automotive components, where there is a direct correlation between fuel consumption and vehicle weight. Similar benefits may therefore be expected by adopting lightweight gas containment solutions for alternate fuel vehicles.

2.1 Cylinder Construction and Technology Options

Different cylinder technology options are available, depending on the ultimate application and the importance of 'lightweighting' to the end user. Monolithic all-metal structures referred to as Type I cylinders, are perfectly suitable for many stationary and some portable applications such as fire extinguishers, industrial and beverage gas storage. As stated above, such products are typically manufactured using some form of impact extrusion technology, followed by a warm forming process to provide the neck closure. Considerable efforts have been made to understand and optimize the thermomechanical process stages for both manufacturing efficiency and microstructural control [6, 7]. Type II or hoop-wrapped cylinders consist of a metallic liner, similar in nature to the Type I cylinder, which is subsequently overwrapped along its parallel section with FRP composite material, usually carbon fibre embedded within an epoxy resin matrix. The cylinder is typically designed such that the metallic liner bears around half the load when subjected to internal pressure. Type III cylinders differ from Type II in that they are constructed with a much thinner metallic liner, which is then completely encased with composite material over its domed ends and straight walled section. In this case, the liner bears only around 10% of the load when the cylinder is pressurized. Since the liner in a Type III cylinder is so thin, alternative metal forming processes are required to avoid additional machining or further downstream operations after producing the initial part. For small or portable cylinders, liners may be formed by deep drawing from sheet and then spinning the open end to provide the neck closure. For larger cylinders (above about 300mm diameter), such as those used in alternate fuel vehicle applications, it is common to start with an extruded tube section and then close both ends by spinning. In all cases, particular care must be taken to thermomechanical processing parameters to ensure adequate control of microstructure and properties in the finished product. In addition to the three types described above, it should be noted that Type IV cylinders also exist. These are similar in nature to fully wrapped Type III parts but have a polymeric liner overwrapped with carbon or glass fibre composite. In this case, it is usual for a metallic “boss” to be integrated between the polymeric liner and the FRP composite layers, in order to provide a sufficiently robust interface for accommodating the cylinder valve. Schematic representations of Type II and III cylinders are depicted in Figures 1 (a) and (b) below. Note the increased thickness of the aluminium liner in the Type II cylinder when compared to a Type III product. In addition, Figure 1(b) shows the carbon fibre composite layer being present in the helical or longitudinal orientations rather than simply being in the hoop direction. Storage efficiency increases when advancing through the different cylinder construction types, as seen in Figure 2. This can be exploited in either of two ways; firstly by providing a lighter weight package for a given volume of gas or, by moving to higher pressure in order to contain more gas for a given size or spatial envelope. One way of expressing storage efficiency of high pressure gas cylinders is to plot the weight per litre against capacity. Figure 2 below shows weight-to-volume performance of the four different types of cylinders commonly used for CNG storage (note that the Type I and Type II data is based on steel cylinders and liners) [8].

(a) (b) (c)

Fig. 1, (a) Schematic representation of Type II (hoop-wrapped) hybrid composite cylinder, (b) Type III (fully-wrapped) cylinder; (c) photograph showing installation of a Type III CNG cylinder onto a passenger bus.

