Franz Held and Ulrich E. Klotz
fem Research Institute for Precious Metals and Metals Chemistry

Franz Held (September 01. 1956) studied metallography at the Max-Planck-Institute in Stuttgart. He worked for different precious metal refiners (Degussa, Heimerle + Meule) and has a long-term experience in practical research and testing. He works in the Department of Physical Metallurgy at the Research Institute for Precious Metals & Metals Chemistry (fem) in Schwaebisch Gmuend, Germany.

Silver alloys are widely used in jewelry and are showing some distinct production issues. The paper aims to provide guidelines to the manufacturer of silver products as well as to the goldsmith to achieve high quality products with reduced reject. At first an overview on the metallurgy of silver and silver alloys with a focus on some specific properties of silver, for example the high gas permeability, will be given. These specific properties are the reason for many production problems such as fire scale or different type of porosity. The variation of the silver content in the typical range from 925-935Ag and the role of alloying additions will be highlighted. The metallurgical basis will provide guidelines to the define conditions for the manufacturing of silver products by different processes, such as melting & casting, hot and cold deformation, annealing, quenching, ageing and brazing. Typical failure sources will be identified and illustrated by examples of defective samples. As a consequence the requirements on alloys, equipment and processes will be described and proper working conditions in industrial production as well as in the goldsmith' workshop will be given.

"Understanding the properties and improving the processing of silver alloys"

Franz Held and Ulrich E. Klotz

fem Research Institute for Precious Metals and Metals Chemistry

Schwaebisch Gmuend, Germany

INTRODUCTION

Silver alloys are widely used in jewelry and are showing some distinct production issues. Many papers have been presented about silver alloys at the Santa Fe Symposium® in the last 30 years. They cover the aspects of metallurgy,[1,2] tarnishing,[3-5] alloy development[6,7] and investment casting.[8,9] The cited references are just a selection of many more papers that were presented about silver alloys. Our paper is based on this wealth of information and aims to provide guidelines to the manufacturer of silver products as well as to the goldsmith to achieve high-quality products with reduced rejects.

First, an overview on the metallurgy of silver and silver alloys will be given with a focus on some specific properties of silver, for example, its high gas permeability. These specific properties are the reason for many production problems such as firescale and different types of porosity. The variation of the silver content in the typical range from 925-935 Ag and the role of alloying additions will be highlighted. The metallurgical basis will provide guidelines to define conditions for the manufacture of silver products by different processes such as melting and casting, hot and cold deformation, annealing, quenching, aging and brazing. Typical failure sources will be identified and illustrated by examples of defective samples. As a consequence, the requirements on alloys, equipment and processes will be described and proper working conditions in industrial production as well as in the goldsmith' workshop will be given.

2. BASIC PROPERTIES OF SILVER AND ITS ALLOYING ELEMENTS

2.1 PHYSICAL PROPERTIES

Some basic properties of precious metals and copper are given in Table 1. Silver belongs to the low-melting precious metals with low density. All precious metals are characterized by their low hardness and high thermal conductivity, which is highest for silver, followed by copper and gold. Compared to the other precious metals, silver has a very low price that allows the production of mass jewelry for the consumer market.

Property		Ag	Cu	Au	Pd	Pt
Melting point	[°C]	962	1083	1064	1554	1772
Density [g/cm³]	solid (20°C)	10.49	8.94	19.32	12.02	21.45
	Liquid (at T_m)	9.35	7.98	17.19	10.49	18.91
Volume change at melting [%]		5.0	5.1	5.5	5.9	.5
Hardness	[HV1]	26	37	25	50	48
Thermal conductivity (20°C) [W/Km]		418	398	310	75	73
Price (Nov. 2017)€ / g		0.46	0.007	35.07	27.78	25.83

Table 1 Selected properties of precious metals and copper[10-12]

2.2 Phase Diagrams and Gas Solubility

Phase diagrams are considered roadmaps for materials design. They show the stability of certain phases as a function of temperature, composition, pressure and other variables under the conditions of thermal equilibrium. A phase is defined as a homogeneous material with certain chemical and physical properties, such as crystal structure. Figure 1 shows the phase diagram of the Ag-Cu system that consists of the three phases— liquid, silver-rich solid solution (Ag) and copper-rich solid solution (Cu). The (Cu) single phase field is not shown, but the coper rich solid solution (Cu) is present in the two-phase region marked by "(Ag) + (Cu)". All phase diagrams shown in this paper were calculated using the software Thermo-Calc and the SNOB3 database. The alloying of copper to silver reduces the melting temperature of pure silver and opens a melting range, where (Ag) is stable together with the liquid (region "L + (Ag)"). After reaching a certain copper content the solidus temperature reaches a stable value. At this temperature the melt finally solidifies into a mixture of the phases (Ag) and (Cu) in the so-called eutectic reaction, L => (Ag) + (Cu). It is shown by the red line in Figure 1a at 779°C. This reaction occurs for all compositions between 8.8 and 92 mass% copper. At the eutectic composition of 28.1% copper the melt directly transforms into a finely dispered mixture of the two solid phases (Ag) and (Cu), designated as "eutectic" or often wrongly as "eutectic phase". In fact the eutectic is a mixture of two phases. At compositions with lower copper content, the melt first precipitates a silver rich solid solution phase (Ag) with a dendritic shape. As the dendrites are growing the remaining melt enriches in copper until it reaches the eutectic composition, where it finally solidifies to form islands of eutectic between the dendrites. On the copper rich side of the eutectic the copper rich dendrites are precipitated instead of silver rich dendrites.
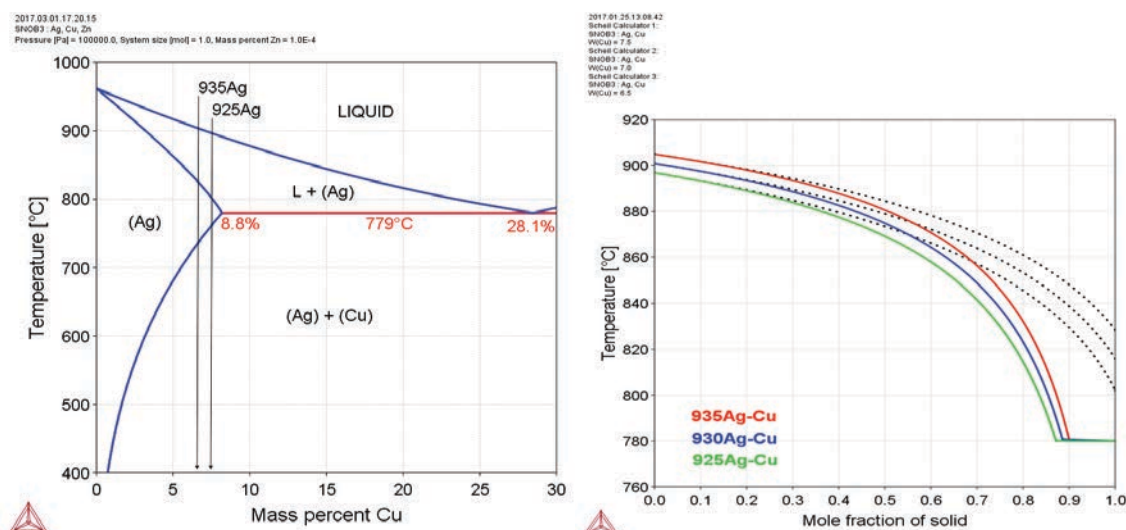

Figure 1a. Silver-rich side of the Ag-Cu phase diagram. b. Comparison of equilibrium (dashed lines) and non-equilibrium (solid lines) melting ranges of silver-rich alloys (Thermo-Calc simulation)

Considering conventional sterling silver (925 Ag), the phase diagram in Figure 1a shows that this alloy should start solidifying at 897°C (liquidus temperature) and that the solidification should be finished at 799°C (solidus temperature). Therefore, the eutectic reaction is not expected under the conditions of thermal equilibrium. However, in practice this thermal equilibrium is not reached during cooling of the melt because the diffusion of copper in solid silver is too slow to allow compositional homogeneity. The higher cooling rate causes copper to segregate to the melt, which results in a reduction of the liquidus temperature and the occurrence of the eutectic reaction. This non-equilibrium solidification is simulated using the so-called Scheil model that assumes no diffusion in the solid phase takes place during cooling. In practice, this assumption is not fully valid because some diffusion still occurs depending on the cooling rate. A comparison of the equilibrium and the non-equilibrium solidification is given in Figure 1b. According to the calculated non-equilibrium solidification, about 12% of the microstructure should consist of the eutectic phase mixture. This content reduces with increasing silver content. The occurrence of the eutectic reduces the solidus temperature of the alloy to the eutectic temperature. The effect of cooling conditions and heat treatment on microstructure and properties is described in detail in the following sections. Silver alloys are often melted or annealed in an oxygen-containing atmosphere. Nitrogen is inert with silver and copper, but oxygen shows certain solubility and reactions with silver and copper. Therefore, the phase diagrams Ag-O and Cu-O were considered. Phase diagrams involving gases are dependent on the gas pressure as an additional variable. The silver-oxygen phase diagram is shown

in Figure 2 for two different oxygen pressures. The oxygen solubility in liquid silver is quite high under a normal pressure of 1 bar and drops to about 80 ppm in solid silver. If the pressure is reduced, the oxygen solubility is decreased significantly. For instance, the solubility is only 3 ppm at a pressure of 1 mbar. Melting under vacuum can therefore reduce the oxygen content in silver.
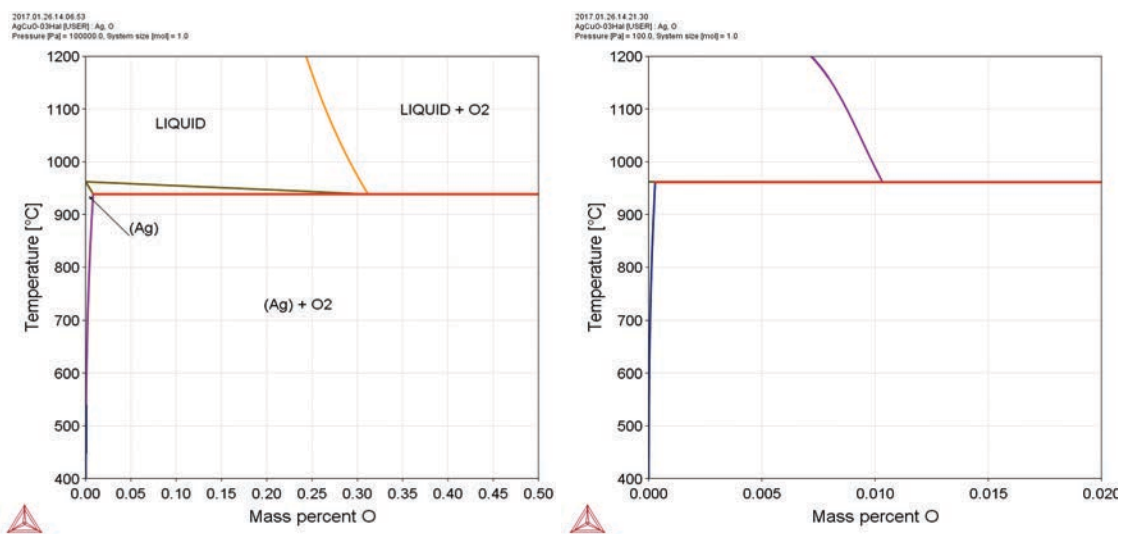

