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Liquid metal embrittlement studies on model systems with respect to the spallation target technology: The importance of nanometre-thick films

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Abstract - Liquid metal embrittlement (LME) is illustrated on the Cu-Bi and Cu-PbBi systems at 300°C using either constant strain-rate tests at 10^{-4} s^{-1} or constant load tests at 25% of yield stress. Intergranular penetration was studied in the Ni-Bi system at 700°C and was shown to result in the formation of slowly growing micrometre-thick and rapidly growing nanometre-thick films. Both induce very strong intergranular brittleness but only micrometre-thick films are visible by SEM on polished cross-sections. Nanometre-thick films were analysed by Auger electron spectroscopy after "in situ" fractures within the spectrometer; in particular, a series of analyses on an Ni bicrystal proved the constant thickness of this film over several hundreds of microns. The severity of embrittlement due to bismuth penetration was confirmed in the analysis of the Ni-PbBi system. Based on these results, it is underlined that technological systems like T 91 steel / Pb or T91 / PbBi should work at temperatures below the wetting transition temperature (T_W), i. e. in the temperature range where intergranular films can't form. If it is not the case, nanometre-thick films should be taken into account, both in the evaluation of the kinetics of embrittlement and in the modelling of intergranular penetration and LME.

Key-words: LME, liquid metal embrittlement, intergranular penetration, wetting, thin films, AES, spallation target, hybride systems, Cu-Bi, Cu-PbBi, Ni-Bi et Ni-PbBi.

Résumé - Etude de la fragilisation par les métaux liquides sur des systèmes modèle en relation avec la technologie des cibles de spallation : l'importance de films d'épaisseur nanométrique. La fragilisation par les métaux liquides est illustrée dans les couples Cu-Bi et Cu-PbBi à 300°C, en utilisant deux types de tests : traction à 10^{-4} s^{-1} ou fluage sous une charge correspondant à 25% de la limite d'élasticité. La pénétration intergranulaire en l'absence de contrainte appliquée a été étudiée dans le système Ni-Bi, à 700°C. Deux types de films intergranulaires ont été identifiés, d'une part des films d'épaisseur micrométrique à croissance lente et, d'autre part, des films d'épaisseur nanométrique à croissance rapide. Les deux induisent une importante fragilité intergranulaire, mais seuls les films d'épaisseur micrométrique peuvent être détectés au microscope électronique à balayage (MEB) sur les coupes polies. Les films d'épaisseur nanométrique ont été analysés par spectrométrie Auger après rupture "in situ" dans le spectromètre; en particulier, une série de mesures effectuées sur un bicristal de nickel a permis de prouver que l'épaisseur de ce film était constante sur une distance de l'ordre de quelques centaines de microns. Le fort effet endommageant du bismuth est confirmé par l'analyse du couple Ni-PbBi. En se basant sur l'ensemble des résultats, on souligne que les couples d'intérêt technologique comme l'acier T91/Pb ou T91/PbBi devraient fonctionner à une température inférieure à la température de transition de mouillage (T_{TM}). Dans le cas contraire, les films d'épaisseur nanométrique doivent être pris en compte à la fois dans l'évaluation de la cinétique d'endommagement et dans la modélisation de la pénétration intergranulaire et de la fragilisation par les métaux liquides (FML).

1. INTRODUCTION

Hybride systems are a new concept for energy production and nuclear waste incineration [1]. They consist of an accelerator and a subcritical nuclear reactor where lacking neutrons are produced by a spallation process i.e. the decomposition of heavy liquid metal nuclei under irradiation by high energy protons (GeV) [2]. This process takes place in the spallation target, where a liquid metal (Pb or PbBi eutectic) is in contact with a solid metal (T91 martensitic steel) at relatively high temperatures (up to 475°C), under irradiation and stress, in general well below the yield stress [3].

One of the main requirements, from the materials point of view, is to ensure that T91 steel can withstand such complex operating conditions. This requirement can best be checked under simulated experimental conditions, as in the LiSoR experiment [4], or real "in service" conditions, as in the Megapie project [4], including post-irradiation tests. While such experiments can validate the T91/Pb or T91/PbBi solutions for a relatively short-term operation, there is a need for understanding all potential damaging mechanisms to ensure the reliability for a long-term operation. The critical points are related either to irradiation effects like hydrogen induced cracking and embrittlement due to helium bubbles or heavier spallation products, or to the liquid metal embrittlement (LME).

We are mainly interested in LME because of potentially unpredictable fractures that can be induced by this phenomenon [5]. In fact, as the spallation target has to contain several tons of liquid metal, the T91steel has to withstand applied or residual stresses under contact with liquid metal and therefore is potentially exposed to the LME phenomenon, i.e. damage of the solid metal due to the synergetic action of stress and liquid metal [6], which can result either in purely transgranular or purely intergranular cracking and fracture. This distinction in the fracture path is less clear in the martensitic microstructure of the T91 steel, where even apparently transgranular cracks might be a result of the weakening of the martensite/martensite interfaces by penetrating liquid metal. Consequently, studying intergranular penetration (IGP) i.e. replacement of grain boundaries by liquid films and LME, appears as most representative of real operating conditions. As we are concerned with stresses, in general, they will be relatively low and erosion-corrosion phenomena might be of prime importance [7], but in some severely loaded points, like the window for protons, they can be only slightly below the yield stress.

IGP studies should be done without stress in a first step and under a fraction of the yield stress in a second step, at a temperature corresponding to the operating conditions. Such conditions applied to systems of technological interest for a relatively short time, compatible with a laboratory scale of time, can't result in any significant embrittlement. In order to study the mechanisms of LME and IGP, those phenomena must be accelerated, either by an adequate structural transformation (for example by heat treatment or by strain hardening) of the solid metal [8] or by the use of model systems, which is the way we have chosen [9, 10].

