Leaded copper alloys for automotive applications: a scrutiny

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Goal and scope of the report

In 2010 the *European Copper Institute* commissioned a report to give an overview of the value of lead as an alloying element in copper alloys for automotive applications. It should review its use, its benefits and weaknesses, its sustainability as well as the general evolution of lead and lead-free alloys.

Although the general description of the situation described four years ago still holds, new technical data about lead and lead-free alloys were obtained and gathered since then. They allow to clarify some specific issues and to strengthen various arguments previously put forward.

Thus it appeared necessary to rewrite the 2010 report in order to cover these new aspects. Whereas the general considerations will only be summarised in this scrutiny for the sake of a better understanding, it offers the opportunity to give a clearer perception how the new findings have to be evaluated.

The inputs to the present report of several OEMs, suppliers to the automotive industry, fabricators of copper based semi and cast products, trade associations and metallurgical research and testing institutions are gratefully acknowledged

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1. Some basic considerations about selecting materials

Selecting the optimal material for a given application is a complex issue. The designer of the component which will integrate the material has to take into account a large variety of aspects. It starts with the right perception of the technical system for which he designs the component. In a second step, he has to consider all the specific constraints which the system puts onto the material.

1.1. The technical system of automotive components

An automobile is a mass produced system. To give a figure: in 2013 approximately 13.3 million new cars were registered in the EU 27 and EFTA (source: ACEA). In general, a component, like a tire valve or a pin for an electrical connector, which is usually made from leaded brass, occurs more than one time in a car. Thus we speak about global production volumes of some 100 million units for each component. Even at the level of an individual OEM, large production volumes must be considered: this is due to the trend to standardise more and more the components for the various car models. Furthermore, although a car is an expensive product, each component is a low cost object. Thus a car bears similarities to consumer electronics, household appliances or plumbing devices. They also are mass produced units based on low cost components. But contrary to those systems, a car must be extremely safe and hence reliable. One difficulty results from the fact that a vehicle is exposed to harsh environmental conditions. These are varying outside temperatures, large temperature gradients, vibrations, pH values ranging from acidic to basic surroundings, humidity enhanced by corrosive agents like salts and fumes and, last but not least, specific aggressive automotive fluids. In this sense, a vehicle as a system shares more similarities with aerospace and military ones.

A comparison of the American standard USCAR-21 for testing the performance of automotive electrical connectors with the more general focused European standard EN 60352-2 for crimped connectors illustrates the enhanced requirements for automotive systems. Just to give two examples: the highest test temperatures are 175 °C *vs.* 125 °C and the number of temperature cycles are 100 *vs.* 5 for the two standards, respectively.

A characteristic of mass produced, low cost components is that quality control cannot be performed for each individual unit. Once the process parameters have been set, the operator must be confident that the produced parts have the expected properties within a given tolerance range. Statistical process control helps to achieve this goal. Furthermore, the cost pressure makes that the different subcontractors need a raw material which allow them to run their equipment in a fully automated regime for a sufficient long time - typically a night shift. Thus it makes no sense to provide them for example with a material which demands a tool change every half hour.

Materials - like brass rods - used for manufacturing low cost products must also be as cheap as possible. This means that their properties exhibit some variability, independently whether it is due to the quality of the starting material or to small parameter fluctuations within the production chain. For instance, leaded brass rods for free machining and hot forging are fabricated almost exclusively with recycled brass (either old scrap coming from end of life systems or new scrap occurring during the manufacturing of components), low quality copper and zinc scrap. This aspect will be discussed in more details in § 5.1. The intensive use of scrap has both financial and sustainable advantages within a circular economy. But nobody can guarantee that all the scrap batches have similar qualities.

Notwithstanding severe scrap acceptance standards in the brass mills and analytical control of the melt in the casting furnace aimed to insure the basic specifications, small variations must be accepted. Consequently the chemical composition and microstructure of the material needs to be elastic enough to fulfil the requirements of the subsequent process steps and of the service life of the component. It is thus important to having a good perception of the relationship between a given property and the concentration of the purposely added property controlling element. Figure 1 shows schematically the most common behaviour of the impact of an alloying element which improves the performance of the material.

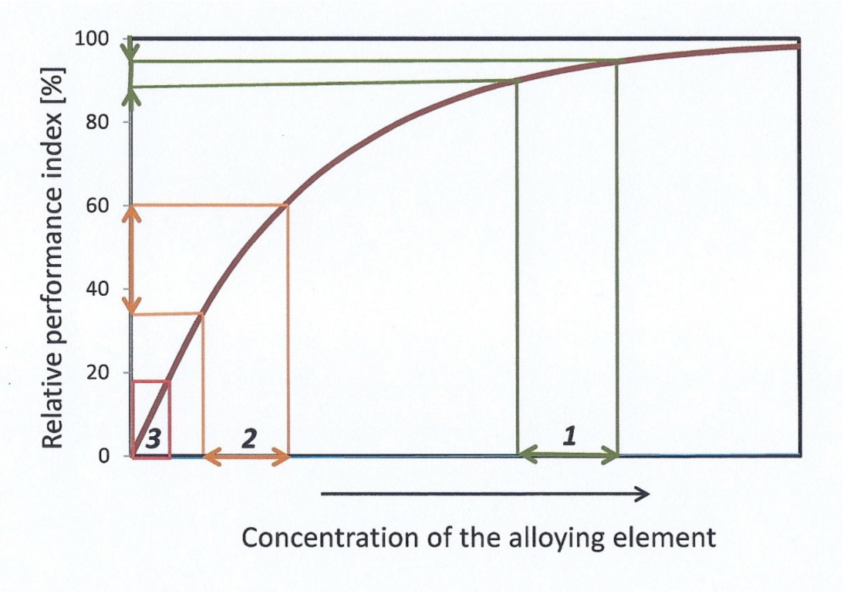

Figure 1: *Dependence of a specific material's property (expressed as a relative performance index) on the concentration of an alloying element (like lead) emphasising the three zones 1, 2, 3.*

Three concentration zones can easily be recognised in the diagram.

- Zone 1: at high concentrations, we observe a saturation regime; on one hand, the performance index is maximal, on the other hand, even large fluctuations of the property controlling alloying element have only a small impact on the performance index, i.e. the element has a damping behaviour and its concentration must not be controlled very strictly; thus, this is the zone of maximal benefit – specifically when it comes up to mass production.
- Zone 2: at intermediate concentrations the relationship is almost linear with the consequence that concentration fluctuations induces similar fluctuations of the performance index: this requires a more stringent control of the concentration;
- Zone 3: the problem with vanishing concentrations is not only that the (absolute) performance index is minimal, other metallurgical parameters like impurities, grain sizes, phase morphologies etc. start to have an strong impact on the performance of the material (such a situation was observed during machining tests, see § 4.1.2.); therefore, these parameters have to be put under control – if possible - for demanding applications or even modified.

The concentration axis is purposely not scaled, because the critical concentrations depend on the alloying element and on the specific property.

Figure 2 illustrates the dependence of the metal removing rate in a standard turning operation on the lead content; precision machining like deep hole drilling or fine groove milling are not considered.

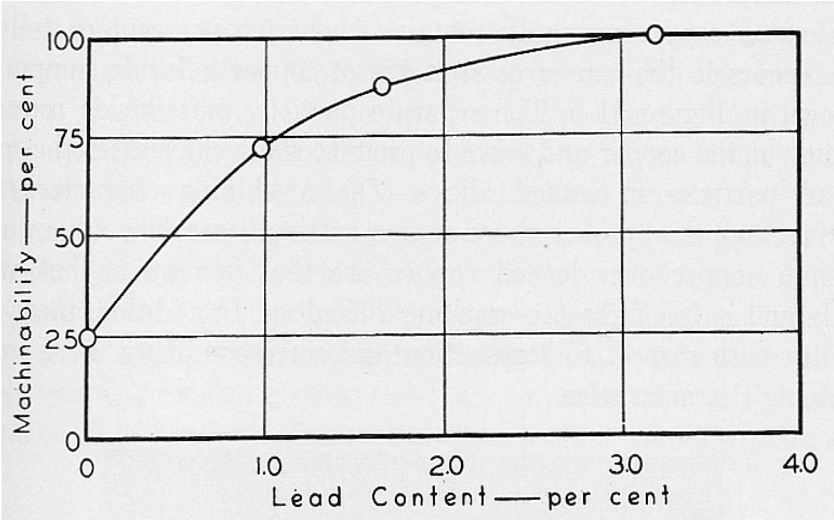

Figure 2: *Lead concentration dependence on the machinability of free-cutting brass CuZn36Pbx (Crampton 1944).*

In case that increasing contents of an alloying element affect negatively a property, the sensitivity curve which is shown in figure 1 decreases from 100 to 0 %. Evidently, the concentration of this element has to be kept at a low level. This can lead to conflicting situation, e.g. when the constraints of cold forging and micro-machining like drilling are competing. High lead concentrations easily generate cracking during cold forging, whereas micro-drilling needs high lead contents. Experience has shown that a lead concentration around 2 % represents the optimal situation. A real case will be described in § 4.1.2.

The influence of lead concentration on the polarisation resistance of brass exposed to two different media is shown in figure 3. Whereas the resistance starts to saturate in the range of 2 to 3 % of lead in a sulphuric environment, it continues to increase in a chlorine environment even when the lead concentration exceeds 3 %.

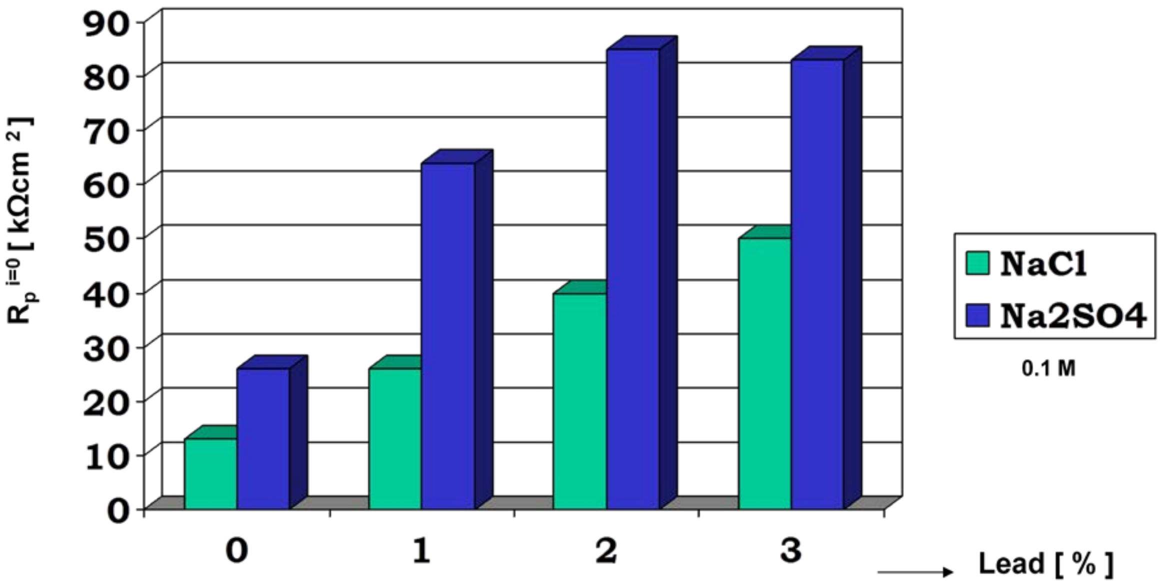

Figure 3: *Lead concentration dependence on the electrochemical polarisation resistance of CuZn38Pbx in two different media (Welter 2010). The polarisation resistance can be considered as an indicator for the electrochemical stability of the surface.*

On the other hand, figures 2 and 3 demonstrate that a lead concentration above 3 % is best when a component has to be machined and exposed during service-life to harsh corrosive environments. In the next chapter the complexity of finding the right material for a given application will be outlined in more details.