Figure 2 Silver-oxygen phase diagram for different pressures of 1bar (left) and 1mbar (right). The oxygen partial pressure is 0.21 bar and 0.21 mbar. The oxygen solubility in solid and liquid silver increases significantly with increasing oxygen pressure. (ThermoCalc simulation using data from references 13-15)

Compared to silver, liquid copper shows a very high solubility of oxygen of several percent (Figure 3). During solidification, the solubility drops significantly and results in the precipitation of the red copper oxide Cu_2O in the eutectic reaction, $L => (Cu) + Cu_2O$ at a temperature of 1066°C. Solid copper has an oxygen solubility of about 60 ppm at maximum. In the case of sterling silver alloys, the low oxygen solubility in copper and silver results in the formation of copper oxide, even at low oxygen levels. This effect is well known in the jewelry industry as firestain.
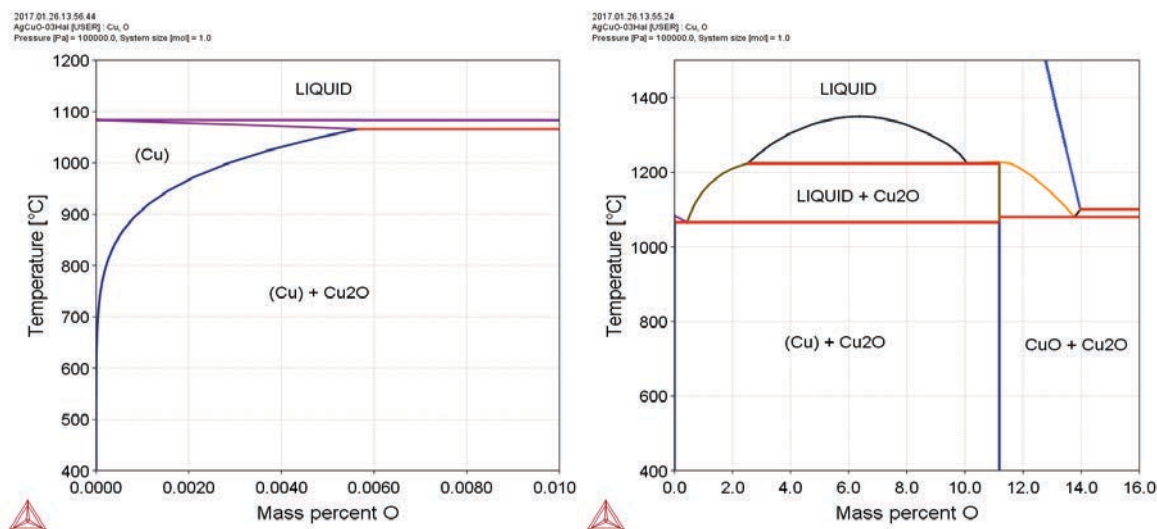

Figure 3 Section of the Cu-O phase diagram on the copper-rich side at a pressure of 1 bar according to Thermo-Calc calculations using data from Reference 15. The right plot shows a magnification of the phase diagram (left plot) for oxygen contents between 0 and 100 ppm.

Metallic alloys form a lattice of close-packed spherical atoms. The metal atoms are of similar size and therefore replace each other in so-called solid solutions. Gas atoms are much smaller compared to metal atoms. Some typical atomic radii are given in Table 2. Therefore, some gases can be dissolved in metals on interstitial sites, i.e., in the gaps between the spherical metal atoms. The solubility increases exponentially with temperature and strongly depends on pressure (Figure 4). Other gases, such as hydrogen, show much lower solubility in silver. The solubility of hydrogen in silver is about 100 times lower compared to oxygen.16
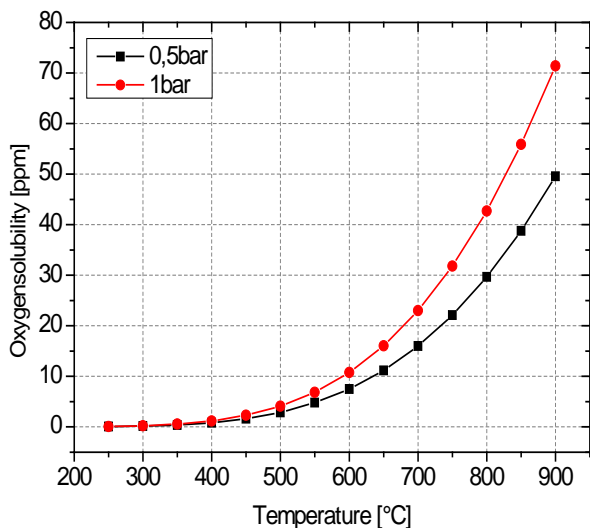
Figure 4 Oxygen solubility in solid silver as a function of temperature and pressure. Data taken from Reference 13 and converted to ppm, mass-fraction.

2.3 Diffusion

Diffusion in solid metals describes the transport of atoms through the metallic matrix. It is controlled by the crystal structure of the matrix, the atomic size, the type of atom diffusing, and temperature. Silver crystallizes in a face-centered cubic (FCC) structure where the atoms are positioned at the edges and the face centers of a cube (Figure 5). Two principal diffusion paths have to be distinguished, namely substitutional diffusion and interstitial diffusion. In substitutional diffusion the matrix atoms are diffusing. Each crystal lattice has some imperfections such as vacancies, i.e., empty lattice sites. These vacancies allow atoms to jump from one lattice site to another. The number of vacancies increases exponentially with temperature. Interstitial diffusion occurs on the interstitial sites, i.e., in the gaps between the matrix atoms. These gaps are much smaller than the atomic radius. Therefore, only smaller atoms are able to occupy these sites and diffuse between the matrix atoms.

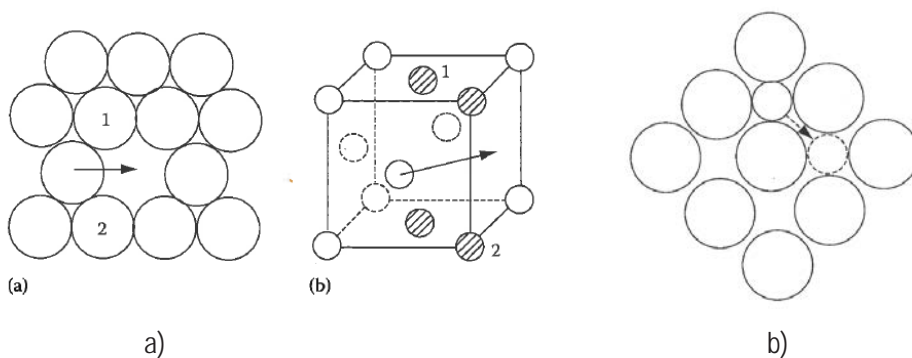a)   b)

Figure 5 Diffusion mechanisms of substitutional (left) and interstitial diffusion (right)17

The movement of an atom from one lattice site to another requires the displacement of the surrounding atoms. With increasing temperature, the vibration of the atoms on their lattice site increases and the resistance against displacement reduces. Therefore, temperature appears to be the most important factor influencing the diffusion rate. The diffusion coefficient D can be described by equation (1). The frequency factor D0 and the activation energy Q are material parameters that depend on the type of atom and the matrix in which diffusion takes place. R is the universal gas constant (8.3144 J/mol·K) and T is the temperature in Kelvin. As D0 and Q are constant, the diffusion coefficient of a certain atom only depends on temperature. Some values for the diffusion of Ag, Cu, H and O in silver are given in Table 2. The large elements Ag and Cu have to diffuse by substitution on the vacant lattice sites of the silver lattice. The activation energy Q for this process is rather high compared to the activation energy for the diffusion of H and O in silver, which are diffusing interstitially.

Arrhenius equation:[17]

$$D = D_0 \cdot e^{-\frac{Q}{RT}} \tag{1}$$

$$\log D = \log D_0 - \frac{Q}{2.3 \cdot RT} \tag{2}$$

Diffusion depth:[17]

$$\bar{x} = \sqrt{Dt} \tag{3}$$

Taking the logarithm of equation (1) turns it into the simple linear equation (2). If logD is plotted over 1/T it turns out that logD0 is the y-axis intercept while -Q/R is the slope of the line. Figure 6 shows the diffusion coefficient of these elements as a function of temperature. The larger the diffusion coefficient D, the faster is the diffusion of the atoms. Silver and copper have a very similar diffusion rate, while hydrogen and oxygen are diffusing much faster. At a temperature of 727°C, the diffusion rate of hydrogen and oxygen is 3 million times and 100,000 times faster than that of silver or copper.

