Interface Reactions Between Au-based Filler Alloys and Ti, Ni Substrates

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Abstract

The present study focused in diffusion soldering of Ti and Ni substrates using low melting point eutectic Au–Si and Au–Ge filler alloys. Au–Ge–Sn and Au–Ge–Sb foils were produced by melt spinning and also used as filler metals in the joining process. Ti substrates were used as well as Ti coated with layers of Ni or Ni and Au. A series of them were annealed to improve adhesion of the coating. The main objective of this work is to characterize the joining interfaces from a microstructural and mechanical point of view.

The joining process was performed at 400ºC with a holding period of 10 minutes and under a vacuum pressure of 4x10^{-6} mbar.

The microstructure was characterized by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The chemical composition of the present phases was analyzed by energy dispersive X-ray spectroscopy (EDS) by means of point measurements, and through wavelength dispersive X-ray spectroscopy (WDS) were performed linescans of the interfaces. The applied foils were also analyzed by SEM and EDS and the evaluation of the melting points of the filler alloys was carried out by differential scanning calorimetry (DSC). Mechanical evaluation of the joints was done by means of shear tests and microhardness measurements.

Using Au–28Ge filler alloy, Ni/Ni joints showed a perfect connection and achieved the best mechanical performance with 201MPa. Ti/Ti, on the other hand, did not exhibit such good performance. The observed bad wetting behavior seemed to result in areas of the joint without any connection. However, using Au–19Si, the performance with Ti substrates increased.

When comparing not coated Ti/Au-Ge/Ni with coated Ti/Au-Ge/Ni joints, the (annealed) coating of the Ti substrate had a significant effect in the microstructure and consequently in the mechanical behavior.

The production of Au–Ge–Sn and Au–Ge–Sb foils was successful as well as the soldering with Ni and Ti substrates. It was observed that addition of Sn or Sb to Au–Ge alloy decreases the melting point even more.
Resumo

O presente estudo incidiu na união, por diffusion soldering, de substratos de Ti e Ni, usando para tal ligas de adição eutécticas de Au–Ge e Au–Si, de baixo ponto de fusão. Au–Ge–Sn e Au–Ge–Sb foram também produzidos por melt spinning e aplicados como ligas de adição na produção das uniões. Substratos revestidos de Ti foram também utilizados e estes foram revestidos com camadas de Ni ou Ni e Au. Uma série destes substratos foram recozidos para melhorar a adesão dos revestimentos. O objectivo principal deste trabalho é então caracterizar as uniões produzidas de um ponto de vista microestrutural e mecânico.

O processo de união foi realizado a 400°C com estágio de 10 minutos e sobre uma pressão de vácuo de 4x10⁻⁶ mbar.

A microestrutura da interface foi caracterizada por microscopia electrónica de varrimento (MEV) e por microsonda electrónica (EPMA). A composição química das fases presentes foi analisada por espectroscopia de dispersão de energias de raios-X (EDS) e através de espectroscopia por comprimento de onda dispersivo (WDS). As ligas de adição foram também analisadas por MEV e EDS e a avaliação dos seus pontos de fusão foi feita por calorimetria diferencial de varrimento (DSC). A avaliação mecânica das uniões foi efectuada por ensaios de corte e medições de microdureza.

Usando a liga de adição Au–28Ge, as uniões Ni/Ni demostraram uma ligação perfeita e alcançaram o melhor desempenho mecânico com 201MPa de resistência ao corte. Uniões Ti/Ti, por outro lado, não exibiram tão bom desempenho. A reduzida molhagem de Au–28Ge em substratos de titânio pareceu resultar em áreas da união onde a conexão foi inexistente. No entanto, usando Au–19Si, o desempenho das juntas de Ti aumentou.

Quando comparadas uniões Ti/Au-Ge/Ni (não revestido) com uniões revestidas Ti/Au-Ge/Ni, o revestimento (recozido) do substrato de Ti teve um efeito significativo na microestrutura e consequentemente no comportamento mecânico.

A produção de folhas de Au–Ge–Sn e Au–Ge–Sb foi bem-sucedida, bem como a união com substratos de Ni e Ti. Foi observado que a adição de Sn ou Sb à liga de Au–Ge reduz ainda mais o seu ponto de fusão.
Motivation of study

Soldering offers various possibilities of joining similar and dissimilar metal substrates, without the necessity of high process temperatures. A strategic selection of filler metals and process parameters allows producing highly loaded bonds of different basis materials without changing their properties significantly. For several decades high Pb content alloys have been widely used in electronic and automotive industries as soldering materials for high temperature applications. Considering the toxicity of lead and its difficult and problematic recycling, it is an urgent priority to develop high temperature lead-free solders [1, 2].

Au-based filler alloys are an attractive alternative due to their excellent properties such as good mechanical properties, high-temperature oxidation resistance, high thermal and electrical conductivity. [3, 1]. Eutectic alloys like Au–28Ge (at.%) and Au–19Si (at.%) show particular interest because the exhibit extremely low melting points. This is a clear advantage because not only the time and energy consumption of the process is reduced, but also residual stresses, due to differences in thermal expansion coefficients, are minimized. Furthermore, Chidambaram et al. showed that the addition of metals like Sb or Sn to the Au–Ge alloy decreased the melting point even more and improved its ductility [1].

Scientific investigations of Au-based alloys are still lacking. Thus, the goal of this investigation is to gain knowledge about Au-based filler alloys and their soldering behavior with different metallic substrates.

Frequently used metals were chosen as basis materials for soldering - titanium and nickel. These are also widely used as substrates in electronic components. Coating layers of Ni and Au were applied to Ti substrates to ensure wetting by the Au-based solder alloy; further annealing of the coated substrates was done to improve adhesion. Studies with uncoated Ti were also carried out. The combination of these materials makes them suitable for applications in electronic, sensor and space technology.

In the present work, the analysis and characterization of the joints interfaces was carried out to determine interface reactions and to understand the influence of the developed microstructure on the mechanical behavior. Therefore, shear tests were also essential to characterize the bond strength of the produced joints. This whole understanding is crucial for new technology developments.
1. State of research

1.1 Diffusion soldering

According to the American Welding Society (AWS) [4], brazing can be defined as a “joining process that takes place above 450ºC using filler metals or alloys which flow by capillary forces and whose melting temperatures are lower than the solidus temperature of the base materials.”

The fundamental concepts like metallurgy and surface chemistry are similar between soldering and brazing. Both employ the same bonding mechanism, that is, the use of a molten filler metal that wets the mating surfaces of a joint and reacts with the base material, usually alloying, and forming metallic bonds at the interface [5]. The substrate materials, with a higher melting point than the filler metal, remain solid during the joining process. However, in contrast to brazing, soldering uses filler metals with a liquidus temperature that does not exceed 450ºC [6].

Soldering is performed in many industries, from applications in aerospace, semiconductors and sensors to jewelry or plumbing. Due to the temperature restrictions of electronic components and substrates, soldering is the only metallurgical joining technique suitable for mass manufacture of electrical interconnections. [7].

However in brazing and soldering, the wetting of the components surface is not always easy to reach. Moreover, the reaction between the filler metal and the components can cause excessive erosion of the base material or embrittlement of the joint, due to the formation of phases with inferior mechanical properties, and other undesirable effects. The higher working temperature of the ensemble can also be compromised by the presence of the filler metal, with lower melting point. On the other side, brazing and soldering have the advantage of being able of filling joints with irregular dimensions and produce round fillets on the extremities [5].

Diffusion bonding avoids the need of wetting and spreading by the filler metal. Once produced, the diffusion bonded joints are stable at high temperatures, so that the working temperature can, in fact, exceed the temperature peak of the joining process, without the risk of remelting the joint. However, diffusion bonding tends to be limited as production process, since it’s not tolerant to joints of variable width and, furthermore, its reliability deeply depends on the state of cleanliness of the surface. High loads (10-100 MPa) have to be applied during the bonding cycle to ensure perfect contact along the interface. In addition, the duration of the heating cycle is typically in the range of hours, compared to seconds for
soldering and brazing, because the solid state diffusion is much slower than the wetting of a solid by a liquid. This features, and the non-existence of remarkable fillets on the extremities, for reducing the stress concentration, widely restrict the applications of the diffusion bonding [5, 6].

Diffusion soldering (or transient liquid phase joining) is a hybrid joining process, based on the principles of isothermal solidification, that combines the beneficial features of both soldering and diffusion bonding. It associates good joint filling, the formation of fillets, and surface preparation tolerance of soldering, along with a great flexibility of service temperature, as well as metallurgical simplicity of diffusion bonding [5].

Its high temperature analogue, diffusion brazing, is a well-known process, applied to many metallic systems, with varied range and geometries, and which has been used for decades to join and repair components in aerospace industry and semiconductor applications [8, 9].

In diffusion soldering, a low melting temperature metallic interlayer is applied between the mating surfaces of the components, so that, initially, this molten filler metal fills the joint gap, but during the heating cycle it diffuses into the components material to form intermetallic compounds (IMCs). Due to the higher melting points of these IMCs compared to the initial low melting point interlayer, the joint re-melting temperature is elevated and, therefore, usage at higher temperatures can be achieved. To initiate the melting process it’s favorable that the phase constitution of the solder includes a relatively low melting point eutectic reaction. [10, 11].

Diffusion-soldering is not regularly found but is used commercially. In most of the published studies of diffusion soldering, the emphasis has been on lowering the process temperature to make the joining operation suitable for attachment of dies and other electronic components, which are temperature-sensitive [5].

1.1.1 Process principles of diffusion soldering

The joint configuration normally includes the two parts of the component (substrates) to be joined and the filler metal inserted between them. The components should be fixed together with a low compressive stress that ensures the correct position of the parts to be joined. The set is then heated above the liquidus temperature of the filler, which melts, wets the joint surfaces and fills the clearance in between them, producing small fillets on the extremities [5, 6].
Owing to the formation of a liquid in the joint, the necessary applied pressures are normally much inferior than those needed for diffusion bonding, and generally between 0.5 and 1MPa. This is important for two reasons: there is no need for highly demanding equipment for the joining operation and since the necessary pressure is only a small fraction of the yield stress of the base metal deformation is avoided [5].

As a result of diffusion of one or more constituents of the liquid solder into the base metal, and vice versa, isothermal solidification occurs due to a change in composition and melting temperature with time [5].

Diffusion soldering, being a liquid-phase joining, offers a means to fill joints that aren’t fully flat or smooth, at the same time offering greater flexibility with respect to process temperature in relation to the service temperature of the product. Due to the referred features of the process the following advantages can be highlighted [5, 6]:

- Good reproducibility of the process.
- High degree of dimensional control of the joint width.
- Remarkable joint filling over large area joints, ensuring leak tightness (the joint works as a hermetic enclosure).
- Obtainment of very narrow joints, normally less than 10µm, benefiting properties like thermal conductivity and mechanical properties, while compared to conventional solder.

1.1.2 Wetting and spreading

The adhesion of soldered joints depends on the phenomena of wetting and spreading. The joining of two materials involves the formation of an interface where bonding occurs and the nature of this interaction can be simply mechanical, physical (reversible Van der Waals forces) or chemical (chemical reactions between solid and liquid) [12].

Other major factors that must also be considered include the state of the solid surface in terms of the presence of oxide films, surface roughness and their effects on wetting and spreading [7].

In the absence of barriers to wetting such as the referred oxide films or even grease or dirt, molten metals will wet metallic substrates whatever the intensity of interaction between the liquid and the solid [13]. Wetting in this kind of systems can be discussed according to the classical model of wetting, using the Young-Dupré equation: The liquid will spread over the
solid surface until the surface tensions between liquid and the solid substrate, the liquid and the atmosphere, and the solid substrate and the atmosphere are in balance. This model contains several approximations which make it only a rough description of the actual system. According to the wetting equation (Equation 1) and as can be seen in Figure 1, a wetting angle of $\theta < 90^\circ$ corresponds to $\gamma_{sv} > \gamma_{sl}$, which means that this imbalance is the driving force for the wetting and spreading of the molten filler metal over the surface of the base material. From a practical point of view, wetting is assumed when $\theta < 70^\circ$. On the other hand, if $90^\circ < \theta < 180^\circ$, some wetting is said to occur but the liquid will never spread on the solid surface [6, 12, 13].

