ALLOY DEVELOPMENT STRATEGIES FOR JEWELRY: WHAT CAN WE LEARN FROM OTHER INDUSTRIES

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INTRODUCTION

1.1 The compositional space

Alloy development is a very complex process. Many different parameters are important (composition, processing conditions, thermomechanical treatment, microalloying and more) to find suitable compositions for a specific purpose. The development of new alloys still remains a huge and nearly unexplored field of science. In view of the fact that mankind has been using metals and alloys for several thousand years, this statement may seem bold. However, a simple consideration of the number of possible phase diagrams in multicomponent alloys confirms it. Figure 1 shows the number of possible phase diagrams C based on the number of alloying elements n, which can be mathematically expressed as:

$$C = (n¦k) = n!/(k!\cdot(n-k)!) \qquad (1)$$

Consider a ternary system, such as Au-Ag-Cu, which forms the basis for most gold and silver-based jewelry alloys. Understanding this ternary system requires the knowledge of three binary and one ternary system. Binary systems can be described easily described using2D plots of temperature versus composition. A ternary system is represented by a three-sided prism with the triangle and the z-axis forming composition field and temperature, respectively. A quantitative graphical representation is achieved by 2D slices along constant temperature (isothermal section) or composition (isopleth section). To achieve the composition of a Ni-free, age-hardenable white gold alloy, two additional elements must be added: nickel and zinc, which increases the number of systems for a full description to 10 binary, 10 ternary, 5 quaternary and 1 quinary

system. The possibilities for alloying are immense. The complete description of this five-component system is a practically unsolvable task with countless parameters.

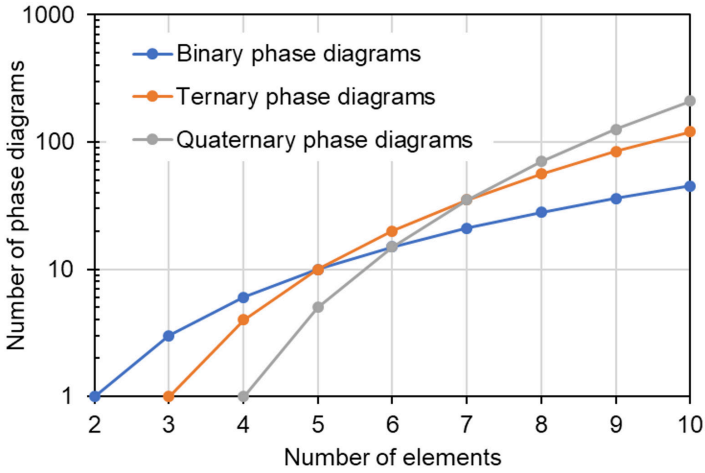

Figure 1: Combinations of alloying elements and the number of possible binary (k=2), ternary (K=3) quaternary (k=4) phase diagrams. Please note: number of phase diagrams is plotted on a logarithmic scale.

1.2 Solid solution based alloys

Experience shows that soft and malleable alloys are most often formed around the "corners" or "edges" of the compositional field of multicomponent alloys were one major or two elements form a solid solution phase that dissolves all other alloying elements. If more elements are added, they may form additional phases that induce embrittlement to the alloy. However, a certain and fairly controlled amount of additional elements is required to improve hardness and strength to acceptable levels. The above-mentioned five component system Au-Ag-Cu-Pd-Zn is then the basis for five groups of alloys based on the major solid solution phase of Au, Ag, Cu, Pd or Zn, respectively. Obviously, these five groups of alloys show very different characteristics.

A different group of solid solution based alloys was described in 2004 and is known as high entropy alloys (HEA) or complex concentrated alloys (CAA)[1]. HEA are defined as alloys with five or more elements that each have a concentration between 35 and 5at.-% ("multi-principal element alloys", MPEAs). A mixture of so many principal alloying elements is said to stabilize a solid solution phase by a high configurational entropy ("high entropy alloys") and the wide compositional range opens "the vast, unexplored central regions of multi-principal element composition and phase

space" [1]. What makes such alloys interesting is their often claimed to superior properties (high strength, high magnetic saturation or high electrical conductivity at low temperatures). The topic gained enormous interest with many studies that were published in recent years, including some work on noble metals alloys[2–5]. The sheer number of possible alloy compositions has spurred researchers to find new alloys with particularly outstanding compositions.