1.2. How to choose the right material

Having defined the general requirements of the technical system, the designer can proceed to analyse the specific constraints, respectively requirements, imposed on the material. First of all, the component is part of a larger system which has to fulfil the expectations of the customers. Car manufacturers have to provide to their customers a transportation mean which nowadays has to be

- safe,
- reliable,
- comfortable,
- economic,
- environmentally friendly.

For finding the most suitable material for a specific application (this is the goal), the designer should follow an evaluation scheme as outlined in figure 4. It gathers the constraints into four basic first-level groups of constraints. Each group will usually comprise further second-level constraints. Almost each of the constraints will exhibit a similar behaviour for any alloying element as outlined in figure 1.

The first group relates to the service-life of the component. Aspects to be considered are electrical and thermal conductivities, mechanical properties including creep and mechanical relaxation, resistance to deterioration and damage occurring in aggressive atmospheres or due to wear, ability for smooth sliding, aesthetic look... As the component has to be manufactured, fabrication aspects are gathered in the second group. They concern all aspects of machining, both for basic forming and as a finishing step, casting ability for piece moulding, brazing. The third group concerns economic aspects. Even if the price of the material is important (this includes the possibility of using scrap instead of virgin material), the ease of producing good quality material with small tolerance intervals, as was discussed in the previous chapter is often even more important. Furthermore, in the case of the automotive sector, it is crucial to obtain it consistently worldwide from different fabricators. The fourth group addresses socio-cultural issues like laws and regulations, know-how and experience with the material etc.

It is obvious that not only the list of constraints – especially at lower hierarchical levels – but also their importance may change from application to application. Besides correctly listing the constraints, the designer has to set priorities before checking the best material among possible alternatives. Nowadays different mathematical algorithms are available to support the decision making steps. One has always to be aware, that the selected material represents a compromise and that even nobody can ever be certain to find an acceptable material on the marketplace. In such a situation the solution is to look for a different design approach to the component or, in a worst case scenario, to give it up. The history of techniques is full of good ideas which could not be realised due to a lack of an adequate material.

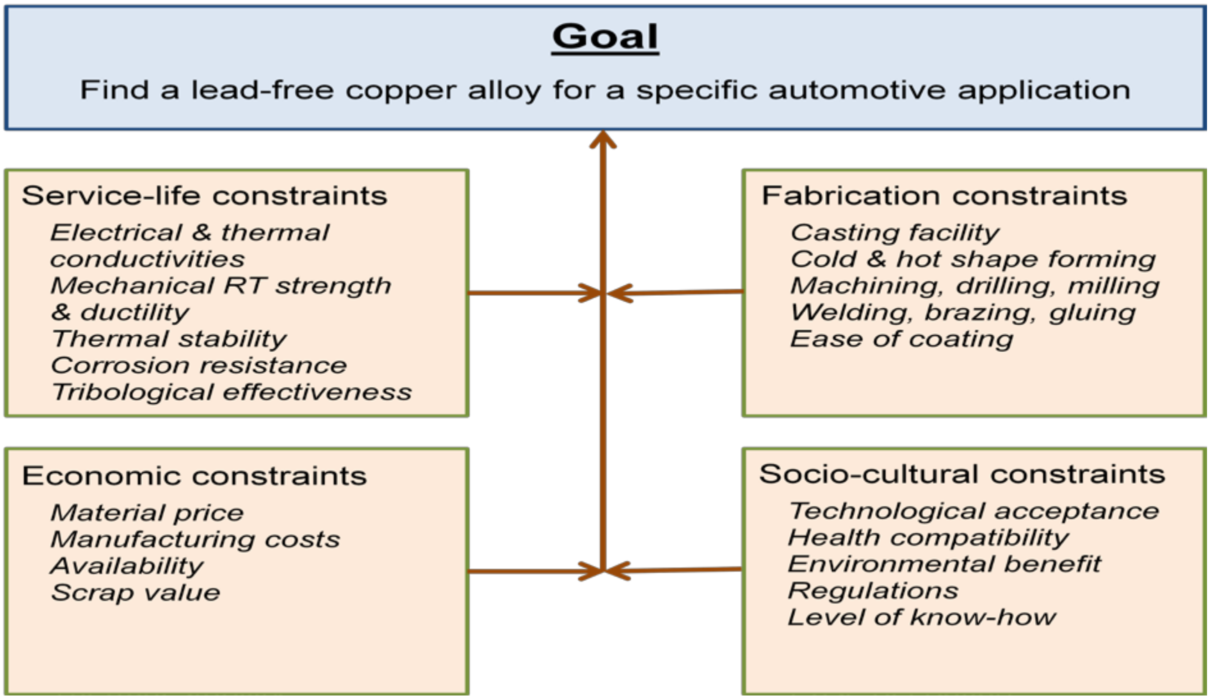

Figure 4: *Hierarchical constraint tree for choosing the optimal material for a specific application.*

A further important issue results from the fact that a vehicle is a multi-material system. Therefore the compatibility between materials (and fluids) is an overall controlling constraint which has to be carefully considered. Critical situations may occur when two materials are in close static or dynamic contact. Galvanic corrosion, loss of adhesion or jamming between partners may create severe damages. These aspects will be reconsidered in § 4.2. Thus changing one partner needs to reconsider also the second one and to adapt both to the new situation. Often there is no simple material solution and the whole sub-system has to be redesigned. An example will be given in § 2.1.

Even if the approach for selecting a material or a combination of materials is rather clear, this does not mean that in real life the selection process is well documented in the various companies. It is a fact that not only in industrial development departments, but also in research laboratories, negative results are ill or even not recorded. This increases the difficulties of the OEMs to trace the reasons which lead to choosing a given material, because the selection of materials for components and subsystems are usually made at tier 2 or 3 levels.

The learning curve for the OEMs and their suppliers needs time, the duration of which is often strongly underestimated. A good example are new steel sheets for the car bodies giving improved weight saving, mechanical properties and formability. Both the automotive and steel industries (for whom such sheets represent a huge market) are very keen to keep development times as short as possible. As figure 5 emphasises, the experience of the last decades has shown that even for very successful developments 20 to 25 years elapsed between the more basic applications oriented materials studies and the large scale implementation into the car production. For other materials, this period may be slightly different. Nevertheless, the point is that material development for industry is a long lasting process which is often not perceived such as.

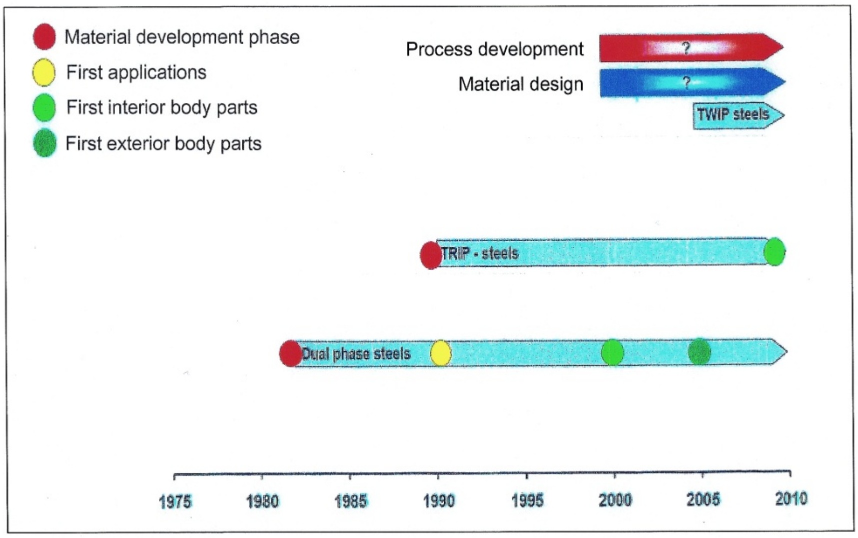

Figure 5: *Development and implementation phases for new steel sheets for car bodies (source: EHK Institute – RWTH Aachen).*

In the following, the scheme outlined in figure 4 will be used to discuss whether lead-free copper alloys can replace in all situations leaded alloys. Before doing so, the actual situation of copper alloys present on the market will be shortly reviewed, with a special focus on the lead issue. A survey of the technical literature will allow to evaluating the evolution of lead-free alloys.

2. Copper alloys for automotive components

The use of copper and its alloys in vehicles was recently very well summarised by Lipowsky and Arpaci (2007). In the next chapter only a short resume will be given emphasising the role of lead. Before going into more details, it should be remembered that copper and its alloys are functional materials chosen first of all for their excellent electrical conductivity, corrosion resistance and ease of joining. They have the drawbacks for the automotive industry for being rather heavy and expensive. As they do not really fit into the general objective of weight and cost reduction, their use just means that there are no technical alternatives for they high performance benefits they offer. Sometimes even the OEMs had to come back to copper alloys, because the alternatives did not convince. Examples are tire valves (from aluminium to leaded brass) and guides for valve shafts (from steel to specialty brass). The latter case illustrates very well that the substitution of a given material is not a singular step, but that it involves the whole system: when steel started to replace brass, it became very rapidly evident that the valve shafts had to be hard chromium plated, which means the use of Cr^{6+}.