In order to get an idea how fast the atoms are diffusing, the average diffusion depth was calculated using equation (3), where is the average diffusion depth and t is the time. The data in Table 3 illustrate that oxygen and hydrogen can penetrate silver jewelry items at 750°C quite easily. If, for instance, a flask is taken from the furnace too early, oxygen can diffuse deeply into the matrix and internally oxidize the copper to form firestain. Data for the oxidation speed of 925 Ag in air as a function of temperature are given in Figure 20. The concentration profile of oxygen diffusing into silver at a certain temperature and time can be calculated by solving Fick's second law of diffusion using the boundary conditions: COx (at x = 0) = CS and COx () = C0. COx denotes the concentration of oxygen at the distance x, CS denotes the surface concentration of oxygen and C0 denotes the oxygen concentration in the matrix. CS was set to the maximum solubility of oxygen at a certain temperature (see Figure 4) and C0 was set to 10 ppm as the typical value for degased high-purity silver. The concentration profiles were calculated according to equation (4). The term "erf" stands for error function, which is an indefinite integral that is tabulated in books of standard mathematical functions.

Concentration profile:[17]

$$C = C_S - (C_S - C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{4}$$

Element	D_0 [10^{-4} m²/s]	Q [kJ/mol]	Temperature range	Atomic radius [nm]
Ag	0.278	181.7	765 – 945°C (1409 – 1733F)	144
Cu	1.230	193.0	717 – 945°C (1323 – 1733F)	128
	0.029	164.1	426 – 624°C (799 – 1155F)	
H	8.55·10^{-3}	30.1	674 – 850°C (1245 – 1562F)	37
O	3.66·10^{-3}	46.1	407 – 867°C (765 – 1593F)	63

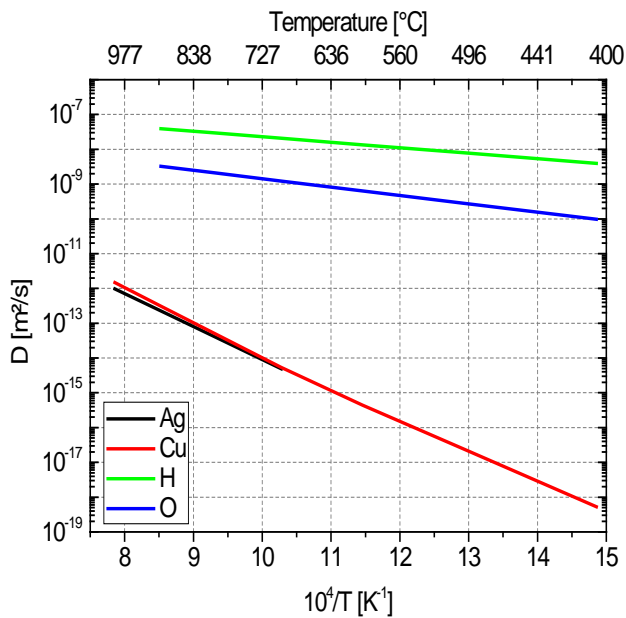Table 2 Diffusion constants of selected elements in silver with the temperature range of validity[10]

Figure 6 Diffusion coefficients of selected elements in silver as a function of temperature[10]

Element	Diffusion depth @ 750°C [μm]		
	1 min	3 min	10 min
Ag	1.3	2.3	4.2
Cu	1.4	2.5	4.5
H	1726	2990	5459
O	441	764	1394

Table 3 Diffusion depth in solid silver at 750°C for different elements as a function of time using the data from Table 2

The concentration profiles given in Figure 7 show a strong dependence on temperature and time. At temperatures of 550°C or below, the oxygen solubility is smaller than the typical oxygen level of 10 ppm in the matrix. Oxygen should therefore diffuse out of the material. At 600°C or above, oxygen is dissolved in silver and a typical concentration profile forms. Due to the high diffusion rate of oxygen, the penetration depth reaches several millimeters. The kinetics of oxygen diffusion is shown in the right figure for a temperature of 750°C. Even for a short time of only 1 minute, oxygen penetrates into the matrix up to a depth of about 1 mm. The depth of penetration increases in a non-linear manner with time. If the typical thickness of a piece of jewelry of 1⎯3 mm and if penetration occurs from either side, it appears that it only takes 1⎯3 minutes until complete penetration of the piece has occurred at a temperature of 750°C.
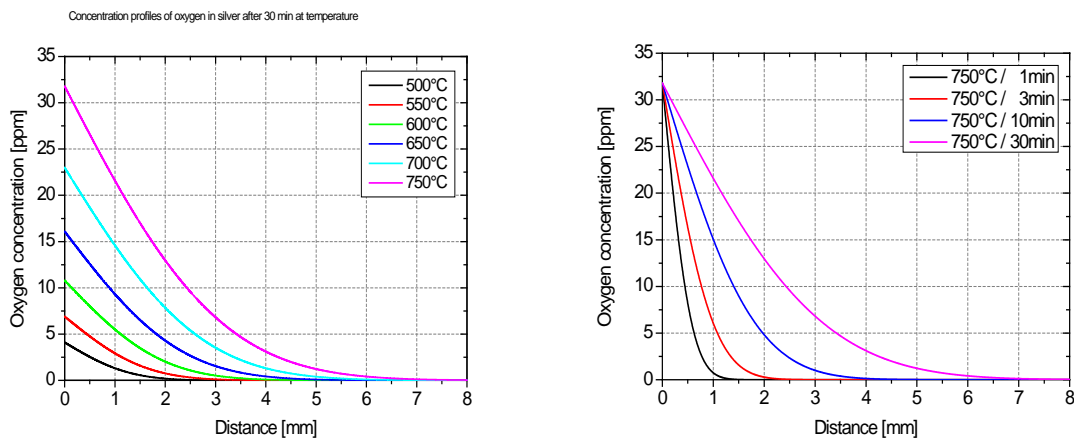

Figure 7 Concentration profiles of oxygen in silver calculated according to equation (4) after annealing in air at normal pressure.
Left: Effect of temperature after annealing for 30 minutes in air. Right: Effect of time at a temperature of 750°C.

3. MELTING AND CASTING

The processing of silver alloys differs significantly between industry and workshop. The following sections therefore distinguish between the different handling processes and describe specific challenges. The main processes are melting and casting of alloys from raw materials, their thermo-mechanical treatment and the final processing steps such as joining. The response of the material on these processing steps is illustrated by typical microstructures and properties after certain processing steps. Typical defects occurring during processing and measures to avoid such defects are described.

3.1 PRIMARY MATERIALS

The primary or raw materials are the alloying elements that are typically bought from a refinery to prepare an alloy of a certain composition. The primary materials are available in different sizes and shapes, such as electrolytic silver, granules (casting grain), sheet, etc. (Figure 8). The oxygen content of these qualities varies. In electrolytic silver the oxygen content is highest due to the deposition process.

Figure 8 999 Ag raw material for melting. Left: Electrolytic silver, oxygen content 400 ppm. Center: Silver granules, oxygen content 250 ppm. Right: Vacuum-melted silver bar, oxygen content <10 ppm.

Granules are a material of choice because they are easy to handle and to dose during the weighing of the alloying elements. They allow for easy mixing of the alloying elements in the crucible and melt homogeneously. Granules are prepared by casting the melt into water. Many gravity casting machines allow the preparation of granules by a dedicated granulation unit. The casting of hot metal into water has some drawbacks, especially in the case of silver alloys. The high solubility of oxygen and the high diffusivity of oxygen and hydrogen in silver were described above. During quenching of the hot metal, some water might be trapped inside the granules, and water can be disintegrated into its elements hydrogen and oxygen. The microstructure of a typical granule in the as-delivered condition is shown in Figure 9. At lower magnification (left), the typical micro shrinkage porosity is visible. The oxygen level was determined to be 250 ppm, which is much higher than the solubility values given in Figure 4. This can be explained by a continuous line of gas pores visible at the grain boundaries inside the granule (Figure 9, right). The actual oxygen content of silver granules is expected to depend on the production conditions and might vary from batch to batch and from one producer to another.
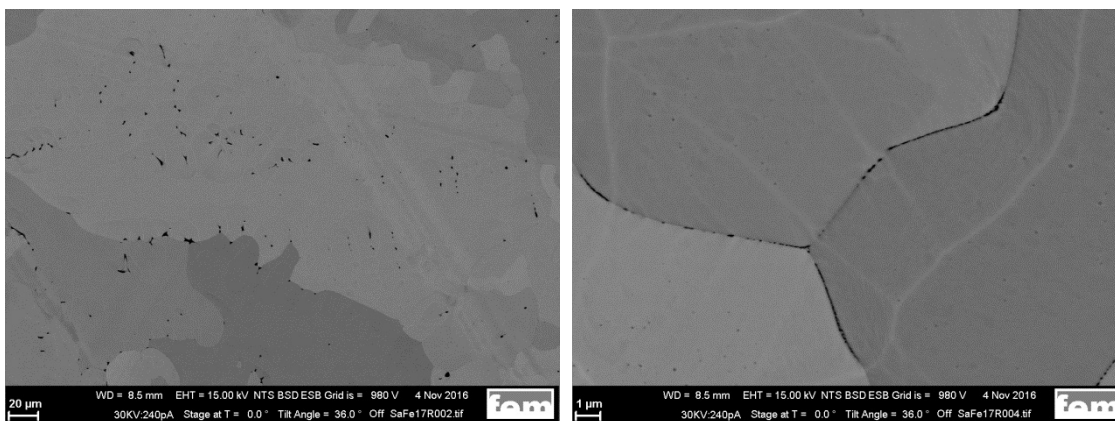

Figure 9 SEM images of granules as delivered from refinery with an oxygen content of ca. 250 ppm

The lowest oxygen content is achieved by melting under vacuum. The entrapped gases evaporate during melting and are removed by the vacuum pump. This results in oxygen levels below 10 ppm. Figure 8 (right image) shows the electrolytic silver after melting under vacuum. The surface is white and shiny and all impurities are collected in the dross on the right side of the bar. Instead of using granules for alloying, it's better to use silver sheet as primary material because its oxygen content is much lower.

