Feasibility, processing properties and thermal behavior of Ni nanopastes produced by ultrasound-enhanced dispersing

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Abstract. Nickel nanoparticles are materials that can be used for a novel type of joining, so called nanojoining, as an alternative to conventional brazing. The physical characteristics of these nano-sized particles lead to a lower melting temperature compared to nickel bulk material and even lower than typical brazes, without the need for melting point depressants. Such elements like boron or silicon cause issues due to formation of brittle intermetallic phases. In order to be able to use Ni nanoparticles in practical applications, they have to be in forms such as suspensions, e.g. pastes. In the present work, therefore, a series of Ni nanopastes is prepared and investigated with emphasis on the solvent systems. These suspensions consist of Ni nanoparticles (mean diameter 20 / 90 / 180 / 300 nm) and organic compounds. The examinations show the feasibility of producing such nanopastes using ultrasound-enhanced dispersing, as well as margins for adjusting their processing properties. In addition, first results of the thermal behavior of the Ni nanopastes, measured by simultaneous DSC/TG, are shown.

1. Introduction

In high-temperature applications, nickel base superalloys are heavily employed due to their high-temperature strength and great resistance to oxidation and creep [1,2]. For joining of these alloys, a range of welding and brazing techniques are available, but there are some points to consider. For example, several Ni base superalloys show segregation issues during solidification when welded due to its high diffusion rate, which weakens it’s strength [3]. According to manufactures, brazing processes in the range of 1200 °C negatively affect properties of single-crystal Ni base materials, due to recrystallization effects above 1100 °C. Brazes also limit the maximum operating temperature of joined components and can cause brittleness when intermetallic phase formation takes place at the centerline of the joint [4,5].

Therefore, this paper deals with viscous suspensions consisting of pure Ni nanoparticle and organic additions, which are intended to be used in nanojoining processes. Nanojoining is an alternative method and similar to brazing resp. soldering but possess, besides some challenges, specific advantages. Nanoparticle in general show lower melting and sintering temperatures compared to the corresponding bulk material due to their high specific surface area or high surface-to-volume ratio, respectively [6–8]. In comparison to brazing fillers no melting point depression elements like Si or B are needed. After Ni nanoparticles coalesce during the joining process, the resulting metal regain almost the properties of the bulk material. This is beneficial for joining purposes, because the process can be carried out at relatively low temperatures while the maximum operating temperature of the joint is not strongly affected [9,10]. In contrast to many previous papers dealing with low viscosity suspensions (e.g. nano inks) or...
suspensions as a reagent in order to produce nanoparticles bottom-up [11–13], this work here presents results of paste-like, higher viscosity Ni nano suspensions.

Mixing Ni nanoparticles with solvents and stabilizers (dispersing agents) is necessary to cover their surfaces and to keep them separate from each other in order to avoid agglomeration before the actual joining process takes place [14,15]. Furthermore, for a reliable joining process handling, it is necessary to use nanoparticles in the dispersed form of a suspension, comparable to common brazing pastes.

2. Experimental and materials

2.1. Starting materials

For examination here, pure Ni nanoparticles in different mean diameters and several organic solvents and agents are used. In the following, Ni nanoparticles is abbreviated to “Ni-NP”. The mean diameters of the particles are 300, 180, 90 and 20 nm, delivered by manufacturer Amogreentech Co., LTD. (South Korea) and M K Impex Corp. (Canada), respectively. A summary of all organic materials is provided in Table 1.

| Compound                              | formula            | CAS No.       | Supplier               |
|---------------------------------------|--------------------|---------------|------------------------|
| Polyethylene glycol 400 (PEG 400)     | C_{2n}H_{4n+2}O_{n+1} | 25322-68-3   | Carl Roth GmbH (GER)   |
| Polyethylene glycol 600 (PEG 600)     | C_{2n}H_{4n+2}O_{n+1} | 25322-68-3   | Carl Roth GmbH (GER)   |
| Terpineol, pure                       | C_{10}H_{15}O      | 8000-41-7    | Carl Roth GmbH (GER)   |
| Dihydroterpineol (DHT)                | C_{10}H_{20}O      | 498-81-7     | MuseChem (USA)         |
| Ethyl cellulose (EC)                  | - (more complex)   | 9004-57-3    | Carl Roth GmbH (GER)   |