2.1. Categories of copper based alloys used in vehicles

The European standardisation scheme distinguishes three categories of copper alloys (besides master alloys and scrap): wrought alloys which are shaped by removing matter or by mechanical deformation, ingots for piece mould casting and filler alloys for brazing (CEN 2003). The latter are nowadays basically lead-free. Casting alloys exhibit (until recently) a very large spectrum of lead contents. High strengths alloys for industrial applications, which are often multi-element precipitation hardened materials, contain only a very small amount of lead (usually less than 2 %). It helps in the final machining step and improves service-life behaviour. Some components cast with such alloys – like forks for gear boxes – can be found in a vehicle. An example and the efforts to reduce the lead content will be described below in § 4.1.1. High amounts of lead – up to 8 % - were often found in plumbing devices made predominantly by sand casting tin containing alloys. The reason is that the large interval of solidification leads to a highly porous casting microstructure. Because lead is insoluble in copper alloys, it migrates during solidification into the pores and insures the tightness of the device. Even higher amounts of lead – as a lubricating element – were added to alloys intended for the fabrication of bearings.

This is no longer an issue for the automotive sector. In this specific situation no lead-free substitute could be found. Therefore, modifications of the geometry of the bearings and more complex, multi-material constructions allowed to obtaining acceptable alternatives to leaded materials. Furthermore, the whole lubricating system (first, the entire oil pump) had to be redesigned to cope with higher temperatures and flow speeds of the oil. Components manufactured from wrought pure ETP copper (mainly the electrical wires and cables) and copper alloys semi-products represent by far the predominant category of copper products found in a vehicle. Concerning lead, “pure” means here a content of less than 50 ppm. Broadly speaking, the semi-products can be subdivided into sheets, tubes and bars on one hand and rods and alloy wires on the other hand. The first category contains basically no lead. Exceptionally some lead is added to brass sheet used for making small toothed wheels for watch making (and similar devices – see § 2.3.). Thus most of the lead introduced into a car with copper alloys has its origin in large and small gauge brass and bronze rods.

According to a statistical survey made by some car manufacturers a few years ago, the amount of leaded copper alloys which was present in cars was up to 2 kg with a mean lead concentration of 2 % (Welter 2010). The same companies conducted recently a refined survey. It reveals that presently the mean weight of leaded copper alloys is approximately 1 kg for standard and 1.3 kg for fully equipped cars. The mean lead concentration within these alloys slightly increases from 1.4 % to 2,1 % for the two model categories, respectively. The most popular brass alloy is CuZn39Pb3 (in Asian the standards allow up to 3.7 % lead without explicitly specifying it) used to make some 50 % of the brass components. Second to it is CuZn38Pb2. The next group consists of a series of brasses with zinc concentrations varying from 36 to 40 % and lead from 0 to 2 %. Bronzes like CuZn4Sn4Pb4 are further speciality alloys (see § 23). It should be noted that presently some 100 different lead containing copper alloys are produced worldwide, often aimed to very specific applications.

Two conclusions can be drawn from those figures.

The first one is that the OEMs continue their efforts to reduce the amount of leaded copper alloys. It appears that this is done predominantly for parts which already have a low lead content and where alternative solutions could be found. The efforts are thwarted by a higher demand and imposition for more electronic control units, sensors and actuators to make driving safer and more comfortable. High leaded copper alloys are mainly – but not exclusively – used in such devices. As it was already said, they are full of small items like connector pins, motor axles, valves etc made from wrought brass products with 2 to 4 %. This explains why their mean lead concentration increases from 2,5 % to 2,8 % in standard and fully equipped models, respectively. They weigh less than 10 g and usually even less than 1 g. As those small parts represent some 75 % of all the parts made from leaded copper alloys, their contribution to the total amount of lead given previously is small. The obvious conclusion is that technical requirements make it harder to reduce lead in the high concentration end of the exemption. Furthermore, referring to figure 1, lead contents in this range give also the highest quality insurance.

The second one is that the average content of residual lead originating from leaded copper alloys ranges nowadays between 14 g and 36 g. The average value should be less than 20 g because only some 20 % of the cars are fully equipped models. This is a much lower lead content than the one arising from other materials, either as being added purposely or as being an unavoidable tramp element. With a yearly automotive registration of 13,3 million new units in Europe, the cars contain altogether less than 20 000 tons of such copper alloys. Thus, the total lead content is roughly 245 t. During the elaboration of components, the rods are heavily machined. Therefore it is estimated that the brass mills fabricate some 30 000 t of brass rods for the automotive market. The difference between produced and consumed brass goes back as turnings to the brass mills and is recycled in rod production as so-called new or run-around scrap. This amount of brass rods for the automotive market represents a small fraction of the European brass production, which ranges around one million tons.

2.2. Leaded alloys and the morphological specificity of lead

The advantage of adding a few percent of lead to copper alloys and more specifically to brass was recognised more than one and a half century ago and is well documented. One of the oldest references to the beneficial effect of lead in brass goes back to 1859. In the *Dictionnaire Universel Théorique et Pratique du Commerce* *et de la Navigation* one can read that unleaded brass greases the rasp, i.e. that it sticks into the interstices of the teethes and hinders their biting: the addition of 2 to 3 % of lead makes that this inconveniency disappears, and hardens also the alloy (Dictionnaire 1859). Two years later, the well-known English metallurgist John Percy wrote in his metallurgical treatise on copper, zinc and brass: *It is usual to introduce a small quantity of lead into brass intended for this purpose [i.e. turning], in order that the turnings may "leave the tool easily". About 3 ozs of lead are added to 10 lbs of brass;..*. This gives a lead content of some 2 %. Percy illustrates his saying by reporting the analysis of a brass sample with 2.15 % of lead (Percy 1861). The key point of those two references is the tribological asset of lead, because it strongly reduces the sticking of the metal to the machining tools. Most recently, actual production trials made by Supplier-05 with lead free brass have confirmed the importance of lead for performing good industrial sawing.

The reason why lead was beneficial was only discovered at the end of the 19th century with the upcoming of metallographic and thermodynamic investigation equipments. They allowed the detection of the presence of lead as segregated micrometer large metallic nodules in the microstructure of copper (and other metal) alloys – mainly in the grain boundaries and on the surface. The metallic character of the lead nodules gives them a low shearing module and a negative standard electrode potential. It is the large size of lead ions which limits very strongly its solubility in most metals. On the other hand, lead is soluble in the brass melt which makes homogenisation easy. Other soft materials like graphite are unfortunately not soluble in the melt. Even sophisticated casting techniques like centrifugal casting or spray forming did not allow to obtaining the same degree of homogeneity of lead. The isotropic softness (this is also an advantage in comparison to graphite) of the nodules allows them to follow the deformation path of the matrix. In cold drawn rods the nodules can easily acquire an elongated shape along their axis. This is a preferential stopping orientation for cracks progressing from the surface (Lipetzky and Schmauder 1993). All these properties explain to a large extent the advantages of lead as an alloying element, but also some inconveniences as will be discussed below. Furthermore, small amounts of lead can easily be squeezed out from the bulk onto the surface leading to the formation of a µm thick layer (Welter 2010).

The smearing property of the lead nodules and the surface film allows minimising the use of lubricants. Indeed, the presence of lead strongly facilitated the occurrence of micro-lubricated and lubrication free machining without a real loss in performance. On the other hand, as it will be shown below, acceptable machining of lead-free alloys can require complex lubrication systems. Obtaining short turnings was apparently not an issue during the 19th century. Nowadays, as highly automated machining centres are used, this aspect is getting much more important to evacuating the turnings and reducing safety hazards in the machining shop. Furthermore, small chips must be produced when sophisticated forms are manufactured like deep, small diameter holes in connector pins. Going back to the two 19th century references, it is interesting to note that basically the lead content did not change until nowadays in wrought semi-products with a standard concentration range between 2 and 4 %.

2.3. The driving force for lead reduction and the portfolio of lead-free alloys offered by the copper industry

Because practical experience has confirmed since the 19th century the overall good properties of leaded free machining brass (as well as of leaded casting alloys), there was no need to question the presence of lead. Furthermore, lead was not considered to represent a real health hazard: the main reason is that lead is imbedded into the matrix as a metallic particle. This was particularly true for lead-containing copper alloys aimed for fabricating plumbing devices. The situation is therefore different from the one of chemical lead compounds which can easily be dissociated e.g. by gastric fluids. The debate about leaded copper alloys came up during the 1980s when the World Health Organisation (WHO) lowered the acceptable lead content in drinking water from 50 to10 µg/l. In view of the large amounts of leaded brass used worldwide for plumbing devices, the copper associations (Dresher 1992) and the brass mills initiated rapidly research programs to look for alternatives.

As early as 1990, bismuth appeared potentially as a substitute for lead (LoIacono and Plewes 1990). The reason was that like lead, it is almost insoluble in brass and forms metallic particles. To improve the limited benefit of bismuth, alloys containing both bismuth and lead (McDevitt 1992) or elements like selenium (US-CDA 1995) or indium, which modify the precipitation of bismuth, were developed. Besides health and sustainability related problems (Welter 2010), a major drawback of bismuth for the recycling of copper is that minute traces have one of the highest propensities to segregate into the grain boundaries of copper and are responsible for generating cold and hot cracking. Thus bismuth is much more “toxic” than lead. The standards acknowledge this detrimental property the upper limit for bismuth in ETP copper is 5 ppm, for lead 50 ppm. For all these reasons bismuth did not become really popular. In the USA and in Eastern Asia small quantities of items made from bismuth containing cast and wrought brass are fabricated. In Europe bismuth was never considered, neither by the industry nor by the regulators, to be a viable solution to the lead issue. Thus no bismuth containing alloys were included in recent test programs.

More or less at the same time, “old” silicon containing copper-zinc alloys were optimised in Japan, both as a casting and as a wrought alloy (Oishi 1998). The idea was to use the co-precipitation of copper, zinc and silicon to form rather hard particles helping to fracture the turnings. This gives, at least as far as short turnings are concerned, an industrially satisfactory alloy. New results confirm the advantages and disadvantages of this alloy for automotive applications as having been described in the previous report (Welter 2010). They will be reported below. Although in Europe copper alloys with lead contents in the 2 to 4 % range are well used for plumbing applications (the upper limits being somewhat different for wrought and cast alloys), a new push for low-lead alloys was initiated recently in California through the Bill AB 1953 signed in 2006. The new regulation states that after January 2014 the wetted surface of components in contact with drinking water should contain less than 0.25 % of lead. For other pipes and fittings lead-free still means less than 8 %. The demand for silicon brass increased, and a company like Chicago Faucets is strongly investing in equipment to low pressure die-cast this alloy (Junker News 2014).

The European brass mills active in the USA predominantly (but also American ones) prefer to offer reduced-lead or lead-free binary brass, in which lead was compensated by an higher amount of zinc. A full series of brasses with 0.25 to 1 % of lead are proposed to fittings and fixture manufacturers. A typical representative alloy is CuZn42. As this family of alloys was known for years to most brass mills as a speciality, little development had to be made. They can be produced on the same production lines as the leaded brass, the accepted minimal content in lead allows some flexibility with the quality of the raw materials and the returned new scrap can be recycled in both alloy families (see also § 5.1.).

