

MSL compatible isothermal furnace insert for high temperature shear-cell diffusion experiments

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Abstract. For long-time diffusion experiments shear-cell techniques offer more favourable terms than the traditional long capillary techniques. Here, we present a further developed shear-cell that enables the measurement of diffusion coefficients up to temperatures of 1600 °C. Hence, diffusion experiments can be carried out at temperatures not accessible until now by conventional capillary or shear-cell techniques. The modified shear-cell, which can contain up to six samples of a total length of 90 mm and a diameter of 1.5 mm, is built of 30 shear discs of 3 mm thickness each. It is operated in an isothermal furnace insert which can be accommodated in the Materials Science Laboratory of the International Space Station. This provides the opportunity that the shear-cell can be applied to microgravity and to ground-based experiments, respectively. The heater insert with an overall length of 518 mm and a diameter of 210 mm consists of four heating zones with a total power of 3.5 kW. Temperature homogeneity along the graphite sample compartment is better than 2 K at 1600 °C. Details of the new design are discussed and results of first successfully performed heating and shearing cycles are presented.

1. Introduction

Diffusion is a vital topic in solid-state physics, chemistry, metallurgy and materials science [1]. A thorough understanding of diffusion in the liquid state of multicomponent metallic alloys and semiconducting alloys is crucial for materials development and engineering [2]. Traditionally, diffusion coefficients are measured using long capillary techniques [2]. This technique, whereby the spatial distribution of a tracer or the spatial dependence of composition along a thin rod-like sample is determined after a full heating, annealing, and cooling cycle, proved highly successful for solids [1]. However, for determining diffusion coefficients in liquids a number of problems are encountered that negatively influence the accuracy of the data. Segregation during heating, microstructure and shrinkage hole formation during solidification and density changes between liquid and solid are just a few of the important ones. For binary systems accurate diffusion coefficients can be obtained by in-situ monitoring the long capillary with X-ray radiography [3]. However, for alloys with no X-ray contrast, alloys that feature a complex phase diagram upon heating with e. g. largely differing melting points for the two samples constituting the diffusion couple, or multicomponent alloys, the use of the so-called shear-cell method is indispensable

to determine accurate diffusion coefficients. Successful shear-cell experiments on measuring self diffusion in liquid mercury [4] and impurity diffusion in liquid Sn and Cu were reported in the past [5]. Moreover, for multicomponent alloys shear-cells were used to determine chemical diffusion coefficients [6, 7]. For binary samples with X-ray contrast the shear-cell technique can now also be combined with X-ray radiography [8]. In a shear-cell the two different samples of a diffusion couple are separately melted. After some time for homogenization the samples are brought into contact with each other starting the diffusion process. In case of non in-situ imaging with X-ray radiography the diffusion process is terminated by shearing of the diffusion couple into numerous sections after some annealing time. Thereby the diffusion profile of the liquid is frozen in. The individual sections of the solidified sample are then analyzed for their composition. Even so all of the previously mentioned problems encountered for classical long-capillary experiments on liquid samples can be overcome by the shear-cell technique, the measured diffusion coefficients might still be erroneous due to buoyancy-driven convective flow. The latter can only be overcome by performing experiments under reduced-gravity conditions which allows purely diffusion conditions [6]. To this end, a shear-cell has already been successfully used aboard a FOTON satellite up to maximum temperatures of 770 °C [7] and up to 850 °C on ground [9]. The FOTON setup with its small diameter relied on direct heating via a molybdenum-wire resistance heater brought in contact with the cartridge surface. The cartridge and heater were tightly wrapped in Al₂O₃-felt insulation [10]. In order to reach higher temperatures and to be able to process more samples simultaneously the original FOTON design has to be modified. Here, a further developed version of a shear-cell is presented that now enables to simultaneously measure diffusion coefficients for up to six samples at temperatures of up to 1600 °C. In order to achieve these higher temperatures and to enable processing of the required larger-sized shear-cell an isothermal furnace with a large bore diameter has to be used. Details of the complete experimental facility developed by Astrium GmbH and partners and performance parameters from first tests are presented.