1.3 Intermetallic and amorphous alloys

Next to solid-solution based alloys there are intermetallic alloys, which are alloys based on chemical compounds formed by different metals. Brass and bronze are the most widely known example. These intermetallic compounds form an enormously large group of sometimes malleable, but mostly hard and brittle materials, depending on the chemical bonding of the elements. The development of aircraft engines and turbochargers is inextricably linked to the development of alloys based on intermetallic phases, such as titanium and nickel aluminides. Intermetallic compounds give rise to abrupt changes in a material's behavior. This becomes most obvious, if an alloy suddenly changes its color due to the formation of an intermetallic compound (Figure 2).

Figure 2: Jewelry based on intermetallic compounds of AuAl2 (purple) and AuIn2 (blue)

Some elements dramatically impair the properties of alloys, even if they are only present in minute traces. Silicon is a typical example in 18 karat gold alloys as it causes hot tearing and cracking. Ott and Raub have carefully investigated the effects of small amounts of many elements on the properties of gold alloys[6–9]. It is the irony of alloy development that it was the addition of large amounts of silicon that led to the discovery of a new class of metallic materials – so-called amorphous metals or metallic glasses[10]. These alloys are extremely brittle, but if they are cooled rapidly they form metallic alloys of extremely high elasticity. Not only gold but also platinum alloys form such metallic glasses with exceptional properties, if large amounts of phosphorous are added (Figure 3)[11,12].

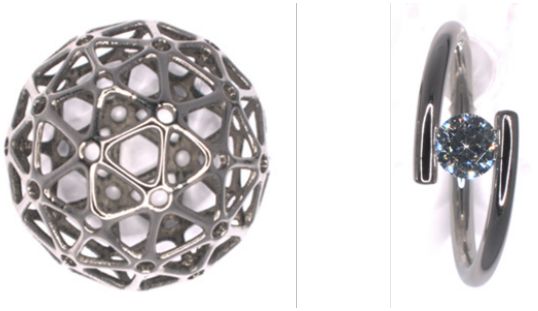

Figure 3: Jewelry made of platinum based bulk metallic glass alloys

2. Alloy development approaches

The development of new alloys for luxury goods is driven by the following and other factors:

- Improvement of the alloy properties (hardness, scratch resistance, tarnish resistance), e.g. tarnish resistant silver alloys[13]
- New manufacturing techniques, e.g. alloys suitable for additive manufacturing[14]
- New, exclusive properties, e.g. alloys of special color[15,16]
- Laws and regulations, e.g. limitation of nickel release to avoid allergic reactions[17]

In the past, materials were primarily developed through empirical methods, relying on educated guesses and a bit of luck. This conventional alloy development approach is suitable for simple alloys that are based on 2-3 elements. Minor additions of functional elements (grain refiners, desoxidants). The development is based on adding one additional element after the other and explore their role. The experimental alloy optimization can be supported by simulation tools. One of the most important tools is based on the thermodynamics of alloys and is known as the so-called CALPHAD approach (CALculation of PHAse Diagrams)[18]. This is one of the most established and highly developed techniques for phase diagram calculation.

An example Figure 4 shows the silver-rich side of the binary, eutectic phase diagram of silver-copper alloys (black line). The addition of copper reduces the solidus and liquidus temperature of silver and opens a melting range. The red line marks the eutectic reaction at 781°C, with the composition of traditional Sterling silver being located just at the Ag-rich end of the eutectic line. If a constant amount of zinc is added to the alloy, this will shift the phase equilibria. The phase diagrams in blue and green color are for constant zinc content of 2% and 4%, respectively. These diagrams are sections through the ternary diagram along a temperature-con-

centration plane, so-called isopleth sections. It appears that for a constant Ag-content the liquidus temperature is slightly lowered while the solidus temperature is slightly increased – the melting range is becoming narrower. The eutectic line is degenerated to a three-phase field and shifted to lower temperatures. At the same time the single-phase field in the solid state is strongly increased. With the ability to read phase diagrams, such calculations allow the experienced metallurgist to qualitatively assess, for example, the age hardenability of sterling silver when copper is reduced to increase tarnish resistance, or to find the optimum heat treatment conditions.