Both silicon and high zinc brass alloys have acceptable (as will be seen below) – and even some outstanding – properties for manufacturing plumbing devices. Little (rough) machining is needed. A reason is that the European manufacturers use predominantly near net shape hot forging and casting technologies. Corrosion resistance against aggressive waters is important, but neither electrical conductivity nor sliding ability. Low thermal conductivity can even be an asset to reduce heat losses. And, first of all, the very stringent safety requirements as for vehicles do not exist.

As these alloys satisfy the regulations and as brass for plumbing applications represents one of the most important markets, there is little need and no meaningful reason for the brass mills to look for new alloys.

In the previous chapters attention was focused on leaded copper-zinc brass. It was shown that potential alternatives were more or less successfully developed for specific applications like plumbing devices. For industrial applications, special leaded brasses have been developed by adding further elements (thus the silicon brass can be considered as a lead free special brass). For these alloys, no lead free alternatives exist. A first example for such a special brass is leaded nickel silver. Around 10 % of nickel is added to the brass in order to increase its strength and to shift its colour to silver like tones. The alloy is used for fabricating internally cut security keys. Some 2 to 3 % of lead is needed for precision milling the encoded grooves. Furthermore lead improves the sliding of the key into the lock. A second example is machining bronze. Tin has been added, while strongly reducing the amount of zinc. Machining such a high strength and corrosion resistant alloy is very difficult. Therefore it contains 4 % of lead and the overall composition is CuZn4Sn4Pb4. The alloy is used for machining predominantly small parts weighting less than a gram, mainly for gear boxes and electronic systems. It should be noted that when this alloy is used to cast parts, the lead content may even be somewhat higher. The reason is that the long freezing range of the alloy (in comparison to tin free brass, which has a short range freezing range), generates in the microstructure some porosity. Lead, which is not soluble in copper alloys as stated previously, precipitates into the pores and insures the soundness of the cast.

It will be more and more difficult to find substitutes for lead, because, nobody, as well in the brass industry as in academia, seems to have presently an idea in which direction to investigate for finding a viable alternative. The now well-known reason is that the list of possible alloying elements is extremely small and that possible candidates have been studied, evaluated and – unfortunately - rejected. This situation is confirmed by looking into the technical literature.

3. Information from the technical literature

For the reasons mentioned in § 2, no real technical or scientific investigations were realized during the last century to demonstrate the beneficial role of lead as a minor alloying element. One of the few laboratory investigations undertaken during the early 20th century is the work of Crampton (Crampton 1944). It clearly demonstrates that in free-cutting brass machinability starts to drop significantly with decreasing lead contents, especially when its concentration is reduced below 2 %. The views expressed 1954 in the section "Lead in Copper Alloys" in Butts' monograph on *Copper: the science and technology of the metal, its alloys and compounds* saying that the optimal content ranges between 3 and 4 % still hold today (Butts 1954). It is only since the 1980s, when the debate on the impact of lead on the quality of drinking water came up, that some papers were published in the technical and scientific literature, reporting comparative experiments on leaded and unleaded copper wrought and casting alloys. A recent literature survey had allowed to gathering a small number of relevant publications beyond those listed in the previous report. They focus mainly on "new" alloys containing bismuth, selenium, silicon as alloying substitutes to lead. Even more exotic elements like titanium, phosphorus, or graphite (Li 2011, Rohatgi, Saigai, Dürrschnabel 1991) were evaluated. Because all those alloys were primarily developed as substitutes for casting yellow and red brasses used for plumbing devices, the first property which was investigated was their ability to be cast. Second to it came their ease to be machined in a finishing step. Obviously, the corrosion resistance in drinking water was also tested. As we have seen, in the automotive sector mainly wrought copper alloys are used with a completely different microstructure generated through complex thermo-mechanical treatments. Therefore most of the findings are irrelevant for the presently discussed problem.

Nevertheless, it is worthwhile to present some of those papers. Further papers will be introduced in subsequent parts of the report. One of the first newer studies about leaded and unleaded free machining α/β-brass was motivated by concerns about the sliding behaviour of unleaded brass (Gane 1981). It confirms the old 19^{th} century findings. The addition of 2.9 % of lead to brass reduces the friction coefficient by half. The consequence is that the rake's face friction in machining drops by a factor of five. The beneficial role of lead as reducing cutting forces and hence the need for excessive lubrication has been shown by various researchers. A first overview on the behaviour of copper-base alloys was given almost twenty years ago (Kuyucak 1996) and reconsidered again more recently (Klocke 2012 - 1, Nobel 2014). A further study has shown that 3 % of lead in an α-brass outdo 0.5 % in an α/β-brass as a force reducing agent by at least a factor of three – and this rather independently of the temperature in the range 0 to 200 °C (Masounave 2007). The fact that lead reduces the adhesion of copper on the cutting tool was pointed out again (Ando and Azumi 2004, Klocke 2012-2). Lead free copper alloys strongly increase the wear of the cutting tool – even if the presence of zinc reduces somewhat this deleterious effect. The absence of lead does not only shorten the life-time of the tool, but first of all it leads to poor surface quality. This becomes very apparent in a finishing operation with small feed speed and cutting depth. The only way to maintain an acceptable surface quality is to flood with a high pressure jet of lubricant the cutting edge of the tool. Furthermore, the tool has to be coated with polycrystalline diamond – a technology the technical, economic and ecologic justification of which can be questioned.

A smooth surface finish is mandatory to improve the resistance of copper alloys to corrosion damage like dezincification in a chlorine environment, independently of the lead content (Karpagavalli and Balasubramaniam 2007, Kumar 2007). Whereas lead seems not to affect the corrosion resistance of brass in comparison to the corrosion inhibitors tin and arsenic, the situation changes in a sulphuric environment (Ismail 2005). The reason is the formation of a lead sulphate layer on the surface which strongly reduces the corrosion rate. The effect is pronounced for lead concentrations above 2.5 %. This confirms elder findings where the samples have been exposed to sulphate environments (Badawy 1995). Leaded brass behaves also better in ammoniac containing Mattson's solution known to initiate easily stress corrosion cracking (You 2002). Lead is also a better corrosion damage inhibitor than bismuth in synthetic tap water (Kwon 2000). An EIS investigation allowed to getting a better insight why lead improves the corrosion resistance of brass in various solutions (Badawy 1997). More recently, the dezincification and stress corrosion behaviour of various brass alloys were tested in tap water containing minute amounts of ammonia (Brandl 2009). It was found that dezincification is much lower in CuZn39Pb3 than in CuZn40Pb2, which is probably due to both the higher lead content and the induced finer grain structure. The only alloy prone to stress corrosion cracking was CuZn36Pb2As, although arsenic strongly inhibited dezincification.

Although these studies have emphasised the beneficial role of lead when machining, friction or corrosion aspects are concerned, it was also made clear that lead deteriorates the mechanical behaviour of brass - nevertheless to a lower extent than bismuth (Jang 2004). Lead hinders also stud welding (Kerry 1985). Occasionally, a trade-off must be done to optimise the lead content: an example is when both good machining and cold forming capabilities are asked for (Akin 1993).

Some new alloys like silicon containing brass have on one hand better mechanical and corrosion resistance properties, but on the other hand also some significant drawbacks, as will appear in the following chapters. Nowadays such brass alloys are no longer considered as a substitute for leaded free machining brass, but for stainless steel (Hofmann 2005, Wieland 2005, and Scharf 2007). To complete the survey, one should mention the bismuth and selenium containing red brasses, which were developed in the USA and Canada as a substitute for high leaded red brass used predominantly to cast plumbing devices (Sadayappan 2002, Sadayappan 2005). Besides the fact that they are lead-free, they have proven to be inferior in all respects to leaded brass.

Once again, the information gathered from literature has shown that there is no "universal" alloy which can match leaded free machining brass. Thus this alloy has to be considered as an optimal material for specific applications and there is little hope to find technical alternatives within the next 30 years. The reason is that unfortunately no perspective for new families of lead-free copper alloys could be identified in the survey.

4. An overview of recent experimental investigations

Although much general information about lead-free brass can be found in the data sheets provided by the brass mills (mainly aimed to the plumbing industries), the automotive industry and their suppliers financed since the last revision of ELV/exemption 3 different comparative investigations on leaded and lead-free copper alloys ("lead-free" means in the following a maximal lead content of 0.1 %).The reason was to have a better understanding of the behaviour of these alloys in specific automotive related situations. The investigations were done in close cooperation with the trade associations of the copper industry both within external metallurgical laboratories like universities (basic research) and within OEM and supplier companies (applied research),

4.1. Production related results

4.1.1. Casting

Gear box shift forks are often made by pressure die-casting complex brasses with a microstructure rich in inter-metallic compounds like CuZn42Al2Mn2Fe1, containing some 2 % of lead. Industrial tests limited to a few thousand units were undertaken with the lead free alloy. To obtain a good casting, melt temperatures had to be increased by some 50 °C. Evidently, this will have a negative impact on the life time of the moulds and more generally on the equipment. On the other hand, the melt was running more freely and injection parameters had not to be changed, but a higher amount of slag was generated. The absence of lead had four consequences. The separation of the parts from the feed system was more difficult, the length of the chips increased from 1 up to 50 mm (which could be dangerous for the workers and processes), dry machining was not possible (which means a return to emulsion lubrication) and the life-time of the cutting tools was shortened (Supplier-02 2013).

As far as manufacturing the forks is concerned, the absence of lead is not a prohibitive issue, even if many technical hazards strongly complicate the process.

Concerning service-life, first tests in a gear box however have shown that the lead-free forks do not fulfil the specifications because of excessive wear (OEM-01 2014).

4.1.2. Machining

First of all it should be made clear, that all copper alloys can be machined with different degrees of difficulty and levels of productivity. This has led to subdivide the alloys into three broad categories. The two alloys CuZn36Pb3 and CuZn39Pb3, which belong to category I, have the best ranking (Deutsches Kupferinstitut 2010). They demonstrate that with a sufficiently high lead content, the details of the microstructure (pure α-phase and mixed α+β phases, respectively) become less important. Thus the issue is not whether lead-free alloys can be machined, but to find parameters which possibly allow machining them as successfully as their leaded counterparts. Various aspects of machining leaded, low lead and lead-free alloys were addressed previously, both in this report as well as in the previous one. As machining is a complex topic including processes going from rough turning to precision drilling, a laboratory study was undertaken to evaluating how different wrought and cast copper alloys would behave (RWTH Aachen 2013, 2014). One should be aware, that only a limited number of some 1000 samples could be machined within each run. Machining shop experience has shown that as a rule going to industrial series generates worse conditions. As already mentioned in § 1.1., reasons are the larger variability in material and process parameters.