2. Isothermal Furnace

The isothermal furnace with an overall length of 518 mm and a diameter of 210 mm offers a bore of 68 mm diameter for the experimental cartridge insertion. It consists of four independently operated heating zones with a total power of 3.5 kW. The heating zones consist of four meandered graphite heaters. Using these heaters a maximal temperature of 1600 °C at the sample position can be achieved at a maximal heating rate of 60 K min⁻¹. With this maximal temperature determining diffusion coefficients of high melting point alloys like Al-Ni and Si-Ge becomes possible. As verified experimentally the furnace provides a homogeneous temperature zone of 90 mm length at 1600 °C with a gradient of less than 2 K axially. This equals to a gradient of less than 0.02 K mm⁻¹ axially. The furnace can be operated under vacuum or under inert gas atmosphere (Ar or He), respectively. Typically, the vacuum is better than 9·10⁻⁵ mbar at ambient temperature and 1.2·10⁻⁴ mbar at experimental temperature. All measured data are monitored and saved by a closed loop control process computer. The process unit also controls several experiment environment values and allows online telecommanding. The isothermal high temperature furnace insert, shown in figure 1, is fitted in a process chamber fully compatible to the one used in the Materials Science Laboratory (MSL) aboard the International Space Station (ISS). The furnace is further fully compatible with power, cooling, vacuum, and gas supplies available in the MSL. For ground-based diffusion experiments the process chamber is mounted on a decoupled optical table and can be brought into a vertical position. This is required for aligning the capillary axis parallel to the gravitational force. As a result a stable density layering of the liquid column is achieved. This helps to suppress convective flow in ground-based experiments.

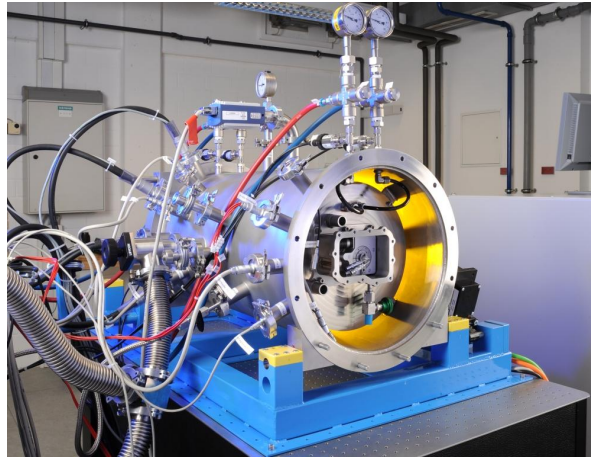


Figure 1. Process chamber with integrated isothermal high temperature furnace and open ended experimental cartridge in horizontal position. As described in the text the entire chamber can be tilted vertically for the experiment.



Figure 2. Newly designed high temperature shear-cell. The graphite articulation tube with lead-through for holding bolts is shown. The front part shows individual shear discs as they are integrated in the shear-cell. Cut-outs for disc motion as well as holes for diffusion samples are visible.

3. Shear-Cell

The here presented modified shear-cell is based on the original FOTON design [11, 12]. Its size and operating mechanism were modified according to MSL requirements. The novel shear-cell consists of 30 graphite discs each with a thickness of 3 mm and a diameter of 30 mm. Graphite is chemically inert for a large number of melts of interest. It can be precisely machined and shows moderate friction for shearing. The discs have six equally spaced holes of 1.5 mm diameter at a distance of 8.5 mm from the disc centre. Hence, a total of six different diffusion couples can be simultaneously processed. If required, the diameter of the capillary holes can be modified within certain limits for future application without compromising functionality or stability of the shear-cell.

The shear discs and reservoirs are mounted on a middle axle and integrated into a slotted, articulated tube, shown in figure 2. The middle axle also carries three type-S thermocouples at