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Equation 1: Wetting equation; $\gamma_{sv}$ – surface tension between solid and vapor, $\gamma_{sl}$ – surface tension between solid and liquid, $\gamma_{lv}$ – surface tension between liquid and vapor.

Figure 1: Contact angle and surface tension forces acting when a liquid droplet not wets ($\theta > 90^\circ$) and wets ($\theta < 90^\circ$) a solid surface (left and right side, respectively), according to the classical model [7].

A low contact angle, which indicates wetting, is only one significant aspect of the soldering process. Viscosity of the filler metal is also important. Eutectic compositions are known to have lower viscosity than adjacent compositions, being this desirable for the spreading of the filler metal onto the substrate. This can be explained by the instant melting of the eutectic alloy, without any gain on its viscosity, so that the spreading of the molten alloy is then driven by interaction with the substrate [6, 7].

Surface roughness is also known to reduce the contact angle $\theta$, but for each material there is an optimum roughness that will aid the wetting and spreading of the filler. The texturing produced by network of thin channels may raise the capillary force between the filler and the mating surfaces [6].
1.2 Applied Materials

1.2.1 Filler alloys

1.2.1.1 Au–Ge

As can be seen in Figure 2 the Au–Ge system exhibits a deep eutectic with a eutectic temperature of 361°C (around 28 at.% Ge), a value much lower than the melting points of the alloy’s constituent elements Au and Ge having a melting point of 1064°C and 937°C, respectively [14]. This eutectic temperature can be further decreased with the addition of a third element, such as Sn or Sb [15, 16]. Chidambaram et al., for example, reported that the addition of Sb to the Au–Ge eutectic would not only decrease the melting point, but would also improve the ductility of the alloy significantly [1].

Besides the low melting point, Au–Ge based alloys also possess many interesting properties that are required for high temperature solders. Au–Ge is among the earliest known metallic glasses [17] and does not contain any stable intermetallic compound (IMC). Furthermore, the good heat conductivity of Au based alloys is essential for transferring heat away from the device, which is suitable for devices like power circuits.

Au based alloys also possess a good corrosion and oxidation resistance in the presence of high humidity at elevated temperatures, good mechanical properties, and excellent biocompatibility and workability for environment and health considerations. Therefore, and despite their cost, Au–Ge alloys have been proposed as possible high-temperature lead-free materials for highly loaded components such as high-power micro-electromechanical systems (MEMS), but also in applications for space technology [18, 19, 20]. Au–Ge eutectic alloys are also used as a catalyst for producing Ge nanowires, for applications in nanotechnology [21].

Au–Ge alloys used as solders have been proposed only recently, and rather limited research has been published. Shimaoka et al. [22] reported that the tensile strengths of Au–Ge solders are more than five times higher at 24°C and 10 times higher at 120°C than that of Pb–Sn solder. The thermo-physical properties of Au–Ge alloy, such as surface tension and wettability, have been investigated to a very limited extent only. The wettability of Au–Ge alloy on SiC substrates has been studied in [23] and the wetting and soldering behavior of Au–28Ge on Cu and Ni substrates has been studied in [24].

Although the initial cost associated with gold-based alloys is high, there is on the other hand a value to the recycled product and no disposal cost associated with the solders, resulting in lower lifetime costs for the product. However, a systematic investigation of Au–Ge based
solders, including their wettability and mechanical properties as well as the microstructure evolution at the interface with different substrates, is still lacking.

Au–Ge-based alloys are very interesting from both a scientific as well as technological point of view. However, they are scarcely used because of the high price of gold.

![Figure 2: Au–Ge equilibrium phase diagram [14].](image)

### 1.2.1.2 Au–Si

The binary system Au–Si also shows an extremely deep eutectic point (363°C, with concentrations of Si and Au of about 19 at.% and 81 at.%), far below the melting temperature of pure Si (1414°C) [14]. The reasons for this unusual deep eutectic point are still not fully understood. It has been speculated to be related to the high stability of the liquid phase, which is supposed to be a result of the presence of a well-defined chemical short-range order as a function of temperature [25, 26]. Phase equilibria in the binary Au–Si system are well established and were summarized by Predel [27], mostly based on an earlier review by Okamoto and Massalski [28]. After slow cooling below the eutectic point, the liquid separates into crystalline Au and Si with a rather limited solid solubility and no stable intermetallic compounds, whereas amorphous Au–Si phases can be achieved by rapid quenching with a variety of techniques, including splat quenching and evaporation [29].

The eutectic Au–Si alloy was the first ever discovered metallic glass-forming alloy [30], but they are not only interesting from a scientific point of view. They have also gained
an increasing importance for a number of practical application purposes. In the recent past, Au–Cu–Si based bulk metallic glasses were developed. In further studies, Au–Cu–Si–Ag–Pd alloys showed good processability, a high corrosion resistance, good mechanical properties and an excellent wear and scratch resistance, making them attractive for jewelry applications [31, 32, 33].

Au–Si alloys have attracted a particular interest in nanotechnology. For example, the catalyzed growth of Si nanowires or nanotubes from gold nanoparticles via vapor–liquid–solid mechanism has been subject of intensive research worldwide [34, 35, 36].

The low melting point of eutectic Au–19Si and the lack of intermetallic crystalline compounds make it also an interesting candidate for joining of highly loaded micro-electromechanical systems (MEMS) or optoelectronic devices by a soldering process. Besides the characteristics mentioned above, Au$_{81}$Si$_{19}$ has very good sealing and reliability making it an optimum candidate for this type of applications [37]. However, despite its interesting properties, only a few results concerning the use of Au–Si for joining relevant substrate materials are reported in the literature. For example, Tiensuu et al. reported on the application of eutectic Au–Si for assembling three-dimensional Si based MEMS devices with bond strengths of up to 65 MPa [38]. In the recent past, eutectic Au–Si (like eutectic Au–Ge alloy) has been mentioned as an interesting candidate for novel high temperature lead-free solder alloys.

![Figure 3: Au–Si equilibrium phase diagram [14].](image)
1.2.2 Substrate materials

1.2.2.1 Titanium

With a melting temperature of 1670°C and a density of 4.5g/cm³ (60% of steel or nickel-base superalloys), titanium has found its place in many industries, due to the combination of high strength-to-weight ratio, excellent corrosion resistance and mechanical properties, over competing materials such as aluminium, steels, and superalloys [39, 40]. Some important characteristics of titanium compared to other structural materials can be seen in Table 1:

Table 1: Titanium characteristics compared to other structural metallic materials (Fe, Ni, Al) [40].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Ti</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Temperature (°C)</td>
<td>1670</td>
<td>1538</td>
<td>1455</td>
<td>660</td>
</tr>
<tr>
<td>Allotropic Transformation (°C)</td>
<td>β</td>
<td>α</td>
<td>γ</td>
<td>-</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>bcc</td>
<td>hex</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>Room Temperature (GPa)</td>
<td>115</td>
<td>215</td>
<td>200</td>
<td>72</td>
</tr>
<tr>
<td>Yield Stress Level (GPa)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.5</td>
<td>7.9</td>
<td>8.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Comparative Corrosion Resistance</td>
<td>Very High</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Reactivity with Oxygen</td>
<td>Very High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Price of Metal</td>
<td>Very High</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Titanium can be alloyed with several elements, like vanadium, aluminium or molybdenum to produce strong lightweight alloys for applications in many fields, from aerospace (spacecraft, jet engines) to military, automotive, chemical and petro-chemical, biomedical devices, and technical instruments. Commercial pure titanium, with a lower mechanical strength but a higher corrosion resistance than its alloys, represents 20% of the titanium alloys applications with plates and sheets for aerospace industry, components for petro-chemical industry and architecture. Furthermore, commercial pure titanium and the alpha-titanium are the most weldable of the titanium family and may be joined by other techniques including brazing. [39, 40].

Although titanium has the highest strength-to-weight ratio among structural materials, its relatively high cost (four times that of stainless steel, but comparable to superalloys) has hindered wider use. This is due to the fact that titanium has a high reactivity with oxygen, requiring the use of vacuum or inert atmosphere during its production process. On the other hand, this high reactivity leads to the immediate formation of a stable oxide layer resulting in an excellent corrosion resistance, often exceeding the resistance of stainless steel in most aggressive environments [39, 40, 41].
The four different grades of CP titanium differ with respect to their oxygen content in order to increase the yield stress. Oxygen can, in fact, be considered as an alloying element when it is used to obtain the desired strength level. This is especially true for the different grades of CP titanium.

In this work, according to the certificate of analysis by the manufacturer, was used titanium with a purity of 99.2 wt.% and a oxygen content of 0.11 wt.%, which makes it grade 2. CP titanium grade 2 have an ultimate tensile strength of about 550MPa, equal to the common low-grade steel alloys, but having the advantage of being 45% lighter. However, certain titanium alloys can achieve tensile strengths of about 1400MPa [41, 42].

1.2.2.2 Nickel

Pure nickel is a ductile material with a melting temperature of 1453°C and a high density of 8.9g/cm³. It’s one of the most important industry metals, because of its ability to alloy with a wide range of metals, like steels, cast irons and nonferrous alloys. In fact, the most important industrial use of nickel is that of an alloying element in ferrous alloys. With properties like an excellent corrosion resistance and high strength even at severe operating conditions, nickel alloys are particularly interesting of aerospace applications where superior elevated temperature properties are needed [41, 43].

Commercial pure nickel is characterized by high density, good electrical and magnetic and magnetostrictive properties compared to nickel alloys. It has also a good thermal conductivity, being useful for heat exchangers in corrosive environments or electronics. However, one drawback of nickel is its high price [41].

Nickel and nickel alloys are used in a variety of applications, mainly involving corrosion resistance and/or heat resistance, such: aerospace aircraft, gas and steam turbines, medical applications, chemical and petro-chemical industries, nuclear power systems, among others. Another relevant application of nickel is its usage in coatings, providing corrosion resistance [41, 43, 44, 45].

In this work commercial pure nickel substrates with a purity of 99.5 wt.% (Nickel 200) were used. With an ultimate tensile strength of 462MPa and a yield strength (0.2% offset) of 148 MPa, it has good mechanical properties and excellent resistance to many corrosives. It’s mainly used for chemical and food processing, electronic parts and aerospace equipment [41, 45].
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates
2. Materials and experimental procedure

This section will describe the applied materials and the experimental procedure adopted for the execution of the joining process and for the microstructural and mechanical characterization of the interfaces. Moreover, the techniques and applied procedure for the production of the Au-Ge-based foils: Au–Ge–Sn and Au–Ge–Sb will be also described.

2.1 Substrates

Three kinds of substrates were used in this work: uncoated substrates, coated substrates and annealed coated substrates.

Ti and Ni substrates were produced by Alfa Aesar GmbH & Co KG (Karlsruhe, Germany) with a purity of 99.2 wt.% (commercial pure titanium grade 2) and 99.5 wt.% (commercial pure nickel). Cutting of these substrates was carried out by RTERO GmbH (Feuerthalen, Switzerland) using electrical discharge machining (EDM), providing substrates with two different dimensions: 20x10x1mm and 4x4x1mm (± 0.05mm).

2.1.1 Uncoated substrates

The non-coated substrates were ground and polished in order to eliminate defects and the oxidation layer from the cutting process. The small substrates were ground by hand down to a 2500 mesh abrasive paper, while the big substrates were ground and polished using a mechanical polishing machine, down to 6µm diamond suspension.

2.1.2 Coated substrates

In this study 20x10x1mm Ti substrates were coated with Ni layers or with Ni and Au layers. This process was done by Collini AG (Dübendorf, Switzerland) using an electrochemical process and the thickness of the layers was around 2 - 4µm of Ni and 1 - 2µm of Au (please see Figure 4 (a) and (b)). These substrates were further cut at EMPA Dübendorf, using mechanical cutting.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

Figure 4: Scheme of the Ti coated samples with a layer of (a) Ni and (b) Ni and Au.

2.1.3 Annealed coated substrates

Annealing of the titanium coated substrates was performed at 500ºC for 60 minutes, in a vacuum furnace, in order to improve the adhesion properties of the coatings. It can be seen in [46] that this process promotes interdiffusion between the coating layers.