The turning of samples has emphasised the difficulties to obtain short chips. No set of parameters could be found to bring the chips of lead-free alloys to the dimensions of CuZn39Pb3. Furthermore, much higher temperatures of the tool and of the material arose. Suggestions were made to cool the cutting spot with lubricants at high pressures or to use even cryogenic cooling. There is no need to point out that this is inappropriate as well from environmental as from energy saving points of views. An important result was also that at low lead contents, a variation of 0.05 % of the lead concentration in an almost lead free alloy led to a large scatter in machining behaviour – which obviously is inacceptable for mass production.

A key machining process for the small objects needed in vehicles is the drilling of long, small diameter holes. For various reasons micro-drilling results of the lead-free alloys CuZn21Si3P, CuZn38As and CuZn42 were worse than with CuZn39Pb3. The results of laboratory tests shown in figure 6 make clear that drilling such holes in CuZn21Si3P and CuZn42 demands complex process strategies: the drill had to be withdrawn up to 10 times from the hole in order to avoid frequent break of the drill. The reason for tool breaks is still unclear, because the chip length was rather comparable to the one of the leaded brass. Slightly longer chips were formed with CuZn38As. In any case, besides a strong loss of productivity the necessity of attacking 10 times the hole leads to a loss in surface quality and in diameter tolerance.

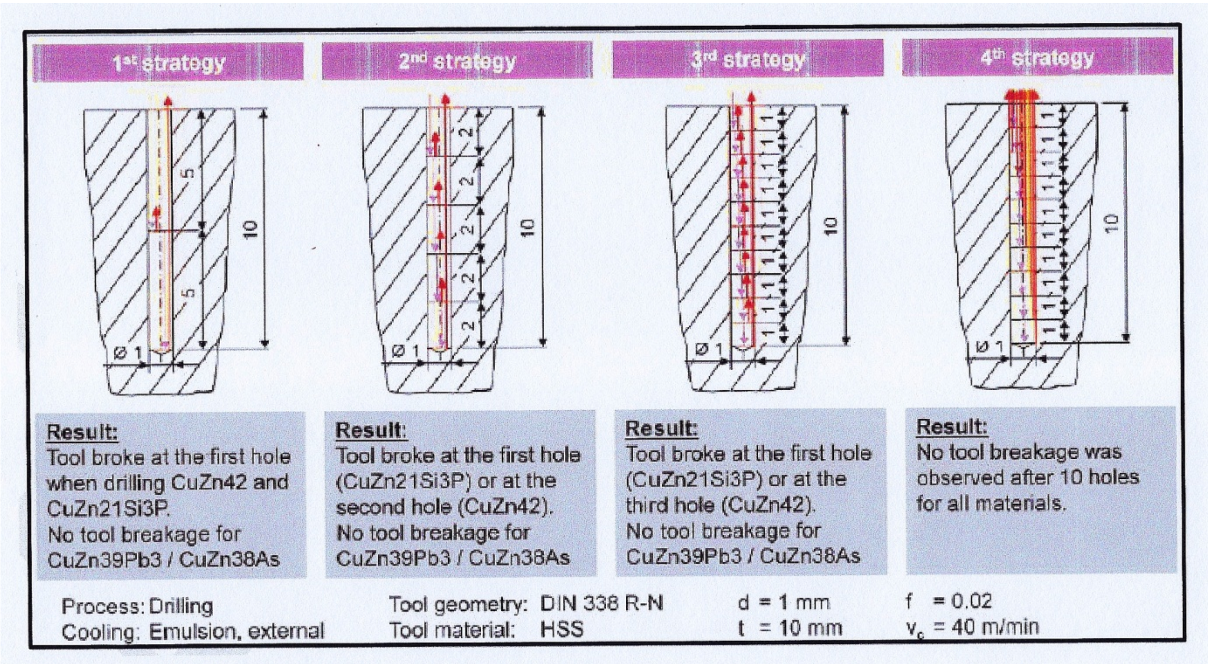

Figure 6: *Attack and withdraw strategies for the drill in leaded and lead-free brass alloys aiming to avoid tool breaking while drilling deep, small diameter holes.*

On the other hand, feed forces were significantly higher for these alloys in comparison to CuZn39Pb3, especially when the drill arrived to the bottom of the holes (e.g. up to a factor of four for CuZn38As). High abrasive wear of the drill was observed for CuZn21Si3P and high adhesive wear for CuZn38As, respectively (RWTH Aachen 2014). The tests will be continued in 2015 with public grants focusing on micro-machining. Understanding micro-machining of lead-free alloys is still in infancy. But it is “the” issue for more than 90 % of automotive brass components. The involved processes are more complex than for macro-machining (even when lead is present). It may take years before acceptable industrial operation parameters will be found. Little help is to be expected from the brass mills, because of a lack of practical experience as micro-machining is not critical for components going into large volume application markets, like the one for plumbing devices.

As already mentioned in § 1.1., the high amount of lead needed for good machining can be limited by other constraints. A specific component for which such a conflict of constraints exists is the crimped connector. The stranded wire is inserted into a deep hole drilled into the connector and then crimped. This is a cold deformation process which excludes using brass with high lead contents. Because the diameter of the cable can vary considerably, the tolerance of the diameter of the hole must be kept in very close limits. Supplier-04 drilled holes with a diameter of 0.6 mm in four brass alloys with different compositions, i.e. CuZn37Pb0.5, CuZn35Pb1, CuZn35Pb2 and CuZn37Pb2, in order to evaluate the lowest possible amount of lead needed to fulfil the tolerance requirements. The two low lead brasses had to be rejected because the constancy of the diameters could not be guaranteed. From a machining point of view the alloy should contain at least 2% of lead – but not more, because cracks could easily occur during the cold deformation process! It is interesting to see that the brass mill rated the overall machining index of the four alloys 60%, 75 %, 80 % and 85 %, respectively in comparison to the 100 % of CuZn39Pb3. The test shows that for specific machining processes, like micro-drilling, a yes/no situation exists: here a general machining index is meaningless. A further interesting aspect revealed by these the test was that other elements besides lead have to be considered for selecting an adequate brass, The low zinc brass exhibited an increasing scatter of the contact resistance cable/connector during temperature cycling. The alloy had also to be rejected. Apparently, changing the zinc content from 35 to 37 % is sufficient to modify the microstructure (presumably minute amounts of β-phase are generated) in such a way that a narrower variance of the contact resistance is obtained.

Battery clamps are a further connector system. Supplier-01uses presently CuZn39Pb2, but tested as alternatives the lead-free alloys CuZn42 and CuZn37. For CuZn42 the major problem was not so much that machining times were more than doubled and the life-time of the tools was reduced by a factor of two, but the occurrence of micro-cracks in specific area of the connector. Evidently they may lead to a failure of the clamp. Similar observations were made with CuZn37. Furthermore, a surface enhancing treatment according to OEM requirements could not be achieved.

4.2. Service life related results

4.2.1. Electrical conductivity

For a material used for fabricating electrical terminals, not only the bulk conductivity has to be high (for this reason CuZn21Si3P is not considered as an acceptable alloy: its electrical conductivity is only some 8 % of the one of copper, whereas leaded brass is up to 25 %), but also the contact resistance should not increase significantly during service-life. It is well known that the electrical current flows through surface contact spots. The better these can be deformed, the higher the true contact surface is. A softer material like CuZn39Pb3 is therefore advantageous. Furthermore, the lead segregated on the surface fills partially the inter-spot regions.

4.2.2. Corrosion resistance

The advantage of the presence of lead in brass as a corrosion damage inhibitor in various aggressive environments has been pointed out by different researchers. As an example, lead up to a content of a few percent in CuZn38 reduces significantly the corrosion rate when brass samples are in contact with dilute sulphuric acid: passivation results from the formation of a lead sulphate film on the surface (Ismail et al. 2005).

Nevertheless, as no corrosion experiments exists comparing different lead-free alloys to standard CuZn39Pb3 brass, various investigations were conducted during the last years.

As it was pointed out, compatibility between the different materials and fluids used in a vehicle is a key constraint. Thus the best combination of materials is the one for which galvanic corrosion is minimised. The aluminium alloy AlSi9Cu3 is used in large quantities in a vehicle. As aluminium has a very negative electrochemical potential, it appeared necessary to investigate how it behaves when put into contact with different brass alloys in a salty medium like a 3.5 % NaCl solution. CuZn42 has the worst galvanic corrosion behaviour and attacks strongly aluminium. CuZn38As and CuZn21Si3P behave better and the lowest corrosion current is observed with CuZn39Pb3 (see table 1).

	Electrochemical potential vs. SCE electrode (mV)	*Mixed potential vs. SCE electrode (mV)*	*Galvanic current after 600 min (µA)*
AlSi9Cu3	– 640 ± 5	– 640	
CuZn39Pb3	– 237 ± 7	– 267	21
CuZn21Si3P	– 243 ± 15	– 223	42
CuZn38As	– 260 ± 12	– 233	110
CuZn42	– 292 ± 21	– 225	347

Table 1: *Galvanic corrosion in a 3.5 % NaCl solution of four brass alloys coupled with aluminium.*

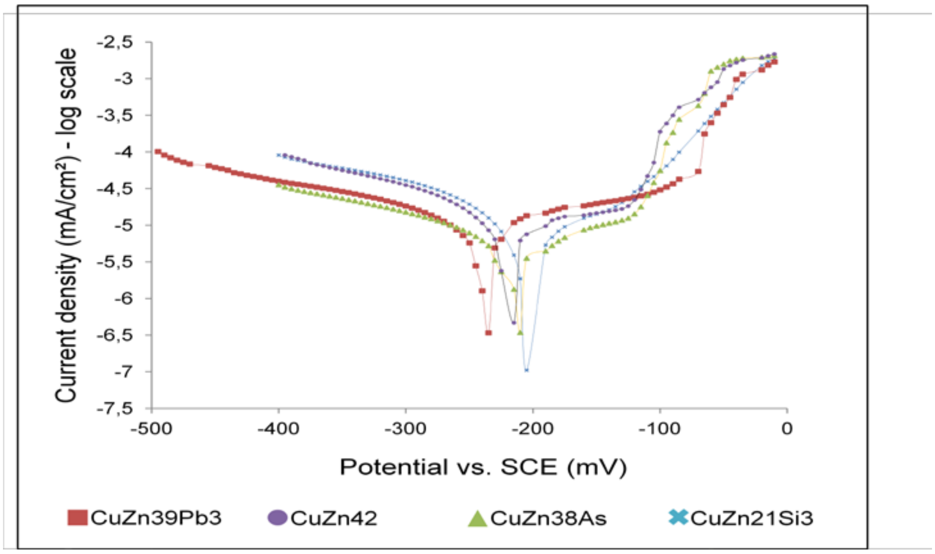

Figure 7: *Polarisation curves in a 3.5 % NaCl solution of four brass alloys*.