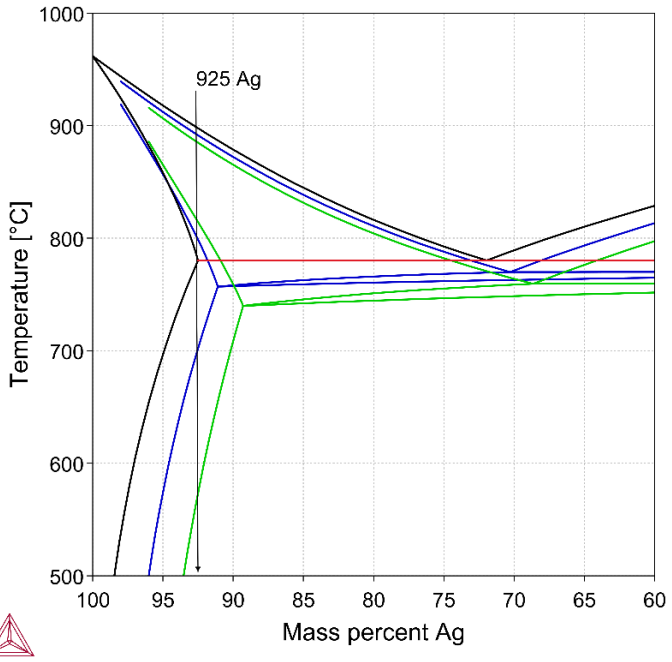

Figure 4: Effect of the addition of zinc to silver-copper alloys. Overlay of three phase diagrams: binary silver-copper alloys (black), alloys with 2% zinc (blue) and with 4% zinc (green). The red line marks the eutectic reaction in binary silver-copper alloys. ThermoCalc v2023b, TCNOBL3 database.

2.1 Material properties

Many simulation tools for process optimization require material properties that are very difficult to determine experimentally. Simulation tools with embedded physics-based material models can provide such data much easier. Examples of such properties are phase fractions, thermal conductivity, viscosity or volume that are important for other simulation tools like casting simulation[19]. The experimental determination of such properties, especially as a

function of temperature is demanding and time consuming. Some important properties require the experimental determination of several other properties. For instance, the thermal conductivity λ, is a product of density ρ, thermal diffusivity a and specific heat capacity c_p. The determination density is done by dilatometric measurements or by the sessile drop technique[20], thermal diffusivity requires laser flash measurements and finally heat capacity is obtained by differential scanning calorimetry (DSC).

The determination of these properties for at least four temperatures requires a tremendous amount of experimental work and expenditure of material. Above that, considering the non-linear behavior and the abrupt change at solidus and liquidus temperature do not allow a simple interpolation or extrapolation of the values. The measurement techniques in the solid state are more elaborated and widely available in well-equipped laboratories. However, measurements of liquid alloys are often only performed by specialized laboratories or even require low-gravity conditions[21].

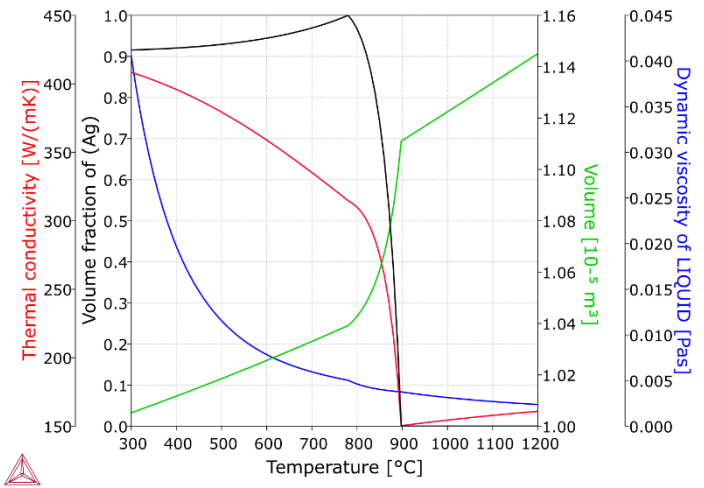

Figure 5: Properties of 925 Sterling silver as a function of temperature calculated by the CALPHAD technique. ThermoCalc v2023b, TCNO-BL3 database.

