

An overview of the ESA-ESRF-ILL collaboration in the framework of the IMPRESS Integrated Project

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ABSTRACT

Three intergovernmental research organizations from the EIROforum collaboration: the European Space Agency (ESA), the European Synchrotron Radiation Facility (ESRF) and the Institut Laue-Langevin (ILL), are cooperating to perform advanced experimental characterization in the field of materials science within the framework of the IMPRESS Integrated Project. This project aims to develop and test two distinct prototype-based intermetallic materials: (i) γ -TiAl turbine blades for aero-engines and stationary gas turbines, and (ii) Raney-type Ni-Al catalytic powder for use in hydrogen fuel cell electrodes and hydrogenation reactions. The opportunity to carry out investigations combining the use of both synchrotron radiation at the ESRF and neutrons at the ILL provides unique experimental data to complement other benchmark experiments performed on the ground and in microgravity. We present an overview of the different synchrotron X-ray and neutron characterization techniques implemented at ESRF and ILL to study the solidification and subsequent processes leading to the final products for these two materials.

INTRODUCTION

EIROforum is a partnership regrouping Europe's seven largest intergovernmental research organizations. Among them, the European Synchrotron Radiation Facility (ESRF) and the Institut Laue Langevin (ILL) both located in Grenoble France, and the European Space Agency (ESA) have combined resources in order to perform key materials science experiments for the benefit of the IMPRESS Integrated Project [1,2]. IMPRESS is an acronym for Intermetallic Materials Processing in Relation to Earth and Space Solidification [3,4]. This project is coordinated by ESA within the European Commission's 6th Framework Programme (FP6). The main scientific objective of IMPRESS is to gain a better understanding of the strategic links between material processing routes, material structure and final properties of intermetallic alloys. Technically, the project aims to develop and test two distinct prototype-based intermetallic materials (i) TiAl and (ii) NiAl.

In the case of (i) structural turbine blade applications, titanium aluminides have been investigated for many years and most effort is now concentrated on γ -TiAl with various alloying additions. These alloys offer excellent mechanical properties at high temperature up to 750°C, combined with low density and non-burn. They have the potential to replace nickel superalloy turbine components, in turn offering substantial weight reduction for gas turbine components.

In the case of (ii) catalytic applications, intermetallic materials such as Raney-type nickel-aluminide alloys have been used since the 1920s in the chemical industry [5]. Conventionally, Raney-type catalytic powders are produced by a cast-and-crush method

followed by leaching with aqueous sodium hydroxide in order to remove aluminum atoms randomly at the unit-cell level revealing a highly porous skeletal structure of activated nickel. In IMPRESS manufacturing routes such as gas-atomization and nano-particle synthesis are being explored as new ways of producing powders with improved activity and selectivity. One of the unique parts of IMPRESS is the ability to perform benchmark experiments in space thereby removing the effects of gravity. Space experiments on MAXUS sounding rockets are in preparation to study solidification phenomena affected by gravity, for example, the settling or flotation of grains/inclusions in the melt. It is equally important for the development of reliable computer models of solidification to have accurate measurements of thermophysical properties of liquid metals. In this area, use is being made of a containerless melt processing technique known as electromagnetic levitation (EML) regularly used in microgravity on the ESA/DLR parabolic flight campaigns and TEXUS sounding rockets. The final class of experiments being carried out in microgravity involves the production of Ni-based nanoparticles from the vapour phase. Under weightless conditions and without convective effects, the agglomeration kinetics of the nanoparticles can be studied, including the magnetic interactions between particles.

Carrying out extensive investigations combining the use of the intense neutron source available at the ILL and the powerful synchrotron X-ray source of the ESRF to complement the experiments performed by the IMPRESS partners on the ground and in microgravity is an exceptional opportunity to create a research capability unparalleled in the world. Details of the individual instruments named below can be found in [6,7]. This paper describes a number of different characterization techniques applied so far in the IMPRESS Project.

CHARACTERIZATION TECHNIQUES

Synchrotron X-ray diffraction using a 2D-type detector

Hot Isostatic Pressing (HIPping) is a densification technique widely used in the metallurgical industry, for example, to remove the internal porosity generated during casting. In recent work [8] it has been found that the pressures used during such a process can alter the equilibrium proportion and thus the properties of phases in a Ti-Al-Nb alloy. Precise measurements of the lattice parameters of the various phases present at room temperature and at the HIPping temperature were performed on beamline ID15B of the ESRF using an induction furnace and a 2D detector to calculate the corresponding variation in atomic volume and thus determine the change in volume fraction. Furthermore, the 2D image and integrated diffraction pattern contain more information than traditional powder patterns by enabling the rapid viewing of a large solid angle of detection within a single collection frame as shown in figure 1.