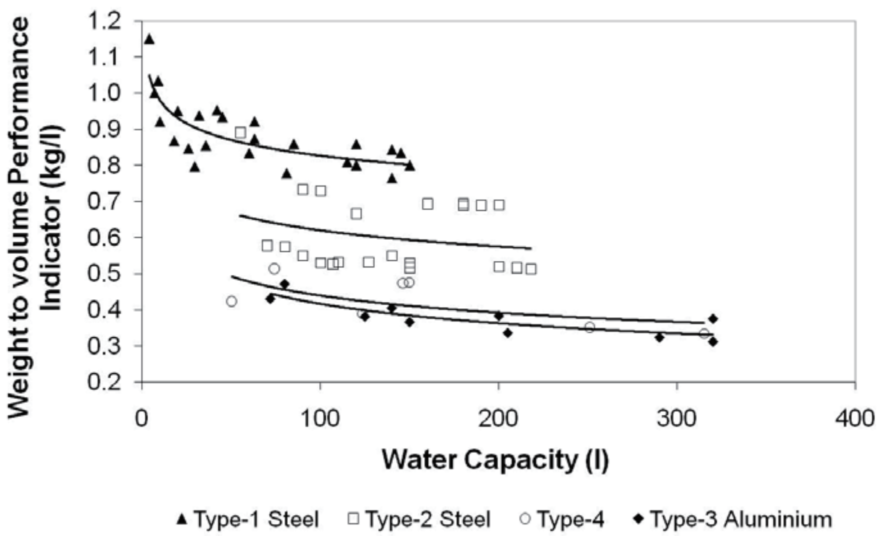


Fig. 2, Cylinder weight (kg) / cylinder volume (water capacity, l) performance indicator as a function of cylinder water capacity for different cylinder construction types.

3. High Strength 7xxx Series Alloy and Technology Developments

The advent of the seamless aluminium Type I cylinder was a breakthrough product for the beverage industry, and other new applications for lightweight high pressure gas containment soon followed. As new markets requiring greater portability emerged, the requirement to reduce weight still further over steel became of significant commercial interest. This resulted in the development of high strength alloys; the most successful of which have been AA7032 and AA7060. Today, high pressure cylinders fabricated from these materials are used extensively to provide convenient, compact and lightweight medical oxygen containers for people suffering from lung disorders and also within hospitals and the emergency services. The alloys were the product of large research and development programmes, conducted with the backing of major global aluminium suppliers. Firstly, the ability to manufacture products utilizing existing equipment and processes was an important consideration. This was achieved with comprehensive fundamental studies of the thermomechanical processes involved in cylinder manufacture [6]. Models were developed to simulate the various metalforming processes involved and ultimately predict microstructural features within post-heat treated components [9]. Once manufacturing capability had been demonstrated, but before placing product into the market, extensive analysis and performance-based characterization was required to demonstrate that the new alloys were of at least equivalent safety to the more conventional cylinder materials. The testing included quantitative damage tolerance and fracture toughness assessment to determine the burst (overpressurisation) and cycle life characteristics on both virgin and flawed components; and resistance to intercrystalline corrosion, stress corrosion cracking and sustained-load cracking mechanisms. Such tests are now incorporated into many national and international standards for the design and qualification of new high pressure gas cylinders.

The requirement to meet such stringent toughness and corrosion-resistance related criteria, in order to comply with all necessary standards, dictates that 7xxx series alloys are usually used in a significantly overaged condition for gas cylinder applications. However, efforts to optimize the strength-toughness relationship are ongoing, as a means of providing still further weight savings. In recent years, new understanding of the precise precipitation sequence in 7xxx series alloys and the interdependency of composition, microstructure and performance has been generated [10, 11]. Large experimental, multi-parameter, alloy development programmes can however quickly become time consuming and expensive, therefore data-driven modeling approaches have been used as a means of accelerating development time. In a recent alloy design exercise [12], adaptive numeric modeling (ANM) techniques were successfully used to predict mechanical properties including proof stress, UTS, hardness and kahn tear test unit initiation energy (UIE), used as an indicator of toughness. Full details of the experimental alloy compositions and some of the mechanical test results have been published previously [11]. Two aspects were identified as being particularly important for this next phase of work; firstly the quality of the input data (and therefore the experimental design); and secondly the requirement for some degree of model 'transparency' so that the results are able to be interpreted in relation to meaningful physical parameters, as opposed to simply being a 'black box' data processing model. The modeling process itself involves a thorough data processing stage and this highlighted the importance of capturing accurate data from the physical experimentation. For example, an enhanced method of interrogating kahn tear test specimens using time-lapse photography and image analysis techniques was used in order to yield more reliable crack growth data than crack opening displacement obtained via clip gauge. An example of the process is shown in Figure 3 below.

After exploring several ANM techniques, a particular methodology known as Support Vector Machine Regression (SVR) was found to give increased model accuracy over a more conventional multiple linear regression approach for the generated dataset. In addition to its predictive capabilities, this new multidimensional analysis allowed enhanced visualization techniques to be utilised, such as the contour plots depicted in Figure 4, and an optimum alloy composition to be proposed. By running a simulation using the best-performing SVR model, maximum toughness was attained in an overaged condition and with a major alloying element combination of 0.7Cu, 1.75Mg and 2.6Zn (at.%). The relative influence of the individual input parameters can be seen in Figure 4. Although not shown here, similar simulations were also produced for proof stress and hardness. Inevitably, a compromise has to be reached when deciding on the alloy to use for the fabrication of gas cylinders both in terms of manufacturing and final performance requirements. By using techniques such as the developed model, it is possible to apply a 'reversed optimization' approach to statistically selecting the optimal composition and ageing conditions, by first defining the levels of properties required and then simulating the compositions necessary to achieve the target balance of strength (and hardness) versus toughness.