In our opinion, there are two main questions that should be experimentally addressed in order to understand this type of damage and predict the remaining lifetime of components: first, the kinetics of grain boundary penetration, of crack initiation and of crack propagation in LME, and second, the physico-chemistry and geometry of intergranular films due to the phenomenon of IGP.

The aim of this paper is to provide a synthetic overview of results obtained in our laboratory in the field of LME and IGP on two model systems: Cu-Bi and Ni-Bi, and to enrich the discussion with respect to the spallation target, on the basis of new results: on bicrystals in the Ni-Bi system, and on polycrystals in the Ni-PbBi system. In particular, we are going (i) to illustrate LME on Cu-Bi and Cu-PbBi systems, (ii) to suggest the way the kinetics of crack initiation and propagation should be studied, (iii) to give evidence for the existence and embrittling effect of the nanometre-thick films formed by IGP in the Ni-Bi system, (iv) to indicate how these results can be used to predict the behaviour in the Ni-PbBi system after a simple observation of a polished cross-section and finally (v) to point out different categories of embrittlement models, with respect to the actual temperature and stress conditions.

2. EXPERIMENTAL

LME in Cu-Bi and Cu-PbBi systems: all tests were done on a polycrystalline oxygen free high conductivity (OFHC) copper. Cylindrical specimens (gauge length of 22 mm and diameter of 5 mm) were heat treated to stabilize the grain size at 50 μm (600°C, 24h) and mechanically polished. Tensile tests were done up to fracture at 10^{-4} s^{-1} and 300°C, either in pure liquid bismuth or pure liquid Pb–Bi eutectic alloy. The total time of contact between solid copper and liquid metal in these tests was between 20 and 30 minutes. The yield stress, as determined from the above mentioned tensile tests is of the order of 40 MPa. Preliminary creep tests at 300°C and 10 MPa applied stress were done to evaluate the possibility of studying grain boundary penetration under stress. The type of fracture surface and the depth of IGP during the tensile tests were assessed through observations of the longitudinal polished sections, before and after room-temperature bending tests.

IGP in Ni-Bi and Ni-PbBi systems: tests were done either on a polycrystalline high purity Ni (C, S, N, C, each < 10 wt. ppm) or on a 26° <110> tilt bicrystal, always at 700°C, which is above all peritectic points. Heat treatments were done in silica tubes sealed under argon, where, after 30 min of temperature stabilization, liquid oversaturated bismuth ($Bi_{0.724}$-$Ni_{0.276}$) was put in contact with solid nickel for a period of 4 or 8 hours. Some shorter heat treatments, between ½ and 2 hours, were done without direct solid/liquid contact, i.e. in presence of Bi vapour. One particular heat treatment was done to check IGP in the Ni/PbBi system, where a drop of a saturated PbBi eutectic alloy (saturation with 5wt% of Ni [11]) was deposited on a Ni surface for 16h at 700°C. The depth of penetration was analysed from observation of polished cross sections before and after room temperature mechanical tests.

Auger spectroscopy: all AES tests were done after "in situ" fracture, either by bending (Ni-Bi) or tensile (Cu-Bi) tests. The thicknesses of the intergranular films were deduced from these measurements using a model of a nanometre-thick film. The details of the quantification procedure are given in [12]. One particular test was done on a bicrystalline specimen heat-treated for 1.5 h (+ 30 min of temperature stabilization), impact broken by bending within the Auger spectrometer main chamber and analysed by point-to-point spectroscopy every 100 μm, from one external surface to the other.

3. RESULTS

3.1. LME in Cu-Bi and Cu-PbBi systems

The effect of a liquid metal on tensile curves of polycrystalline copper at 300°C and 10^{-4} s^{-1} initial strain-rate is shown in *figure* 1. The plastic elongation to fracture ε_R drops from 20% for the test in air down to 7% in eutectic PbBi and 1% in pure Bi. It is striking that the main crack in both cases starts after some plastic deformation, which implies significant strain-induced hardening, and propagates in a brittle manner. A detailed analysis of these curves in terms of crack initiation and crack propagation has been given elsewhere [13]. It is worth to be mentioned that, in the tensile test in PbBi, the nominal stress in the liquid metal, for a given plastic deformation, is systematically lower than in air. Such a behaviour is significant of an important reduction in effective specimen section and was confirmed by the observation of long intergranular films (*figure 2*).