The herein investigated nanopastes are based of two chemical systems. First, a mixture of Ni-NP and PEG, where PEG acts as solvent and stabilizers at the same time. PEG 400 is a macromolecular liquid at room temperature (20 °C) whereas PEG 600 is at its melting point, so appear as a pasty material. Both are miscible, so by combining them the viscosity of the resulting suspension is adjustable within a certain range. Second one is a mixture of Ni-NP, Terpineol or DHT as well as EC for the option to enhance viscosity. For tests of suspensions with EC, the EC must be solved in terpineol/DHT at approx. 85 °C in advance.

2.2. Measurement of viscosity characteristics of solvents

The viscosity range of solvent systems, which can be adjusted by their composition, is important for later applications of the nanopaste in terms of handling. In addition to detailed methods, simplified methods can also be used to determine the viscosity, such as using a viscosity cup or flow tests on an inclined plane [16]. Performing a detailed viscometer measurement is not reasonably for this work, because it would require large amounts of some limited cost-intensive starting materials and further, only a relative comparison is intended.

The measurement method used here is based on the principle of flow due to gravity. A rotatable mounting is used for this, into which sample bottles are inserted, each filled with 1 g of the solvent investigated. The mounting, including the filled bottles, is then tilted by 45° to horizontal position and turned back subsequent. This is recorded digitally and evaluated by using image analysis. The experimental design is shown in Figure 1.
Figure 1. Sample mounting and measurement principle for evaluating viscosity characteristics of solvents.

The duration until the re-flow movement meets a certain criterion, is used as the measured value. Therefore, taking into account the flow front is inclined, a special measuring bar was defined which the flow front has completely to travel. This duration was taken as result. The duration for complete leveling of the solvent seems also as an obvious one, but preliminary tests in this case show an extreme spread of the measured values, since this non-linear process takes a long time towards the end, at least in the case of solvents with higher viscosity.

2.3. Volatility of solvents
The volatility of the solvents that keep the Ni-NP dispersed a suspension, has strong influence on their processing properties and storage capacity, i.e. on drying behavior. In order to obtain appropriate and reproducible results, all solvents were exposed to a defined ambient at elevated temperature to accelerate the process of volatilization. For this purpose, 1 g of each solvent was heated to 85 °C in an open sample tube in a water bath whereas the tubes do not touch the ground. After specified periods of time (between 0 to 30 minutes), the residual mass of the remaining solvent was weighed, so that the loss of mass could be determined as a function of time.

2.4. Preparation of the Ni nanopastes
In order to evaluate the maximum achievable metal content and to carry out thermal analysis, nanopastes were produced by first giving together precisely weighted amounts of Ni-NP and solvents together in a sample bottle. Then the components are mixed by pulsed ultrasound-enhanced dispersing (USP 200, Hielscher-Ultrascall-Technologie) a several times while it’s temperature is controlled by using a water bath. An important variable in this mixtures is the metal content of the nanopastes. Preliminary tests have shown that the metal content cannot be increased up to any value. If the content of solvent is too low, the wetting of Ni-NP is not sufficient to form a viscous suspension. Therefore, in a separate test series PEG 400 was added in small steps to a given content of Ni-NP. After each step, it was attempted to produce a suspension by using ultrasound-enhanced dispersing. If this was not possible, the solvent content was increased and so on. This was repeated with Ni-NP in all different mean sizes to evaluate the maximum achievable metal content.
For thermal analysis, three PEG based Ni nanopastes were produced, see table 2 for details. The investigation of the thermal behavior was carried out by a measuring system from Netzsch, model STA 449 F1 Jupiter. This device record heat flow (DSC) and the weight over temperature (TG, thermogravimetric analysis) simultaneous.