Before the soldering experiments, all substrates were cleaned with ultrasounds in ethanol and acetone solution.

2.2 Filler alloys

2.2.1 Au–Ge and Au–Si foils

Au–12Ge and Au–3Si (wt.%) foils were used as filler metals for performing the diffusion soldering experiments. Au–Ge and Au–Si foils were produced with a thickness of 25µm and 35µm respectively. These foils were later cut by a laser process with the dimension of 5x5mm.

The chemical composition analysis was performed by the manufacturer (Materion, Hungerford, UK), resulting in a purity of 99.9860 wt.% for Au–12Ge and 99.9961 wt.% for Au–3Si, as can be seen in Table 2.

Table 2: Chemical composition of the Au–12Ge and Au–3Si solder alloys.

<table>
<thead>
<tr>
<th>Filler alloy</th>
<th>Element</th>
<th>(wt. %)</th>
<th>(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Ge</td>
<td>Si</td>
</tr>
<tr>
<td>Au-12Ge</td>
<td>87.64</td>
<td>11.85</td>
<td>-</td>
</tr>
<tr>
<td>Au-3Si</td>
<td>97.22</td>
<td>-</td>
<td>2.78</td>
</tr>
</tbody>
</table>

2.2.2 Au–Ge–Sn and Au–Ge–Sb foils

Two ternary alloys from Au–Ge–Sn and Au–Ge–Sb systems were produced for being used as filler alloy for preliminary soldering experiments. Small round samples with approximately 1g each were firstly produced by arc melting.

One composition, with low melting point, of each alloy was selected from the ternary phase diagrams. Table 3 shows the compositions in atomic percent of the selected the alloys. One sample of each composition was prepared for arc melting. Highly pure metal bases (99.999%) and a semi-micro balance (accuracy of ± 0.5mg) were used for the weighing of the elements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>Au–Ge–Sn</td>
<td>15.3</td>
</tr>
<tr>
<td>Au–Ge–Sb</td>
<td>17.0</td>
</tr>
</tbody>
</table>

2.2.2.1 Arc furnace

The weighted samples were then melted in an arc furnace, under argon atmosphere. The electric arc is created by two electrodes. The anode is a movable tungsten needle (with a high melting point) and a copper plate, with several cavities, acts as the cathode. Copper is used due to its high thermal conductivity that allows an efficient cooling. Both electrodes are water cooled. The samples are placed into these cavities that provide proper contact between the pieces of metal to be melted. Figure 5 shows a typical arc furnace.

For the melting process, the chamber is evacuated and purged with argon several times. After applying a potential, an arc is initialized by touching the tungsten tip with the copper plate. To avoid traces of oxygen inside the chamber, a titanium getter is melted before the melting of the samples. In order to ensure a homogeneous distribution of all elements, all the samples are melted three times and turned upside down between each melting. After the melting process, it was found that the mass loses were negligible in all samples. Figure 6 shows the arc melted samples with around 6mm diameter.
2.2.2.2 Melt Spinning

Both Au–13.7Ge–15.3Sn and Au–15Ge–17Sb ribbons were produced by melt spinning at LMPT from ETH Zurich.

Due to the extremely high cooling rates that can be achieved by this technique ($10^4$ - $10^7$ K/s), it can be applied to the production of amorphous ribbons, being very often used to the development of metallic glasses.

The sample is melted inside an $\text{Al}_2\text{O}_3$ crucible, heated by a coil. When it reaches a temperature ~ 150°C higher than the melting temperature of the alloy (measured by an infrared thermometer), a flow of gas (helium) forces the thin stream of liquid metal to be dripped onto a spinning copper wheel (cooled by water), causing rapid solidification of the liquid and the formation of a thin ribbon. By varying a series of parameters ribbons with different characteristics can be achieved. The used parameters, same for both alloys, are given in Table 4.

<table>
<thead>
<tr>
<th>Temperature of molten filler</th>
<th>Pressure crucible</th>
<th>Pressure chamber</th>
<th>Blowing Pressure</th>
<th>Rotation speed (frequency)</th>
<th>Orientation of crucible</th>
<th>Mass of sample</th>
<th>Distance nozzle-wheel</th>
<th>Diameter nozzle opening</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
<td>0.5bar</td>
<td>0.6bar</td>
<td>0.8bar</td>
<td>30Hz</td>
<td>0º</td>
<td>1g</td>
<td>2mm</td>
<td>1mm</td>
</tr>
</tbody>
</table>

Both produced ribbons had a flat surface with apparent homogeneity. In the case of Au–Ge–Sn the obtained ribbon was perfectly continuous and unbroken. Au–Ge–Sb shattered into pieces, but it was possible to attain ribbons with length of some dozens of millimeters. The average thickness of the Au–Ge–Sn foil was about 40µm, whilst the Au–Ge–Sb was of 20µm. The width of both foils was of 2mm.
2.3 Diffusion soldering

2.3.1 Assembly

A jig was used for applying pressure to the assembled parts, providing a uniform contact between the mating surfaces and ensuring sufficient wetting. Therefore, the components being joined were held in the required configuration during the heating cycle.

As can be seen in Figure 7 (a), initially the lower (bigger) substrates are placed onto an Al$_2$O$_3$ plate, preventing any reactions between the substrates and the jig (titanium grade 5). Squares with the approximate dimensions of 20x20mm are used to guarantee the correct position of the two lower substrates (2 joints per square). The foils are then placed over the lower substrate and, using steering parts, the upper substrates are positioned exactly on the top of the foils, parallel to the lower substrate. These steering parts are later removed when all assembly is fixed with vertical compressive stress provided by screws. This correct positioning of the upper substrate is extremely important for the shear tests. Between the screw and the upper substrate an Al$_2$O$_3$ plate is placed to prevent reaction between these two metal pieces. The final prepared jig can be seen in Figure 7 (b). The applied pressure was not measured quantitatively. The only taken concern was to ensure that all the assemblies had an approximately equal compressive stress, which ensures the intimate contact between the surfaces. Thus, the number of twists given to the screws was the same.

![Figure 7: (a) Assemblage steps of the components in the jig (upwards) and (b) final prepared jig.](image)
2.3.2 Diffusion soldering experiments

Diffusion soldering experiments were performed in a vacuum furnace (Cambridge Vacuum Engineering, Model 1218H) with a vacuum pressure of 4x10^{-6} mbar. The jigs were placed inside a molybdenum shield and covered with ceramic plates to prevent direct radiation onto the assembly and metal – metal contact. The corresponding temperature – time curve is shown in Figure 8 and, as can be seen, the joining temperature is of 400°C with a holding period of 10 minutes. The heating rate was 10°C/minute. In total, the samples were exposed to a temperature of 360 to 400°C for 50 minutes. Due to the low process temperature and the big size of the chamber, the stage at 350°C was carried out to ensure an homogeneous temperature distribution. The vacuum furnace used for the joining operations as well as a soldered sample can be seen in Figure 9 and Figure 10, respectively.

Figure 8: Applied cycle for the soldering process.

Figure 9: Vacuum furnace with the soldering jig inside.

Figure 10: soldered sample with the respective dimensions.
2.4 Metallography

For further investigation with Scanning Electron Microscopy (SEM) and Electron Probe MicroAnalysis (EPMA), the samples were embedded for grinding and polishing to obtain a visual flat surface necessary for microscopic examinations.

Firstly, the samples were embedded in an epoxy cold resin. Using a grinding/polishing machine, the samples were ground with silicon carbide (SiC) abrasive paper of 240mesh until it was reached the middle section of the joint, please see Figure 11. Then, the samples were ground stepwise down to 2500mesh SiC abrasive paper. The polishing steps were subsequently performed using 6 and 1µm diamond suspension. Alumina suspension of 0.05µm was also used as final step in order to improve the surface quality. Finally, and before coating the samples with carbon film for electron microscopies techniques, the surfaces were observed with an optical microscope for checking for possible scratches.

![Figure 11: Profile substrate / filler metal / substrate.](image)

2.5 Microstructural characterization and analysis methods

All samples were prepared by standard metallographic techniques already described and then characterized by Scanning Electron Microscope (SEM) and Electron Probe MicroAnalysis (EPMA).

2.5.1 Scanning electron microscopy and electron probe microanalysis

SEM and EPMA are used for imaging of microstructures as well as qualitative and quantitative examinations. The SEM is capable of an extremely high magnification, over 500,000 times, and a resolution better than 0.4 nm [47].

In both techniques a focused electron beam is used, produced from an electron gun, with much reduced diameter and angular aperture, providing a resolving power and a depth-of-filed very superior to those afforded by optical microscopy. Electron guns generate electrons and there are several different used on commercial SEMs. In this work, tungsten and field emission electron guns were used for EMPA and SEM techniques respectively.
Electrons are accelerated by a voltage, (between 0.1kV and 30 kV) and, passing through focusing coils, a fine beam is produced that impinges the surface of the sample, scanning it in a rectangular pattern, line by line [48, 47, 49]. The collisions of the incident electrons with the sample atoms lead to the emission of a variety of signals, being those represented in Figure 12.

![Figure 12: Scheme of resulting radiation of the electron beam/sample interaction](image)

The beam penetrates into the sample to a depth that depends on the accelerating voltage and atomic weight of the specimen atoms. Each type of emitted signal is associated with a certain interaction volume beneath the surface as can be seen in Figure 13.

![Figure 13: Interaction volume of the different emitted signals](image)

Secondary electrons (SE) and back-scattered electrons (BSE) are used for imaging. The secondary electrons, which are ionization products of the sample atoms, have a low energy (less than 50eV) and so they cannot escape from very deep in the sample (typically a depth range of 2 to 10nm for metals) [47, 49]. This way, their given information is surface specific, providing images with strong topographical contrast and, thus, evidencing defects such as cracks and voids that can be present at the joint [48].

The backscattered electrons, on the other hand, result from elastic or low energy loss collisions with the sample, having, this way, a significantly high energy, close to the incident
beam energy. Due to their superior energy, these electrons can emerge from higher depths while compared with secondary electrons. The images obtained with this radiation include two types of information: chemical and topographical. The chemical contrast is given by the different atomic number of the present phases, distinguishing bright areas (with higher atomic number) from dark areas (lower atomic number). The topographical information stems from the relief of the specimens surface [47, 49].

Another type of signal used in this work for the joining interface characterization was the X-rays signal. The X-rays, derived from the entire interaction volume, provide quantitative measurements of elemental compositions. X-ray microanalysis cannot only collect the elemental information, but it can also identify, through linescans or area mapping, the distribution of the specimen’s elements. Depending on the element, several different characteristic X-rays can be emitted [48, 47, 49].

The SEM usage becomes more efficient when applied along with energy dispersive X-ray spectroscopy (EDS), complementing the microstructural imaging with chemical information. The EDS uses the energy of the characteristic X-rays lines, which is specific of the atomic number of the present elements, for its identification. X-ray spectrums can be obtained for the most elements of the periodic table, from beryllium onwards. Since EDS measures the whole spectrum simultaneously it’s a very fast method. The X-rays intensity emitted by the elements of the sample is approximately proportional to the weight fraction of each emitting element. However, it does not reflect the concentration ratio with enough precision so that some manual adjustments are necessary [47, 49].

The EPMA, equipped with wavelength dispersive spectroscopy (WDS) detector, was employed to the determination of characteristic X-rays. This technique uses the diffraction of the characteristic X-rays, in different orientated crystals, for the discrimination of the X-rays spectrum emitted by the sample. An accurate mechanical system positions the crystal so that, by the conditions of Braggs approach, the emerged X-rays from the sample can be selected and reach a detector that registers their intensity [49]. Since the detector and the crystal move while measuring, this method is slower than EDS, but with a much higher resolution, making it promising when there is for example overlapping peaks at EDS and for more precise qualitative and quantitative analysis.

Microstructural characterization of all interfaces was performed using a scanning electron microscope (Philips XL 30 ESEM-FEG) operating with energy dispersive spectroscopy (EDS). The images were in the secondary electron (SE) and backscattered
electron (BSE) mode using an acceleration voltage of 20kV and an aperture of 50μm. EDS measurements of the existing phases were made with a lens aperture of 100μm.