2.2 High-throughput thermodynamic calculations

The thermodynamic calculations can be automated by external scripts that can access the software via an API. In case of the software ThermoCalc this is done by TC-Python. Figure 6 shows the result of applying such a script to calculate the solidus and liquidus temperature of Ni-based alloys. Over 20,000 compositions were tested with a variation of eight elements. The results within that multi-dimensional composition room were then filtered for alloys

that fulfilled certain pre-defined criteria, which included a maximum liquidus temperature, a specific melting range, a maximum allowed phase fraction of intermetallic compounds and much more. The selection criteria can be tailored to the application of interest.

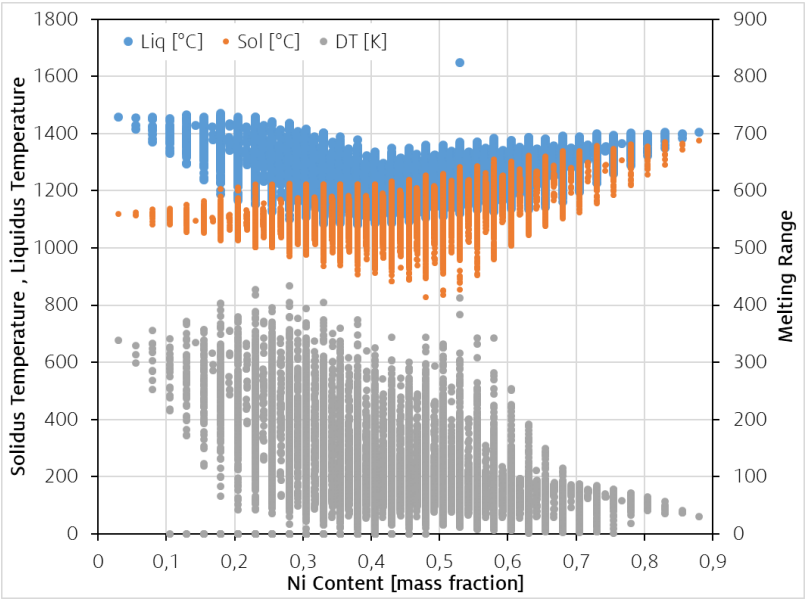

Figure 6: Automated calculation of solidus temperature, liquidus temperature and the melting range DT of Ni-based alloys. ThermoCalc v2023b, TCNI11 database[22].

3. Experimental and simulation-based high-throughput techniques

Many complex alloys were discovered as a result of a failed / unplanned experiment or a "strange" behavior of a material, e.g. bulk metallic glasses or age-hardenable aluminum alloys[23]. In the latter case, Al-Cu-Mn alloys were extensively used before the reason for their special properties were fully understood. Finding such compositions based on available experience is impossible, if the mechanism for their properties remains unclear. Even simulation tools can only build bridges between the "islands of knowledge", but are not useful to discover "new continents". For instance, a thermodynamic simulation technique like CALPHAD can only handle phases that have been previously described. New phases cannot be discovered by that approach. Therefore, experimental high throughput techniques are required to bridge that gap. Such techniques use two basic approaches that are described now.

Classical experimental techniques for material development are very powerful in generating detailed datasets of individual compo-

sitions. Such information is crucial for the detailed understanding of material behavior or for the optimization of processing conditions. The one-by-one modification of the experimental parameters provides the maximum information about a specific material and system. However, the elaborate preparation routes for each sample are slow, and material and labor-intensive. Therefore, such techniques are not ideal for the search of new materials.

3.1 Experimental high-throughput techniques

Experimental high-throughput techniques provide an overview of the general material properties by a screening of thousands of compositions[24–26]. There are two basic approaches:

1. Multi-material samples with concentration profiles, e.g. diffusion couples: One sample, many compositions, high resolution characterization techniques
2. Automated manufacturing of individual samples (combinatorial alloy development): Robotic techniques, high material expenditure, ...

The first approach requires the in-situ preparation of a library of material compositions within one sample. In materials science two main technologies have been used for that purpose: co-sputtering of thin films[26–29] and the diffusion couple technique[30,31]. In the past, the latter technique has been mainly used to screen complex phase diagrams or to study diffusion properties[32–35]. However, diffusion couples have been used to study the hardness by nano-indentation[36–38], which has recently been used for the development of new, age-hardenable copper alloys[39,40].