Figure 1. 2D diffraction patterns of a Ti-Al-Nb alloy at (a) room temperature and (b) $T = 680^{\circ}\text{C}$

Grazing incidence synchrotron X-ray diffraction (XRD)

A pending issue of Ti-Al based alloys for turbine blades is the degradation of various mechanical properties, especially room-temperature ductility, after exposure to air at temperatures higher than 700°C [9]. The application of a protective coating or alloying are ways to minimize the influence of oxidation [10], however, the origin of the resulting embrittlement of these alloys remains unclear. One assumption is that gas diffusion into the surface modifies the initial lattice. The surface is then put into stress leading to the formation of cracks [11]. Surface investigations were performed on the high-resolution diffraction beamline ID31 of the ESRF. The highly monochromatic beam available was used at different wavelengths to vary the penetration depth and precise $\sin^2\Psi$ measurements were recorded, where Ψ is the angle between the scattering vector and the sample's normal direction. The underlying stress in the sample can be found from the gradient of the graph of d -spacing plotted against $\sin^2\Psi$.

In situ and real-time energy dispersive X-ray diffraction

Despite the two different application areas of the IMPRESS project, the two intermetallic compounds investigated have a common feature; their respective production process are primarily governed by out-of-equilibrium solidification behaviour. The ID15 beamline has been used to perform high-energy-dispersive diffraction on electromagnetically levitated melts. This allowed an *in-situ*, real-time study of solidification from the undercooled melt to be made. Such experiments enabled the determination of phase selection and nucleation undercooling values in various Ti-Al and Ni-Al Alloys [12,13].

High resolution synchrotron X-ray and neutron powder diffraction

Raney-type Ni is obtained by leaching away the aluminum of Ni-Al powders with aqueous sodium hydroxide. The leaching conditions as well as the characteristics of the initial powder have strong effects on the properties of the final catalyst [14]. Gas-atomization is a promising way to obtain a more efficient catalyst by rapidly solidifying fine liquid droplets. Previous experiments combining X-ray and neutron diffraction of atomized powders reported variations in phase fraction with grain size of the droplet as well as the occurrence of phases which could not be identified [15]. Powder diffraction patterns of Ni-Al powders with selected grain sizes and composition, before and after leaching, were recorded on the high resolution beamlines ID31 of the ESRF and D20 of the ILL. The very high angular resolution available on ID31 can separate peaks of unidentified phases which are generally small and overlap the reflections of other phases. Neutron diffractograms can show strong, well-defined diffraction peaks even at high angles and thus provide precise information on the atomic structure and phase fraction through Rietveld refinement analysis.

Synchrotron X-ray microtomography

Analyses by neutron and X-ray powder diffraction are efficient methods to determine average phase content, phase composition and phase fraction but provide limited morphological information on the microstructure, especially in the case of complex dendritic structures. Local investigations at the grain scale were carried out by performing synchrotron microtomography

with the best pixel resolution available on the ID19 beamline of the ESRF (0.17 $\mu\text{m}/\text{pix.}$). 3D reconstructions of an atomized and a Raney-type droplet are shown in figure 2. Phase-fraction measurements can be compared to those obtained from the Rietveld refinement of diffraction patterns. Morphological analysis of the skeletal structure observed after leaching will provide significant parameters such as surface area, porosity and tortuosity which are critical properties affecting the activity of the final catalyst.

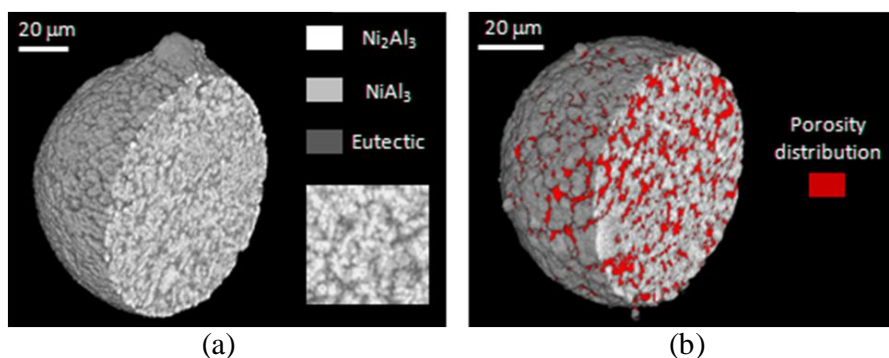


Figure 2. 3D reconstructions of (a) Ni-Al atomized droplet and (b) passivated Raney-type Ni droplet.