3.2 TESTING FOR OXYGEN

In order to assess the effect of oversaturation of the granules with oxygen, some simple tests were done. Some granules were annealed at 800°C in different atmospheres (Figure 10). After annealing in argon and air, the samples looked shiny like before the test. In forming gas the surface became white and dull (Figure 10d). The metallographic section reveals typical indication of hydrogen brittleness for all granules but most severe for the granule annealed in forming gas. The mechanism of hydrogen embrittlement is the formation of water steam by the reaction of hydrogen and oxygen ($2H_2 + O_2 \Rightarrow 2H_2O$). In forming gas there is an excess of hydrogen that diffuses very quickly into the silver granules and reacts with the oxygen in solid solution. Nearly all grain boundaries are decorated with gas pores. At the surface the material swells, resulting in a rough and dull surface. This surface is shown in detail in Figure 11. Numerous pores and the swelling of the material are visible. The pores are preferentially located at the grain boundaries and the stacking faults, because diffusion is a factor of 10-100 times higher at these positions. The cross-section in the focused ion beam shows that the pores are larger close to the surface. The large pores appear spherical, while the smaller pores in greater depth appear angular. The angular shape corresponds to the lattice planes of the face-centered cubic silver lattice and is an effect of surface energy.
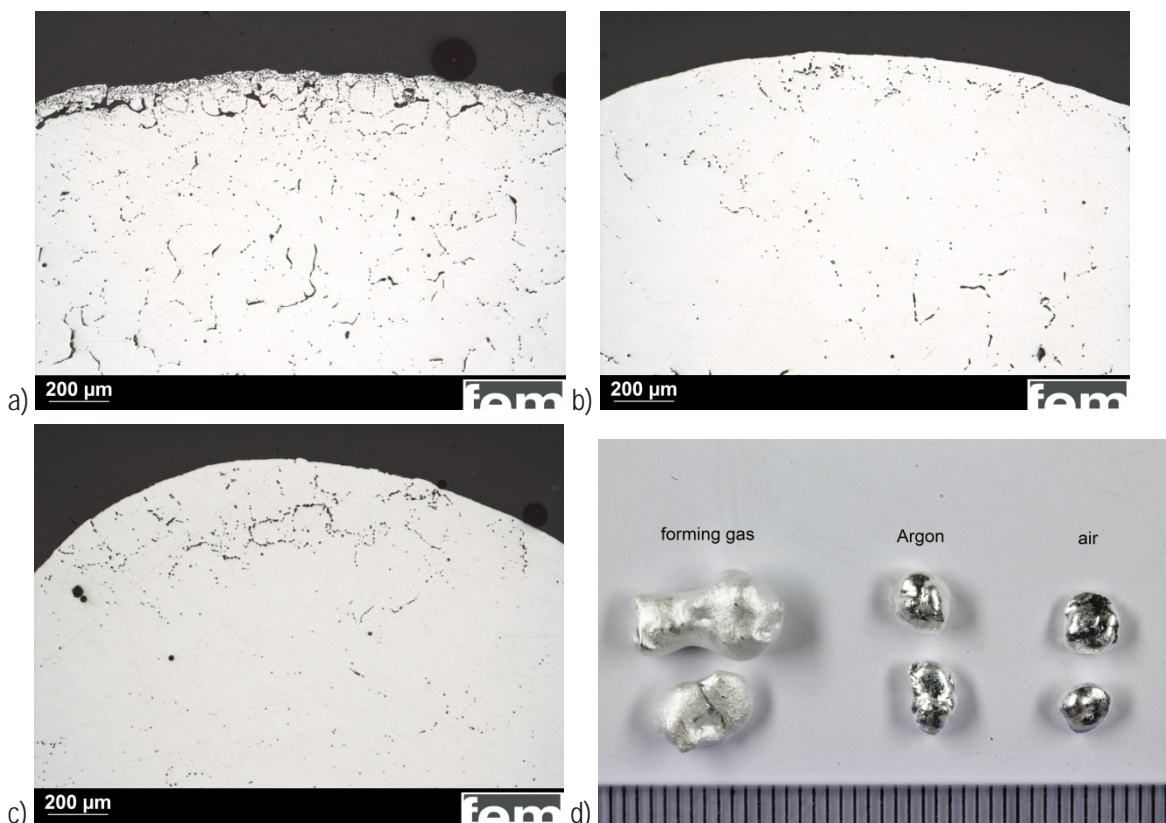

Figure 10 Annealing of silver granules at 800°C for 1 hour in a) forming gas (N2+10%H2), b) argon and c) in air. Appearance of the granules after annealing d) from left to right: forming gas, argon, air.
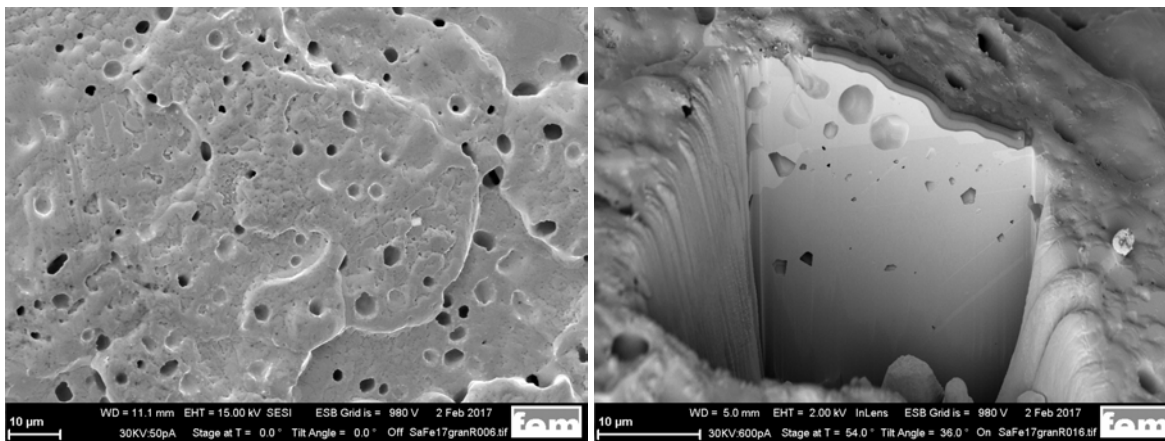
Figure 11 SEM images of a silver granule annealed at 800°C/1 hour in forming gas (N2+10%H2). Left: Surface with numerous gas pores. Right: Focused ion beam section at the surface.

The extent of hydrogen embrittlement in argon and air is much lower. This is because only the entrapped hydrogen atoms are able to react. In spite of this, hydrogen embrittlement is still problematic. During alloying oxygen-containing silver with copper to obtain 925-935 alloys, the oxygen will react with the copper to form copper oxide. The copper oxide will form dross during melting or will be included in the final alloy and cannot be removed by annealing processes. In order to avoid hydrogen embrittlement and internal oxidation of alloys, it is necessary to use oxygen-free silver for alloying.

3.3 MELTING AND CASTING EQUIPMENT

The role of atmosphere during melting was already mentioned. In general, furnaces that can be evacuated before back filling with protective gas (argon or nitrogen) provide the best results and are state-of-the-art in industrial practice. Graphite crucibles are used almost exclusively. They provide a reducing atmosphere due to the reaction of graphite with traces of oxygen. Casting molds are also generally made of graphite, especially for continuous casting. In the case of hand casting, graphite or iron molds are used.

The silversmith in the workshop usually works with small batches. Typical furnaces are electrically or torch heated and alloys are melted in graphite crucibles in air. Due to the missing protective atmosphere, the graphite crucible has to provide the reducing atmosphere. Oxidation and uptake of oxygen into the melt are more likely to occur. The small batch size intensifies such reactions, since the ratio of surface to volume is higher than in large batch sizes.

3.4 GRAIN SIZE, HARDNESS AND MICROSTRUCTURE

A typical microstructure consists of the silver solid solution with primary copper-rich dendrites and a fine two-phase eutectic structure (Figure 12). The fractions of the primary silver-rich phase and the eutectic mixture depend on the cooling conditions. This is illustrated by the Scheil calculation shown in Figure 1. For very slow cooling rates, the fraction of the eutectic mixture will be smaller, while after fast cooling with very limited time for diffusion, a microstructure with a large fraction of the eutectic mixture will occur. Grain size will decrease with increasing cooling rate. Grain refiners such as iridium and boron are important for hand casting and investment casting. In continuous casting, the effect of casting parameters dominates the grain size and grain refiners play a less important role. The hardness in the as-cast condition is typically 60-85 HV1. It depends on the cooling conditions and decreases with increasing cooling rate as shown in Figure 18.
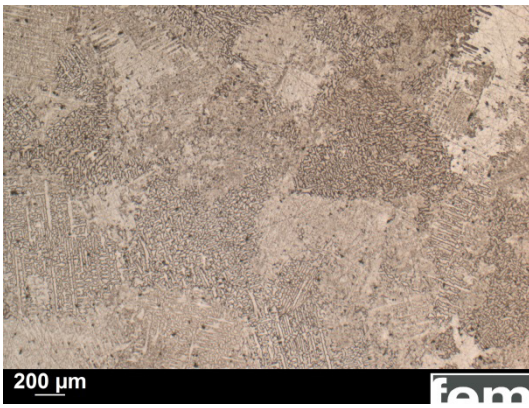
Figure 12 Typical as-cast microstructure of 930 Ag after fast cooling

Generally speaking, the grain size is coarser in investment casting compared to continuous casting. In the present study we cast a rod with a diameter of 15 mm that was swaged to a diameter of 5.1 mm, then annealed at 650°C /30 min/argon and water quenched. The rod was further swaged to a final diameter of 2.8 mm. Further heat treatments were done at different temperatures, holding times, atmospheres and cooling conditions on these cold-deformed rods. Three different alloys, namely 925 Ag-Cu, 930 Ag-Cu and 935 Ag-Cu were investigated and compared. The microstructure of investment cast silver alloys and the effect of grain refiners and further alloying additions is described in detail in the Santa Fe Symposium® paper of Jörg Fischer-Bühner from 2003.[1]

4. THERMO-MECHANICAL TREATMENT

4.1 COLD-WORKING

Sheet or wrought material undergoes a thermo-mechanical treatment after continuous or ingot casting to destroy the casting micro-structure and segregations. Industrial processing is done according to operation routines that describe the single deformation steps and intermediate annealing processes. Silver alloys are usually cold-deformed, e.g., rolled with a thickness reduction of at least 50% before heat treatment. The silversmith in the workshop works with hand rolling mills on small samples. The applied deformation depends on the effort for deformation and the required dimensions. Due to the high ductility, cold-working can be done up to 90% deformation without cracking for most alloys. The hardness increases up to 160 HV1 and sufficient ductility for bending is still maintained. Such high hardness is required for jewelry to obtain scratch resistance and sufficient rigidity of filigree items and stone settings.