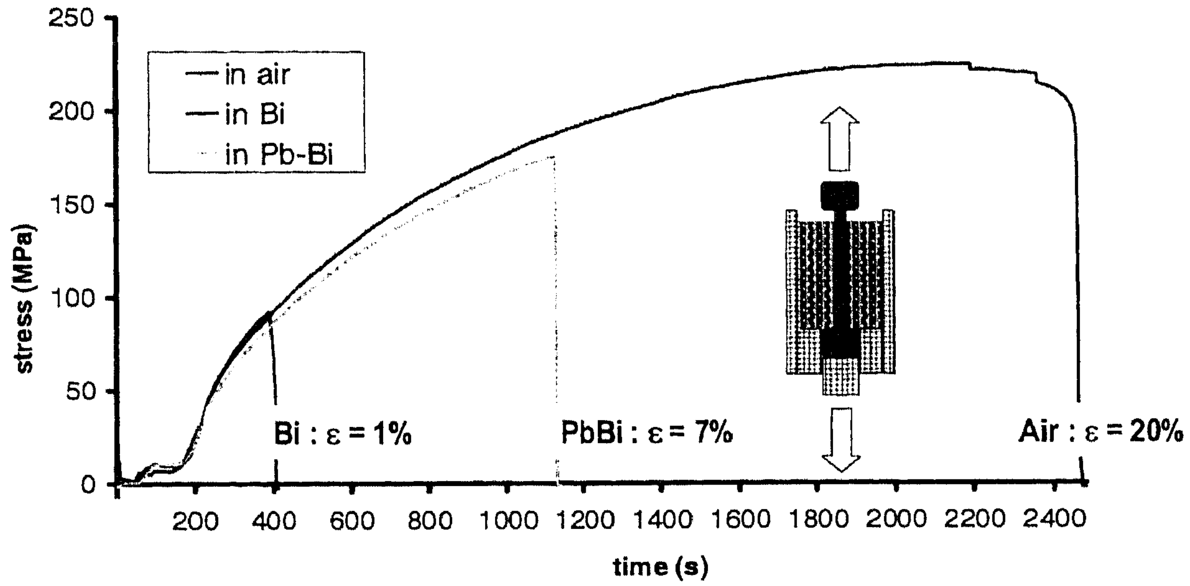


Figure 1. Results of tensile tests at 10^{-4} s^{-1} and 300°C on polycrystalline copper in air (plastic deformation at fracture $\varepsilon_R = 20\%$), eutectic Pb-Bi alloy ($\varepsilon_R = 7\%$) and pure Bi ($\varepsilon_R = 1\%$).

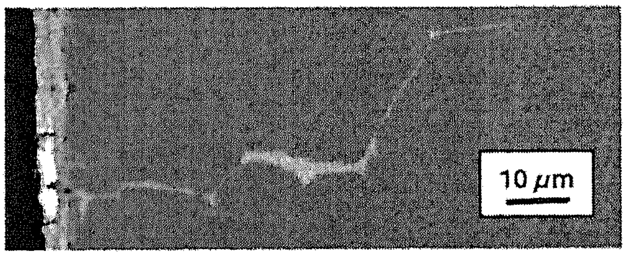


Figure 2. SEM image of a longitudinal polished section of copper specimen after tensile test in liquid PbBi alloy, showing a long intergranular crack filled with liquid alloy.

Such several micrometer-thick films are probably the result of crack formation and filling with liquid metal. On the contrary, in the tensile test in liquid Bi, the nominal stress in the liquid metal is the same as in air, which is significant of limited crack initiation and very rapid crack propagation from one relatively small crack. The final fracture in Bi and in Pb-Bi is purely intergranular.

LME fracture in tensile tests occurs very rapidly because of a relatively high strain-rate, but the stress level that induces fast propagation of a critical crack (90 MPa in Bi and 170 MPa in PbBi) is far above the yield stress of copper (40 MPa). Such experimental conditions are suitable for rapid evaluation of the severity of different environments but do not reproduce the conditions of "in service" solicitation. Consequently, an alternative method to reveal LME, i.e. constant load tests, was used. Tests were performed at 300°C in pure Bi at a stress level as low as 10 MPa, which corresponds to 25% of the yield stress (*figure 3*). Under these conditions, the creep rate of copper in air was of the order of 10^{-9} s^{-1}, however the same thermomecanical conditions, but in liquid bismuth, resulted in a strong acceleration of creep rate and brittle intergranular fracture after 100 hours. These preliminary results indicate a possibility to analyse the degree of embrittlement, as a function of a percentage of the lifetime, by a three step procedure: (i) interrupted constant load tests at 300°C (for ex. 30% of lifetime in *figure 3*), (ii) room-temperature tensile test to open all embrittled grain boundaries and (iii) observation of longitudinal polished cross-sections. Such a procedure allows to reveal the depth of embrittlement (*figure 4a*) and to determine the kinetics of embrittlement expressed as the average depth of embrittlement as a function of the percentage of lifetime at a given stress. However, the analysis of intergranular films in this case is not relevant of the embrittlement process because the crack opening is immediately followed by filling with liquid metal (*figure 4b*). Consequently, the analysis of intergranular films can only be done after tests without any applied stress.

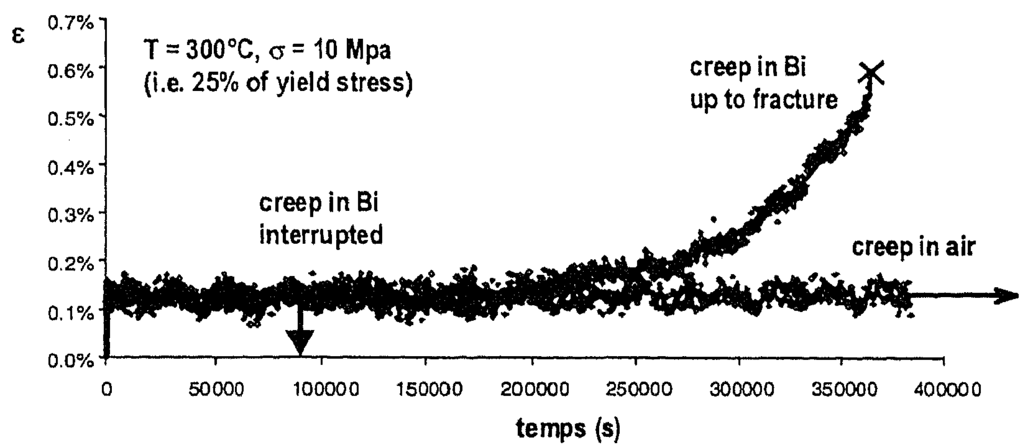


Figure 3. Results of constant load tests at 10 MPa and 300°C on polycrystalline copper in pure Bi with no significant deformation up to 50% of lifetime (interrupted test) and final fracture after 100 hours at $\varepsilon = 0.5\%$ plastic deformation (test on cylindrical specimens immersed in liquid bismuth). Note that the accelerated deformation for (t > 200000s) results from both creep and crack opening.