3.2 Diffusion samples

Diffusion samples are prepared from individual alloys by a diffusion welding process that is well-known in the jewelry industry for the manufacturing of multi-colored wedding rings[41]. Figure 7 shows a series of diffusion samples that were prepared by hot-pressing of rings and cylinders of different copper alloys. The selection of suitable alloy compositions allows combinations of many different alloying elements. The diffusion welding results in an intimate contact of the different alloys. A subsequent annealing treatment forms a diffusion profile where the composition of the alloys are mixing. The metallographic cross-section shows the washed-out color of the different alloys at the interfaces. This gradual color change was caused by interdiffusion of the alloying elements. In the present case this zone has a width of 1-2mm, which is large enough to allow the measurement of a hardness profile across the diffusion zone. A hardness mapping obtained by automated measurement across one triple point of the alloys CuAl5, CuNi9.5 and CuCo4.5 is shown in

Figure 7 (right side).

The chemical composition in the interdiffusion zone around that triple point was determined by energy dispersive x-ray analysis (EDX) in the scanning electron microscope (SEM) and mapped over the hardness data (Figure 8). The representation of hardness as a function of the chemical composition of a quaternary system on a two-dimensional plane is not trivial. The points shown can lie on the plane or above or below it. For a clear representation, a simplification was therefore made by projecting the measurement points onto the plane, as described in[40]. The quaternary chemical composition was also converted into the proportions of the respective binary starting alloys according to EDX. The hardness profiles of the alloy libraries could thus be depicted in the ternary image as shown in Figure 8. There are no pronounced differences in hardness in the solution-annealed state (left image). The hardness is essentially determined by the solid solution hardening, i.e. by the atomic radius difference of the alloying elements. In the range of 50% CuAl5, a slightly increased hardness of max. 120 HV1 can be observed. However, ageing results in an area of increased hardness on the CuAl5 side, which protrudes into the four-component system. A maximum hardness of 224 HV1 was observed during ageing at 455°C. This behavior (low hardness in the solution-annealed condition and increase in hardness due to ageing) indicates a typical precipitation-hardening system. Based on these experimental results, two Cu-Ni-Al compositions were selected for further investigations on solid samples. The alloys are located in the areas of high hardness in the as-aged condition and differ primarily in their Ni:Al ratio and alloy content. For the exact description of individual alloys, the examination of massive samples will continue to be decisive. Thanks to screening, however, only targeted melts are required, which can then be used to concentrate on detailed examination of specific alloys.

The example shows the potential of the screening method for alloy development, as it drastically simplifies the evaluation of entire alloy systems. The method has its advantages particularly in its speed. A major advantage is that metastable precipitation states can also be investigated. These play a special role in precipitation-hardening alloys and generally lead to better properties[23]. Many precious metals alloys are using precipitation hardening or ordering (red gold, white gold platinum based alloys) for the purpose of enhancing the hardness. The potential of using the diffusion couple method to optimize such alloys seems obvious. In the future the local determination of other properties (e.g. color or electrical conductivity) will increase the potential of this screening

method. CIE-Lab color coordinates can be easily extracted from an optical image of a diffusion sample. Figure 9 shows the gradual changes of the L*, a* and b* values between the different copper alloys. Such information is extremely valuable in finding alloys of customized color or to analyze the color gradients during joining processes and to correlate such changes with the chemical composition to identify, for example, deviations from hallmarking conventions.

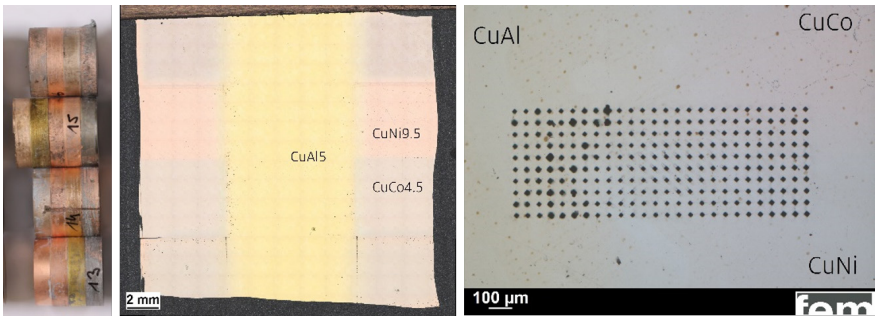

Figure 7: A set of diffusion samples prepared of different copper alloys. The sample diameter is 20mm. Center: Metallographic cross-section of one of the diffusion couple after diffusion annealing. Right: Hardness mapping around one triple point[39,40,42].