Quantitative analysis of the phase compositions present at the interface were performed by an EPMA (JEOL JXA8800), with an accelerating voltage of 20 kV and a probe current of 5.0 x 10^{-8} A.

Pure element standards provided by JEOL were used for the calibration before the measurements. The effectuated measurements have a relative accuracy of about ± 1%. Spatial resolution of the EPMA measurements was around 1 μm, therefore line scans were performed at the interface with a step size of 1 μm, with at least 30 individual points in each line.

2.7.2 Differential scanning calorimetry / differential thermal analysis (DSC/DTA)

Differential thermal analysis is one type of thermoanalytical technique that can measure, in a controlled atmosphere, the temperatures and heat flows associated with transitions in materials as a function of time and temperature. These measurements offer qualitative and quantitative information about chemical and physical changes involving heat exchanges (either endothermic or exothermic processes), or changes in heat capacity [48, 51, 52].

This thermal analysis involves heating up the sample and a reference at a fixed rate until a certain temperature. This happens in a tubular furnace, where both specimen and reference are inside crucibles (Al₂O₃) that don’t react in any way with the materials until, at least, to the maximum program temperature. This temperature should be slightly higher than the melting temperature of the probed material, ensuring full melting. The process is conducted under inert gas (Ar) and a differential thermocouple measures the difference between the temperature of the sample and the reference. If a phase transformation happens, heat is either dissipated or absorbed, and the temperature of the sample will differ from that of the reference, allowing the phase change to be detected. Instead of using a reference material, the empty Al₂O₃ crucible acted as a reference in the performed experiments.

DSC is very appropriate in the determination of phase transitions and eutectic temperatures, as well as other features that are useful for the determination of the equilibrium phase diagrams, but for this work, the real interest in the use of DSC was to be sure that the melting temperatures of the used filler alloys were consistent with the accessed equilibrium phase diagrams. This gave useful information for the determination of the soldering temperature.
The experiments were performed in a Netzsch DSX 404 F3 Pegasus. DSC cells were calibrated using melting temperatures of the pure elements Sn, Zn, Al, Ag and Au. Al₂O₃ crucibles were used to hold the foils. Before each experiment, the DSC cell was evacuated three times and re-filled with high-purity argon. Measurements were performed at a scan rate of 10°C/min for heating and cooling under a continuous argon flow.

2.8 Mechanical characterization of the interfaces

2.8.1 Shear tests

The mechanical strength of the joints was evaluated by shear tests at EMPA Thun. This technique was chosen because it shows high reproducibility and informative results, in addition to quick sample preparation and realization.

The shear strength of a planar joint is a measure of its ability to sustain a parallel applied stress without breaking. The shear strength (τ) could be calculated by the simple relation, where F is the force and A is the area (16mm²):

\[ \tau = \frac{F}{A} \]

Equation 2: Shear Strength.

The maximum force equivalent to the shear stress could be taken out of the force-displacement curve. The shear tests were executed on a walter+bai ag system coupled with the electronic measuring unit Digimess 1000. A customized sample holder, which allows an accurate fixation and alignment of the sample, was employed. Figure 14 shows the test system, as well as the sample holder with a mounted sample.

Figure 14: Shear test equipment and sample holder.
The sample and the sample holder were adjusted in order that the shear blade passed tightly above the bigger substrate hitting the 4x4mm substrate. As a consequence, it is important that both substrates are exactly parallel to each other, avoiding tension peaks on one side of the substrate that would falsify the results. To guarantee the precision of the results eight tests were performed for each material combination, under ambient temperature.

Figure 15 shows an enlargement of the shear blade and the incorporated sample holder. The force direction of the force and the blades speed (0.1 mm/s) are also represented in the same figure.

![Shear blade and corresponding direction and speed](image)

**Figure 15: Shear blade and corresponding direction and speed.**

### 2.8.2 Microhardness Measurements

Vickers microhardness measurements of the different phases were performed with a Fischerscope HM2000 equipment, using a HV pyramid shape indenter. An optimum load value of 10 mN was chosen and it was applied to all the samples for 20 seconds.
3. Presentation of the results and discussion

3.1 Results

In this section microstructural characterization and thermal analysis of the fillers will be presented. Secondly, the microstructural and mechanical characterization of the interfaces will be shown.

Soldering with Ti and Ni uncoated substrates was executed with both Au–Ge and Au–Si foils, while for soldering coated Ti substrates (annealed and not annealed) was only used Au-Ge filler alloy. Ti coated substrates were always used as lower substrates in this work and Ti(Ni/Au) or Ti(Ni) designations will be used regarding their coating layers sequence.

Similar substrates (Ni/Ni, Ti/Ti) were also joined using the produced Au–Ge–Sn and Au–Ge–Sb foils. Their characterization, by SEM and EDS analysis, will be showed at the end of this section. No mechanical tests were performed in these cases due to the reduced width of the foils (2µm).

3.1.1 Microstructural characterization

3.1.1.1 Filler alloys

3.1.1.1.1 Eutectic Au–Ge and Au–Si

The microstructures of the Au–Ge and Au–Si eutectic compositions are presented in Figure 16 (a) and (b). Both alloys showed microstructures consisting of a gold matrix with (Ge) or (Si) grains within. However, (Si) grains in Au–Si alloy are much thinner and homogeneously dispersed compared to (Ge) grains in Au-Ge alloy. The thicknesses of Au–Ge foil is about 25µm, while Au–Si is 35µm. Figure 17 illustrates the DSC curves of Au–Ge and Au–Si foils. During the heating stage, endothermic peaks at 361°C for Au–Ge and 363°C for Au–Si were observed. These reactions are associated to the eutectic temperatures of these alloys and they agree well with the corresponding temperature of their phase diagrams (Figure 2 and Figure 3).
3.1.1.1.2 Au-Ge-Sn and Au-Ge-Sb

Figure 18 (a) and (b) present the microstructure of the produced Au–Ge–Sn and Au–Ge–Sb foils. As can be seen, the foil thickness is about 40µm and 20µm for Au–Ge–Sn and for Au–Ge–Sb respectively. XRD analysis confirmed that both foils were crystalline. However, probably due to the small grain size was very difficult to distinguish different phases at SEM, especially for the Au–Ge–Sb foil. In the Au–Ge–Sn foil (Figure 18 (a)), small round areas with a slightly brighter contrast were observed. However, it was not possible to distinguish different chemical compositions by EDS. The measured compositions were 73at.% Au, 14at.% Ge, 13at.% Sn for Au–Ge–Sn and 71at.% Au, 16at.% Ge, 13at.% Sb for Au–Ge–Sb.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

Thermal analyses were performed with Au–13.7Ge–15.3Sn and Au–15Ge–17Sb as-cast samples and are presented in Figure 19. Compared to Au–28Ge (T$_m$=361 ºC), these two alloys exhibit even lower melting temperatures. The Au–Ge–Sn and Au–Ge–Sb solidus/liquidus temperature are 265ºC/347ºC and 315ºC/335ºC, respectively (please see Table 5). The solidus and liquidus temperatures obtained in this work, calculated by CALPHAD (CALculation of PHAse Diagram) method and from literature are compiled in Table 5, having been observed a slight difference between them. Besides the solidus and liquidus effects, one more endothermic effect at 177ºC was observed for the Au–Ge–Sn alloy. According to CALPHAD calculation of the vertical section at 15.3 at.%Sn, this effect is probably related to the solid-state transformation (Ge)+AuSn+Au5Sn → (Ge)+AuSn+Hcp.

As can be seen in the vertical section presented in Figure 20, the calculated transformation temperature is around 180 ºC, which agrees well with the DSC results.

![Image](https://via.placeholder.com/150)

**Figure 18:** (a) Au-Ge-Sn and (b) Au-Ge-Sb filler alloys microstructures.

![Image](https://via.placeholder.com/150)

**Figure 19:** DSC heating curves of Au–15Ge–17Sb and Au–13.7Ge–15.3Sn.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

Table 5: Solidus (s) and liquidus (l) temperatures of Au–15Ge–17Sb and Au–13.7Ge–15.3Sn obtained by DSC experiments, calculated by CALPHAD and from the literature [53].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>DSC (this work)</th>
<th>CALPHAD [53]</th>
<th>Literature [53]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au–13.7Ge–15.3Sn</td>
<td>265 (^{s}), 347 (^{l})</td>
<td>267 (^{s}), 335 (^{l})</td>
<td>335 (^{l})</td>
</tr>
<tr>
<td>Au–15Ge–17Sb</td>
<td>315 (^{s}), 335 (^{l})</td>
<td>287 (^{s}), 367 (^{l})</td>
<td>288 (^{l})</td>
</tr>
</tbody>
</table>

Figure 20: CALPHAD assessment of the vertical section at 15.3% of Sn.

3.1.1.2 Uncoated substrates using Au-Ge filler alloy

3.1.1.2.1 Ni/Au-Ge/Ni

Similar Ni/Ni joint is homogeneous in all its length, as can be seen in Figure 21. The average thickness of the interface is about 11µm ± 3µm. Neither holes nor cracks were observed and a good connection between both substrates was obtained. The EDS measurements confirmed the existence of a gold solid solution (Au)\(^{*}\) at the middle of the interface, with 4 to 8µm of width. Next to the nickel substrates and at both sides of the interface, two thin layers of intermetallic compounds (IMCs) were also formed: a Ni\(_3\)Ge\(_3\) layer of 2µm and a NiGe layer of 1µm between (Au) and Ni\(_3\)Ge\(_3\) layers.

\(^{*}\) Hereafter, all the chemical compositions of the identified phases, measured by EDS and WDS, can be assessed in Appendix A.
3.1.1.2 Ti/Au-Ge/Ti

The obtained interface when similar Ti substrates were used is showed in Figure 22. The interface shows a TiAu₄ layer with blocks of (Ge) dispersed along the centerline. The joint is not homogeneous in all its extension. Several holes, lacks of material and regions where no connection occurred were observed (please see Figure 22 (b)).

3.1.1.2 Ti/Au-Ge/Ni

The solder area shows some holes and is not homogeneous in all its extension due to the different shapes of the (Ge). As can be seen in Figure 23 (a) (Ge) looks like a “layer” of 3.5µm thick, while on other places of the joint it appears as big size grains, with some
precipitations of (Au) (please see Figure 23 (b)). The center of the joint is mainly constituted by a gold solid solution. At the upper interface, a Ni$_3$Ge$_2$ layer with a thickness of around 1.8µm was formed. At the lower part of the interface, a mixture of 48 at.% Au, 23 at.% Ti, 16 at.% Ge and 13 at.% Ni, represented in Figure 23 (a) as P1, was detected. Another phase with a darker contrast (marked as P2 in Figure 23 (a)) with composition 32 at.% Ge, 30 at.% Ti, 26 at.% Ni and 12 at.% Au was observed as well. Both chemical compositions are showed in Table 6.

![Figure 23: Microstructure of the Ti/Au-Ge/Ni interface showing the different shapes of (Ge).](image)

<table>
<thead>
<tr>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Au</td>
</tr>
<tr>
<td>Ge</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>P1</td>
</tr>
<tr>
<td>P2</td>
</tr>
</tbody>
</table>

Table 6: Chemical composition of the marked points in Figure 23 (a).

3.1.1.3 Uncoated substrates using Au-Si filler alloy

3.1.1.3.1 Ni/Au-Si/Ni

The interface obtained between similar Ni substrates and Au–Si filler alloy is showed in Figure 24 (a) and (b). The interface thickness is around 5µm in all its extension, consisting of a very thin (0.5µm) Ni$_3$Si layer formed close to both Ni substrates and a central gold-rich layer of 4.5µm. NiSi phase is also present and dispersed through all the interface. The microstructure is homogeneous from side to side, showing no defects. An accumulation of the filler alloy at the edges of the joint was also observed, as shown in Figure 24 (b).
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

3.1.1.3.2 Ti/Au-Si/Ti

A wide interface of 40 ± 5µm without defects and with good connection between Ti substrates and Au-Si filler alloy was observed and is shown in Figure 25 (a). It is mainly constituted by a solid solution of gold with lamellar structured “islands” of TiSi2. It is also visible some relief along the joint, probably originated by the final polishing step with alumina suspension. Adjacent layers of 54 at.% Au, 30 at.% Ti, 16 at.% Si (2 - 5µm thick) and 64 at.% Au, 21 at.% Ti, 15 at.% Si (2µm thick) ternary mixtures were detected along the interface with the substrates and their atomic composition can be seen in Figure 25 (b).