4.2 HEAT TREATMENT

After a certain deformation is reached, the material has to be softened by applying a heat treatment. Typical heat treatment ranges can be distinguished and are plotted into a phase diagram in Figure 13. Short-term and long-term annealing are used for the same purpose, namely to soften an alloy by recovery and recrystallization after cold deformation. The atomic defects (so-called dislocations) that were introduced during cold deformation are recovered and new grains are formed. This process is thermally activated and time dependent. Annealing done at high temperature for a short time or at a lower temperature for longer time can achieve the same effect. Depending on the size and shape of the material to be annealed, different furnaces have to be used.
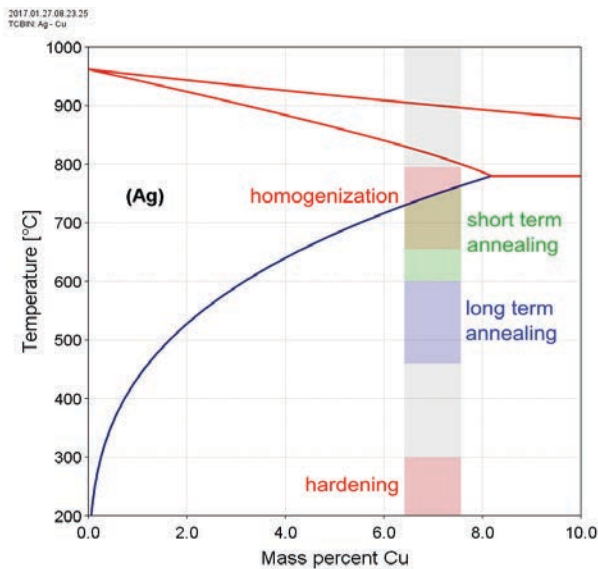
Figure 13 Typical heat treatment ranges for sterling silver alloys

The temperature-time profiles of certain furnaces are shown in Figure 14 and Table 4. Continuous operating furnaces work at relatively high temperatures and short times and are used for small- to medium-sized pieces for recrystallization, hardening or brazing. The furnace atmosphere is controlled and constant. Thermal profiles can be adjusted inside the furnace. Samples can be slowly cooled or quenched into water. During water quenching, the pieces have to be moved to avoid adherent gas bubbles on the surface that reduce the quenching speed. Further and more important, water can be disintegrated into hydrogen and oxygen, which immediately dissolve into the hot pieces. This might result in hydrogen embrittlement during subsequent annealing processes as described above for the granules.
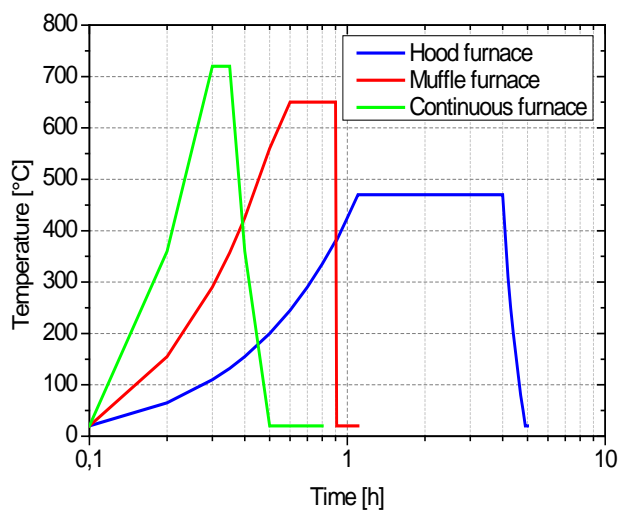

Figure 14 Typical time/temperature characteristics of different furnace types used for heat treatment. The cooling conditions can vary depending if air cooling or water quenching is used.

Furnace type	Temperature range	Annealing duration	Cooling	Atmosphere	Purpose
Hood furnace	420–600°C	Long-term	slow cooling	Closed chamber with inert gas	Recrystallization
Muffle furnace	550°C–800°C	medium/ short-term	quenching in water	Flowing inert gas	Recrystallization, homogenizing, hardening, brazing
Continuous furnace	600°C–780°C	Short-term	slow cooling/ quenching in water	Flowing inert gas	Recrystallization, homogenizing, natural hardening, brazing

Table 4 Furnace characteristics and annealing conditions

Muffle furnaces are used for similar purposes, mainly for smaller batches in the workshop. Some furnaces can be flushed with protective gas. The preheated furnace is loaded and unloaded manually. The parts can be quenched in water, air-cooled or furnace-cooled. The atmosphere is less controlled due to the manual loading that requires opening the hot furnace.
Hood furnaces are suitable for annealing large batches, e.g., complete coils, for the recrystallization between the individual rolling steps. The batch is loaded in a cold chamber that is sealed and evacuated or flushed with inert gas. The actual furnace is a hood that is set over the chamber for heating and cooling.

Under industrial conditions heat treatments are done according to a detailed quality-control chart. Modern equipment allows sophisticated temperature controls in different furnace zones and data recording to ensure reproducibility. Atmosphere and cooling conditions can be controlled. The silversmith doesn't have this type of equipment and the possibility to control. Instead, annealing temperature is controlled by the color of the workpiece, and the duration of the annealing process is estimated. The atmosphere cannot be controlled, so often annealing is done in air or in a slightly reducing atmosphere using charcoal. Additionally, cooling conditions are less controlled and depend on the size of the piece. As a result, the hardness varies from piece to piece and sometimes inside the piece. Oxidation cannot be avoided; therefore, finishing requires more effort to remove firestain.

Homogenization and hardening are part of a two-step heat treatment. The first step of homogenization is done around the solvus line of the copper solid-solution phase (650°-780°C. All or most of the copper-rich phase is brought into solid solution to obtain the highest potential for hardening in the second step of the heat treatment. In order to avoid re-precipitation of the copper-rich phase as soon as the temperature drops below the solvus line, it is mandatory to quench the material from the homogenization temperature. Otherwise, the hardening potential is at least partly lost. During hardening the copper-rich phase precipitates are finely dispersed inside the silver matrix. The effectiveness of hardening depends on temperature and aging time, which is typically 0.5-2 hours. Under optimum conditions (e.g., 300°C) a maximum hardness of about 150 HV1 can be achieved compared to 60-70 HV1 prior to hardening. A detailed description of effects of homogenization and hardening temperature and time, prior cold deformation and alloy composition on hardness and microstructure can be found in Reference 1.

4.3 MICROSTRUCTURE, GRAIN SIZE AND MECHANICAL PROPERTIES
All thermal treatments affect microstructure, grain size and mechanical properties depending on alloy composition. Many microstructure images can be found in Reference 1. One important property that has to be controlled during heat treatment is grain size. In Ag-Cu alloys the copper-rich phase acts as grain refiner during short-term and long-term annealing. Figure 15 shows the sensitivity of grain size to annealing temperature for three different copper contents. The grain size remains below 10 μm up to a temperature of 700°C. At higher temperatures, significant grain growth occurs, most pronounced for 930 Ag and 935 Ag, while 925 Ag maintains a smaller grain size even up to 780°C. According to the phase diagram (Figure 1) the copper-rich phase gets into solid solution at temperatures above 720°C (935 Ag). Obstacles hindering grain growth are then missing and the grain can grow uncontrolled. Alloys with higher copper content show a higher solvus temperature and maintain smaller grain size at the same temperature.
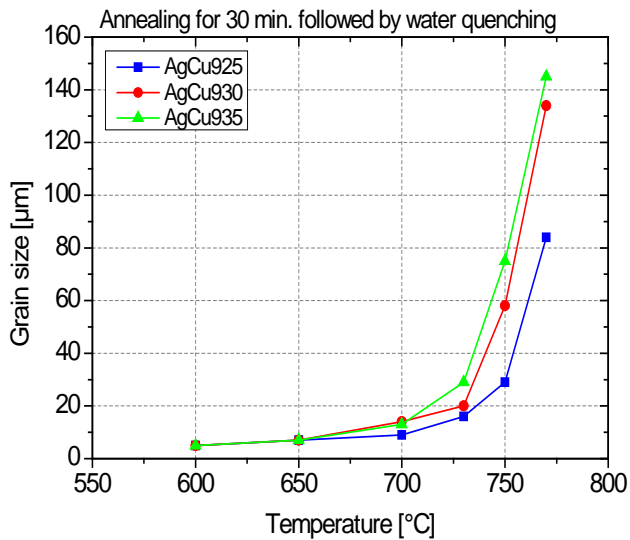
Figure 15 Grain size of different cold-rolled alloys (70% deformation prior to annealing) as a function of annealing temperature