The polarisation curves shown in figure 7 confirm these behaviours. They show furthermore that CuZn39Pb3 exhibits the largest low-current plateau in the cathodic regime (CopperCEEF 2014).

Another critical situation occurs when components contain residual elastic stresses. It should be noted, that even when internal stresses caused during manufacturing could be released by an appropriate thermal treatment, assembly and service-life stresses still occur. To test the resistance of different brass alloys to stress corrosion, small batches of machined screw terminals for electrical wires were exposed to an ammonia containing environment. Ammonia is known to reveal in a very discriminating way the risk of cracking in devices with internal stress. Notwithstanding a somewhat higher torque on the screw, terminals made from CuZn39Pb2 brass show a much lower disposition to stress corrosion cracking than those made from lead-free CuZn42 brass. Whereas none of the terminals made from leaded brass cracked or exhibited crack initiation, two terminals made from lead-free brass failed and on 30 terminals crack initiations were observed – as illustrated in figure 8.

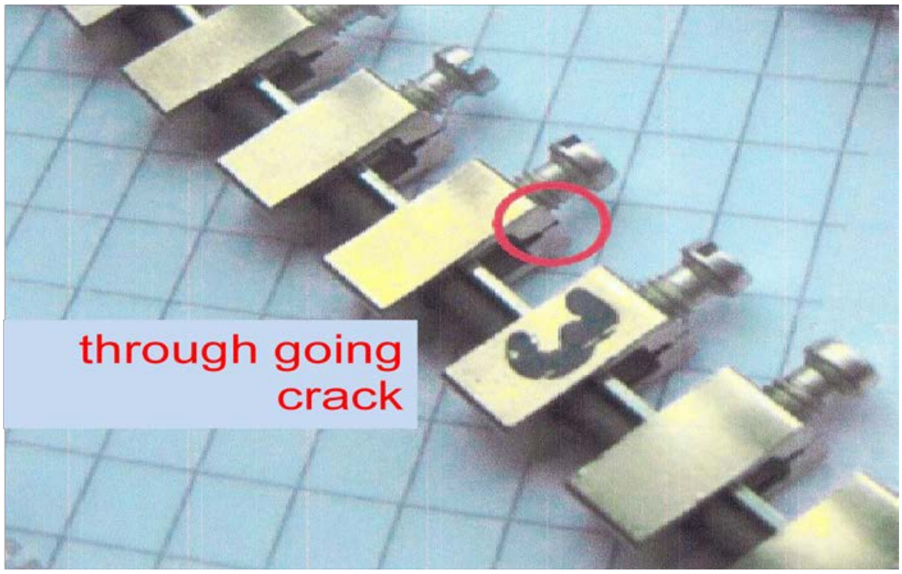

Figure 8: *Stress corrosion cracking leading to complete failure of a terminal made from CuZn42 in an ammonia environment.*

The reason of the good behaviour of the leaded brass could be that the soft lead inclusions limit the building up of internal stresses and give some chemical protection. Furthermore, during machining, the life time of the tools was 20 to 30 times higher for CuZn39Pb2. Silicon brass, which has good corrosion resistance behaviour, was not tested: As it was mentioned in § 4.2.1., its very low electrical conductivity makes the alloy unsuitable for electrical applications (Supplier-05 2014).

As this was a “static” test, a series of dynamic stress corrosion experiments were performed by straining at a very low speed of 1.5 µm/min machined samples of CuZn42, CuZn38As, CuZn21Si3P as well as CuZn39Pb3. The elongation leading to cracking was measured both in corrosive NaCl and Na_2SO_4 solutions and, for comparison, in air. The ratio gives the sensitivity coefficient C_{scc} for stress corrosion cracking. It has the value of 1 for CuZn21Si3P and CuZn38As in both media. It means that both alloys are not sensitive to stress corrosion cracking. The reason for the good behaviour is due to the protective silica layer formed on top of silicon brass and to the role of arsenic as an inhibitor of dezincification (this phenomena usually precedes stress corrosion cracking) of α-phase grains – of which the sample consisted. Leaded brass resisted much less to stress corrosion: C_{scc} drops to 0.3 and 0.2 in NaCl and Na_2SO_4, respectively. For CuZn42 the situation was even worse with values of 0.2 and 0.1 in the two solutions, thus confirming the static tests. The results show that increasing the zinc content and thus the amount of β-phase to substitute lead for better machining has a detrimental effect when it comes to stress corrosion resistance (CopperCEEF 2014).

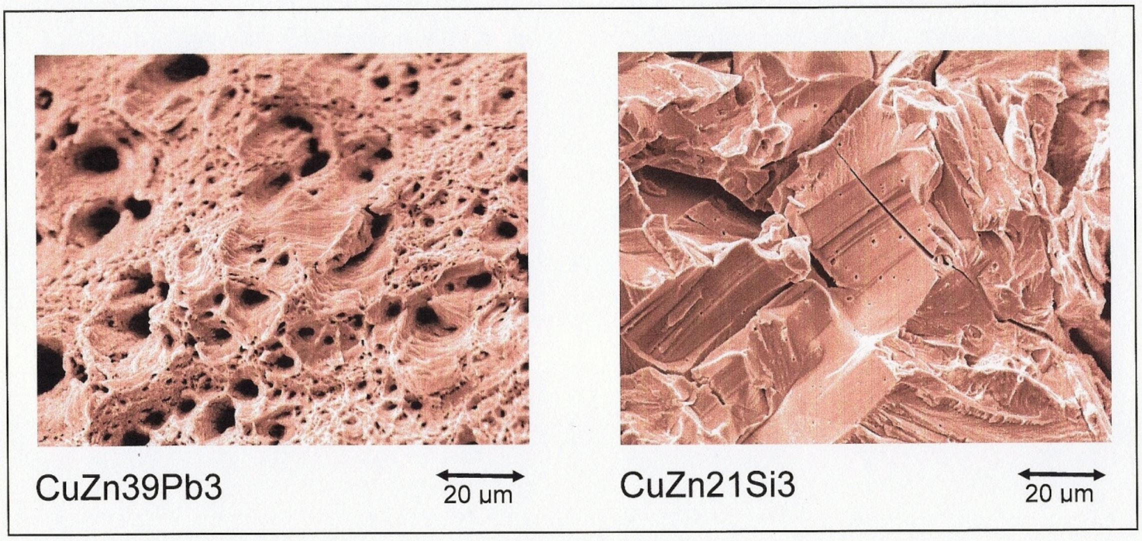

Figure 9: SEM-*micrographs of the fractures of CuZn39Pb3 and CuZnSi3P strained in a corrosive NaCl solution.*

At the macroscopic level only the CuZn39Pb3 sample shows clearly a significant necking before breaking and a curved fracture face as expected for a ductile material. For the other alloys no necking occurred and the faces are rather flat: these are characteristics of fragile breaks. Scanning electron microscope pictures of the fractured faces at micrometric level confirm the ductile and fragile rupture of the samples of CuZn39Pb3 and CuZn21Si3P, respectively (figure 9). For the two other alloys an intermediate situation was observed. CuZn39Pb3 and CuZn42 have basically the same α+β-phase microstructure. The different fracture behaviour can be attributed to the presence of lead. The sockets of the lead nodules appear clearly in figure 9. Although the alloys had a similar half hard/hard metallurgical state, the much higher ultimate tensile strength of CuZn21Si3P (resulting from its precipitation hardening mechanism) could be to some extent responsible for the fragile fracture (see also § 4.2.4.).

The loss of adherence between two materials can also be considered in the broadest sense as a case of corrosion. A recent test series made by OEM-02 (2014) has shown that leaded brass insures the best adhesion of rubber. Tire valve stems were machined from CuZn39Pb3, CuZn40Sn1Pb0.2, CuZn39Sn1Bi2 and CuZn21Si3P and covered with rubber. The valves were exposed to higher temperatures, humidity, diluted sulfuric acid and ammonia for at least 72 hours. The preliminary results have revealed that an unstable situation for the adherence of rubber exists for low lead and lead-free alloys. The worst situation was observed for CuZn21Si3P. Furthermore, stress corrosion cracking occurred for the bismuth containing brass.

All those findings make clear that for some applications, lead-free alloys are often excellent materials. Nevertheless, they cannot match the overall good properties which leaded brass shows in a large range of environmental situations typical for automotive surroundings.

4.2.3. Friction and wear

An important characteristic of materials which has also to be considered pair-wise (and, as we have seen, more generally system-wise) are their tribological properties. It was pointed out that tribology not only impacts service-life behaviour, but also manufacturing. These aspects will be illustrated with the results of three test series.

Semi-industrial tests were undertaken to evaluate whether CuZn21Si3P could be used for press fit bushings. The alloy could be machined by adjusting and increasing the rotation speed and feeding rate by approximately 15 to 20 %, but the life time of the tools was reduced by 5 to 10 %. The strongest drawback came from the generated ductile and up to a few centimetres long turnings, which disturbed the automatic machining process. Figure 8 gives an impression of the different quality of the turnings. Eventually, the whole bushing had to be redesigned because of a lower push force onto the motor shaft (Supplier-06 2013).

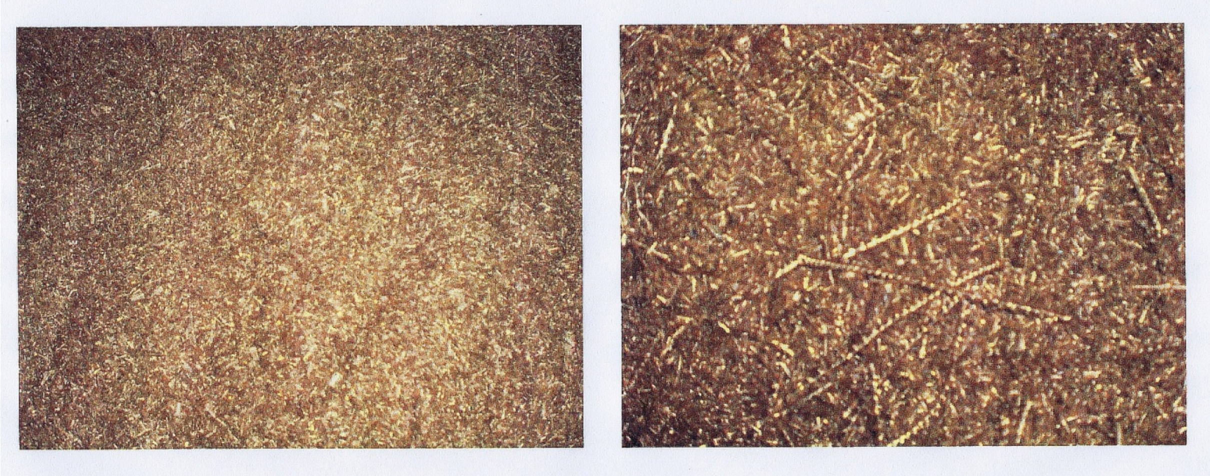

Figure 10: *Turnings obtained when machining CuZn39Pb3 (left) and CuZn21Si3P (right); the length of the lead-free turnings can reach a few centimetres.*

To evaluate the abrasive wear, a system consisting of a brass pinion moving a dented wheel made from an acetal resin (Delrin® 100) was set up. One pinion was made from CuZn39Pb3, a second one from CuZn31Mn2Si1Al. This is one of the many lead-free speciality alloys available on the market.