<table>
<thead>
<tr>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>P1</td>
</tr>
<tr>
<td>P2</td>
</tr>
</tbody>
</table>

Figure 25: (a) SE image from Ti/Au-Si/Ti joint microstructure and (b) chemical composition of the layers represented as P1 and P2 in (a).
3.1.1.3 Ti/Au-Si/Ni

As can be seen in Figure 26, dissimilar joints between Ti and Ni substrates showed good connection with both substrates without cracks or holes. A gold solid solution is the main constituent of the joint microstructure. TiSi₂ phase, with a lamellar shape, and (Si) grains, represented with the darkest contrast in the corresponding Figure 26 (a), were observed at the interface. A 3µm thickness layer with the composition of 63 at.% Au, 22 at.% Ti and 15 at.% Si was observed at the Ti interface. At the Ni interface a layer with the composition of 57 at.% Au 20 at.% Si, 13 at.% Ti and 10 at.% Ni was measured and can be seen in Figure 26.

![BSE image from Ti/Au-Si/Ni joint microstructure and respective chemical compositions of point P1 and P2.](image)

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>P1</th>
<th>P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>63</td>
<td>57</td>
</tr>
<tr>
<td>Si</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>13</td>
</tr>
<tr>
<td>Ni</td>
<td>n.d.</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 26: (a) BSE image from Ti/Au-Si/Ni joint microstructure and (b) respective chemical compositions of point P1 and P2.

3.1.1.4 Coated titanium substrates using Au-Ge foil

3.1.1.4.1 Ti(Ni/Au)/Ti

In Ti(Ni/Au)-Ti joints, the formed soldering zone is heterogeneous. Some areas mainly consist of TiAu₄, while at other areas big shattered Ge-rich grains are visible, as can be seen in Figure 27 (b). Part of nickel remain along the lower titanium substrate with variable width from 0.5 to 3µm, but apparently the gold layer of the coating totally diffused to the center helping to form TiAu₄. The Ni₅Ge₃ phase is also visible along the lower part of the interface and above the Ni layer, with a constant thickness of 3µm. At the upper part of the joint Ti₆Ge₅ and Ti₅Ge₃ phases with 1.5µm of width were formed as well as a layer of
unknown dark precipitates. Its identification revealed to be impossible since they have an extremely small size.

![Figure 27 (a) and (b): BSE image from Ti(Ni/Au)/Au-Ge/Ti joint microstructure, showing different zones of the interface.](image)

3.1.1.4.2 Ti(Ni/Au)/Ti annealed

After annealing of the Ni-Au coated Ti substrate, the formed interface grew from $24 \pm 5\mu m$ to $68 \pm 8\mu m$ of thickness. The appearance of holes close to the lower substrate and adjacent to (Ge) grains was also observed. On the other hand, a successful connection with the upper uncoated Ti substrate was observed. The (Ge) grains have now a bigger dimension and are no longer shattered. Between these grains and the titanium lower substrate $Ni_3Ge_2$ was formed as a connection layer. $TiAu_4$ as well as the dark precipitates (mentioned in the chapter 3.1.1.4.1) are part of the microstructure. The formation of a quaternary mixture of all involved elements was detected: 33 at.% Ge / 31 at.% Ti / 30 at.% Ni / 6 at.% Au and 39 at.% Ge / 29 at.% Ti / 27 at.% Ni / 5 at.% Au, represented in Figure 28 (a) and (b) as points P1 and P2, respectively.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

3.1.1.4.3 Ti(Ni/Au)/Ni

A thin joint with an average joint thickness (without crack) of 9 ± 3µm was observed. Figure 29 (a) shows a crack, along half of the joint, with around 1µm of width, between (Ni) coating layer (1µm) and Ni₅Ge₃ (1µm). Along the upper substrate a slightly thicker (1.5 µm) Ni₅Ge₃ layer was formed. Some porosity can be observed in this layer and between Ni₅Ge₃ and (Ni) coating layer on the lower substrate (please see Figure 29 (b)). The centerline of the soldering zone consists of a solid solution of gold with 4 to 6µm of width.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th></th>
<th></th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
<td>Au</td>
<td>Ge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>6</td>
<td>33</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>P2</td>
<td>5</td>
<td>39</td>
<td>29</td>
<td>27</td>
</tr>
</tbody>
</table>

Figure 28: (a) BSE image from Ti(Ni/Au)/Au-Ge/Ti (annealed Ti coated substrate) joint microstructure and (b) chemical compositions of points P1 and P2.

Figure 29: (a) BSE image from Ti(Ni/Au)/Au-Ge/Ni joint microstructure showing a crack and (b) without crack, although is visible some porosity.
3.1.1.4.4 Ti(Ni/Au)/Ni annealed

After annealing, the crack along the joint is no longer formed. In addition to the known phases (presented in the chapter 3.1.1.4.3) the formation of the Ni$_3$Ge$_2$ phase was detected. The joint thickness slightly increased to 11 ± 3µm; (Ni) raised its thickness from around 1µm (before annealing of the Ti substrate) to 2µm and the middle gold solid solution increased from nearly 5 to 6µm. On the other hand, the upper Ni$_3$Ge$_3$ layer got 0.5 µm thinner. The entire interface is homogeneous, showing a good connection with both substrates, without defects.

![Figure 30: BSE image from Ti(Ni/Au)/Au-Ge/Ni (annealed Ti coated substrate) joint microstructure.](image)

3.1.1.4.5 Ti(Ni)/Ti

The produced joint shows an average thickness of approximately 24µm with large and round voids within the TiAu$_4$ layer. Some islands of TiAu are also visible along the centerline of the joint. A layer with a thickness of 2.5 - 7µm of NiGe was detected between TiAu$_4$ and the titanium lower substrate. As can be seen in Figure 31 (a), a 1.5 to 3µm thick upper reaction layer was formed, consisting of a mixture of 34 at.% Ti, 31 at.% Ge, 26 at.% Ni and 9 at.% Au. The bright dots in the same area, close to the substrate, were noticed to have a higher at.% of Au, being a mixture of 39 at.% Ti, 33 at.% Au, 16 at.% Ge and 12 at.% of Ni. Due to their small size and the influence with the surrounding elements it was difficult to measure their exact compositions via EDS.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

3.1.1.4 Ti(Ni)/Ti annealed

After annealing a high growth of the joint region, from 24 to 65µm, was observed as well as the formation of big (Ge) grains. The same behavior was already observed in Ti(Ni/Au)/Ti. It is also well visible in Figure 32, with the darkest contrast, voids with the shape of a crack resulting, this way, in only some points of contact with the Ni$_5$Ge$_3$ reaction layer. Below that, apparently, the nickel coating layer remains unconsumed for the formation of other phases, except for Ni$_5$Ge$_3$. Both (Ni) and Ni$_5$Ge$_3$ have thicknesses of around 2µm. The dark precipitates on the upper part of the joint appeared again as was already observed for the combination Ti(Ni/Au)/Ti.

![Image](image.png)

Figure 32: BSE image from Ti(Ni)/Au-Ge/Ti (annealed Ti coated substrate) joint microstructure.
3.1.1.4.7 Ti(Ni)/Ni

The joint between Ti(Ni) and Ni substrates is homogeneous along its complete length. A crack between pure nickel, remaining form the coating layer, and Ni$_5$Ge$_3$, as well some porosity along the upper Ni$_5$Ge$_3$ reaction layer was observed. The middle of the interface consists of a gold solid solution with variable width from 4 to 9µm. With around 12µm, the average joint thickness is relatively low.

![Figure 33: BSE image from Ti(Ni)/Au-Ge/Ni joint microstructure.](image)

3.1.1.4.8 Ti(Ni)/Ni annealed

It can be seen in Figure 34 that the execution of the joining process with the annealed titanium substrate led to the non-formation of the crack between the nickel coating and Ni$_5$Ge$_3$ layer. The reaction layers continue to be of the same products, but with lower thicknesses compared with the one before: 5 - 7µm, 1.5µm and 1µm for (Au), (Ni) and Ni$_5$Ge$_3$, respectively. The entire joint is homogeneous with a reduced thickness of 10µm.

![Figure 34: BSE image from Ti(Ni)/Au-Ge/Ni (annealed Ti coated substrate) joint microstructure.](image)
3.1.1.5 Similar uncoated substrates using Au-Ge-Sn filler alloy

3.1.1.5.1 Ni/Au-Ge-Sn/Ni

A homogeneous joint of 22µm thickness was produced. A significant amount of porosity along the interface and the substrates was observed (please see Figure 35 (a)). A central layer of around 88% of gold and 12% of tin (please see P1 in Figure 35 (b)) with adjacent layers of Ni₃Ge₃ and NiGe was measured. A thin bright line of a mixture Au, Sn and Ni, outlining the joint, can be seen in the same figure and its composition is represented by P2 in Figure 35 (b). The detected high amount of Ni is possibly due to the beams interaction with the substrate since this is a very thin layer to be measured.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Point</th>
<th>Au</th>
<th>Ge</th>
<th>Sn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>88</td>
<td>n.d.</td>
<td>12</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>21</td>
<td>n.d.</td>
<td>8</td>
<td>71</td>
<td></td>
</tr>
</tbody>
</table>

Figure 35: (a) BSE image from Ni/Au-Ge-Sn/Ni joint microstructure and (b) respective chemical compositions of point P1 and P2.

3.1.1.5.2 Ti/Au-Ge-Sn/Ti

Figure 36 (a) shows the microstructure of the Ti/Au-Ge-Sn/Ti joint. A central layer of TiAu₄ was observed, with some islands of a ternary composition represented by point P3. Titanium also reacted with gold to form another Ti-Au IMC: TiAu₂. TiAu₂ was formed in some areas of the side layers, represented by points P1 and P2. These layers are around 2.5µm thick and their atomic composition can be seen in Figure 36 (b). As can be verified both have a very similar quaternary composition. Furthermore, the existence of another ternary composition, with the darkest contrast in Figure 36, is represented by point P4. A thick joint with 21µm of thickness without defects was produced.
3.1.1.6 Similar uncoated substrates using Au-Ge-Sb filler alloy

3.1.1.6.1 Ni/Au-Ge-Sb/Ni

A middle layer of (Au) is the main constituent of this interface. Grains of NiGe and NiSb were also detected along the interface with both substrates. Other grains, which sometimes cross the whole width of the joint, can be seen in Figure 37 (a) with a light grey contrast and their composition is represented by point P1 in Figure 37 (b), with 60% of Sb, 30% of Au and 10% of Ni. The interface had no defects and a thickness of 36 ± 3µm.
3.1.1.6.2 Ti/Au-Ge-Sb/Ti

A very thin 8µm joint without any defects was produced. TiAu$_4$ “islands” with different sizes and geometries were formed in the middle of the interface and can be seen in Figure 38 (a) with the lightest contrast. A mixture of around 50% of Au and Sb that surrounds the TiAu$_4$ phase was detected (please see P1 in Figure 38 (b)). (Ge) was also identified in the center of the interface and can also be seen in the same figure with the darkest contrast. Two layers with close compositions delimit the joint with both substrates. These are represented by P2 and P3 in Figure 38 (a) and as can be seen in Figure 38 (b), P2 has a ternary composition of 40 at.% Ge and 30 at.% of Sb and Ti, while in P3 the at.% of Sb decreases 5% for the appearance of 5at.% of Au.

<table>
<thead>
<tr>
<th>Point</th>
<th>Au</th>
<th>Ge</th>
<th>Sb</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>55</td>
<td>n.d.</td>
<td>45</td>
<td>n.d.</td>
</tr>
<tr>
<td>P2</td>
<td>n.d.</td>
<td>40</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>P3</td>
<td>5</td>
<td>40</td>
<td>25</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 38: (a) BSE image from Ti/Au-Ge-Sb/Ti joint microstructure and (b) chemical composition of point P1, P2 and P3.
3.1.2 Mechanical characterization

3.1.2.1 Shear test results

Shear test results performed for 8 samples per each combination are compiled at Table 7 to Table 10 and graphically represented at Figure 39 to Figure 42.