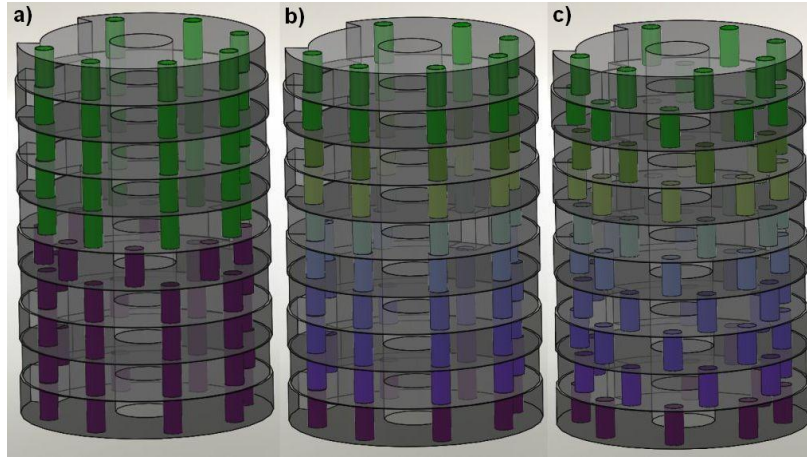


Figure 3. Visualisation of the shear-cell mode of operation: a) Separated diffusion couples with one shear-disc out of alignment for separate melting during heating and followed by a homogenisation phase. b) Diffusion pair in contact during diffusion annealing. c) Termination of the diffusion process by shearing of every other disc, effectively freezing in the liquid diffusion profile. The last step is followed by cooling.

either end and at the center of the diffusion couple. Graphite bolts are gearing through the slots into cut-outs on the shear-discs, limiting the elbow-room of each disc. A mechanical rotation of the articulated tube by a boron nitride driving shaft moves every other disc on the middle axle. In a typical starting position all discs but one are aligned at the end position in clockwise rotation direction. Hence all but one of the capillary holes are aligned for each diffusion couple. The one disc located e. g. in the center of the disc stack is displaced by 30° counterclockwise [cf. figure 3 a)]. With the samples fully melted and homogenised clockwise rotation of this displaced disc brings into contact the two initially separated samples. As a result diffusion is initiated and a diffusion profile develops with time [cf. figure 3 b)]. Counterclockwise rotation of every other disc by 60° terminates the diffusion process [cf. figure 3 c)]. The total length of the capillary rods is 90 mm with reservoirs on each end. The reservoirs are pre-stressed by graphite felt pushing on pistons to balance volume expansion or shrinkage and to minimize free surfaces. Free surfaces can otherwise cause Marangoni convection significantly altering the measured diffusion coefficient [13, 14].

The shear-cell assembly is housed in a rhenium cartridge of an outer diameter of 60 mm and an overall length of 510 mm. The cartridge can be inserted into the previously described isothermal furnace. Boron nitride spacer bars (cf. figure 2) are keeping the graphite cell at distance from the rhenium tube surface to avoid corrosive reaction of graphite with the metal. The driving shaft is connected to a five-stage epicyclic gear which is driven by a direct-current motor. Both are mounted at the far end of the cartridge. To minimize heat flow from the heating zones to the drive system unit the boron nitride shaft is embedded in a solid graphite insulation foam itself separated from the cartridge surface by a boron nitride slotted tube. Three cartridges have been designed which are fitting the furnace. These are shown in figure 4. Cartridges FM-01 and FM-02 enable high temperature operation up to 1650°C . Cartridge EM01 is available for demonstration purposes. Cartridge FM-01 is fully MSL compatible. It can be vacuum tightly sealed with a leakage rate of less than 10^{-8} mbar \cdot l \cdot s $^{-1}$. It can be operated both with vacuum or inert gas inside the cartridge. In addition a thermocouple and a signal cable lead-through are available. Cartridge FM-02 has the same size and specifications as FM-01. However, it is designed with open access to the driving unit. Cartridge FM-02 is easier to assemble and to handle than cartridge FM-01. Hence it is mainly used for ground-based experiments. Also

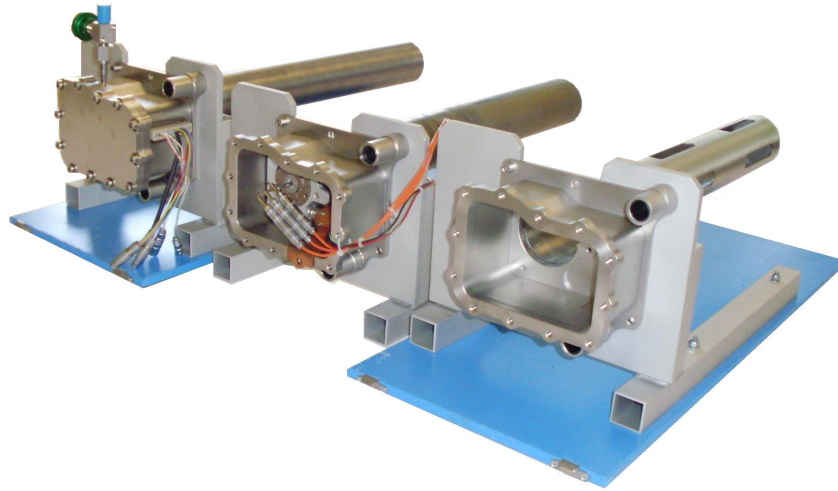


Figure 4. High temperature cartridges. Left to right: FM-01 fully MSL compatible; FM-02 for ground-based experiments; EM-01 engineering model.

modifications during the test phase can be easily carried out. Cartridge EM-01 has a slotted tube to enable visible inspection of the shear-cell in demonstration mode.