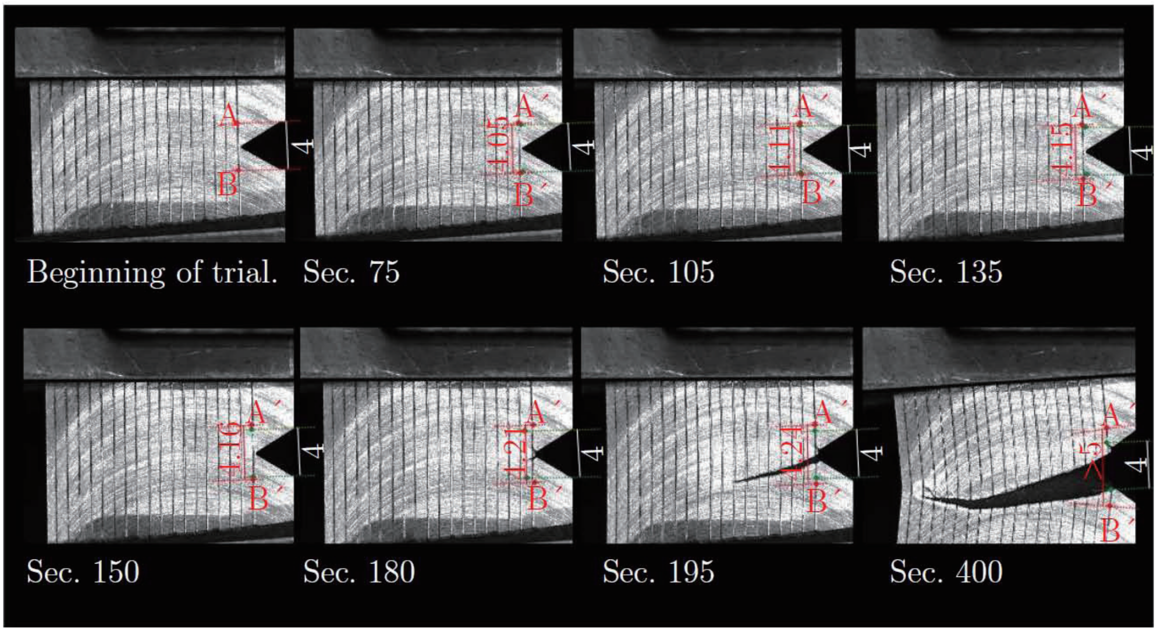


Fig. 3, Time-lapse photography of kahn tear test specimen. In the example shown, crack initiation was recorded after 180s [12].

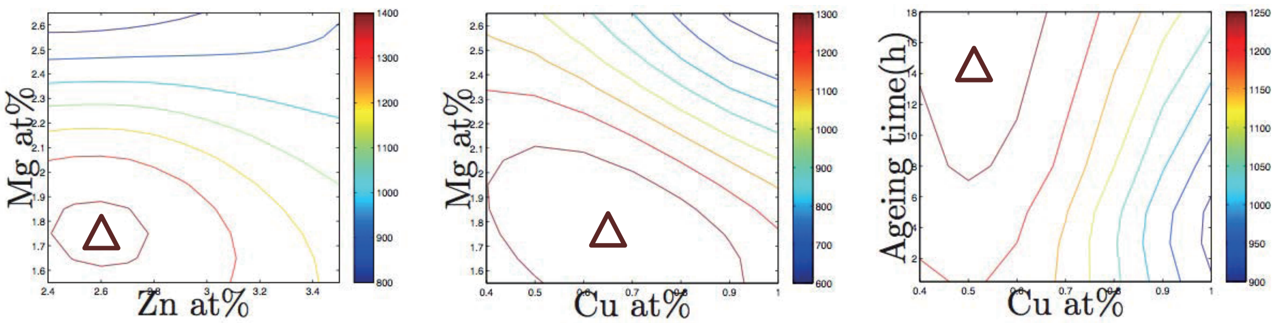


Fig. 4, Example contour plots showing the influence of various model input parameters on alloy 'toughness.' Δ symbol denotes contour region of maximum unit initiation energy value.