Table 2. Composition of Ni nanopastes used for thermal analysis.

| Nanopaste   | Ni-NP   | solvent | Type  | Weight | Resulting metal content |
|-------------|---------|---------|-------|--------|-------------------------|
| Ni90_PEG400 | 90 nm   | 2.518 mg| PEG 400 | 1037 mg | 70.83 %                |
| Ni90_PEG600 | 90 nm   | 2.497 mg| PEG 600 | 1039 mg | 70.62 %                |
| Ni20_PEG400 | 20 nm   | 2.500 mg| PEG 400 | 1781 mg | 58.40 %                |

3. Results and discussion

3.1. Measurement of viscosity characteristics of solvents

All re-flow tests, like described in section 2, took place at room temperature (20 °C) and three measurements were carried out for each solvent, so 3 sequences were captured, evaluated and a mean result was formed. Results are shown in figure 2, please note EC additions are in weight percent and the 20:80 proportion is by weight too.

Figure 2. Results of the re-flow tests for evaluating viscosity characteristics of solvents, all solvent quantities refer to weight.

The re-flow durations are to be interpreted in this way, that a higher value corresponds to a higher viscosity of the liquid. Pure terpineol and pure dihydroterpineol (DHT), show the lowest values and behave very similarly. If only 1 wt.-% ethyl cellulose (EC) is added, the re-flow duration increases to more than four times in both cases. An addition of 2.5 wt.-% EC leads to a further large increase, which is even greater in case of DHT. The significantly more viscous properties of terpineol and DHT with additions of EC are also clearly noticeable during the experimental handling. In summary, the system [terpineol/DHT] + EC provides a good viscosity range that can be set to application desired values with relatively small amounts of EC.
Polyethylene glycol (PEG) 400 has a slightly higher viscosity than the terpineol or DHT without EC. At room temperature, PEG 600 is at the transition to the solid and does not flow. If PEG 400 and PEG 600 are mixed together, the melting point can be shifted or the viscosity of the mixture can be adjusted as desired. For example, a mixture of PEG 400 and PEG 600 in a ratio of 20:80 by weight shows a re-flow duration that is more than twice as long as pure PEG 400. Pure PEG 600 is also suitable for processing a usable suspension, but for dispersing with Ni nanoparticles, the temperature must increase above the melting point (e.g. 40°C) while mixing.

For a better assessment of the values, it should be stated that all solvents are more viscous than water at room temperature. In general, the behavior is strongly dependent on temperature, which was observed, for example, when terpineol or DHT are heated to 80°C during the dissolution of EC. At this temperature, their viscosity is comparable to that of water, despite the EC content. The PEGs show a sensitive viscosity behavior particularly around their melting point.

3.2. Volatility of solvents
The investigation was carried out with all solvents of which the viscosity was characterized. The figure 3 shows the loss of mass after 5 / 10 / 20 / 30 minutes.

![Figure 3. Volatility of solvents heated to 85 °C, measured as loss of mass over time.](image)

It can be observed that the PEGs show almost no loss over the entire exposure duration of 30 minutes; this is true for pure PEGs as well as the 80:20 mixture (PEG 400: PEG 600). Terpineol solvents shows mass losses that are roughly linear over time. The same applies to DHT based solvents, but with a higher rate of loss. Pure DHT lost 109 mg of mass after 30 minutes, that is over 10% based on the initial mass of 1g. A significant influence of the EC on the volatility cannot be identified. The generally higher volatility of terpineol- and DHT-based solvents is also clearly seen in the processed form as Ni nanopaste during experimental handling. Small amounts of suspension of this kind dry up quickly, whereas PEG based suspensions are still stable after exposition to air for weeks. This behavior is an important aspect as it is crucial for the long-term viscosity properties and dispersion stability of nanopastes.
3.3. Maximum metal contents and thermal analysis of PEG based Ni nano suspensions

First, according to the method described in experimental, an evaluation of the maximum metal content for Ni nano suspensions with PEG 400 as solvent was carried out. The results are listed in Table 3.

| Mean diameters of Ni-NP | Max. metal content in wt.% |
|-------------------------|---------------------------|
| 300                     | 89.2                      |
| 180                     | 85.2                      |
| 90                      | 78.2                      |
| 20                      | ~58.4                     |

Compared to other publications [12,17,18] it turns out that relatively high metal contents are feasible, but it depends on the particle size. So, the smaller the mean diameters of the particles, the more solvent is necessary to obtain a suspension. In other words, the maximum realizable metal content decreases with decreasing particle sizes. The mixture which consists of 20 nm particles does not show any clear suspension forming behavior, since strong agglomerations were observed, so this value is uncertain.