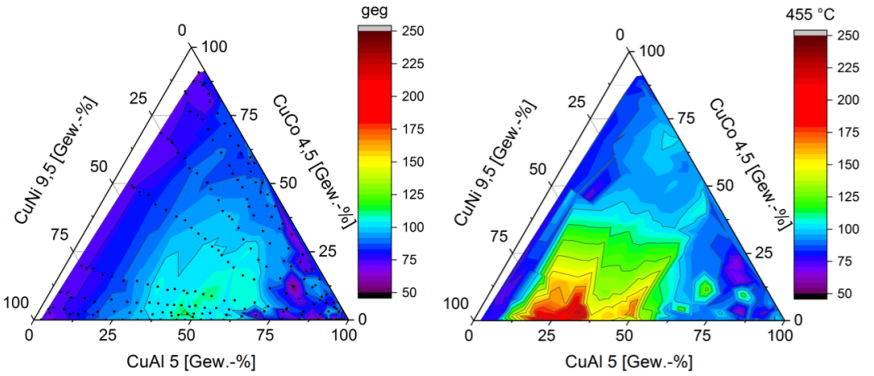

Figure 8: Hardness as a function of alloy composition. Left: annealed condition. Right: after age hardening at 455°C [42].

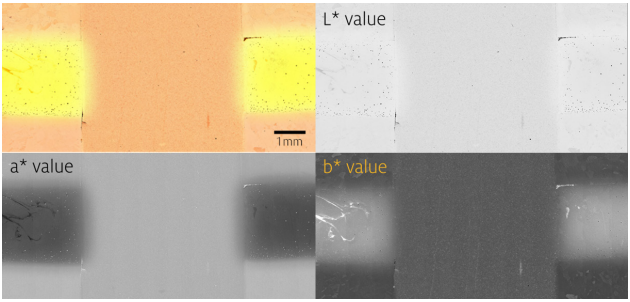

Figure 9: CIE-Lab color parameters of a diffusion sample of three different copper alloys.

3.3 Thin film coatings by co-sputtering

The PVD technique is a proven technique for the deposition of thin films of material onto substrates[43]. The thickness of the deposited layer is depending on the distance of the substrate position from the target. The use of multiple PVD-targets arranged around the substrate (so-called co-sputtering) enables the deposition of multi-material layers. Thin film co-sputtering is a proven and powerful high-throughput technique used in various fields of materials science[28,29]. This technique was applied at the fem Research Institute to find gold alloys of special color (Figure 10, see also[15,16]). Three PVD-targets of gold, indium and aluminum were positioned around a square glass substrate of approx. 20x20cm on the lower left, the right and the top side, respectively. After sputtering the gold-rich corner is easily identified by its specific color. The In-rich and Al-rich corners appear blueish and grayish, respectively. The color gradients are rather smooth without any specific colors, because the as-deposited film have a high concentration of point defects on the atomic level. Therefore, annealing at 400°C is required to reveal the color of the different compositions. After annealing the Al-rich changes its color into the typical purple gold color of the intermetallic compound AuAl2 (compare to Figure 2). The different colors are now clearly separated depending on the stability range of the particular phase that determines the color.

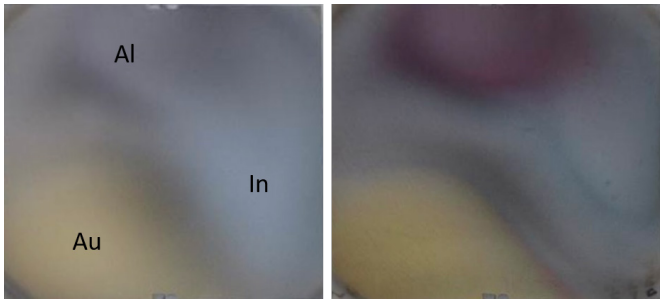

Figure 10: Co-sputtered thin film coatings of gold, aluminum and indium. Left: as-sputtered condition. Right: formation of purple colored AuAl2 phase after annealing at 400°C/1h.[44].

