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Intergranular penetration and embrittlement of solid nickel through bismuth vapour condensation at 700°C

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Abstract

Grain boundary penetration of liquid bismuth in polycrystalline nickel is investigated at 700°C. The contact between the two metals is ensured by bismuth transport through vapour phase. The formation of a nanometre-thick Bi-rich layer on external surfaces of solid nickel is revealed by glow discharge optical spectroscopy. This layer is the consequence of Bi vapour condensation on nickel substrate at 700°C. The liquid Bi/solid Ni contact leads to grain boundary penetration of liquid bismuth in the form of a film of nanometric thickness as revealed by Auger electron spectroscopy. The presence of these intergranular films causes strong room temperature brittleness of nickel, as shown by tensile and bending tests. The comparison with results due to the direct contact between solid nickel and bulk liquid bismuth-rich alloy indicates that in both cases intergranular penetration rate and embrittlement are of the same magnitude. Based on these results, a concept of a new device for liquid metal embrittlement (LME) tests is outlined.

1. Introduction

Liquid metal spallation target is a complex device where neutrons are produced by highly accelerated protons [1,2]. Neutrons are needed either in fundamental research (European spallation source (ESS) [3], spallation neutron source (SNS) [4]) or in accelerator driven system (ADS) for power generation [5] or nuclear waste incineration [6]. Spallation targets constitute an alternative, as opposed to the nuclear reactors, for neutron production with an advantage of a pulsed source. Neutrons are produced by spallation reaction i.e., collisions between pulsed high-energy protons (of the order of GeV) and heavy metal nucleus. Liquid metal spallation target (Hg, Pb or Pb–Bi) are preferred because of the higher neutron production rate, easier cooling system and increased lifetime with respect to the solid target. However, one of the critical points of such a system is the compatibility between liquid metal target and solid metal container, usually called window (i.e., the entrance for high-energy protons). This compatibility must be ensured under complex loading conditions including residual stresses, irradiation and thermal fatigue. It also requires: (i) limited liquid metal corrosion i.e., relatively homogeneous attack and dissolution of solid metal by stagnant or flowing liquid metal and (ii) resistance to the liquid metal embrittlement (LME) [7] i.e., preferential transgranular (rare) or intergranular (frequent) rapid penetration of liquid metal under stress and consecutive failure. In some model systems (Al–Ga [8], Cu–Bi [9]), this penetration can even occur without external stress and result in low temperature brittleness.

Two types of liquid target/solid container systems are considered for the design of the spallation target:

(i) liquid mercury in contact with 316L austenitic stainless steel, in SNS project [4,10]. Liquid mercury is a good candidate as spallation target, because of relatively low-working temperatures (typically between 60°C and 150°C) and materials lifetime and neutronic performance are increased compared to water-cooled solid target [4]. 316L stainless steel is chosen as mercury container, because it exhibits good performance while

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simultaneously exposed to the intense flux of high-energy protons and neutrons [4] and to the flowing liquid mercury [10].

(ii) liquid lead [11–13] or lead–bismuth eutectic alloy (Pb–55.5 wt% Bi) [12,14] in contact with ferritic steel, in the MEGAPIE project [2] and GEDEON program [15,16]. Liquid Pb–Bi spallation target is also considered as possible neutron source in the concept of undercritical hybrid reactor [6]. The range of working temperatures (350–550°C) is higher than for mercury target, but an important advantage of Pb–Bi target is the increased neutron production rate as compared to pure lead or mercury. Nevertheless, the compatibility between these liquid metals and ferritic steels as container is the critical point and some papers [12,17], that compared the damaging effects of liquid Pb and liquid Pb–Bi on different steels, underlined that the addition of Bi was at the origin of LME.

Our effort is aimed at the understanding of LME phenomenon on a model system: liquid bismuth/solid nickel [18–20]. The advantage of this couple is that it is possible to separate grain boundary liquid penetration, taking place at elevated temperature, from the resulting intergranular embrittlement at room temperature, which allows grain boundary analysis by Auger electron spectroscopy. Grain boundary liquid penetration was typically obtained by direct contact between solid Ni and liquid Bi-rich alloy [18,20]. Direct contact results in the formation of relatively short intergranular films of micrometric thickness and long intergranular films of nanometric thickness [20]. Although only micrometric films are visible by scanning electron microscopy (SEM), both films result in strong intergranular brittleness [20]. These results underline the key role of nanometric films in the assessment of LME phenomena, but it requires quite complex experimental device due to the direct contact procedure.