3.1 7xxx Series Manufacturing and Formability Improvements

The alloy design exercise described above was primarily focused on enhancing performance by maximizing mechanical properties. However, the fundamental understanding of 7xxx series thermomechanical processing behaviour generated during the earlier development stages [6] has recently been applied and extended in order to develop a new 7xxx series liner for a Type III composite cylinder. In this case, a thin-walled liner is produced via a combination of backward extrusion and drawing / ironing process steps. This liner is then spun to form the neck closure and heat treated prior to filament winding with carbon fibre, as shown in Figure 5(a). The resultant 7xxx series liner technology has successfully been used to develop a new lightweight medical oxygen cylinder, offering a weight saving of around 15% over the previous generation of 6xxx series based composite cylinders. Other recent studies have looked at upstream billet supply options, where ‘melt conditioning’ approaches can generate more favourable microstructures for deformation processing. This technique is also being evaluated as a means of refining the distribution of Fe and Si containing intermetallic phases in aluminium alloys, thereby increasing the performance of alloys prepared with higher levels of recycled material [13]. Figure 5(b) shows the as-cast microstructure in a melt conditioned 7xxx series billet. The equiaxed, fine cellular structure has performed well in commercial scale manufacturing trials.

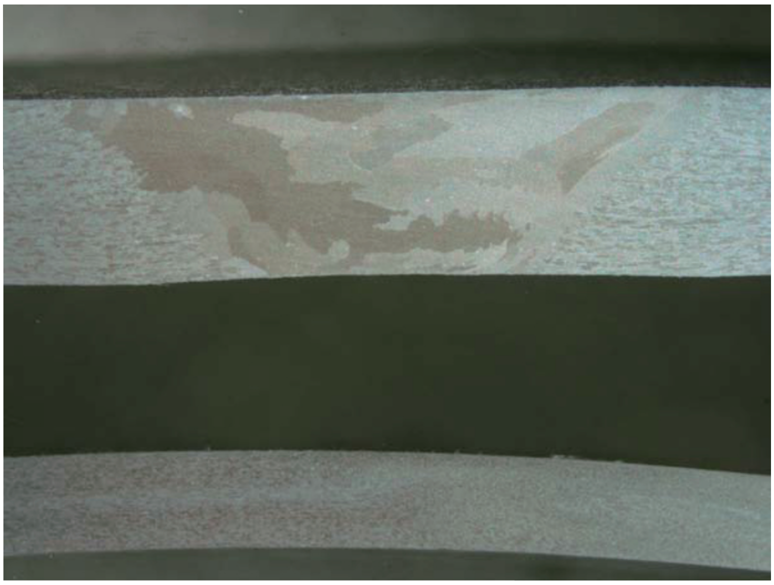
(a) (b)

Fig. 5, (a) section through 7xxx series Type III liner and composite cylinder; (b) microstructure of a melt-conditioned 7xxx series billet in the as-cast condition.

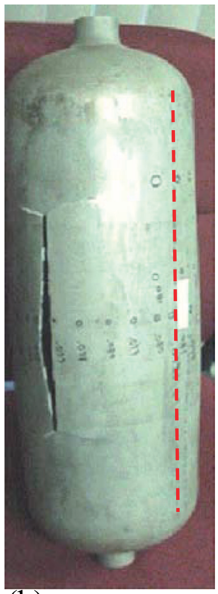
4. Considerations for Large Diameter Alternative Fuel (AF) Cylinders

The environmental and economic benefits of natural gas as a vehicle fuel are becoming increasingly recognized, with more than 11 million natural gas vehicles now on the roads [8]. Growth is being driven by environmental benefits, since the emissions of a dedicated natural gas vehicle typically include significant reductions of up to 70% in carbon monoxide (CO), 90% in non-methane organic gas (NMOG), 90% in nitrogen oxides (NOx), 95% in particulate matter (PM) and almost 20% in carbon dioxide (CO2) compared to gasoline vehicles [14].