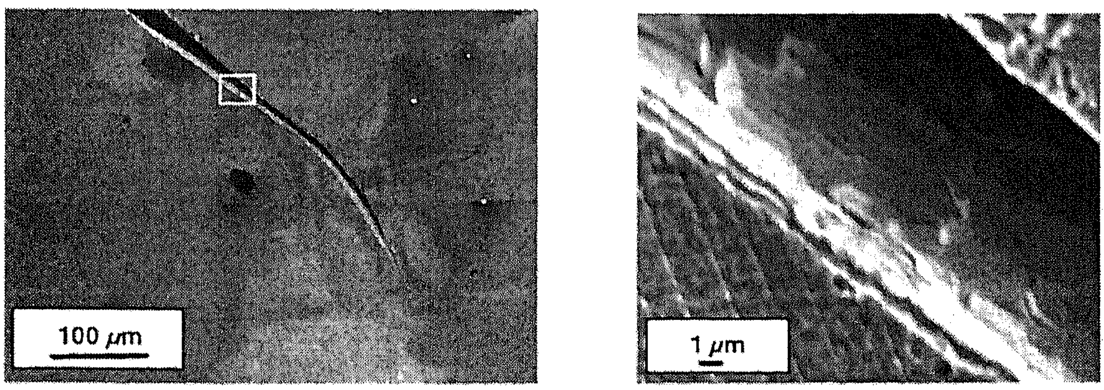


Figure 4. SEM images of longitudinal polished sections of a copper specimen after interrupted constant load test in liquid Bi and subsequent room-temperature tensile test, showing important intergranular cracks (left) and presence of intergranular, submicrometer-thick films (right, which is an enlarged view of the area marked by a white rectangle). The presence of a bismuth film within the crack is a result of crack opening immediately followed by filling with liquid bismuth.

3.2. Intergranular penetration in Ni-Bi

A series of preliminary tests [14] and the analysis of literature [15, 16] has allowed to choose the Ni-Bi system at 700°C to study the phenomenon of IGP, first, because it was apparently very easy for experimental observation on polished cross-sections and second because bismuth itself and its intermetallic compounds are inherently brittle, therefore the analysis of the area ahead of the visible penetration front [16] was in principle possible by Auger Electron Spectroscopy (AES).

In general, the contact between liquid metal and solid metal always results in grain boundary grooving and formation of a dihedral equilibrium angle. With increasing test temperature, these angle drops down to zero at a so-called wetting transition temperature (T_W). Above this temperature, grain boundary replacement by a liquid film is energetically favourable even without any applied or residual stress and results in the formation of intergranular films, like those of micrometric thickness after heat treatment of 1h at 700°C, easily observed on a polished cross-section (*figure 5*). Characteristic features that differentiate these micrometre-thick films from intergranular grooves are the important length-to-thickness ratio (here almost 100) and the existence of two roughly parallel solid/liquid interfaces. The very acute tip of these films is compatible with the thermodynamical condition of IGP (dihedral angle equal to zero). As the composition of the Bi-rich liquid ($Bi_{0.735}$-$Ni_{0.265}$) is close to that of the Bi_3Ni intermetallic brittle phase, intergranular films are supposed to induce intergranular brittleness, at least up to the tip of these micrometre-thick films.

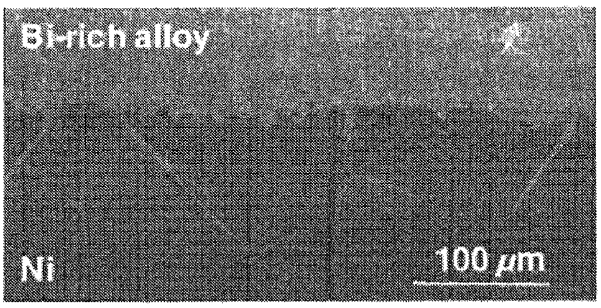


Figure 5. SEM micrograph of a polished cross-section of a nickel specimen after 1h contact at 700°C with saturated Bi-rich alloy, showing several micrometer-thick films, due to the phenomenon of intergranular penetration (without any applied stress).

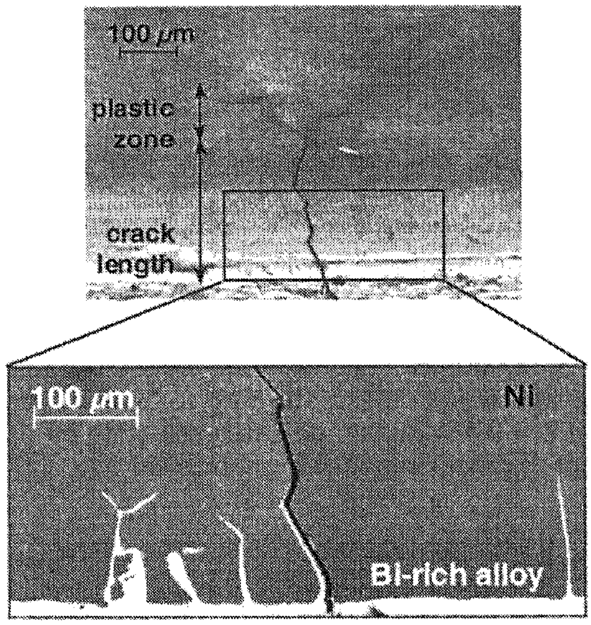


Figure 6. SEM micrographs of polished cross-sections of a nickel specimen after 1h contact at 700°C with saturated Bi-rich alloy and subsequent room-temperature bending test showing that the depth of embrittlement is much longer than the length of micrometre-thick films.

The result of the room-temperature bending test on Ni specimen, previously heat treated for 1h at 700°C in direct contact with liquid Bi-rich alloy, is very striking (*figure 6*). In fact, cracks start before general yielding and open up to a well defined depth, far in excess of the length of the micrometre-thick films. Increasing the bending displacement doesn't result in further increase of the embrittlement depth, but only leads to a wider crack and clearly reveals the plastic zone in front of the crack (*cf. figure 6*). It must be underlined that the depth of embrittlement (here 400 μm) is much more important that the average length of micrometre-thick film (here 100 μm). While it is clear that the embrittlement in the first 100 μm is due to the presence of the micrometre-thick film, the origin of the embrittlement between the tip of this film and the tip of the crack was assessed by AES.