The microstructure images corresponding to Figure 15 are shown in Figures 16 and 17. Figure 16 shows the effect of annealing temperatures for 925 Ag-Cu. After annealing at 400°C, the grain size is well below 10 μm. The copper-rich phase is very finely and homogeneously dispersed. At 600°C, the copper-rich phase coarsens, turning into a cellular arrangement along the direction of rolling. The copper-rich phase starts going into solution as the temperature increases to 700°C and the distance of the cellular copper-rich precipitates increases. The grain size grows accordingly. At 750°C, the copper-rich phase is completely dissolved in the silver solid solution and uncontrolled grain growth and grain coarsening occur.
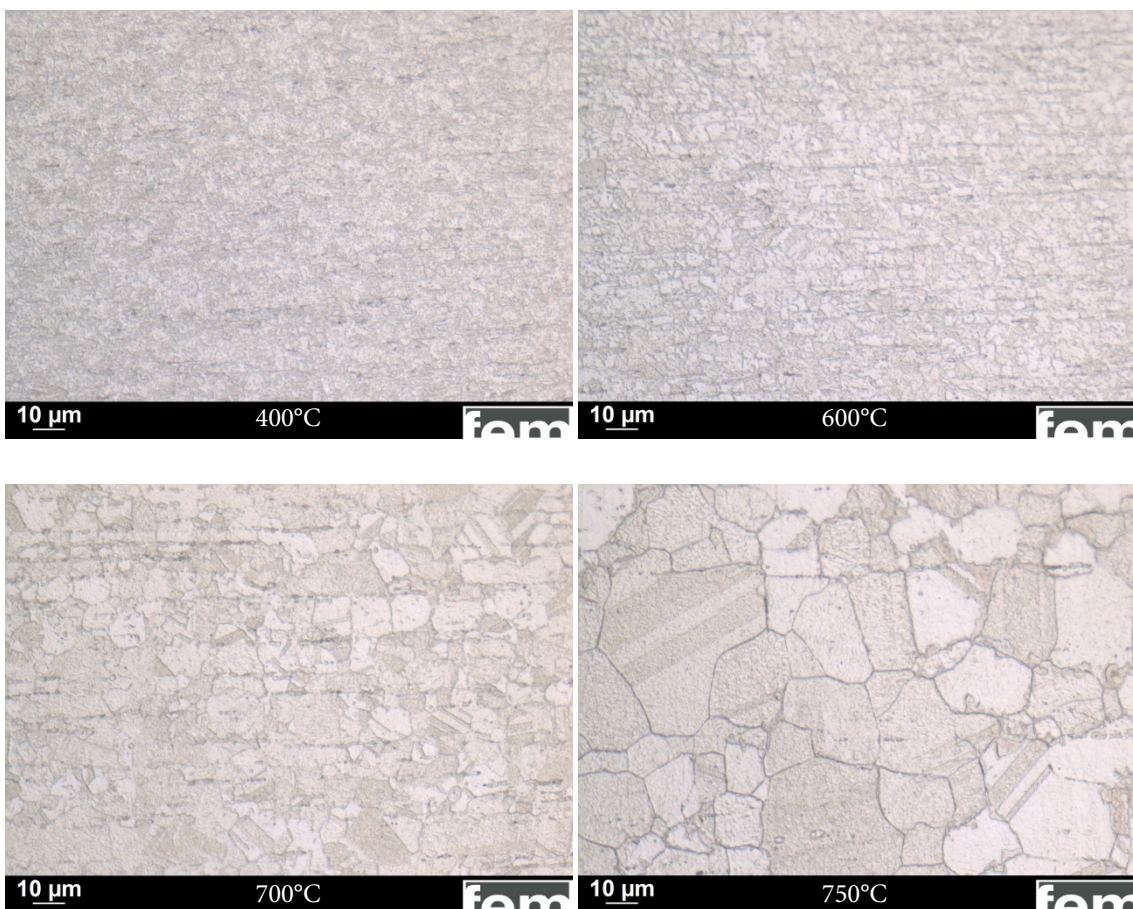

Figure 16 Microstructure of cold-rolled alloy 925 Ag-Cu (70% deformation prior to annealing for 30 minutes followed by water quenching) as a function of annealing temperature

Figure 17 shows the effect of alloy composition for an annealing temperature of 750°C. Significant grain growth has occurred in alloys at this temperature, because most of the copper-rich phase was already in solid solution. The kinetics of grain growth are directly correlated with the kinetics of the dissolution of the copper-rich phase. The alloy 925 Ag-Cu exhibits the highest fraction of the copper-rich phase according to the phase diagram (Figure 1). The dissolution process requires higher temperature and 925 Ag-Cu is therefore showing significantly smaller grain size compared to the alloys 930 Ag-Cu and 935 Ag-Cu. For the same reason, the grain size of 930 Ag-Cu is slightly smaller compared to 935 Ag-Cu.

The recovery of dislocations and the formation of new grains result in a reduction of strength and hardness (Figure 18). With increasing annealing temperature, the hardness drops to 60 HV1, corresponding to the soft annealed, homogenized condition. A short annealing time (30 minutes, water quenching) is sufficient and the hardness drops independent from the annealing duration (30 minutes or 180 minutes). It is important to note that the complete solution of the copper-rich phase is not required to obtain low hardness. Even at an annealing temperature of 750°C, the grain sizes remain as small as 30 µm. If the samples are air cooled after annealing, softening follows the same curve as for water quenching at low temperatures between 500 and 600°C. However, after annealing at temperatures of 700°C and above, significant hardening is observed after air cooling. Such hardening is caused by the in-situ re-precipitation of the copper-rich phase during cooling as the solubility of copper in the silver matrix decreases with decreasing temperature. The diffusion speed of the copper atoms is high enough to form small precipitates that provide enhanced hardness. The cooling speed, therefore, has to be chosen depending on the purpose of the heat treatment.
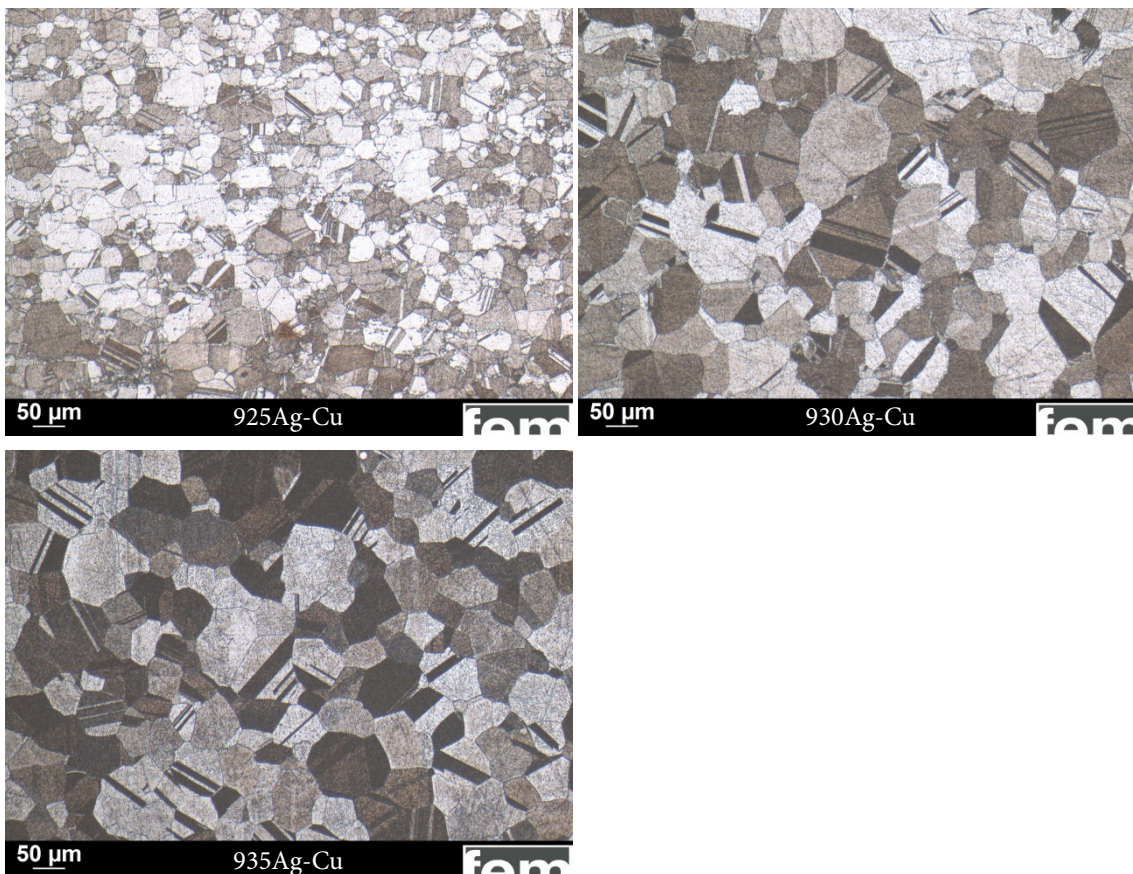

Figure 17 Microstructure of different cold-rolled alloys (70% deformation prior to annealing at 750°C/30 minutes followed by water quenching) as a function of alloy composition

If the material should be soft for further mechanical treatment, quenching is required. If certain hardness should be maintained after the heat treatment, air cooling can provide it. It is important to notice that the hardness achieved during air cooling is lower than that achieved in a two-step hardening procedure (100 HV1 compared to 150 HV1). In some cases a two-step homogenization + hardening treatment might not be necessary. However, the in-situ hardening during cooling depends on cooling speed and, therefore, sample volume. For repeatable results on pieces of different size, the two-step heat treatment provides more uniform mechanical properties. The atmosphere, the temperature and the cooling conditions during heat treatment significantly affect the surface quality of the heat-

treated parts. Figure 19 shows samples that were annealed for 30 minutes in argon at different temperatures and afterwards cooled in air. The samples cooled from 750°C exhibit a black surface layer of copper oxide. This oxide layer is about 3 µm thick, although the cooling requires only a few seconds. Samples that were treated at 650°C show a brownish surface, but no visible oxide layer in the metallographic cross-section. This example demonstrates that overheating considerably increases the reaction rate of oxidation as the diffusion rate of oxygen increases exponentially with temperature.
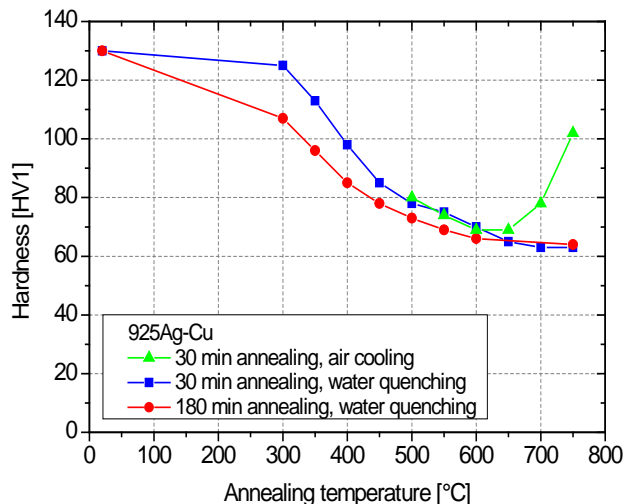

Figure 18 Softening of a cold-rolled 925 Ag-Cu alloy (70% deformation prior to annealing) depending on annealing time/temperature and cooling conditions
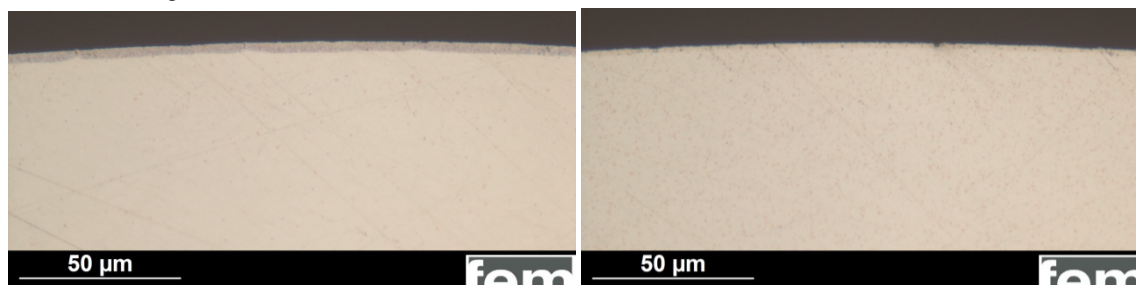

Figure 19 Oxidation during air-cooling after annealing in argon for 30 minutes. Left: Annealing temperature 750°C. Right: Annealing temperature 650°C.