Table 7: Average shear strength, minimum, maximum and standard deviation of Ti/Ti, Ni/Ni and Ti/Ni joints using Au-Ge as foil.

<table>
<thead>
<tr>
<th></th>
<th>Ti/Ti</th>
<th>Ni/Ni</th>
<th>Ti/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>12.9</td>
<td>201.7</td>
<td>37.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>3.9</td>
<td>139.4</td>
<td>22.9</td>
</tr>
<tr>
<td>Maximum</td>
<td>27.6</td>
<td>238.2</td>
<td>48.3</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>7.3</td>
<td>34.7</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Figure 39: Comparison graphic of the obtained shear strengths between Ti/Ti, Ni/Ni and Ti/Ni joints, using Au-Ge as foil.

With average shear strength of 201.7MPa, the similar Ni-Ni joints substrates joint, using Au-Ge solder, was the one with distinctly best results among all tested combinations. Even its minimum result is higher than any other mean shear strength. Although it had the best value, it’s visible in Table 7 that the standard deviation is much wider than that of Ti/Ti and Ti/Ni combinations.

Figure 39 shows that dissimilar uncoated Ti and Ni substrates had, between this three tested combinations, the second best result with 37.8MPa, but still far away from Ni/Ni. At last, Ti similar substrates had the lowest result with an average of 12.9MPa.
Table 8: Average shear strength, minimum, maximum and standard deviation of Ti/Ti, Ni/Ni and Ti/Ni joints using Au-Si as foil.

<table>
<thead>
<tr>
<th></th>
<th>Ti/Ti</th>
<th>Ni/Ni</th>
<th>Ti/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>67.1</td>
<td>92.0</td>
<td>121.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>7.0</td>
<td>52.4</td>
<td>60.8</td>
</tr>
<tr>
<td>Maximum</td>
<td>118.3</td>
<td>151.4</td>
<td>176.1</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>41.1</td>
<td>40.6</td>
<td>43.0</td>
</tr>
</tbody>
</table>

Figure 40: Comparison graphic of the obtained shear strengths between Ti/Ti, Ni/Ni and Ti/Ni joints, using Au-Si as foil.

Figure 40 shows that the best mean shear strength among uncoated substrates, when Au-Si was used as filler alloy, was obtained by the dissimilar combination of Ti and Ni with 121.8MPa, followed by the similar combinations Ni/Ni (92.0MPa) and Ti/Ti (67.1MPa). However, the minimum value of Ti/Ni is below the other two averages. The Ti/Ti minimum is around 7.0MPa, which is very close to zero. It is also important to refer that all these three combinations had a large scattering (please see standard deviation at Table 8).

It should be noticed that using both Au-Ge and Au-Si as interlayers, the combination Ti/Ti always got the lowest values. However, 67.1MPa is more than five times higher than 12.9MPa, value achieved by Ti/Au-Ge/Ti. The combination Ti/Ni worked better with Au-Si, reaching better values in this case. The opposite happened with Ni/Ni getting better results using the Au-Ge filler alloy.
Table 9: Average shear strength, minimum, maximum and standard deviation of the joints using coated Ti (Ni and Ni/Au) as lower substrate and using Au-Ge as foil.

<table>
<thead>
<tr>
<th>(MPa)</th>
<th>Ti(Ni/Au)/Ti</th>
<th>Ti(Ni/Au)/Ni</th>
<th>Ti(Ni)/Ti</th>
<th>Ti(Ni)/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td>10.4</td>
<td>15.1</td>
<td>24.2</td>
<td>37.4</td>
</tr>
<tr>
<td><strong>Minimum</strong></td>
<td>0.3</td>
<td>1.2</td>
<td>9.5</td>
<td>16.9</td>
</tr>
<tr>
<td><strong>Maximum</strong></td>
<td>35.9</td>
<td>42.4</td>
<td>39.7</td>
<td>63.1</td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td>11.3</td>
<td>13.9</td>
<td>9.1</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Figure 41: Comparison graphic of the obtained shear strengths of the joints that use coated Ti (Ni and Ni/Au) as lower substrate (using Au-Ge as foil).

The two highest averages in this group of coated Ti substrates, using Au-Ge filler alloy, were achieved by the combinations that used nickel as coating: Ti(Ni)/Ni and Ti(Ni)/Ti, with 37.4MPa and 24.2MPa, respectively. Ti(Ni)/Ni had the best maximum result of 63.1MPa.

The 37.4MPa obtained by Ti(Ni)/Ni is a value very close to the average got by Ti/Au-Ge/Ni uncoated substrates (37.8MPa), as can be compared in Table 8. However, the standard deviation, using the Ti coated substrate, was higher in this case (15MPa comparing to 8.4Mpa).

The second lower average was 15.1MPa of Ti(Ni/Au)/Ni and the worst one was obtained by Ti(Ni/Au)/Ti, with 10.4MPa. As can be noticed in Table 9 and Figure 41, the minimum values of Ti(Ni/Au)/Ti and Ti(Ni/Au)/Ni were close to 0MPa. In the case of Ti(Ni/Au)/Ti, the maximum value (of 35.9MPa) was more than three times higher than its average. In the case of Ti(Ni/Au)/Ni, the maximum result was 42.4MPa, more than double of the average.
Table 10: Average shear strength, minimum, maximum and standard deviation of the joints with coated and annealed Ti (Ni and Ni/Au), as lower substrate (using Au-Ge as foil).

<table>
<thead>
<tr>
<th></th>
<th>Ti(Ni/Au)/Ti</th>
<th>Ti(Ni/Au)/Ni</th>
<th>Ti(Ni)/Ti</th>
<th>Ti(Ni)/Ni</th>
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<tbody>
<tr>
<td>Average</td>
<td>22.5</td>
<td>64.6</td>
<td>11.6</td>
<td>121.2</td>
</tr>
<tr>
<td>Minimum</td>
<td>5.8</td>
<td>23.9</td>
<td>3.3</td>
<td>72.9</td>
</tr>
<tr>
<td>Maximum</td>
<td>49.0</td>
<td>124.2</td>
<td>20.5</td>
<td>164.9</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>18.4</td>
<td>31.9</td>
<td>6.5</td>
<td>30.2</td>
</tr>
</tbody>
</table>

Figure 42: Comparison graphic of the obtained shear strengths of the joints that use coated and annealed Ti (Ni and Ni/Au) as lower substrate (using Au-Ge as foil).

After annealing of the coated Ti substrates the shear strengths increased in all material combinations, except for Ti(Ni)/Ti (please see Table 10 and Figure 42). All four combinations reduced their standard deviation, which means that the annealing also helped to reduce the scattering of the shear test results.

Ti(Ni)/Ni continued to have the best average, now with 121.2MPa (more than three times than before) and with a best maximum strength of 164.9MPa. The average in Ti(Ni)/Ti joints decreased to 11.6MPa which is half of the value of the joints with not annealed substrates.

Ti(Ni/Au)/Ni increased its mean shear strength from 15.1MPa to 64.6MPa - more than four times, and with a maximum value higher than the Ti(Ni)/Ni average. Ti(Ni)/Ti also improved to 22.5MPa (twice as high without annealing of the coated Ti substrate).
3.2 Discussion

In this chapter, the mechanical behavior of the produced joints will be explained based on the analysis of the microstructures. Microhardness measurements of the phases were also performed, but due to the small thickness of some layers the results could be influenced by the adjacent layers. Therefore, these hardness values should only be taken into account as a qualitative comparison. In some cases, SEM pictures of the samples after the shear tests will also be used in order to try to understand better where the failure occurred.

The discussion will be separated in the same way as the presentation of the results: uncoated substrates (using Au-Ge and Au-Si filler alloys) followed by coated Ti and coated and annealed Ti substrate combinations (using Au-Ge filler alloy). No discussion of the joints using Au-Ge-Sn and Au-Ge-Sb foils will be done, since no mechanical tests were performed in these cases.

3.2.1 Uncoated substrates using Au-Ge filler alloy

3.2.1.1 Ni/Au-Ge/Ni

Due to the homogeneity of the produced joint, showing a perfect connection with both substrates without any visible defects, Ni/Au-Ge/Ni got the best mechanical performance, with mean shear strength of 201.7MPa. Though, the physical integrity of the joint itself does not entirely explain these results.

Germanium in the Au-Ge filler alloy is prone to react with Ni to form Ni-Ge intermetallic compounds (IMCs) close to the substrates/soldering zone interface. Because of the high affinity of Ge to Ni, Ge diffuses from the filler alloy to Ni substrates, and vice-versa, forming IMCs like NiGe or Ni₅Ge₃. The measured Vickers hardness of these compounds was 1028HV and 759HV, respectively. These values are much higher when compared to the one of pure Ni substrate (383HV). Hereupon, it can be assumed that the presence of Ni-Ge IMCs, could be critical for the joint performance. On the other hand, the fact that all the Ge migrated from the middle of the interface, leaving a layer of a gold solid solution, helped to balance the presence of these hard Ni-Ge phases and reaching such good mechanical performance. The measured hardness of (Au) was about 162HV. A wide ductile layer like this, located in the middle of interface, played a major role helping to accommodate the deformation caused by the shear stress.
Mean shear strength values of 30MPa were referred by [24] for Ni/Ni soldered joints, using Au–Ge filler alloy, although the size of the substrates was different, which could have influenced the mechanical performance. It was also mentioned that the spreading of Au–Ge alloy over Ni substrates was rather extensive, resulting in a significant amount of the solder alloy flowing out of the joint gap and spreading over the lower substrate. The same could be observed in this study, showed by Figure 43, when compared with the spreading behavior over Ti substrates. This explains the reduced width of the produced Ni/Au-Ge/Ni joint.

Figure 43: Spreading behavior of Au–Ge over Ti and Ni substrates.

In Figure 44 (a) the lower substrate of a Ni/Au-Ge/Ni shear sample can be seen. It is visible that the fracture happened along NiGe layer and close to the lower Ni substrate, represented by point P1, with 80 at.% of Ni and 20 at.% of Ge (Figure 44 (b)). The analysis of the upper substrate was also made and confirmed that the crack also reached the upper reaction layers, with Ni₃Ge₃ being also visible. An area of gold can be seen in Figure 44 (a), revealing that the joint failure happened across all layers and resulting in a cohesive fracture of the joint.

<table>
<thead>
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<th>Atomic %</th>
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<tr>
<td>Point</td>
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<tr>
<td>P1</td>
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</table>

Figure 44: (a) SE image from the lower substrate from a Ni/Au-Ge/Ni shear sample and (b) chemical composition of point P1.
3.2.1.2 Ti/Au-Ge/Ti

All the detected voids and zones without connection were certainly the main cause of the joint failure.

Moreover, in the Ti-Ge equilibrium phase diagram almost no solubility exists between these two elements at 400°C, resulting in favored reactions between Ti and Au, and segregation of (Ge). Therefore, a 23µm thick matrix of TiAu₄ (523HV), with a hardness more than 3 times superior to (Au), with big brittle (Ge) grains (967HV) along the interface, are formed. This was also the reason for such low (12.9MPa) shear strength values.

Figure 43 shows that no spreading of Au-Ge filler alloy over Ti substrate occurred, instead, the filler alloy was completely sucked inside the joint gap. Along with the dissolution of the Ti substrate to the formation of TiAu₄ IMC, this results in a wider interface.

The fracture surface of a shear samples is presented in Figure 45 (a) and (b). As can be seen in both images, a bad wetting behavior is obvious, with areas where no connection occurred between the substrate and the filler alloy. When the foil starts to melt, located melting happens with a high contact angle, which can be seen in both images as droplet shaped points of material. Figure 45 (b) is an enlargement of the squared green area marked in Figure 45 (a). The joint failure happened along the middle of the soldering gap, through TiAu₄ and the (Ge) grains.