Later Furrer et al. demonstrated the effect of the Au and Pt content on the color of alloys with a constant content of 66 at% Al[45]. The addition of Pt changes the color gradually from purple on the Au-rich side to yellow on the Pt-rich side. Thin film co-sputtering is therefore proving to be a powerful screening method for alloy development. Compared to the diffusion couple technique, the library of alloys is spread over a much larger area, so that the analysis is less sensitive to the position on the sample. However, film thickness and substrate material must be carefully selected. Therefore, both techniques should be considered complimentary.

4. Digitalization in Materials Science

Digitalization has significantly changed many areas of our lives and work. Many things are now digitally connected. In the future, products will also be developed digitally, from the molecule to the finished component. In order to realize this, a digital material data space will be created. The "Plattform MaterialDigital"[46] is coordinating the necessary work in the field of materials science in Germany. The aim is to achieve a virtual material design along entire value chains and to support materials throughout the product life cycle. A digital description of these processes from the real world in the digital world generates a digital twin that can be used for simulation, design and optimization of real-world processes.

This is illustrated with an example of the mold casting of an aluminum part. The casting process was optimized by employing casting simulation tools. The casting quality was assessed by computer tomography, metallography and mechanical testing. Figure 11 shows a graphical representation of how all these data were integrated into a digital twin of the sample. By using manufacturing process data, precise component behavior predictions become possible. Integrating hybrid, simulation-based, and data-driven methods provides accuracy comparable to conventional approaches without

substantial computational overhead. The higher forces achieved in the example could be used in the product design phase to save material in terms of lightweight construction.

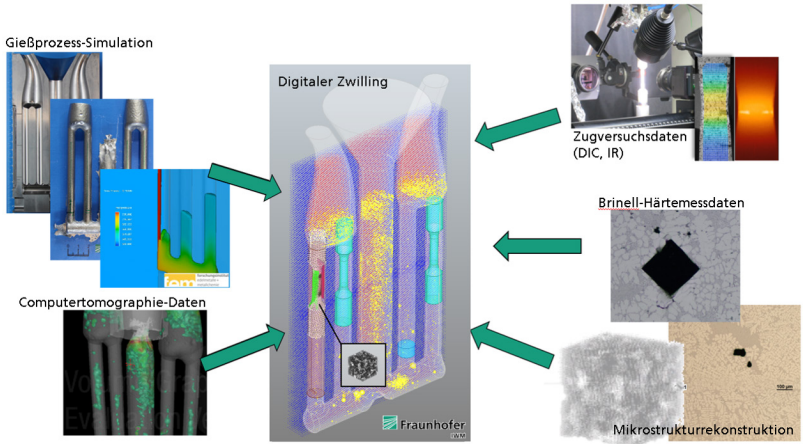

Figure 11: Creating a digital twin by data fusion from simulation and measurement data along the process chain[47].

The integration of the various processes requires linking through a standardized description, a so-called onthology. The foundations for this are currently being laid as part of various pilot projects on different material classes. In this framework the fem Research Institute is coordinating the work on copper alloys in the project "KupferDigital"[48], which includes creating a method for handling and evaluating data from high-throughput methods. This work is of fundamental importance and can also be applied to other materials in the future.

5. Summary and conclusions

The development and optimization of alloys and processes is still one of the driving forces in jewelry technology. However, the mere optimization of existing alloys and processes will not lead to disruptive changes. Therefore, new approaches are required with which the properties of a large number of alloy compositions can be simulated or experimentally investigated in a short time. This is made possible by the use of high-throughput methods.
The application of thermodynamic simulation tools was illustrated with several examples. The solidus and liquidus temperatures, various thermophysical properties and the content of certain phases were determined for over 20,000 alloys. This allowed the optimization of the composition within an eight-component alloy system. So far, many processes cannot be optimized simply on the basis of simulations, but require input from experimental high throughput

techniques. For precious metal alloys, methods that require only a small amount of material (diffusion pairs and thin film co-sputtering) are particularly suitable. The examples explained the development of a precipitation-hardenable Cu alloy and the discovery of gold alloys with special colors.

In order to make effective use of the very large volumes of data generated, the data obtained using high-throughput methods must be represented in a digital twin in future. In Germany, the foundations for the creation and use of corresponding data spaces are currently being laid as part of the "MaterialDigital" platform. The aim is to enable virtual material design along entire value chains in the future. The luxury goods industry now has a favorable opportunity to take up such methods and integrate them into its material and process development strategy.

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