A series of heat treatments in air were conducted at different temperatures in order to get an idea of the oxidation kinetics (Figure 20). These conditions are expected to provide the strongest oxidation at a specific temperature. The experiment shall help to select a temperature range suitable for brazing and heat treatment processes in air without excessive firestain formation.

During annealing, at first the oxygen in solid solution in the alloy (typically 10 ppm for high purity, vacuum-melted silver) is consumed by the formation of very small copper-oxide precipitates throughout the complete sample. Once the oxygen in solid solution is consumed, further oxidation requires the diffusion of oxygen from the surface into the material. According to equation (1), the diffusion rate increases exponentially with temperature. The depth of oxygen diffusion is nearly linear with temperature, according to equation (3) and Figure 7. At an annealing temperature of 500°C, no visible oxidation occurred. Visible oxidation started at 550°C. At the surface the oxide density appears to be higher and decreases towards the center of the sample (Figure 20, right). The dependence of the oxidation depth on temperature is experimentally confirmed and its linearity is shown in Figure 21. During oxidation dissolved oxygen is consumed. This accelerates the diffusion into the material. The calculated diffusion profiles indicate that this process is very rapid and the final oxygen content of the material is therefore much higher than the equilibrium solubility.
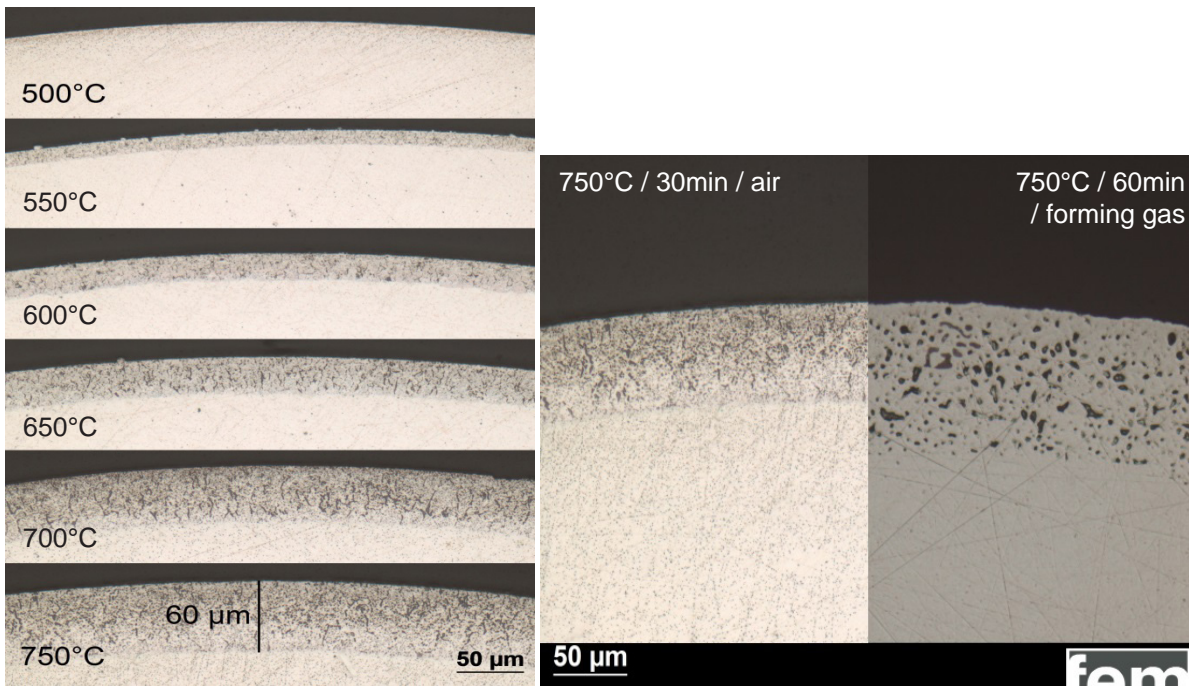
Figure 20 Left: Firestain formation on 925 Ag-Cu during annealing in air for 30 minutes at temperatures between 500°C and 750°C. Right: The wire annealed at 750°C was afterwards annealed in forming gas to remove the oxide layer.
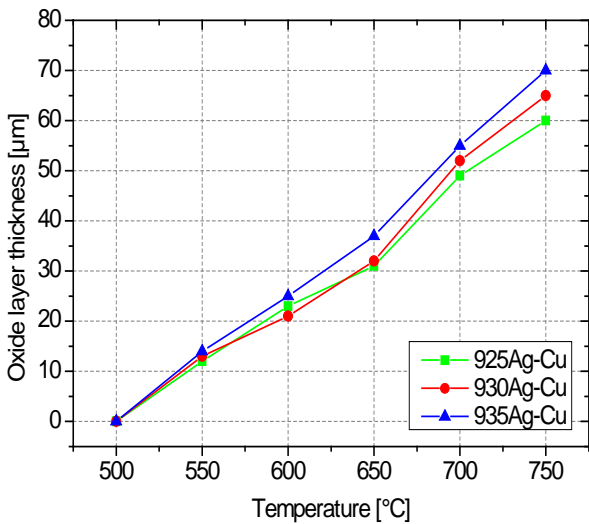

Figure 21 Thickness of the firestain layer after annealing for 30 minutes in air as a function of temperature for different Ag-Cu alloys

The oxide layer can be reduced by a subsequent annealing under forming gas. Figure 20 (right) shows a comparison of a sample that was first annealed at 750°C for 30 minutes in air and subsequently annealed at the same temperature in forming gas ($N_2+10\%H_2$) for one hour. The hydrogen in the forming gas is able to reduce the copper oxide freeing the oxygen atoms so they can react with the hydrogen to make water in the form of steam, and the steam forms gas bubbles in the region of the former oxide layer. Although the copper oxide is removed, the annealing under forming gas is not a suitable repair for firescale oxidation. The sample swells and gets a rough surface or even gas bubbles and blisters that ruin the piece. Therefore, care has to be taken to avoid excessive temperature during annealing or brazing in air in the workshop.

The growth of the oxide layer occurs linearly with temperature (Figure 21). It slightly depends on the copper content. The oxide layer becomes slightly thicker if the copper content decreases. This is surprising at first, because a higher copper content should result in a thicker oxide layer. However, it has to be kept in mind that the growth of the layer is diffusion controlled. The formation of an oxide layer requires diffusion from outside into the surface were it immediately reacts with copper. The effective cross-section of the silver matrix is thereby decreased and further diffusion of oxygen is hindered. If the copper content is higher, the effective cross-section of the silver phase is more strongly reduced and diffusion of oxygen is hindered more strongly, resulting in a thinner but denser oxide layer in 925 Ag-Cu compared to 935 Ag-Cu.

5. FURTHER PROCESSING STEPS

Any jewelry piece requires further processing steps such as joining, stone setting or at least finishing. In this section some typical examples of sterling silver jewelry and possible defects are shown. Brazing of silver alloys (commonly called "soldering" by jewelers) is done with silver-based brazing alloys of different working temperatures. In American literature brazing and soldering are just distinguished by the working temperature. Soldering is done below 840°F (450°C) by definition and brazing above 840°F (450°C). If several brazing steps are required for a certain piece, then brazing alloys of different working temperatures are required. In order to lower the working temperature, the copper content of the brazing alloy can be increased, but this is limited to the eutectic temperature. Therefore, additional alloying elements such as zinc are required to adjust the working temperature for a given silver content. The working temperature ranges from 660°C–770°C as shown for alloys provided by one manufacturer (Table 5).

Ag content	750	675	600	600	550
Brazing temperature	770°C	730°C	710°C	680°C	660°C

Table 5 Typical working temperature of cadmium-free silver brazing alloys[18]

Under industrial conditions, brazing is most often done in continuous or muffle furnaces under protective gas. The brazing alloy is applied as a paste using a dispenser unit. This guarantees constant quality and very limited oxidation. In the workshop, jewelry is brazed using the torch in order to melt small pieces of the brazing alloy. Cooling is achieved by reduced heating, air cooling or water quenching. As a consequence, firestain is often an issue that needs to be removed during finishing. The objective is to work with reduced temperatures and under the best possible conditions in order to keep the oxidation low and so avoid firestain removal during finishing. Firestain removal during finishing can be challenging due to the complex shape of some jewelry pieces assembled by brazing (Figure 22). Silver electroplating is sometimes the only method to hide defects that cannot be removed.
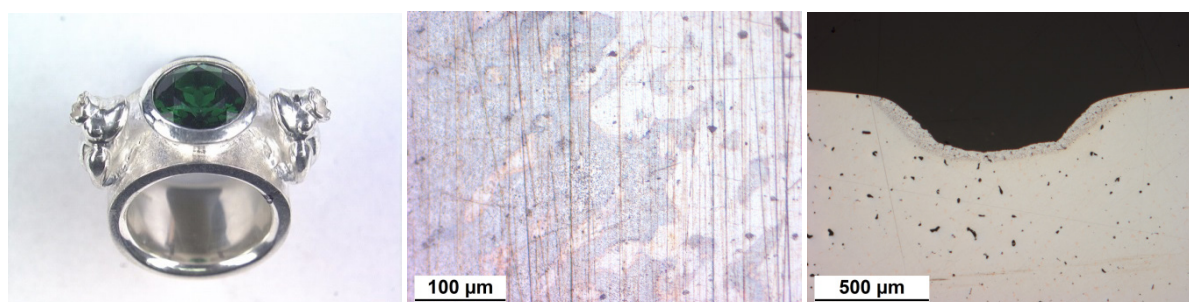

Figure 22 Left: Complex silver jewelry piece with brazed stone settings.
Center: Surface area with firestain. Right: metallographic cross-section. The
firestain layer was removed during polishing, but inside the groove it is still present.