In order to perform AES measurements, heat treatments were done for a time long enough to induce fully intergranular fracture. *Figure 7* represents the result of AES measurements in the middle of a square 2x2mm^2 section of an Ni specimen after heat treatment (8h at 700°C in contact with liquid Bi-rich alloy) and "in situ" impact bending fracture in the main chamber of the Auger spectrometer. Only bismuth and nickel were detected. The quantity of bismuth, expressed by the bismuth-to-nickel ratio (here I_{Bi}/I_{Ni} = 10), is far above a monolayer thickness and consequently a model of a nanometre-thick film was proposed. A detailed analysis of this model has resulted in a quantification procedure that allows to determine the thickness of the film from the experimentally measured I_{Bi}/I_{Ni} ratio (*figure 8*). After 8h of direct contact with a Bi-rich alloy at 700°C, this thickness was calculated to be between 2 and 4 nm depending on the Auger electron collection angle (which can't be known because of the use of polycrystals).

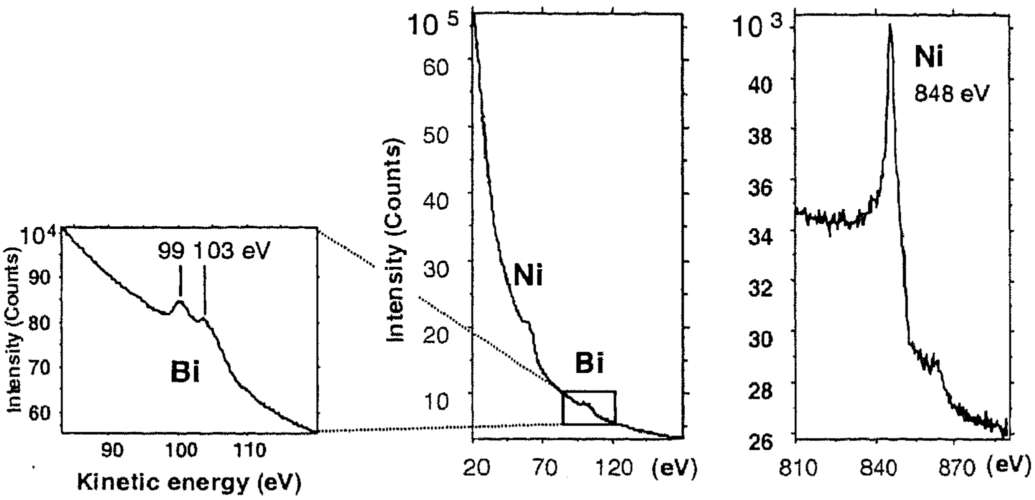


Figure 7. Results of Auger electron spectroscopy measurements on Ni fracture surface after 8h heat treatment at 700°C in direct contact with Bi-rich alloy and subsequent "in situ" fracture, showing that in the area ahead of the tip of the micrometre-thick film, only Bi and Ni were detected.

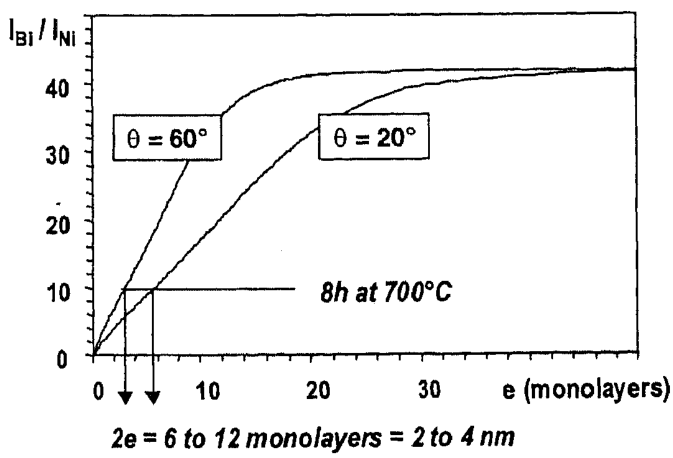


Figure 8. Result of a quantification procedure based on the model of nanometer-thick films, which allows a determination of the actual thickness of the film from the experimental I_{Bi}/I_{Ni} ratio. The value of this ratio after 8h at 700°C is equal to 10, which corresponds to a total thickness between 2 and 4 nm, depending on the unknown (measurements on polycrystals) Auger electrons collection angle - θ.

AES results clearly demonstrate that the embrittlement, in the area ahead of the micrometre-thick film, is due to the presence of bismuth as a nanometre-thick film. It must also be pointed out that this measurement was done at one point only, situated at a distance of 1 mm from the external surface, which doesn't allow to answer the question whether the thickness of this film is constant or not (a question of two parallel solid/liquid interfaces, one of the characteristics of IGP).

4. DISCUSSION

4.1. The interest of studying intergranular penetration

A very damaging effect of IGP is due to the extreme localisation of this phenomenon at grain boundaries and to the nature of the intergranular films that are formed. It has been shown that micrometre and nanometre-thick films have the same effect on room-temperature mechanical properties, namely they induce strong intergranular brittleness under applied tensile stress. At high temperature the situation is even worse because these films are liquid and cannot withstand any applied stress. The localized nature of IGP together with the inability of liquid films to transfer the stress make it very dangerous. Additionally, the existence of very long nanometre-thick films makes almost impossible the prediction of the depth of embrittlement from the observation of polished cross-sections. The application of room-temperature tensile tests appears necessary, in particular in the case of embrittlement through bismuth vapour, where only nanometre-thick films are present [10]. The kinetics of intergranular film formation (micrometre-thick and nanometre-thick) must be known in order to predict the remaining lifetime for a given solid metal / liquid metal system. It must be also underlined that real structures should work at a temperature below T_W, even if the overall thermodynamical conditions ensure the formation of a protective layer.