While aluminium alloys have been used very successfully for several decades as liners for Type II and Type III high pressure composite cylinders, with many millions in service around the globe, the alternate fuel (AF) sector presents several new challenges. For example, simply gaining acceptance in the automotive supply chain requires some effort. The design and approval considerations for a CNG storage cylinder are far more critical than those for a traditional fuel tank, primarily to ensure the safe containment of the fuel at a pressure of 200-250bar in temperatures from -40°C to +85°C, and during scenarios such as high impact or fire. Next, there is a commercial driver to carefully optimize cylinder design in order to minimize costs, given that the majority of the cost in a Type III cylinder is in the materials of construction. Finally, the physical size of the cylinders used in bus and truck installations (currently 300-400mm diameter, with demand for larger sizes) requires investment in capital equipment, process control and also a different approach to metal supply. Liners for Type III AF cylinders are usually manufactured from seamless 6xxx series aluminium tube. The tube is typically drawn and then either spun or flow formed to give the required geometry. This process does allow for some increases in diameter and modification of wall thickness, however, it is true to state that the restricted commercial availability of tube stock is currently limiting finished Type III cylinder sizes. For this reason, cylinders greater than about 400mm in diameter tend to be manufactured from Type IV construction, with a plastic rather than metallic liner beneath the carbon fibre composite structure. In many cases, the vehicle manufacturer or systems integrator simply wishes to purchase a specified volume of gas within a given spatial envelope. So, while the use of aluminium tube in the manufacture of Type III AF cylinders is undoubtedly a growing market, significant additional volume potential exists, should a cost-effective solution become available for diameters beyond 400mm. One approach to resolving this issue is to exploit the benefits of a high integrity joining technique, such as friction stir welding [15-17]. Recent studies have demonstrated the ability to fabricate a high pressure liner from a 6xxx series plate, which is then roll-formed, friction stir welded, drawn, spun and heat treated. Extensive characterization on liners fabricated in this manner has shown mechanical properties at least equivalent to the parent metal, combined with a favourable homogeneous microstructure in the post-heat treated component, as can be seen in Figure 6(a). Furthermore, high pressure burst tests consistently exhibited failure locations away from the original friction stir weld line, shown clearly in the specimen depicted in Figure 6(b). This approach could offer a viable route to large diameter aluminium liners for Type III cylinders.



(a)



(b)

Fig. 6, (a) macro-etched grain structure of a friction stir welded liner wall section, before and after drawing; (b) example of a burst test conducted on a friction stir welded liner. The dashed line indicates the location of the original friction stir weld line.

5. Concluding Remarks

Advances in the fundamental understanding of aluminium alloy design, manufacturing techniques and thermomechanical processing have led to sustained commercial success since the introduction of the first mass-produced CO_2 beverage cylinder 50 years ago. New gas containment markets have been opened throughout this period, and genuine improvements realized for the many millions of end users worldwide. The future is expected to see greater use of high strength 7xxx series alloys in those applications that demand lightweight products such as medical oxygen cylinders, breathing apparatus and associated healthcare products. Lower material costs and increased manufacturing efficiencies will enable wider penetration of these materials into the traditional cylinder markets.

The greatest growth, however, could come from the alternative fuel (AF) sector, where the challenge is to provide large scale and lightweight, yet cost-effective, hybrid carbon fibre composite structures. Today, significant commercial opportunities exist for compressed natural gas (CNG) storage. The industry – as a complete supply chain from material supply to systems integration – must respond rapidly to the challenges faced. The experience and understanding generated therein will provide a sound foundation for longer term alternative fuel solutions, such as bulk gas transportation and hydrogen storage, as growing societal and political will drives the transition towards cleaner transport and greater use of renewable energy sources.

6. Acknowledgments

The authors wish to thank Professor SJ Harris and Dr B Noble (University of Nottingham), Professors PAS Reed and I Sinclair (University of Southampton) and Professor JV Wood (Imperial College) for their inspirational supervision and contribution to the fundamental research; Professor Z Fan (BCAST, Brunel University) and Dr GM Scamans (Innoval Technology) for the provision of melt-conditioned materials; and finally the generous financial support of both the Royal Commission for the Exhibition of 1851 and the Engineering and Physical Sciences Research Council.

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