![Figure 45: (a) SE image from the upper substrate from a Ti/Au-Ge/Ti shear sample and (b) SE image of the square zone seen in (a) with a higher magnification.](image)
3.2.1.3 Ti/Au-Ge/Ni

Regarding its microstructure and mechanical performance, it can be said that Ti/Au-Ge/Ni is in between Ti and Ni similar substrates joints. The presence of some holes, acting as stress concentration sites, compromised the mechanical behavior. Moreover, the presence of a soft gold-rich central layer balances the presence of brittle grains of (Ge). In some places the Ge grains are more than 70µm in length and represent about half of the joint width (please see Figure 23), causing a comparably small shear strength value of 37.8MPa. As can be seen in Figure 46, a cohesive fracture happened through the middle of the joint where the (Au) layer and (Ge) grains are present.

![Figure 46: SE image from the upper substrate of a Ti/Au-Ge/Ni shear sample.](image)

3.2.2 Uncoated substrates using Au-Si filler alloy

3.2.2.1 Ni/Au-Si/Ni

Like Ge in Au–Ge filler alloy, Si is also prone to react with Ni to form Ni-Si IMCs. Thus, all the silicon from the Au–Si filler alloy was consumed to form Ni₃Si and NiSi phases, leaving a gold-rich layer correspondent to 80% of the joint width. This soft middle layer, similar to the case of Ni/Au-Ge/Ni, helped to accommodate the deformation caused by the shear stress. Due to the low thickness of Ni₃Si and NiSi it was not possible to get reasonable hardness values and, therefore, relate their influence to the mechanical behavior. The fact that the joint showed no defects, with an homogeneous microstructure along all length also contributed to the good mechanical performance, reaching a mean value of 92MPa in the performed shear tests.
The low joint thickness of 5.5µm can be explained by the large accumulation of filler alloy at the edges of the joint (please see Figure 24 (b)), resulting in less filler material to react with the Ni substrates, and this way producing an extremely thin joint. However, this is not a synonym of good spreading, because Figure 48 shows that the spreading of Au-Si on Ni substrates was inexistent as the foil maintained almost its initial dimensions.

3.2.2.2 Ti/Au-Si/Ti and Ti/Au-Si/Ni

As can be seen in Figure 25 (a) and Figure 26 (a), Ti reacted with Si to form TiSi2. However, no phases between Ti and Au were observed, resulting in the formation of a gold central solution and lamellar TiSi2 phase.

In the case of Ti/Au-Si/Ti, the formation of big TiSi2 islands with a lamellar shape, along the whole joint, was vital to the shear test performance. As the measured hardness was 980HV, it can be said that we’re in the presence of a brittle Ti-Si intermetallic compound. When the shear stress is applied, these differently angled lamellas will be the first zones to break, helping the crack propagation in all directions and justifying, this way, the lowest shear test results among the 3 different Au-Si joining combinations (67.1MPa).

Figure 47 (a) and (b) are images from a Ti/Au-Si/Ti shear sample. Figure 47 (b) shows an enlarged BSE image of the square area in Figure 47 (a) pointing out that the fracture occurred along the (Au) layer and the TiSi2 islands, although parts of the Ti upper substrate are also visible, which means that the failure also happened along some zones of the interface with the substrate, resulting in a mixture of adhesive and cohesive fracture.

Figure 47: (a) SE image from a Ti/Au-Si/Ti shear sample and (b) BSE image of the square zone seen in (a) with a higher magnification.
Ti/Au-Si/Ni had the best mechanical behavior with 121.8MPa. When analyzing this microstructure, a few segregated Si particles with round shape were detected and lamellar shaped TiSi₂ phases were found. The quantity of TiSi₂ phases was much less than in Ti/AuSi/Ti joints. A 40µm thick solid solution of gold is now the main constituent of this interface, helping to stop the propagation of the crack when brittle (Si) or TiSi₂ break.

In both cases, the produced joints had no defects, showing a perfect connection with the base materials. However, the geometry of the formed phases and their amount were the key for the different mechanical behaviors.

As can be seen in Figure 48, the Au–Si filler alloy, like Au–Ge, was sucked inside the joint gap when using Ti substrates, resulting in no spreading and a wider joint compared to the spreading on Ni substrates.

![Figure 48: Spreading behavior of Au–Si over Ti and Ni substrates.](image)

### 3.2.3 Coated substrates

The need for these coatings is related to previous space applications where oxidation is not allowed. Ti is very reactive with oxygen, easily forming an oxide layer on the surface of the substrates, and thus reducing the quality of the produced joints. On the other hand, by coating the titanium substrates with gold, the wettability is increased. Other reasons for the use of gold as wettable metallization are due to its nobility, metallurgical compatibility with the filler alloys and ease of deposition. Nickel is required as first layer in order to get sufficient adhesion for Au and also improve wettability by the Au-Ge alloy. The understanding and the comparison between coated and uncoated substrates is very important for further projects.
3.2.3.1 Ti(Ni/Au)/Ti and Ti(Ni/Au)/Ti annealed

It was observed that the annealing of the Ti coated substrate had a diminished positive effect on the shear strength of this combination, increasing from 10.4MPa (without annealing) to 22.5MPa. The microstructure didn’t get any better than before, due to the appearance of holes, close to the coated Ti substrate, and which led to the growth of the interface (from 23 µm to 68).

Dark precipitates were also detected in both microstructures, probably originated during the solidification of the joint. However, EDS and WDS don’t have enough resolution for an accurate identification. Nevertheless, by means of EDS point measurement and WDS line scans an increase in Ni and Ge content was visible.

When Ti(Ni/Au)/Ti interface is analyzed (please see Figure 27 (a) and (b)), it’s noticeable the same TiAu$_4$ phase, seen in the Ti/Au-Ge/Ti interface, over a large area. Big size (Ge) shattered into pieces, possibly being a consequence from the grinding/polishing steps, will certainly be weak points of this microstructure and where the crack could be easy initiated and propagated. Some nickel from the coating layer diffused a short distance to form Ni$_3$Ge$_3$ phase. This intermetallic layer can also compromise the mechanical behavior of the joint, as already was said before. In fact, Figure 49 (a) and (b), from a sheared sample, show that the crack occurred between (Ni) coating layer and the Ti lower substrate, and within (Ni) and Ni$_3$Ge$_3$ reaching also some zones of the Ti upper substrate.

![Figure 49: (a) SE image from a Ti(Ni/Au)/Au-Ge/Ti shear sample (lower substrate) and (b) from the upper substrate of the same sample.](image-url)
Observing the Ti(Ni/Au)/Ti microstructure, after annealing of the Ti coated substrate, (Figure 28 (a)), it would be reasonable to say that the joint failure happened along the lower substrate, starting at the holes and breaking through the middle of the interface along the brittle (Ge) grains. Indeed, Figure 50 (a) and (b) show that the failure mostly happened between Ni$_3$G$_2$ and the central layer of TiAu$_4$ with (Ge) grains. In Figure 50 (b) some areas are visible where the upper Ti substrate is exposed, indicating that in these areas hardly any connection occurred. These round shape points of connection seem to be related to favored reaction points with high contact angle that are again a sign of bad wetting behavior, like in the case of Ti/Au-Ge/Ti. However, considering the shear test results, the existence of these holes was not as vital as the microstructure of Ti(Ni/Au)/Ti.

![Figure 50: (a) SE image from the lower substrate of a Ti(Ni/Au)/Au-Ge/Ti (annealed Ti coated substrate) shear sample and (b) from upper substrate of the same sample.](image)

### 3.2.3.2 Ti(Ni/Au)/Ni and Ti(Ni/Au)/Ni annealed

Regarding the thicknesses of the interfaces using nickel as upper substrate, much thinner reaction layers are visible compared to the combination Ti(Ni/Au)/Ti annealed and not annealed. The average joint thickness of Ti(Ni/Au)/Ni is about 9µm and 11µm after annealing.

The gold from the filler alloy stays in the middle of the interface and the one from the coated Ti substrate, having just a short distance to travel diffuses to the center of the joint helping to form a central layer of a soft gold solid solution. Germanium has a higher affinity to nickel reacting with the one from the upper substrate and the Ni from the lower coating layer, to form Ni$_5$Ge$_3$, adjacent to (Au). It should be noticed that the temperature of the joining process is low and the holding time is quite short, affecting the diffusion process and
resulting in thin reaction layers. Because no compounds were formed with Ti, it can be assumed that the Ni coating layer acted as a diffusion barrier.

May be suggested that due to different properties between Ni and Ni$_5$Ge$_3$ (e.g. thermal expansion coefficient) a crack is originated between these two layers (please see Figure 29 (a)). This crack was critical for the mechanical behavior of this joint. The shear fracture was initiated there and easily propagated between (Ni) and Ni$_5$Ge$_3$ layers, resulting in 15.1MPa of shear strength.

After annealing of the coated Ti substrate the disappearance of the mentioned crack was noticed, producing an homogeneous joint without any defects (please see Figure 30) and, consequently, the shear strength increased to 64.6MPa. As said in chapter 2.1.3, the composition of the coating layers changes during annealing. Reference [46] showed that an increase of Ti into Ni and Ni into Au is originated. Therefore, after the joining process, the phases remain the same, but the local composition maybe a little bit different compared to the composition before annealing and, consequently, the properties may also slightly change and help to prevent the crack.

Nevertheless, the weakest zone of this microstructure was again between (Ni) and Ni$_5$Ge$_3$. As can be verified in Figure 51 (a) and (b), all the joint failure happened within these two layers.

![Figure 51: (a) SE image from the lower substrate of a Ti(Ni/Au)/Au-Ge/Ni (annealed Ti coated substrate) shear sample and (b) from upper substrate of the same sample.](image)
3.2.3.3 Ti(Ni)/Ti and Ti(Ni)/Ti annealed

This was the only combination that the annealing had an harmful effect to the mechanical behavior of the joint, decreasing the shear strength from 24.2MPa to 11.6MPa. This possibly happened due to two different reasons:

It can be firstly explained by the way how germanium, from the filler alloy, reacted with nickel from the coating layer, forming different compounds in each case. At the not annealed sample, Ge was completely consumed in the reaction with Ni to form a NiGe layer along the lower substrate. After annealing of the Ti coated substrate, the microstructure changed, with some Ge reacting with Ni to form a thin layer Ni$_5$Ge$_3$ as well as the growth of fragile (Ge) blocks.

Secondly, Figure 31 (a) and Figure 32 show that both samples have defects. The first sample contains round holes while the one with the annealed Ti substrate has a continuous void adjacent to Ni$_5$Ge$_3$ layer, which is much more critical to the performance of the joint than a round shape defect. After annealing, it was detected the formation of the same referred dark precipitates at the Ti(Ni/Au)/Ti joints (Figure 27 and Figure 28 (a)).

In this case, the formation of a TiAu$_4$ central layer occurred due to the diffusion of Ti and reaction with the Au from the Au-Ge alloy, as seen already when both Ti substrates are used. Using the not annealed sample, the formation of some islands of Ti-Au IMC with 50 at.% each were also detected along the centerline of the interface.

Analyzing the mechanical failure of the Ti(Ni)/Au-Ge/Ti joint (please see Figure 52 (a) and (b)) it can be said that the crack propagated through all layers. In Figure 52 (a), the exposed Ti lower substrate is visible containing some bright “islands” (point P2) of a mixture with very similar composition to the upper reaction layer, from the cross section seen in Figure 31 (a) (respective composition in Figure 31 (b)). NiGe and TiAu$_4$ were also detected, as well as a mixture of 58at.% Ni and 42at.% Ti (point P2), supposedly at the interface with the lower Ti substrate.

Figure 53 shows the lower substrate from a Ti(Ni)/Au-Ge/Ti (with annealed Ti substrate) shear sample. As suspected, the crack was initiated at the defects close to Ni$_5$Ge$_3$ and propagated along TiAu$_4$ central layer, breaking through the (Ge) grains.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

<table>
<thead>
<tr>
<th>Atomic %</th>
<th></th>
<th></th>
<th></th>
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</tr>
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<td>n.d.</td>
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<td>P2</td>
<td>35</td>
<td>32</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 52: (a) SE image from the lower substrate of a Ti(Ni)/Au-Ge/Ti shear sample and (b) chemical compositions of points P1 and P2.