4.2. Kinetics of intergranular film formation

A series of heat treatments was done at 700°C for times ranging from 15 min to 4h in order to determine: (i) the average length of micrometre-thick films from the observation of longitudinal polished sections and (ii) the depth of embrittlement from the measurement of crack length after bending tests (*figure 9*). For each heat treatment duration, the embrittlement depth is equal to the sum of the length of the micrometre-thick film and of the length of the nanometre-thick film. Even this limited number of measurements clearly indicates that the embrittlement depth increases much faster than the length of micrometre-thick films. The kinetics of depth embrittlement is almost linear while the kinetics of micrometre-thick films follows approximate kinetics of $t^{1/3}$. Consequently, with increasing heat treatment duration, the role of nanometre-thick films becomes more and more important.

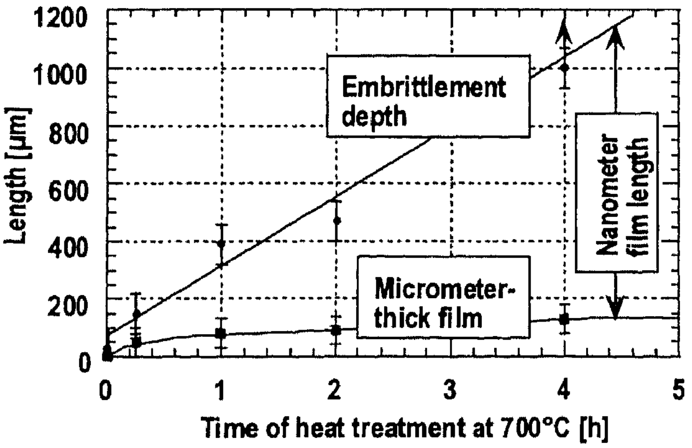


Figure 9. Kinetics of depth embrittlement and micrometer-thick film formation determined from a series of measurements on Ni polycrystals heat treated at 700°C in the presence of bismuth and showing that the length of nanometer-thick film becomes dominant for longer times.

4.3. Geometry of the nanometre-thick films

In order to measure the evolution of the nanometre-thick film thickness as a function of a distance from the external solide/liquid interface for a given heat treatment, a series of measurements was done on a bicrystal heat-treated for 2h at 700°C in the presence of Bi vapour (no formation of micrometre-thick films). Using a bicrystal offers the advantage of having a very long grain boundary with the same crystallographic characteristics, which allows several point-to-point measurements with the same macroscopic orientation of the grain boundary and known Auger electron collection angle (θ = 20°). IGP in this bicrystal appeared to be faster than in the case of polycrystals (*cf. figure 9*): 2h heat treatment resulted in complete embrittlement of an approximately square 1.8x1.8 mm^2 section. AES measurements were done after "in situ" bending fracture, along a line going through the centre of the fracture surface, from on side to the other. AES spectra were collected every 100 μm; the I_{Bi}/I_{Ni} ratios were measured from each spectrum and used in the model of the nanometre-thick film in order to determine its thickness (*figure 10*). All measurements are independent from each other and give a value of 5 ± 1 monolayers for a half-thickness of the film, which corresponds to a total thickness of the order of 3.0 nm. This result clearly indicates that the film is characterized by a constant thickness, i.e. the two solid/liquid interfaces were parallel during IGP.

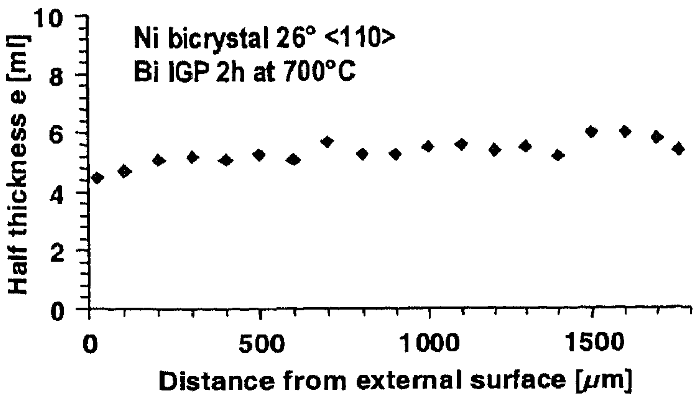


Figure 10. Result of a series of measurements on the fracture surface of 26° <110> tilt bicrystal after 2h heat treatment at 700°C in Bi vapour atmosphere and subsequent "in situ" fracture, showing that the thickness of the intergranular film remains constant (e = 5 monolayers, i.e. 2e = 10 monolayers, which corresponds to 3 nm) across the whole fracture surface.

It is also worth noting that nanometre-thick films are characterized by an extremely high length-to-thickness ratio. For example, the length of the crack in *figure 6* is of the order of 300 μm, while its thickness is certainly lower than 3 nm (only 1h heat treatment at 700°C). It gives a value above 100 000 (!) for the length-to-thickness ratio, which is three orders of magnitude higher than for micrometre-thick films.

Beyond the extreme brittleness induced by nanometre and micrometre-thick films, this strong difference in the length-to-thickness ratio, as well as in the kinetics of formation has at least one theoretical consequence: any model of intergranular penetration has to describe either (i) the formation of micrometre-thick films with very slow kinetics ($l = A.t^{1/3}$) or (ii) the formation of nanometre-thick films with very fast linear kinetics or (iii) both of them, with an explicit parameter that controls the transition between these two behaviours.