An extreme example of internal oxidation is shown in Figure 23. In this case, casting scrap was re-used for investment casting by re-melting and granulation. The material was oxidized from previous casting processes and the copper oxide (CuO) remained in the material. CuO and silver form a eutectic at 946°C as shown in Figure 2 of reference 15. Therefore, copper oxide cannot float to the top of the melt as dross where it could be removed. Instead, copper oxide remains in the melt in further processing steps. As the Ag + CuO eutectic has a lower melting temperature than the original alloy, the oxide inclusions tend to agglomerate in the interdendritic

regions and embrittle the casting. In order to remove the oxide, the material has to be melted under a reducing atmosphere or with a deoxidizer. Even if the copper oxide is removed from the melt, it can be expected that the chemical composition of the alloy is changed. Normally the silver content increases, for instance, to levels of 945‰. As shown above, this will affect the properties and the processing conditions of the alloy. In case scrap should be re-used, great care has to be taken to avoid oxidation throughout the process and to remove oxide layers as much as possible.
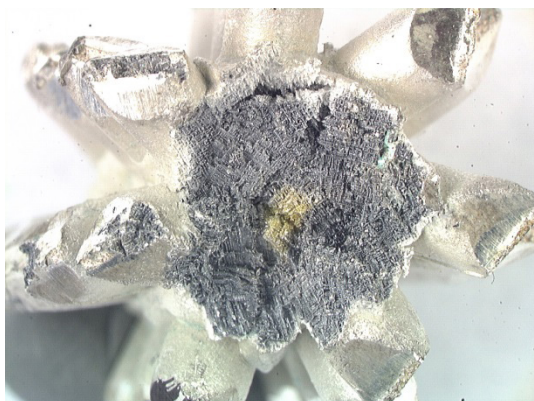

Figure 23 Main sprue of an investment cast tree of 925 Ag-Cu that is fully oxidized due to the re-use of scrap for casting

6. INFLUENCE OF ALLOYING ADDITIONS

Recent developments of silver alloys strive to remove copper partly or fully in order to improve tarnish resistance.3,5,6 Zinc and sometimes indium have been added to silver alloys for a long time to improve castability. Palladium is added to replace copper in tarnish-resistant alloys. The reason for increased tarnish resistance is mainly attributed to the reduction of the copper content. Germanium-containing alloys were the first that claimed to be tarnish resistant and are marketed under the brand name Argentium®. It was claimed that germanium forms a transparent passivating oxide layer.[19]

The effect of the alloying additions on the silver-rich side of the Ag-Cu phase diagram is shown in Figure 24. Elements like zinc and indium lower the eutectic temperature, while palladium increases it. A second influence of alloying is on the solubility of copper in silver. Additions like zinc and palladium are relatively neutral. Indium and germanium, however, reduce the copper solubility in silver. Additionally, these elements are strongly segregating to the melt by forming deeper melting eutectics than the Ag-Cu eutectic. This may result in hot tearing, especially in the case of germanium-containing alloys.
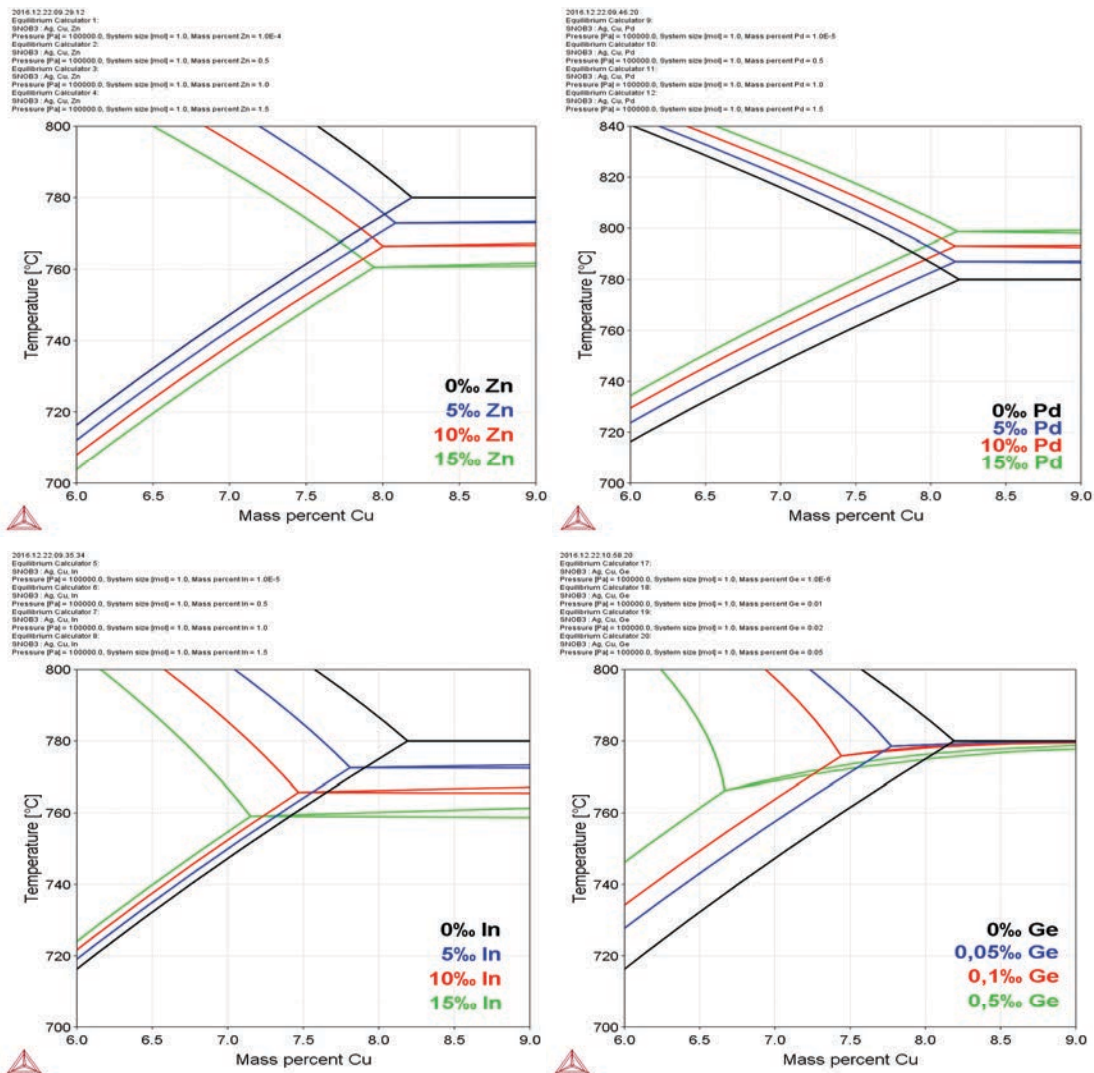
Figure 24 Effect of alloying additions on the solvus line in the binary Ag-Cu system according to Thermo-Calc calculations

Modern manufacturing methods such as additive manufacturing are now introduced into the jewelry market. Silver alloys are among those that are most difficult to be additive manufactured due to their high reflectivity for the laser light and their high thermal conductivity. Alloy development strives to increase the melting range of the alloys to increase the processing window and to reduce porosity. A filigree part produced by additive manufacturing using an unknown 925 Ag alloy was subjected to brazing (Figure 25). A brazing alloy with a working temperature of 750°C was chosen, but it turned out that the part was partially melting during brazing. Metallography revealed a low melting inter-dendritic phase that is rich in germanium.
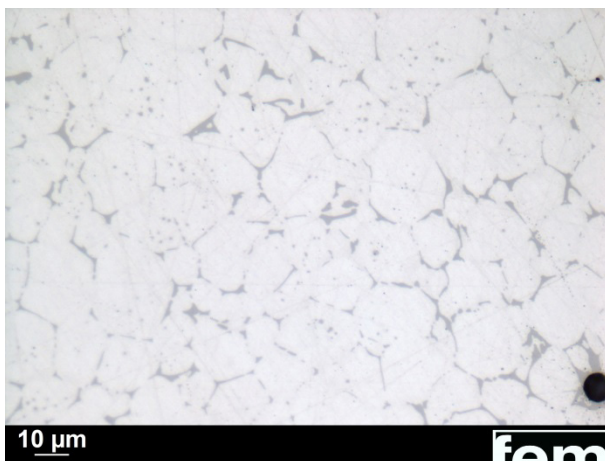

Figure 25 Microstructure of an additively manufactured part of a low-melting 925 Ag alloy

Adjusting the alloy composition in most cases also requires an adjustment of the heat treatment and other processing steps. A typical solution-annealing temperature of 925 Sterling silver of 730750°C might be too high for zinc-, indium- or germanium-containing alloys, while it could be too low for palladium-containing alloys. New manufacturing processes using modified alloys or the newly developed tarnish-resistant silver alloys will require consideration of the processing steps in industry and in the workshop.

7. SUMMARY

This paper describes the properties of sterling silver alloys depending on processing conditions illustrated by the thermophysical properties of silver and its alloying elements and impurities. The focus is on Ag-Cu alloys with a silver content of 925-935‰. The well-known Ag-Cu binary phase explains the microstructure depending on casting and annealing conditions. The high diffusivity of impurities such as hydrogen and oxygen and the high solubility of oxygen in liquid and solid silver are responsible for certain defects that are typical for Ag-Cu alloys. Annealing in air or even air-cooling can result in significant oxidation at the surface and inside the alloy, well-known as firestain.

In industrial processing, the conditions are usually well controlled. In the workshop this is much more difficult due to individual pieces, small batch sizes, limited equipment and high amount of hand work. Firestain or uncontrolled grain growth and thereby loss of hardness are easily occurring. The silversmith should take care not to overheat samples and to use brazing alloys of low working temperature (e.g. 650°C or below), if possible. Oxide layers that formed during processing should be carefully removed by grinding. Annealing of oxidized material under reducing atmosphere, such as forming gas, results in irreparable hydrogen embrittlement. Even the use of granules may cause hydrogen embrittlement due to entrapped water and high oxygen content. The use of oxygen-free raw material such as silver sheet or ready-made alloys from the refinery, careful control of furnace atmosphere and the avoidance of excessive temperature allow high quality under workshop conditions.

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