Figure 53: BSE image from the lower substrate of a Ti(Ni)/Au-Ge/Ti (annealed Ti coated substrate) shear sample.
3.2.3.4 Ti(Ni)/Ni and Ti(Ni)/Ni annealed

These microstructures as well as the interfaces thicknesses are very similar to Ti(Ni/Au)/Ni. The formed reaction layers are the same: a soft gold solid solution in the middle with adjacent layers of Ni$_5$Ge$_3$ phase and a layer of unconsumed (Ni) from the coating. A thin crack, not so pronounced as in Ti(Ni/Au)/Ni, also separates (Ni) from Ni$_5$Ge$_3$ layer (please see Figure 33). However the shear strengths were very different. With the annealing of the Ti coated substrate, the formed phases did not changed, but the crack was not created, showing a perfect connection with both substrates and resulting in the increase of the shear strength from 37.4MPa to 121.2MPa. These values were the highest obtained among the coated and coated and annealed combinations.

Figure 54 (a) and (b) are secondary electron images from one Ti(Ni)/Au-Ge/Ni (annealed Ti coated substrate) shear sample. From their analysis can be said that the mechanical failure of the joint happened between (Ni) and Ni$_5$Ge$_3$ layers and along (Au) central layer.

![Figure 54: (a) SE image from the lower substrate of a Ti(Ni)/Au-Ge/Ni (annealed Ti coated substrate) shear sample and (b) from upper substrate of the same sample.](image-url)
4. Summary and perspective

A good wetting and spreading behavior of Au–Ge alloy on Ni substrates was observed. On the other hand, Ti substrates showed poor wetting and spreading. Using Au-Si filler alloy, no spreading was observed on both Ti and Ni substrates.

Ni/Au-Ge/Ni joints showed a perfect connection, without any defects, and achieved the best mechanical performance among all tested combinations, with mean shear strength of 201MPa. Uncoated Ti substrates, on the other hand, did not exhibit such good performance when joined with Au-Ge filler alloy, achieving only 13MPa. The bad wetting behavior seemed to result in areas of the joint without any connection.

Using Au–Si filler alloy, Ti substrates appear to have a better performance. However, the developed microstructure in Ti/Au-Si/Ti joints, of lamellar TiSi$_2$ islands, seemed to have a prejudicial effect on the mechanical performance and justifies the 67MPa of shear strength. Among these combinations, Ti/Au-Si/Ni joints had the best shear performance with 122MPa and with similar Ni substrates 92MPa were achieved.

A crack between Ni$_3$Ge$_3$ and Ni coating layers in Ti(Ni/Au)/Au-Ge/Ni and Ti(Ni)/Au-Ge/Ni joints was originated most probably due to different properties, like thermal expansion coefficients, between these two layers. Annealing of the coated Ti substrate had a positive effect on the microstructures, with homogeneous joints being produced, with no crack formation and resulting in the best mechanical performances among the combinations using Ti coated substrates: Ti(Ni)/Au-Ge/Ni raised its mean shear strength from 37MPa to 122MPa and Ti(Ni/Au)/Au-Ge/Ni from 15MPa to 65MPa. Still, the mechanical failure continued to happen between the referred layers.

The presence of defects and the formation of big size (Ge) grains appeared to be critical for the performance in Ti(Ni/Au)/Au-Ge/Ti and Ti(Ni)/Au-Ge/Ti joints. The annealing in these cases didn’t seem to have the same beneficial effect that was seen when Ni is used as upper substrate. In fact, Ti(Ni)/Au-Ge/Ti was the only combination that even decreased the mean shear strength from 24MPa to 12MPa.

Annealing of the Ti coated substrate had a diminished but positive effect on the shear strength of Ti(Ni/Au)/Au-Ge/Ti joints, increasing from 10MPa to 23MPa. Areas without any connection were observed and the same high angle droplets of material, seen in Ti/Au-Ge/Ti joints, which seem again to be a sign of bad wetting.

When comparing dissimilar Ti/Au-Ge/Ni with Ti(Ni/Au)/Au-Ge/Ni and Ti(Ni)/Au-Ge/Ni joints, can be said that the annealed coating of the Ti substrate had a significant effect
in the microstructure and consequently in the mechanical behavior, increasing the shear strength from 38MPa to 65MPa and 121MPa, respectively.

The same cannot be said about the comparison of the mechanical behavior of similar Ti/Au-Ge/Ti with Ti(Ni/Au)/Au-Ge/Ti and Ti(Ni)/Au-Ge/Ti (coated and annealed Ti) joints. An increase of the shear strength was observed in the first case, from 13MPa to 23MPa. When compared to Ti(Ni)/Au-Ge/Ti, the shear strength decreased after annealing to 12MPa.

The main advantage of eutectic Au–Si and Au–Ge filler alloys is, indeed, the relatively high mechanical strength that can be achieved with low process temperatures. Therefore, time and energy consumption of the joining process can be decreased and distortions of assembled components are prevented. Since the price of gold is the main problem of this filler alloys, Au-Ge-based alloys reduce the price with the addition of elements such Sn or Sb.

The production of Au–Ge–Sn and Au–Ge–Sb foils, by melt spinning, was successful as well as the performing of the joining with Ni and Ti similar substrates. It was also verified that the addition of Sn or Sb to Au-Ge alloy decreases the melting point even more. Since their melting point was 335°C for Au–Ge–Sb and 347°C for Au–Ge–Sn, it would be interesting to try to lower the process temperature to 350°C. Although joints with apparent physical integrity were produced at 400°C, shear tests would still be necessary to evaluate the joints mechanical performance.

Due to the small thickness of some reaction layers a technique like transmission electron microscopy (TEM) would be useful to a more precise chemical identification of the present phases.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

References


Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates


[49] C. Sá, Caracterização morfológica, microestrutural e microanalítica de materiais por: microscopia electrónica de varrimento (SEM) e microanálise por raios-X – EPMA: EDS/WDS, CEMUP.
Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates

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## Appendix A

**Figure 21:**

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<tbody>
<tr>
<td>TiSi&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3</td>
<td>63</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>(Au)</td>
<td>97</td>
<td>-</td>
<td>3</td>
<td>-</td>
</tr>
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</table>

**Figure 26 (a):**

<table>
<thead>
<tr>
<th>Point</th>
<th>Au</th>
<th>Si</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2</td>
<td>64</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>(Au)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Si)</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 27 (a) and (b):

<table>
<thead>
<tr>
<th>Atomic %</th>
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<tbody>
<tr>
<td>Point</td>
</tr>
<tr>
<td>TiAu₁₂₄₅</td>
</tr>
<tr>
<td>Ni₁Ge₁₂₅</td>
</tr>
<tr>
<td>Ti₅Ge₂₆</td>
</tr>
<tr>
<td>Ti₅Ge₁₇</td>
</tr>
<tr>
<td>(Ni)</td>
</tr>
<tr>
<td>(Ge)</td>
</tr>
</tbody>
</table>

Figure 28 (a):

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Point</td>
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<tr>
<td>Ni₁Ge₁₂₅</td>
</tr>
<tr>
<td>TiAu₁₂₄₅</td>
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<tr>
<td>(Ge)</td>
</tr>
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Figure 29 (a) and (b):

<table>
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<tbody>
<tr>
<td>Point</td>
</tr>
<tr>
<td>Ni₅Ge₃₆₇₈ (upper layer)</td>
</tr>
<tr>
<td>Ni₅Ge₃₆₇₈ (lower layer)</td>
</tr>
<tr>
<td>(Au)</td>
</tr>
<tr>
<td>(Ni)</td>
</tr>
</tbody>
</table>

Figure 30:

<table>
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<tr>
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<tbody>
<tr>
<td>Point</td>
</tr>
<tr>
<td>Ni₅Ge₃₆₇₈ (upper layer)</td>
</tr>
<tr>
<td>Ni₅Ge₃₆₇₈ (lower layer)</td>
</tr>
<tr>
<td>(Au)</td>
</tr>
<tr>
<td>Ni₅Ge₂₆₇₈</td>
</tr>
<tr>
<td>(Ni)</td>
</tr>
</tbody>
</table>

Figure 31 (a):

<table>
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<tbody>
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<td>Point</td>
</tr>
<tr>
<td>NiGe</td>
</tr>
<tr>
<td>TiAu₁₂₄₅</td>
</tr>
<tr>
<td>TiAu₁₂₄₅</td>
</tr>
</tbody>
</table>
Figure 32:

<table>
<thead>
<tr>
<th>Point</th>
<th>Au</th>
<th>Ge</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>35</td>
<td>2</td>
<td>63</td>
</tr>
<tr>
<td>TiAu&lt;sub&gt;2&lt;/sub&gt;</td>
<td>80</td>
<td>-</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>(Ni)</td>
<td>97</td>
<td>-</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>(Ge)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

Figure 33:

<table>
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<tr>
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<th>Au</th>
<th>Ge</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt; (upper layer)</td>
<td>-</td>
<td>37</td>
<td>-</td>
<td>63</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt; (lower layer)</td>
<td>-</td>
<td>37</td>
<td>-</td>
<td>63</td>
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<tr>
<td>(Au)</td>
<td>92</td>
<td>3</td>
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<td>5</td>
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<tr>
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<td>95</td>
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Figure 34:

<table>
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<th>Ge</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt; (upper layer)</td>
<td>3</td>
<td>35</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt; (lower layer)</td>
<td>-</td>
<td>37</td>
<td>-</td>
<td>63</td>
</tr>
<tr>
<td>(Au)</td>
<td>95</td>
<td>2</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>(Ni)</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>98</td>
</tr>
</tbody>
</table>

Figure 35:

<table>
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<th>Au</th>
<th>Ge</th>
<th>Sn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>37</td>
<td>-</td>
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</tr>
<tr>
<td>NiGe</td>
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</table>

Figure 36 (a)

<table>
<thead>
<tr>
<th>Point</th>
<th>Au</th>
<th>Ge</th>
<th>Sn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAu&lt;sub&gt;2&lt;/sub&gt;</td>
<td>63</td>
<td>-</td>
<td>-</td>
<td>37</td>
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<tr>
<td>TiAu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>82</td>
<td>-</td>
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</table>
**Interface Reactions Between Au-Based Filler Alloys and Ti, Ni Substrates**

Figure 37 (a)

<table>
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<th>Atomic %</th>
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<tbody>
<tr>
<td>Point</td>
<td>Au</td>
<td>Ge</td>
<td>Sb</td>
<td>Ni</td>
</tr>
<tr>
<td>NiGe</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>NiSb</td>
<td>46</td>
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<td>54</td>
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Figure 38 (a)

<table>
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<tbody>
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<td>Point</td>
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<td>Ge</td>
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Figure 44 (a):

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<tbody>
<tr>
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<td>Ge</td>
<td>Sb</td>
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Figure 45 (a):

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</thead>
<tbody>
<tr>
<td>Point</td>
<td>Au</td>
<td>Ge</td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>TiAu₄</td>
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<td>-</td>
<td>20</td>
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<tr>
<td>(Ge)</td>
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<td>100</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Ti</td>
<td>-</td>
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<td>-</td>
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</table>

Figure 46:

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</tr>
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<td>Ge</td>
<td>Ni</td>
<td>Ti</td>
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<td>5</td>
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<tr>
<td>(Ge)</td>
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Figure 47 (a) and (b):

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<th></th>
</tr>
</thead>
<tbody>
<tr>
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<td>Au</td>
<td>Si</td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
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<td>-</td>
<td>33</td>
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Figure 49 (a) and (b):

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<th>Ni</th>
<th>Ti</th>
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</thead>
<tbody>
<tr>
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<td>-</td>
<td>37</td>
<td>63</td>
<td>-</td>
</tr>
<tr>
<td>(Au)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ni)</td>
<td>-</td>
<td>-</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Ti</td>
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<td>-</td>
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<td>100</td>
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Figure 50 (a) and (b):

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<th>Ge</th>
<th>Ni</th>
<th>Ti</th>
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</thead>
<tbody>
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<td>Ni₃Ge₂</td>
<td>-</td>
<td>33</td>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td>(Au)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>97</td>
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Figure 52 (a):

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<tr>
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Figure 53:

<table>
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<th>Ti</th>
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<tr>
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Figure 54 (a) and (b):

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<th>Ti</th>
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<tbody>
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<td>Ni₃Ge₂</td>
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<td>66</td>
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