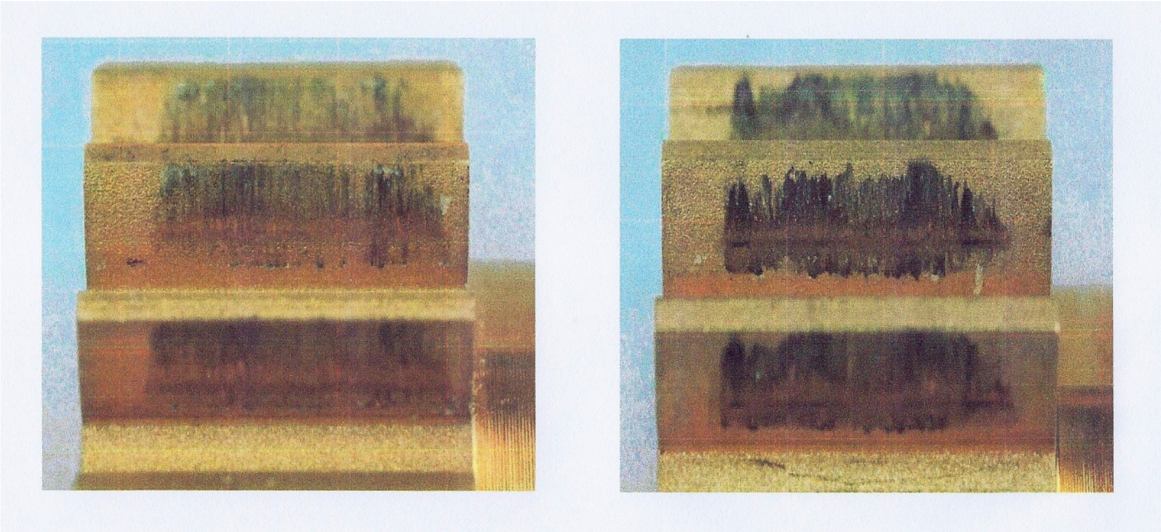

Figure 11: *Wear marks on pinions made from CuZn39Pb3 (left) and CuZn31Mn2Si1Al1 (right).*

In the lead-free combination the flanks of both the pinion's and wheel's teeth show higher wear marks and abrasion, respectively, than their counterparts in the leaded combination. Figure 11 makes the difference very clear for the pinions (Supplier-06 and FAU Erlangen-Nürnberg 2014).

In a third test the friction and wear resistance was obtained from classical pin and disc experiments (TH Ingolstadt 2014). A pin made from high strength chromium rich steel was pressed against discs made from CuZn39Pb3.3, CuZn42 and CuZn21Si3P and was animated by an oscillating movement. Three kinds of information were gained from these experiments.

For all three materials, the friction coefficient dropped with increasing pin pressure. The leaded brass had the lowest coefficient in all situations, whereas the silicon brass had the highest one. This result can easily be understood considering the lubricating lead film and the hard silica like layer formed on the surface of the two alloys, respectively. This explains also why the highest mass loss was measured for the leaded brass, especially at high contact pressures. On the other end, a very high mass transfer from the disc to the pin occurred for the high zinc lead-free brass due to adhesive wear. It was lowest for CuZn39Pb3. The benefit of lead is that it hinders excessive micro-welding. This is in complete agreement with the observations made when sawing such materials.

4.2.4 Mechanical resistance

The presence of large lead nodules in copper alloys can be advantageous or not depending on the kind of mechanical solicitation. As an example, at low strain rates, the nodules can reduce internal stresses and the initiation of crack tips (see stress corrosion cracking). At high strain rates the resilience resistance is lower than in lead-free alloys having a similar microstructure, because it is reduced by any inclusion (see figure 12). The resilience of CuZn21Si3 is even lower than the one of CuZn38Pb2, but higher than the one of CuZn39Pb3. The highest values are obtained for single phase brass like CuZn37 and even more predominantly for CuZn10. The resilience does not correlate with hardness (indentation is a low rate process), but much more with the propensity for chip breaking during machining. Indeed CuZn21Si3 and (to a lower extent) CuZn39Pb3 show the highest Brinell hardness.

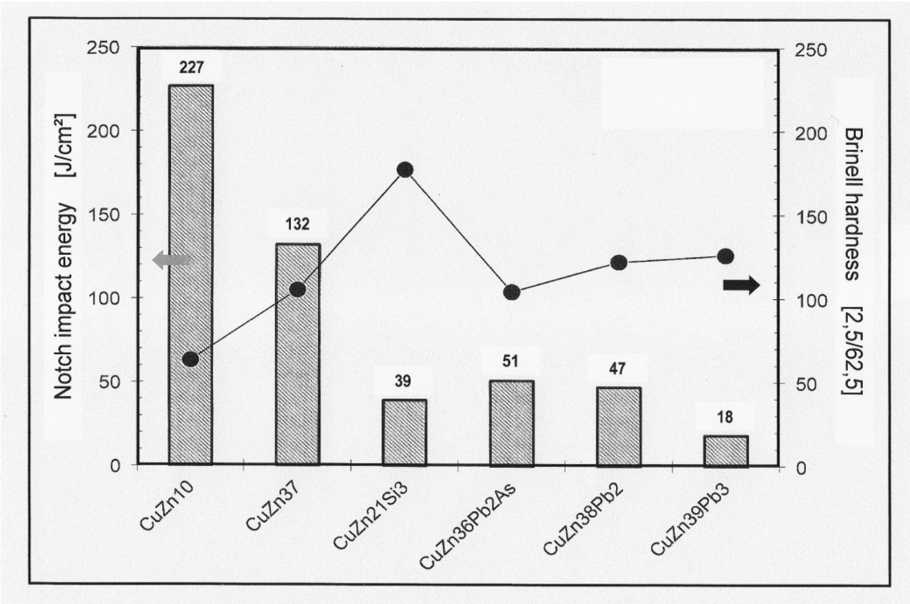

Figure 12: *Notch impact energy (columns) and Brinell hardness (dots) for brass alloys with increasing zinc and lead contents.*

At room temperature similar levels of ultimate strength R_m in the 400 to 500 MPa range can be achieved for CuZn39Pb3, CuZn42 and CuZn38As. As expected, higher values up to 700 MPa can be obtained with CuZn21Si3P. When test temperature is increased to 150 °C, R_m drops for all four alloys down to some 400 MPa for the silicon free alloys and to some 500 MPa for CuZn21Si3P. As a general comment, CuZn39Pb3 exhibits among all four alloys intermediate values (TU Ingolstadt 2014).

It appeared useful to test two further high temperature properties of these alloys, creep and mechanical relaxation. In comparison to tensile tests, which are performed within a few minutes, the two phenomena reflect long term behaviours. They are thermally activated and the properties deteriorate with increasing temperature and time.

At 150 °C, CuZn39Pb3 creeps more rapidly through grain boundary sliding - due to the segregation of highly malleable lead nodules in the boundaries - than CuZn42 and CuZn21Si3, which have almost the same long term behaviour. Creep describes the strain of the material for a given constant stress. The experiment has shown that after 1000 hours the tensile strain of CuZn39Pb3 was at least twice as high as the one of the two other alloys, although the imposed stress was lower. The higher creep rate of the leaded brass may be deleterious in some situations, in other ones it may help the material to adapt better to the stress field (TH Ingolstadt 2014).

For the design of connecting elements, especially for spring loaded terminals, high mechanical relaxation is a drawback. It reflects the reduction of internal stress when the material is deformed elastically through an imposed strain. The elastic stresses are needed to insure that the female element, acting as a spring, closes well the connector.

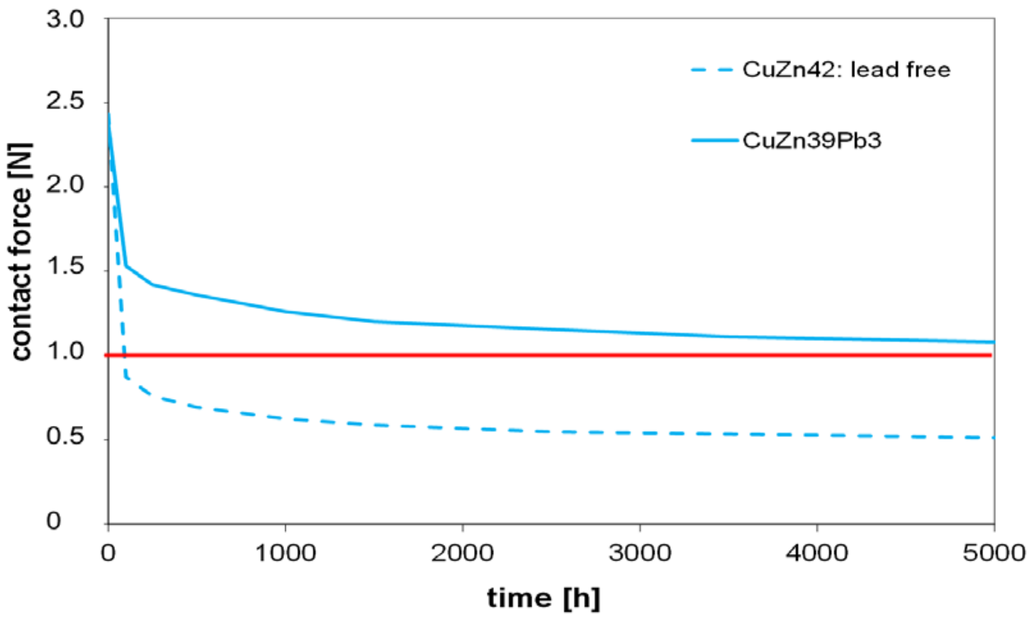

Figure 13: *Decrease of the contact force induced by mechanical relaxation in spring loaded connector elements made of leaded and lead-free brass; the required residual contact force of the elements after an exposure of 5000 hours at a temperature of 125 °C is 1 N.*

Tests with terminals made with CuZn39Pb3 and CuZn42 at 125 °C have shown that even after 5000 hours the leaded alloy relaxes less than the maximal allowed design value (figure 13). The spring strength of CuZn42 drops after some hundred hours below the required value (Supplier-03 2013).

A comparison of the test results emphasises once more that the choice of the optimal material depends on the application: a material which works best in one situation does not necessarily do it in another one. Indeed, although creep and mechanical relaxation are thermally activated processes, in the first situation the material is stressed under constant load and in the second one under constant deformation.