In situ and real-time neutron diffraction

Previous studies have shown that the activation process of Raney nickel is very fast in its initial stage (of the order of a few seconds) [14]. In order to predict catalytic activity, the transformation of Ni-Al alloys to metallic nickel requires characterization of the starting alloy and the phase content of the powders directly during the leaching process. Thus, dynamic *in situ* neutron diffraction was performed on the D20 instrument at the ILL whilst Ni-Al powders of selected composition and size were leached with aqueous sodium deuterioxide of various concentrations. The large and intense neutron beam available on D20 illuminates a sufficient amount of product during the reaction and provides sequences of diffractograms that display the evolution of the different species with time, as shown in figure 3. The amount of Ni_2Al_3 decreases while Raney nickel forms, inducing a decrease in intensity of the peaks related to Ni_2Al_3 and the development of a broad peak related to Ni, accompanied by the appearance of small-angle scattering.

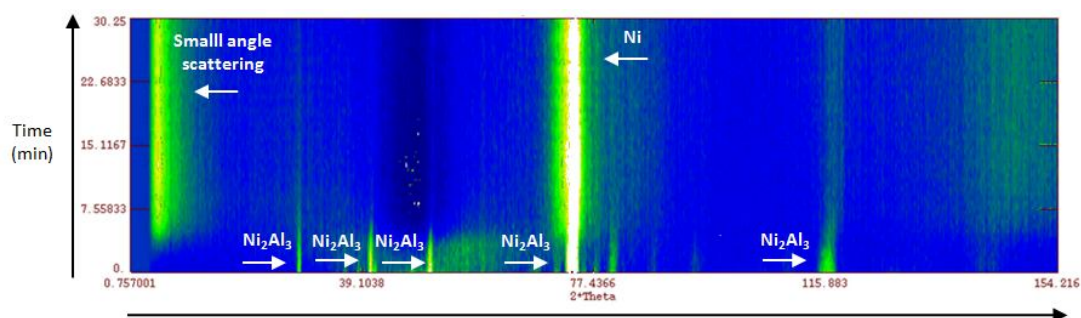


Figure 3. Typical sequence of diffractograms showing a decrease of Ni_2Al_3 and formation of Raney nickel.

Small-angle neutron scattering

Strong scattering at small angles is often observed in the powder diffraction patterns of leached Raney nickel. The cause of this can be the presence of very small particles (10 to 200 Å) which cannot be characterized using X-ray or neutron diffraction or tomography at the micron scale. For this reason, experiments to determine the mean particle size and shape were performed on the small-angle neutron scattering instrument D11 of the ILL. Additional information will be obtained on the surface area of all the particles as well as on the porosity of powders.

MICROGRAVITY RESEARCH

Nickel and its alloys with high specific surface area are interesting catalysts for anodic/cathodic reactions in fuel cells. Evaporation from the melt in an inert gas environment is one of the options to produce such highly porous catalyst metals. In this process nanoscale particles grow and agglomerate via Brownian motion of the nanoparticles and cluster-cluster aggregation via van der Waals, electrostatic or magnetic interactions. Since evaporation takes place at high temperature, convective flow of the hot aerosol occurs. In addition larger agglomerates tend to sediment out. Both processes dominate particularly at low flow rates, i.e., at extended agglomeration times. Therefore microgravity is employed effectively to suppress both convective motion and sedimentation of the larger agglomerates [16]. A custom-built, microgravity-compatible inert-gas condensation source has been flown onboard an Airbus A300 during three ESA parabolic flight campaigns. Samples of Ni agglomerates have been grown during the microgravity phase of the parabola from an aerosol uninhibited by the effects of gravity [17]. Aircraft parabolic flights provide repetitively periods of up to 20s of reduced gravity during ballistic flight manoeuvres and are used to conduct, amongst other things, short microgravity investigations in Physical and Life Sciences and Technology. Their use is complementary to other microgravity platforms, such as drop towers, sounding rockets, low-earth orbit (LEO) capsules and the International Space Station (ISS) [18]. Samples made in microgravity have been measured at the ESRF using magneto-optical Kerr effect (MOKE) and XRD whilst experiments are planned to perform X-ray magnetic circular dichroism (XMCD) on the samples in order to determine the contribution of spin and orbital moment to the total magnetic moment.

CONCLUSION AND PERSPECTIVES

Many investigations in several scientific research areas are being performed at the ILL and the ESRF in the framework of the IMPRESS Integrated Project. Precise measurements and valuable information are being collected which will be used to validate multi-scale numerical models. Further analysis will improve the general understanding of the different phenomena occurring during the manufacture of Ti-Al turbine blades and Raney-type Ni catalysts. The utilization of novel processing routes such as gas atomization, sophisticated EML techniques and benchmark experimentation in space puts IMPRESS at the forefront of materials development. Combined with the rich environment at Grenoble, the most intense continuous neutron source in the world and one of the highest resolution synchrotron powder X-ray beamlines, this collaboration will continue to generate results at the cutting-edge of science.

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