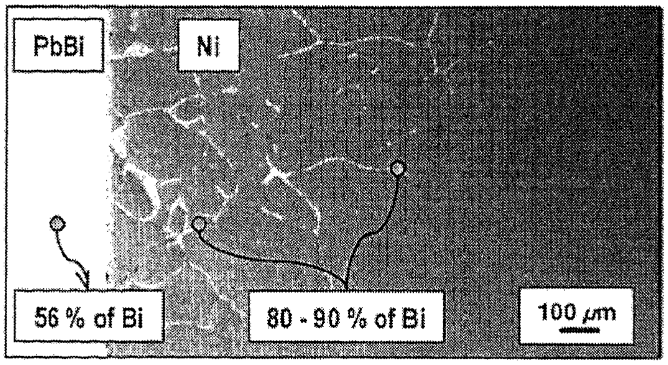
4.4. The interest of using model systems: example of the Ni-PbBi system

The aim of all studies on model systems is not only to collect reliable experimental data in order to check the validity of existing models and propose a new one, but also to offer a qualitative and quantitative prediction of the behaviour for a new system. In the field of IGP studies, only some qualitative predictions are possible at present. As we are concerned with a spallation target technology, a T91/Pb system has been chosen, but there are at least two reasons to replace pure Pb by the Pb-Bi eutectic: much lower melting point (125°C instead of 327°C) and higher resulting neutron flux [4].

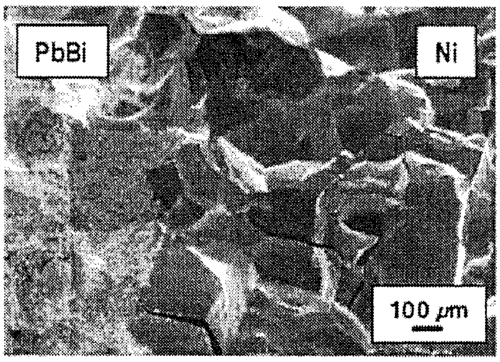
To answer the general question whether replacing liquid lead by liquid lead-bismuth eutectic can be harmful in any way to a solid metal, we propose to analyse the behaviour of the Ni/Pb-Bi system with respect to the Ni/Pb system.

It is known from literature data [17, 18], that the contact between solid nickel and liquid lead at 740°C results in IGP with the formation of micrometre-thick films, the geometry of which is very similar to that of films formed in the Ni-Bi system. This similarity suggests the possible existence of nanometre-thick films that can induce LME, if they are in a liquid state. There is also an important difference with respect to the Ni-Bi: as lead is ductile and there is no intermetallic compounds in the Ni-Pb phase diagram, such films shouldn't result in room temperature intergranular brittleness.

A contact between solid Ni and a drop of saturated PbBi-rich alloy was realized for 16h at 700°C. The observation of polished cross-sections revealed an extensive IGP with formation of micrometre-thick films for depths up to 900 μm (*figure 11a*), depending on the distance with respect to the position of the drop. The analysis of the composition of these films by energy dispersive X-rays spectroscopy (EDX) revealed an important enrichment in bismuth, with up to 90 wt% Bi at the tip of the micrometre-thick film, as opposed to 56 wt% Bi at the former solid/liquid interface (eutectic composition of the bulk liquid alloy). Such an enrichment leads to the fact that the conditions at the tip of the micrometre-thick films are very close to those in the Ni-Bi system. Consequently, the presence of nanometre-thick films and room-temperature brittleness could be postulated and the brittleness was effectively observed (*figure 11b*). As in the Ni-Bi system, the area of embrittlement, in fact the whole fracture surface presumably covered by a brittle nanometrre-thick Bi-rich film, is dominant with respect to the micrometre-thick film (here only 300 μm wide because of the rupture close to the edge of the drop). As Bi itself is as brittle as its intermetallic compounds in the Ni-Bi system, its presence in the grain boundaries of any structural material must be avoided.



a.



b.

Figure 11. SEM images of a nickel specimen after 2h contact at 700°C with saturated Pb-Bi eutectic:
a. polished cross-section (left) giving evidence of IGP with strong enrichement in Bi at the tip of micrometer-thick films, therefore suggesting the presence of strongly embrittling nanometer-thick films (here invisible and impossible to be detected by EDX),
b. fully intergranular fracture surface, obtained by a room-temperature bending test, which confirms the presence of a nanometer-thick film.

In the spallation target, the solid martensitic steel is supposed to be separated from liquid Pb or Pb-Bi by a protective oxide layer, the existence of which is controlled by the oxygen partial pressure but accidental contact has to be taken into account. The unsuitable presence of liquid films at grain boundaries (Pb or PbBi) and embrittling effect of these films after solidification (PbBi and Bi) implies that the operating temperature for a solid structural steel / liquid metal target must be lower than the wetting transition temperature (T_w). To check whether this is the case with the T91/Pb and T91/PbBi systems, tests should be done under very low oxygen partial pressures that exclude the formation of oxide layers and followed by observations of polished cross-sections and AES measurement after "in situ" fracture, using the procedures developed in this study on a series of model systems.

4.5. Towards models of IGP and LME

The aim of this short paragraph is to point out the existence of some different stress-temperature fields, with in principle an equivalent number of models to describe intergranular penetration or liquid metal embrittlement.

The wetting transition temperature (T_w) can be seen as a frontier, which separates the range of intergranular diffusion (IGD, $T < T_w$) from the range of intergranular penetration (IGP, $T > T_w$) (*figure 12*). These two phenomena can be clearly distinguished by at least three characteristics: (i) the dihedral angle at the emerging grain boundary which defines T_w, (ii) the absolute value of intergranular film thickness, which is of the order of a monolayer for IGD as opposed to several monolayers or even micrometric thickness for IGP and (iii) the evolution of the thickness, which rapidly evolves and drops below a monolayer thickness for IGD as opposed to the constant thickness either in the micrometre-thick range or in the nanometre-thick range for IGP. In both cases the situation can be complicated by composition changes, if the liquid phase is an alloy like an eutectic PbBi alloy.