The alternative way of ensuring the contact between solid and liquid metals is vapour transport in temperature gradient and subsequent condensation on solid substrate. This way can apply for elements with high equilibrium pressure and will be called indirect contact. It has been successfully used in several studies. In particular, bismuth vapours from Cu–1 wt% Bi were used for the controlled doping of copper bicrystals [21], mercury vapours condensation was shown to induce intergranular penetration in alpha-brass [22] and Zn, Cd and Hg were theoretically shown to have the equilibrium vapour pressure high enough to ensure their transport between the specimen surface and the crack tip in the LME phenomena [23].

The aim of this paper is to point out that the indirect contact between solid nickel and liquid bismuth through bismuth vapour condensation results in grain boundary penetration and consecutive room temperature embrittlement of the same magnitude that in the case of the direct contact. It will be also suggested that mechanical testing, as opposed to standard SEM observations, is necessary to reveal grain boundary penetration in the form of nanometre-thick films and that bismuth vapour condensation can be used in a simple device to perform LME experiments.

2. Experimental

Experimental work was carried out on polycrystalline nickel with an average grain size of 150 μm and with less than 100 ppm total impurities (C: 40–60 ppm; S, O and N < 10 ppm). Two types of specimen were used: (i) discs (2 mm thick, 18 mm diameter) mechanically polished down to 1/4 μm on front faces, and (ii) cylindrical polished tensile specimen (4 mm diameter and gauge length: 17 mm). Saturated Bi–Ni alloy (72.4 at.% Bi/27.6 at.% Ni at 700°C, according to the phase diagram [24]) was used as a source of bismuth vapour.

Ni specimen and Bi–Ni alloy were placed in silica tubes sealed under argon (see Fig. 1), so that no direct contact between the two metals was possible during all heat treatment at 700°C in a horizontal furnace. The total pressure of Bi vapour at 700°C is 2.4×10^{-5} atm [25]. At the end of heat treatment, silica tubes were water-quenched to avoid any impurity segregation in nickel.

Glow discharge optical spectroscopy (GDOS), which allows quick acquisition of elemental composition profiles on flat surfaces for depth between 100 μm and 1 nm, was used to analyse the Ni disc surface composition. Those analyses were performed using a JY50 GDOS analyser from Gobin Yvon. The average erosion rate was between 2 and 6 μm/min.

Discs were cut and polished after exposure at 700°C, in order to examine transversal sections by SEM coupled with energy dispersive spectroscopy (EDS). One parallelepipedic specimen ($2 \times 2 \times 18$ mm^3) was cut from a Ni disc and impact broken within Auger spectrometer (analysis performed under 5 keV electron beam with Mac III analyser from Cameca) to analyse grain boundaries composition.

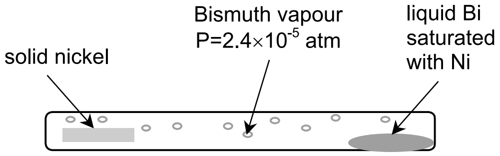

Fig. 1. Experimental procedure: Ni disc and liquid Bi-rich alloy are placed in silica tube sealed under argon so that no direct contact is possible during heat treatment in the furnace at 700°C.

Room temperature bending tests on parallelepipedic specimens ($2 \times 2 \times 18$ mm^3) and tensile test were performed to reveal the influence of Bi vapour environment at 700°C on mechanical properties of solid Ni. Fracture surfaces of specimens were examined by SEM and EDS.

3. Grain boundary penetration and embrittlement due to bismuth vapour condensation

3.1. Bismuth transport through its vapour condensation

The external polished surface of Ni disc after heat treatment in Bi vapour atmosphere during 16 h at 700°C was analysed by GDOS. The result is shown on the graph of Fig. 2, which represents the intensity corresponding to each element from the analysed material as a function of the sputtering time. High peak associated to Bi at the beginning of the sputtering indicates the presence of a Bi-rich layer on Ni disc. The thickness of this layer can be estimated between 4 and 12 nm as calculated from minimum and maximum GDOS erosion rates (such a thin layer can't be detected using SEM and EDS).