The following diagrams in figure 4, 5 and 6 show initially examinations of thermal behavior of the Ni nanopastes (combined curves of DSC/TG). The results for the nanopastes Ni90_PEG400, Ni90_PEG600 and Ni20_PEG400 under an argon shield gas atmosphere at a heating of 10 K/min are presented here, further investigations are in progress.

![Figure 4. DSC / TG signal of nanopaste “Ni90_PEG400”](image1)

![Figure 5. DSC / TG signal of nanopaste “Ni90_PEG600”](image2)

![Figure 6. DSC / TG signal of nanopaste “Ni20_PEG400”](image3)

The TG signal in pastes Ni90_PEG400 and Ni90_PEG600 indicates an almost complete evaporation of the organic components of the suspension, since the mass after the end of the heating process corresponds almost exactly to the mass fraction of the given nickel (metal content). However, carbon
residues from the solvent are to be expected. The evaporation extends over a temperature range of approx. 200 ... 300 °C in both cases and manifests itself in the DSC signal with a corresponding reaction. The weaker exothermic reactions at just below 400 °C cannot be easily interpreted and must be further investigated, but based of former investigations it is assumed to be a sinter reaction of the Ni-NP. At high temperatures, the DSC signals show a clear endothermic reaction at around 1325 °C. This is not the melting reaction of pure nickel with it’s significantly higher melting point at 1455 °C. Due to the assumed carbon residues, this might be the melting reaction of eutectic mass from the Nickel-Carbon binary system. The eutectic melting point in this system is calculated to be at 1326.4 °C according to Franke et al.[19]. Basically, carbon residues, that lowering the melting point, are not desired in later joining applications, but they do not have to occur there due to the higher diffusion activity in thin joining layers. Apart from that, other organic solvents do not show this behavior in DSC signals and instead indicate the melting temperature of bulk nickel [9].

The diagram of the nanopaste Ni20_PEG400 is different. Knowing the thermal characteristics of pastes Ni90_PEG400 and Ni90_PEG600 from their diagrams, a roughly similar behavior can be recognized, but overall it is not that clearly. First, the mass loss according to the TG signal does not match the solvent content of the paste. There is a discrepancy of about 18 wt.-%.

Further, the heat flow signal indicates more distributed reactions, especially no strong reaction at around 1325 °C. It must be stated, that the 20nm Ni-NP show agglomerations, even after ultrasound-enhanced dispersing, so the resulting suspension is not that homogenous like the other ones. This might be a reason for the less defined thermal behavior in comparison to the suspensions consists of 90nm Ni-NP.

4. Conclusions

In this work, organic solvents systems and suspensions of Nickel nanoparticles are investigated. These so called nanopastes are intended to be used for alternative joining methods (“nanjoining”) of Ni base superalloys. It is similar to brazing, but offers several advantages, most notably a significantly lower process temperature and, at the same time, a higher operating temperature of the joint. This is based on the special properties of nanoparticles, which, due to their very high surface-to-volume ratio, have a lower melting point compared to bulk material.

Investigations reveals the viscosity and volatility behavior of two different solvent systems. The first system, terpineol and dihydroterpineol (DHT) with ethyl cellulose (EC) additives provides a wide range of viscosity viscosities that can be tailored to the needs of an application. However, these solvents also show highly volatility during tests in a controlled ambient. Second system is based on polyethylene glycols (PEGs) and also offers a range of viscosity by mixing PEGs of different molecular weights, like PEG 400 and PEG 600 here in this study. Furthermore, it turns out that PEGs are almost non-volatile, even dispersed in a Ni nanopastes after weeks exposed to air.

Ni nanopastes have been successfully prepared using these solvent systems. Results are presented for PEG based nanopastes. The maximum metal content, which can be achieved in these suspensions, is examined. Results show a clearly dependence of the particles mean diameter. Also, results in thermal behavior using simultaneous DSC/TG measurement were shown.

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