As vibrations are inherent to an automobile, the damping behaviour of the four alloys CuZn39Pb3, CuZn42, CuZn38As and CuZn21Si3P was tested (Simetris 2013). Preliminary results of the damping factor measured on vibrating beams as a function of frequency give the following results:

- in the frequency range 400 to 1400 Hz the four alloys exhibit a similar damping behaviour;
- at higher frequencies in the range 3200 to 4500 Hz the two alloys CuZn39Pb3 and CuZn42 have apparently a higher damping factor, although the large scatter of the results does not yet allow a quantitative evaluation.

The conclusion for all those laboratory and industrial tests is that lead is most effective as an alloying element in the concentration range of 2 to 4 %, depending upon the copper alloy and the component to be manufactured. This confirms the trend observed in the use of leaded copper alloys in vehicles, as explicated in § 2.1. Going to the extreme low level of lead asked for by the ELV directive, rises not thus not only concerns about the feasibility of manufacturing components, but also about how good these components will fulfil the requirements. Furthermore, it will also strongly impact the full life-cycle of the material. Some aspects will be discussed in the next chapter.

5. Some comments about the production and use of lead-free alloys

Besides the production and service-life constraints outlined in the previous chapter (and which are directly related to the metallurgical nature of leaded and lead-free alloys), more general economic constraints like recycling and socio-cultural ones like available know-how should also be carefully considered. They may not be decisive for the implementation of the ELV directive, but they have strong implications when it would come up to stronger restrictions for using lead in vehicles or to completely ban it.

5.1. Virgin material vs. scrap

At the vehicle's end of life, as much copper and copper alloys as possible are removed from the vehicle, as well as before (dismantling of sub-systems) and after (shredder scrap sorting) the shredding treatment:

- they are expensive materials and good prices can be obtained by recycling them within well established circuits and recycling schemes: thus waste is kept at a minimum;
- the steel industry limits the copper concentration in automotive steel scrap to 0.25 % by weight; as steel contains 0.10 to 0.15 % of copper as an unavoidable impurity (it is impossible to remove copper from steel), the new scrap has to contain less than 0.10 % of loose copper items.

This means that almost all of the 20 g of lead present in the copper alloys are taken out of the vehicle and recycled in one way or the other. Presently, the leaded copper alloys coming from end of life vehicles represent only a small volume in comparison to the amount of material which has to be elaborated for satisfying the demand from today's car production. Reasons are the long life time of vehicles (10 to 20 years) and the still on-going strong export outside of the EU of a large number of cars arriving at end of life. It is expected that during the coming years the quantity of old scrap will increase, but it can be handled without problems within the presently well organised circular economy.

Nowadays, leaded brass is just melted in the brass mills within the fabrication cycle of new cast or wrought products. The upcoming of lead-free brass in view to fulfil of the ELV requirements will block this possibility. New routes have to be looked for recycling the automotive scrap. Unfortunately, notwithstanding some trials, no convincing technology exists to remove selectively lead without altering the brass matrix (Nakano 2005). This means that one of the two following possibilities have to be considered to get rid of the lead:

- recycling ELV scrap within the material flow of leaded copper alloys for other applications;.
- sending ELV scrap to copper refining furnaces, where impurities are removed by oxidation treatments and trapped into a slag or volatilised as oxides and

collected in efficient filter systems (Langner 2011); this technology is used today to remove gold, silver and copper from electronic scrap.

The first option would not be a fair one. The second option has two major drawbacks. Firstly, zinc, which represents some 40 % of the alloy, is lost as a brass component and must be replaced by new metal. The second one is more important: large amounts of lead are collected into the slag, which is often used in infrastructure construction or goes to landfill. Because lead could be leached out, this is not satisfactory from an environmental point of view. Only the zinc and lead containing flue dust can be treated in zinc production plants to recovering the two metals. It should be noted that at the end of the pyro-metallurgical copper refining process, still some lead will be present in the anodes. When small quantities of scrap are treated, the level is not very important. The situation changes when large volumes will be refined. The lead concentration easily exceeds 0.1 % as we know from processing lead containing copper ore. Lead is eventually removed during the final energy intensive electrolytic refining step to a level well below 50 ppm.

The next challenge is how to deal with the run around leaded scrap – some ten to twenty thousand tons - produced during the past few years in the machining shops and returning to the brass mills as turnings. Nowadays they are considered as being good quality scrap which can be directly melted in the foundry shops of the brass mills. If it comes up to remove lead, only the same two options as for the old scrap exists Hoping to achieve the limit of less than 0.1 % of lead by diluting the run around scrap from the machining shops with lead-free copper and zinc within a short time is unrealistic: It will take at least a decade to achieve the goal and will simultaneously increase the complexity of the scrap circuits.

The production of new brass with less than 0.1 % of lead – either as a binary alloy or as a more complex alternative – for the automotive industries will have an impact on the raw material and scrap circuit, notwithstanding that it represents only a small fraction of the total brass production.

Both types of alloys have to be made from virgin copper and zinc or from high quality scrap. Because this quality of scrap will be no longer available for other applications (in the case of copper e.g. for the fabrication of wire, sheet and tube), it will have to be replaced by virgin metals. This brings up to some extent two negative environmental impacts. The energy consumption of the production cycle will increase. As it was mentioned, copper and zinc ores can contain up to a few percent of lead, an important fraction of which is disappearing into the environment as slag or diffuse flue dust. Thus removing lead from the copper semis for environmental reasons will reintroduce it through the production of primary copper.

Table 2 gives an idea of the impurity levels accepted presently by a major American brass mill (Chase Brass & Copper). Although leaded brass is among all the wrought copper alloys the one which accepts the highest content of impurities (one reason is that the high lead level "smoothes" their impact), the table shows that most of the impurities are well below 0.1 %. The highest concentration of 0.25 % is accepted for iron originating mainly in the abrasion of the machining tools. Such contents are acceptable, as long as elements like manganese, silicon, arsenic, phosphorus … are kept at low levels, because they readily react with iron to form hard inter-metallic inclusions. In alloys, where arsenic and silicon are purposely added to improve corrosion resistance, the allowed iron content has to be drastically reduced. It is also worthwhile to note that in the so-called lead-free silicon brass the lead content can reach the 0,1 % level.

The company insists that the scrap paths should be well segregated from leaded and low-lead brass. It states that "contaminated loads will be rejected at the owner expense". A major European brass mill even provides its customers with specific containers for the turnings generated during machining silicon brass. It informs also the customers that when silicon brass pollutes leaded brass, the whole scrap batch has to be sent to the refining furnaces (Wieland Group). Evidently, the scrap of lead-free binary brass like CuZn42 can be mixed from a metallurgical point with leaded brass (but not the other way round). Nevertheless, from an ecological and financial point of view, this would mean that also this quality of scrap is lost.

impurity	leaded brass	silicon brass
Al	0,01	0,01
Sb	0,025	0,025
Bi	0,02	0,01
Cd	0,01	0,01
Fe	0,25	0,10
Pb		0,09
Mn	0,007	0,01
Ni	0,10	0,10
P		0,15
Si	0,007	
Sn	0,25	0,20
Σ other impurities	0,025	0,025

Table 2: *Allowed impurity levels for run around scrap for standard leaded and lead-free silicon brass (source Chase Brass & Copper).*

As a conclusion, the scrap of special lead-free brasses can be handled with dedicated precautions. This is true because those alloys are still considered as specialities. The situation will change if they should become large volume commodities and will increase - *nolens volens* – the ecological footprint. Hopefully, more in depth going thoughts will be given in the future to environmental and logistic costs and benefits of reemploying lead-free scrap and substituting leaded scrap by virgin material. This is an important aspect, even if one may not consider it to be a decisive one for the implementation of the ELV directive.

5.2. The absence of specific know-how

When the right lead-free alloy has been chosen, component manufacturers have to find the company able to machine the objects. The subcontractors specialised in the field of micro-machining are in general small or medium size companies. Usually they do not have the competences and resources to do the development needed for low cost, high volume production. They have to rely on external expertise and education. Apparently, until now, no activities were started aiming to define the machining parameters for lead-free copper alloys. For instance, in France, the *Centre Technique de l'Industrie du Décolletage* (CTDec) starts to be active when their members come up with specific demands for assistance. The CTDec has developed testing recommendation and sensors for evaluating new materials. The opinion is that the machining shops could rapidly gain their own experience by using these helps and try to deal with lead-free brasses. Besides the loss of productivity, the major problems will be the need to invest in more rigid equipment, to develop software for adjusting the rotation speeds of the machine e.g. to the different steps of the drilling process, as well as to find more convenient cutting tools. Unfortunately, tools have arrived nowadays at a mature level and there is little margin for innovation. In the USA and Germany first publications are coming up in specialised magazines giving some hints how to work with such alloys. Thus, in the USA a paper was published in 2009 discussing the problems occurring when machining lead-free and low-lead brass with 0.25 % of lead (the paper aimed to plants fabricating plumbing fittings and fixtures for the Californian market): the point was that these alloys should not be run like leaded brass, but rather like steel (Free 2009). The paper made some general recommendations, but without giving any detailed information. The same holds for the educational courses organised since 2013 by the German copper trade association (Deutsches Kupferinstitut). Furthermore, some brass mills start also to provide general information about machining (mainly macro-machining) the lead-free brasses. Nevertheless the overall perception is that presently machining shops can expect very little support from outside. Thus the forced modification of processing technologies will lead to a distortion of the market to the profit of large machining companies or of speciality machining shops. It is neither very clear whether the lath, tool and lubricant manufacturers have yet started to develop specific equipment and ancillaries for dealing with these new alloys in a productive way. It will still take many years until both the necessary know-how will be obtained and spread on a larger scale and the money will be available to invest into the production tools adapted to the new situation.

6. Conclusion

The present scrutiny confirms that no convincing overall technical solution came up until now for substituting leaded copper alloys – even if the leaded ones are not perfect in all respects. Unfortunately, considering the ELV directive, there is strong evidence that in the foreseeable future no alternatives will come for such alloys and more specifically for those with 2 to 4 % of lead. The fundamental reason is that no other element exist which is insoluble in copper (and other) alloys and precipitates as soft nodules.

Lead-free alloys are often good material choices, but they cannot match the set of properties needed nowadays in the automotive industry to replace of leaded copper alloys.

Therefore all the accumulated scientific, technical and practical evidence for the benefits of leaded copper alloys strongly support the need to maintain the exemption 3 of the ELV directive.

Furthermore, those results have once more emphasized the necessity to consider carefully any modification of materials in vehicles in relation with their specific constraints. All the stakeholders have to take into account the global value chain from cradle to cradle, in order to avoid contradicting requirements both at technical and environmental levels.

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