The presence of this thin Bi-rich layer on Ni specimen is due to the Bi vapour condensation during heat treatment at 700°C. Indeed, during heat treatment in silica tube, Bi evaporates from saturated Bi-rich alloy, then Bi vapour condenses and finally forms a liquid layer on external surfaces of Ni specimen. Consequently, intimate contact between solid Ni and liquid Bi is ensured and grain boundary penetration becomes possible.

3.2. Intergranular penetration and brittleness at room temperature

Neither secondary electron observations by SEM nor analysis by EDS of Ni specimen transversal sections after heat treatments at 700°C in presence of Bi vapour permit to detect the presence of Bi in grain boundaries. Those observations were done after 1 h, 16 h and 14 d of heat treatment and, even after 14 d of exposure at 700°C, there was no evidence of intergranular penetration (Fig. 3). Then, mechanical tests were done to check whether embrittling effect due to the contact with Bi vapours has occurred or not. Interrupted room temperature tensile test up to 15% plastic deformation was performed on a Ni specimen, after 1 h heat treatment at 700°C. The observations of the longitudinal polished section have revealed several intergranular cracks. An

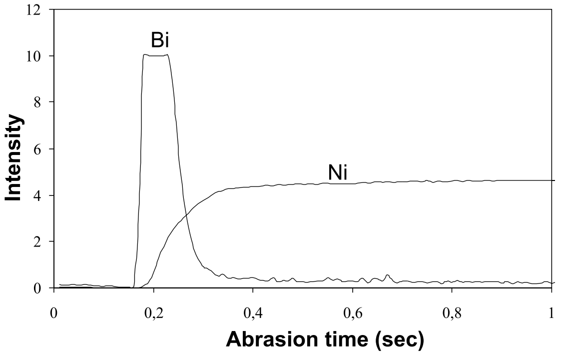

Fig. 2. GDOS graph from the polished surface of Ni specimen after heat treatment at 700°C during 16 h in saturated Bi vapour atmosphere. According to the average erosion rate of 2 to 6 µm/min, the thickness of the Bi layer is between 4–12 nm.

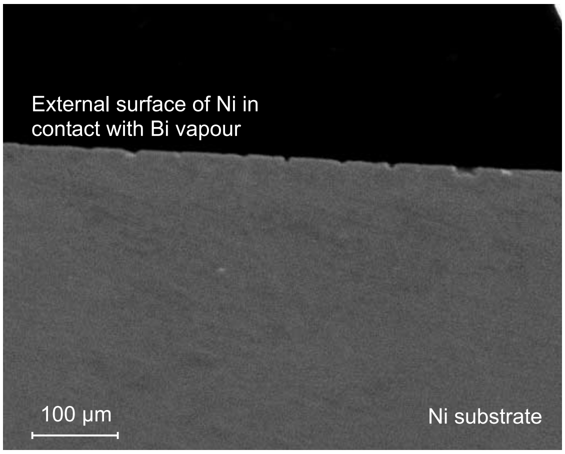

Fig. 3. Transversal polished section of Ni specimen after 14 d heat treatment at 700°C in Bi vapour atmosphere. Note that no intergranular Bi-rich films are visible by SEM; however, grain boundaries will exhibit brittle behaviour (compare with Fig. 4).

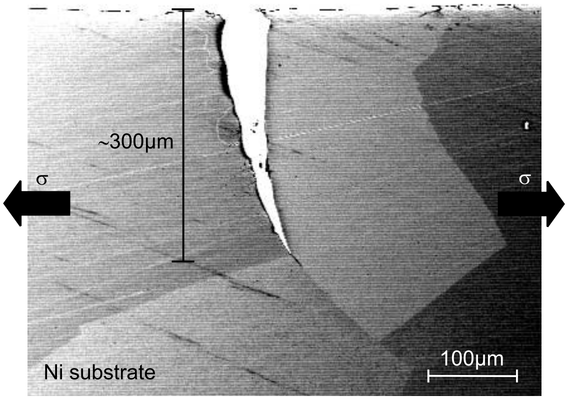

Fig. 4. Backscattered electrons micrograph by SEM of the longitudinal polished section of the tensile specimen (20°C, $\varepsilon = 15\%$) showing one of several intergranular cracks due to Bi penetration (700°C, 1 h, contact through Bi vapour condensation).

example of such a crack is given on the SEM micrograph of Fig. 4: the mean depth of those cracks is 300 μm. It is important to note that SEM observations of polished transversal sections did not permit to detect any grain boundary penetration of bismuth, even after 14 d heat treatment, while tensile test has revealed strong damaging effect of Bi vapour environment even for very short heat treatment (1 h at 700°C).