4. Performance

A thermal furnace heater characterisation up to 1600°C with the aim to calibrate the three type-S thermocouples inside the shear-cell together with showing proper shear-cell function were carried out (cf. figure 5). Temperature homogeneity along the 4 heating zones was currently better than 2 K over the entire temperature range. This equates to a temperature gradient of better than 0.022 K/mm. However temperature gradient on the shear-cell amounted to 5 K. A homogeneous temperature along the shear-cell is required. Individual tuning of the heating elements generated a homogeneous temperature difference on the shear-cell better than 1.2 K axially. With the initial heating cycles the ceramic insulation foam of the process chamber was baked out. The insulation is highly susceptible to moisture. Hence, even with storage under inert atmosphere, the short opening period for cartridge installation is sufficient for moisture ingress into the ceramic insulation. This is verified by slight pressure surges upon heating (cf. figure 6).

A reliable shear-cell actuation was verified. As verified in on-bench tests a hinge moment of 0.8 to 0.9 Nm is required to actuate the empty and cold shear cell in the cartridge for clockwise rotation of the single initially displaced disc. The counter-clockwise rotation of every other disc requires 2.5 Nm of torque. These moments can be achieved by the driving shaft being connected to a five-stage epicyclic gear (1526:1) which is driven by a 12 V direct-current motor. This driving unit provides a maximal torque of 9 Nm which is more than sufficient for a reliable shear-cell actuation even at the highest temperatures. In order to avoid damage by overtightening the shear-cell, a mechanical drive assembly dead stop made of high grade steel is installed. Moreover, the motor current is limited. Hence, on reaching the dead stop the current increase reaches the set limit and the motor is automatically switched off. Increasing shear-cell temperatures should cause higher actuation moments due to thermal expansion of the graphite components. Higher torque should simultaneous cause higher motor currents. Against all odds motor current

decreases on increasing shear-cell temperatures (cf. table 1).

Table 1. Decreasing actuation motor current on high shear-cell temperatures

shearing temperature (°C)	motor current(mA)
20	95-164
700	72-120
1100	68-112
1300	67-90
1500	55-90

First experiments were performed on Al-Cu and Al-Cu-Ag alloys at a diffusion temperature of 700 °C. These particular sample materials have been chosen to enable direct comparison with long capillary experiments carried out in the laboratory using post-mortem analysis and for Al-Cu also with the in-situ technique of X-ray radiography. The volume compensation compartments worked nominally with minimal sample leakage between the discs. Further, the shear-cell actuation worked reliably. The samples were processed with 2 h pure diffusion time. This was based on earlier experience obtained through long-capillary experiments. Diffusion coefficients of $5 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ were expected [3, 15]. The processing time could be estimated using the appropriate solution of Fick's second law of diffusion, the estimated diffusion coefficient and the capillary length of 90 mm. The requirement was a sufficient spread of the profile however without reaching the capillary ends. The diffusion experiments consisted of a heating phase, followed by a sample homogenisation phase (cf. figure 6). At the end of the homogenization phase the two separately melted samples were brought into contact and the diffusion process was started. In the experiments on Al-Cu and Al-Cu-Ag the axial temperature homogeneity was better than 1.2K. After the annealing time the diffusion process was terminated by shearing of the discs and thereby freezing in the diffusion profile of the liquid. This second shearing

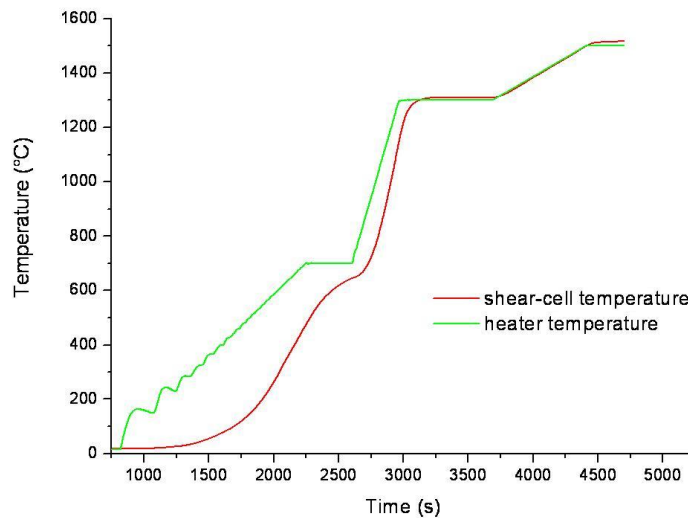


Figure 5. High temperature characterisations and shearing tests at 1500 °C.