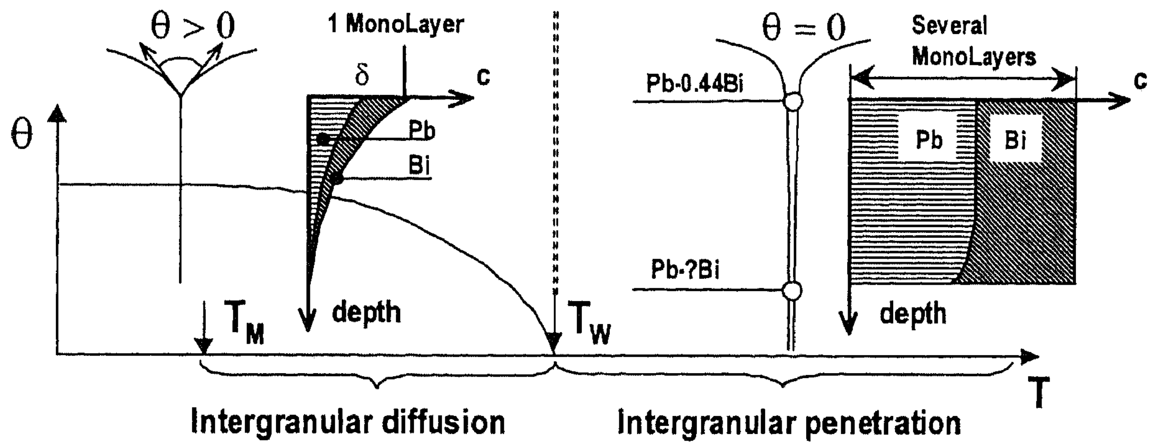


Figure 12. Schematic representation of intergranular phenomena in a solid/liquid (here Pb-Bi) system with respect to T_W, here supposed to be significantly higher then the melting temperature T_M. Below T_W, only IGD occurs. Above T_W, IGP occurs and results in the formation of intergranular films of micrometric and/or nanometric thickness. In both cases the Bi/Pb ratio can vary along the IGD or IGP front.

Both phenomena (IGD and IGP) can occur without any applied or residual stress; in these cases they are driven by thermodynamical forces only [19, 20] and result in modifications of grain boundary chemistry.

These modifications (segregation-like monolayers or intergranular films of nanometric or micrometric thickness) can induce room-temperature brittleness: in this case we are speaking about Liquid Metal Induced Embrittlement and the pertinent studies are those of IGD or IGP.

Both phenomena (IGD and IGP) can also occur in the presence of applied or residual stresses, where crack initiation and propagation are controlled by a synergy between the action of the liquid metal and the applied stress or strain-rate: in this case we are speaking about "true" Liquid Metal Embrittlement and the pertinent studies are those of IGD or IGP under stress (constant load or constant strain-rate or crack propagation tests on compact-tension (CT) specimens) [21, 22].

It is obvious from this schematic presentation that for a given solid/liquid system, there can be at least six different combinations of temperature (below or above T_W) and stress ($\sigma = 0$ or σ applied during the contact with liquid metal or after this contact at room temperature); therefore several models of embrittlement, based on different elementary mechanisms can be proposed. In particular, these models might not be the same depending on which side of T_W the actual analysis is done. Kinetic studies around T_W appear as critical with respect to the modelling of embrittlement due to the presence of liquid metal.

5. SUMMARY AND CONCLUSIONS

1. Liquid metal embrittlement (LME), defined as a rapid damage due to the synergy between liquid metal and stress, was illustrated on pure copper at 300°C by two kinds of mechanical tests:

- first, constant strain-rate tests at 10^{-4} s^{-1}, which resulted in a strong decrease in plastic deformation from 20% in air down to 7% in the Pb-Bi eutectic alloy and only 1% in pure liquid bismuth; such a test constitutes a rapid way to evaluate the severity of liquid metal effects,

- second, constant load tests at 10MPa, i.e. 25% of yield stress, which is representative of "in service" conditions and results in intergranular fracture; it is postulated that a series of such interrupted tests allows to assess the kinetics of crack initiation and propagation.

2. Intergranular penetration (IGP) without stress, which occurs above the wetting transition temperature (T_W) and results in the replacement of the original grain boundary by a liquid intergranular film, was studied in the Ni-Bi system at 700°C and led to the following conclusions:

- intergranular films are composed of short micrometer-thick films (100 μm after 1h at 700°C) and long nanometre-thick films (300 μm after 1h at 700°C),

- the kinetics of nanometre-thick film formation (almost linear) is much faster than that of micrometer-thick film formation (proportional to $t^{1/3}$),

- both films induce strong intergranular brittleness at room temperature, which can be called Liquid Metal Induced Embrittlement (LMIE); it can be explained by the intrinsic brittleness of bismuth or intermetallic compounds formed during the cooling.

3. The eutectic PbBi alloy is potentially dangerous with respect to pure Pb, as indicated by a strong Bi enrichment measured at the tip of the micrometer-thick films in a model Ni-PbBi system and the consecutive room-temperature brittleness.

4. Modelling of embrittlement due to the contact with a liquid metal should be done in a well defined domain of (i) temperature, with respect to T_W and (ii) stress with respect to the yield stress.

5. As LME and LMIE can result in intergranular fracture after a limited plastic deformation, solid metal / liquid metal systems of technological importance like T91 / Pb or T91 / PbBi should be chosen in such a way that the operating temperature is lower than T_W, even if theoretically there exists a protective layer that prevents the liquid metal from a contact with the solid metal.

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