Bending test at room temperature on a parallelepipedic specimen, after 16 h heat treatment in Bi vapour atmosphere at 700°C, has resulted in fully intergranular fracture of Ni specimen (Fig. 5). As Bi could not be detected neither on secondary electrons SEM images nor by EDS on fracture surface, it was concluded that the thickness of the brittle area was in the nanometric range.

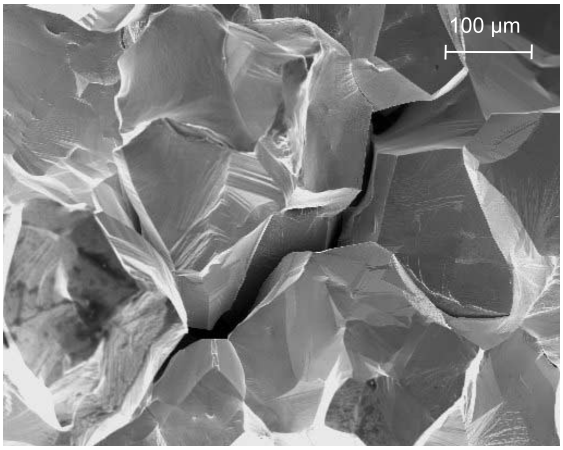

Fig. 5. SEM micrograph of the fracture surface of Ni polycrystal after 16 h heat treatment at 700°C in presence of Bi vapour and room temperature bending test.

Auger analysis was performed at room temperature on one similar specimen (embrittling by Bi vapour condensation, 700°C, 16 h) after in situ bending fracture within Auger spectrometer (Fig. 6). Only Bi and Ni were detected as shown on the AES spectra. Consequently, the brittleness of Ni can be attributed to the presence of Bi in grain boundaries. Whether bismuth is present as a segregation layer or a film of nanometric thickness was analysed in the frame of a quantitative model developed in our previous studies [20,26]. In this model, the accurate determination of the thickness of the brittle area can be obtained from measurements of bismuth to nickel intensity ratios on the fractured surface ($I_{\mathrm{Bi}}/I_{\mathrm{Ni}} = 30$ after 16 h at 700°C) and on the bulk embrittling alloy ($I^*_{\mathrm{Bi}}/I^*_{\mathrm{Ni}} = 43$) of known composition. In the present case, the total thickness of the embrittling area is between 6 and 11 nm. Consequently, it can be concluded that Bi is present in grain boundary as a nanometre-thick Bi-rich film.

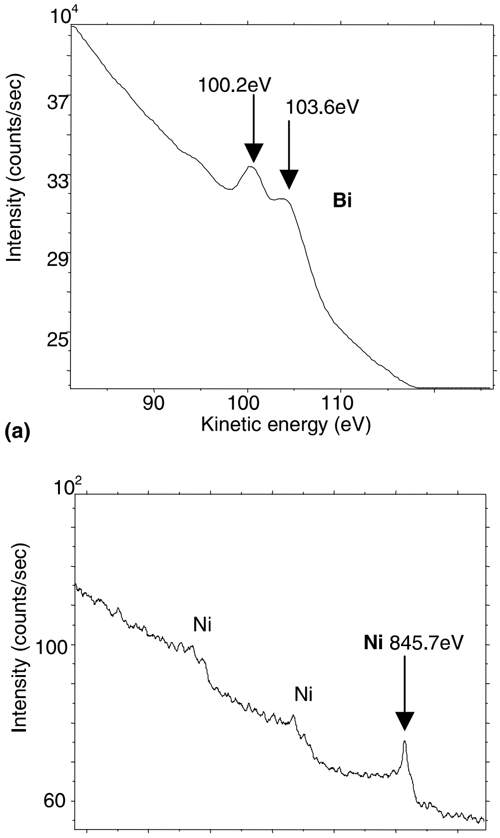

Fig. 6. Direct AES spectra from the surface of the in situ fractured Ni specimen after 16 h heat treatment at 700°C in presence of Bi vapour: (a) Bi peaks and (b) Ni peaks. Double Bi peak at 100.2 and 103.6 eV, and Ni peak at 845.7 eV were used for quantification [21].