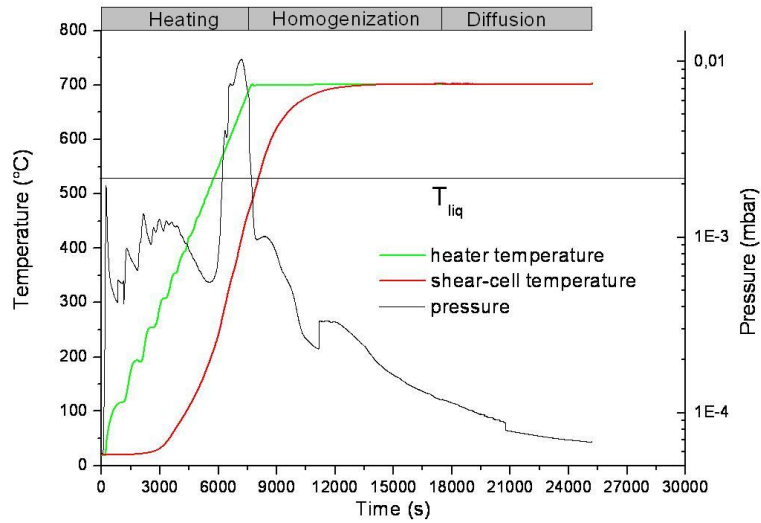


Figure 6. Temperature and pressure processing conditions for a chemical diffusion experiment on a Al-Cu-Ag diffusion pair at 700 °C from start to early stages of diffusion.

processes was followed by shut-down of the heater. As a result the sample was cooled down and solidified. The disassembled small sample cylinders have been weighted for the verification of the compartment filling degree (cf. table 2) and are currently analysed for their composition. Densities calculated for the endmember compositions dividing the measured weight by the compartment volume agree well with densities for Al-Cu melts published in literature [17].

Table 2. Weight of sample cylinders for AlCu7.5-AlCu17.5 after disassembling

Compartment #	1	2	3	4	5	6	7	8
Sample mass (mg)	14.60	14.60	14.64	14.69	14.64	14.74	14.65	14.52
	9	10	11	12	13	14	15	16
	14.99	15.10	15.16	15.60	15.55	16.03	16.77	16.60
	17	18	19	20	21	22	23	24
	16.23	17.08	16.95	16.99	16.84	17.30	16.99	17.09
	25	26	27	28				
	17.07	17.08	17.08	12.61				

For the binary alloy X-ray computed tomography is used as a non-destructive method followed by chemical analysis using atomic absorption spectroscopy. For the ternary sample only chemical analysis is used. Analysis of the samples of these first experiments is currently work in progress.

5. Conclusion

A novel isothermal furnace for the MSL with a large diameter bore capable of steady isothermal conditions for a zone of 90 mm length at temperatures up to 1600°C has been presented. First successful ground-based heating and shearing cycles have been performed using the furnace with a newly designed graphite shear-cell. The experiments have shown the functional capability of

the new isothermal furnace. Proper function of the shear-cell device has been demonstrated. In particular, the proper function of the shear-cell driving unit has been shown. Adequate pressure of the pre-stressed sample reservoirs in the shear-cell minimizes free surfaces in the capillaries. Only marginally material leakage between the shearing discs was observed. Temperature homogeneity of better than 1.2 K along the diffusion couples has been achieved at 700 °C. The samples of the first experiments are currently being analysed for composition. In future experiments on Al-Ni and Si-Ge at higher processing temperatures are planned. This contains also tests of melt containory reactions. Again results of these experiments can be directly compared with in-situ results on diffusion obtained by means of X-ray radiography. For online monitoring of the shear process, further developments of the shear-cell actuator will consist of the integration of a feed-forward control, linked to a rotary angle encoder and a multiphase stepper motor.

Acknowledgments

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