It is important to note that a small quantity of liquid Bi at the external surface of the solid Ni (only 4–12 nm in thickness, as estimated by GDOS) is sufficient to cause intergranular penetration and strong embrittlement of solid Ni.

4. Discussion

4.1. Mechanism of transport through bismuth vapour condensation

The possible scenario for bismuth vapour condensation might be as follows: driving forces for bismuth vapour transport and condensation are respectively (i) the gradient in the equilibrium bismuth vapour pressure due to the temperature gradient within the silica ampoule and (ii) the decrease of the nickel substrate surface free energy. Adsorption of the first bismuth monolayer should be very rapid because (i) any adsorbed element strongly reduces the surface free energy and (ii) bismuth is known to perfectly wet nickel surfaces. Then, the bismuth transfer can only proceed if the equilibrium Bi pressure over the nickel specimen is lower than the equilibrium Bi pressure over the Bi-rich alloy. This situation can be achieved by putting the Bi-rich alloy at the slightly higher temperature (700°C $+ \varepsilon$) than that of the Ni specimen (700°C). The resulting gradient in the Bi vapour pressure leads to the transport of Bi atoms and its condensation on the Ni specimen as a second and following layers of bismuth. In the same time, according to the equilibrium Ni–Bi phase diagram, the nickel substrate should dissolve in the condensed Bi layers and tend to the liquidus composition (i.e., 72.4 at.% Bi/27.6 at.% Ni) at 700°C. This process seems to be continuous and should result in the progressive thickening of the Bi-rich layer. In our case the thickness between 4 and 12 nm was obtained after 16 h at 700°C and is sufficient for intergranular penetration and embrittlement to occur.

4.2. Recall of results on grain boundary penetration and embrittlement due to the direct contact

It was previously shown [20] that direct contact between solid Ni and bulk liquid Bi-rich alloy at 700°C results in rapid intergranular penetration, formation of intergranular films and room temperature embrittlement. SEM micrograph from Fig. 7, corresponding to 1 h heat treatment at 700°C, clearly indicates the presence of micrometre-thick intergranular films, as opposed to the indirect contact through bismuth vapours, where no such features were observable (cf. Fig. 3). Note also that intergranular cracks induced by room temperature bending test extended far ahead of the tip of these films. The area between the micrometric film tip and the crack tip was analysed by AES after 4 and 8 h heat treatment at 700°C and has indicated the presence of films of nanometric thickness. According to our quantitative model [26] the thickness of these films was between 2 and 4 nm after 8 h of direct contact. Consequently, it could be concluded that room temperature intergranular brittleness of Ni is due to the presence of both micrometre-thick and nanometre-thick bismuth-rich films and this is not due to a monolayer segregation.

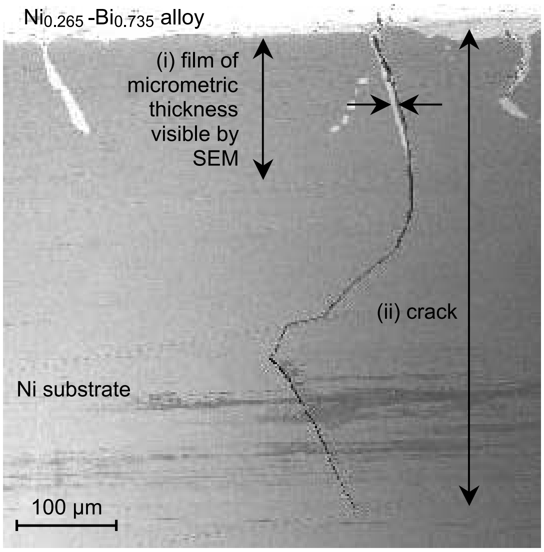

Fig. 7. SEM micrograph showing (i) micrometre-thick intergranular Bi-rich films in a Ni specimen after direct contact with liquid Bi-rich alloy (73.5 at.% Bi–26.5 at.% Ni) at 700°C during 1 h and (ii) an intergranular crack on the same specimen formed after bending test at room temperature. The length of embrittlement is much more important than the length of micrometric films.

4.3. Comparison between direct contact and vapour contact

Heat treatment at 700°C of solid Ni in presence of Bi vapour leads to the formation of a thin Bi-rich layer on external surfaces of solid Ni, ensuring intimate contact between the two metals. The resulting contact seems to differ from the direct contact between saturated liquid Bi-rich alloy and solid Ni, only by the quantity of liquid bismuth on the external surface, i.e., 4–12 nm thick Bi-rich layer instead of bulk liquid. However, both types of contact result in similar intergranular penetration and embrittlement:

(i) *Intergranular penetration of solid Ni by liquid Bi-rich alloy at 700°C.* Direct contact results in the systematic formation of short intergranular Bi-rich films of micrometric thickness and long intergranular Bi-rich films of nanometric thickness [20]. In the case of vapour contact, only long intergranular Bi-rich films of nanometric thickness are formed. No micrometric Bi-rich films were formed, even after 14 d of heat treatment at 700°C.

(ii) *Consecutive room temperature brittleness.* The presence of intergranular Bi-rich films, both micrometre-thick and nanometre-thick, is damaging for the room temperature mechanical properties of solid Ni. In both types of contact intergranular cracks are formed after tensile and bending tests. Note that, following 1 h heat treatment at 700°C, similar average lengths of these cracks are obtained after vapour contact and direct contact.

(iii) *Similar intergranular fracture surfaces.* Both, direct contact and vapour contact result in clearly intergranular fracture surfaces. The only difference lies in the fact that several facets of the fracture surface presented Bi-rich particles after direct contact [20] while no such particles were observed in the case of vapour contact (see Fig. 5) for the same time of heat treatment, i.e., 16 h at 700°C (these particles appear on some facets of Ni fracture surface after a longer time – 3 d – of heat treatment in Bi vapour atmosphere). However, as intergranular fracture occurs even in absence of these particles, their presence is secondary with respect to the intergranular brittleness.

4.4. New concept of high-temperature testing device for LME investigation

It is obvious from the above mentioned results that the nanometre-thick Bi-rich films deposited by vapour condensation on the external surfaces of Ni specimen lead to similar grain boundary penetration rates as from the bulk embrittling alloy. As LME tests require simultaneous action of liquid metal and stress, the phenomenon of Bi vapour condensation could be used in a new concept of testing device, where standard tensile test would be done in presence of Bi vapours. The potential advantage of such a device is much easier operation procedure with the possibility of SEM analysis of cracks and fracture surfaces without the step of liquid metal dissolution, which is essential for the reliable fractographic analysis of LME [27] or other environmentally induced fractures like stress corrosion cracking [28].

4.5. Necessity for low-temperature mechanical testing to reveal intergranular penetration

It appears from this study that neither optical nor standard SEM observations, have adequate spatial resolution to conclude whether nanometric intergranular penetration has occurred or not. The absence of easily observable micrometre-thick films does not imply the absence of intergranular penetration. However, assuming that this penetration results in room temperature brittleness (the case of not embrittling penetration is much more complicated and requires both hydrogen charging and AES analysis), the nanometric films can be easily revealed by any standard mechanical testing as bending or tensile test. It is worth noting that this assumption constitutes the necessary condition for in situ ruptures for AES analysis. The comparison of Fig. 3 (no evidence of intergranular penetration) and Fig. 4 (intergranular embrittlement) strongly supports our point about the necessity of mechanical tests at temperatures where the embrittling material is solidified, to reveal nanometre-thick embrittling films. This approach should be generalised to other potentially embrittling model couples like Fe/Pb, Fe/Bi, Cu/Pb or any industrial couple considered for spallation target in order to check whether intergranular penetration or LME occur or not.

5. Conclusions

1. Heat treatment at 700°C in presence of Bi vapour results in Bi vapour condensation and formation of nanometre-thick layer, as attested by GDOS.
2. Very thin Bi-rich liquid layer (4–12 nm) on specimen surface results in intergranular penetration and consecutive strong intergranular brittleness of solid Ni at room temperature.
3. The embrittlement is due to the presence of intergranular nanometric Bi-rich films (6–11 nm in thickness, for 16 h of heat treatment in Bi vapour atmosphere at 700°C).
4. It is suggested that bismuth vapour condensation can be used in a simple device for LME investigation.
5. Mechanical tests are necessary to reveal nanometric grain boundary penetration, as opposed to standard microscopic observations (SEM, EDS and optical microscopy) on polished sections.

Acknowledgements

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