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Gels of nominal compositions $(Mg_{1-x}Co_x)_2Al_4Si_5O_{18}$ were obtained by the sol-gel method from metallic salts (nitrates) and colloidal silica. The dried gels were melted and the amorphous precursor was annealed to crystallized monophasic cordierite solid solutions. A hexagonal cordierite (indialite) [1] and orthorhombic cordierite (iolite) [2] has been studied by several authors and are very similar; both are built of six-component rings of tetrahedral Si-Al sites perpendicular to c-axis. All these cordierites have several interesting ceramic and optical properties.

X-ray powder diffraction using Cu K α radiation and scanning electron microscopy were used to follow the structural and textural evolution from gels to the final synthetic orthorhombic cordierite solid solutions. Rietveld refinement was started using Cccm space group and structure parameters derived from Terada et al. using the FullProf program [3]. The results confirm the orthorhombic crystal structure and the solid solution formation in the whole range of compositions of these Mg-Co cordierites.

The non-periodicity of nanocrystalline materials can be analyzed using the diffraction line broadening of X-ray diffraction patterns. There are several approaches to obtain microstructural information (crystallite shapes and size distribution, microstrain). We have used an integral breadth method [4], a Fourier method [5] and a statistical method for analysing polycrystalline materials [6]. In all cases the standard line profiles for instrumental line broadening were obtained from LaB₆ (SRM 660a). On average, crystallite size of these orthorhombic cordierite solid solutions is rather similar for different metal contents, but microstrain diminishes when cobalt content increases.

[1] S.P. Meagher, G.V. Gibbs, *Canadian Mineralogist* **1977**, *15*, 43-49. [2] M. Terada., K. Kawamura, I. Kagomiya, K. Kakimoto, H. Ohsato *Journal of the European Ceramic Society* **2007**, *27*, 3045-3048. [3] J. Rodríguez-Carvajal, *CPD Newsletter* **2001**, *26*, 12-19. [4] G.K Williamson, W.H. Hall, *Acta Metallurgica* **1953**, *1*, 22-31. [5] B.E. Warren, B.L. Averbach, *Journal of Applied Physics* **1950**, *21*, 595-599. [6] M.A. Kojdecki, E. Ruiz de Sola, F.J. Serrano, E. Delgado-Pinar, M.M. Reventós, V.J. Esteve, J.M. Amigó, J. Alarcón *Journal of Applied Crystallography* **2007**, *40*, 260-276.

Keywords: sol-gel processes, rietveld refinement, microstructure analysis

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In-situ X-ray diffraction study on the decomposition kinetics in bearing steels

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We have monitored in-situ the austenite transformation kinetics in high-carbon bearing steels undergoing creep phenomena by performing time-dependent X-ray diffraction experiments under tensile load at elevated temperatures using a 70 keV synchrotron X-ray micro-beam. Bearings are nowadays used as key precision components in a broad scope of machinery and gearboxes. The commonly used high-carbon SAE 52100 steel provides the required combination of

high strength and resistance to fatigue to produce bearings with an acceptable lifetime. The room-temperature microstructure of these steels consists of martensite, metastable austenite (10-25 vol.%) and a small amount of carbides (< 5 vol.%). Small dimensional changes in the bearing during operation influences its function and thereby that of the machine in which it operates. One key process that critically affects the bearing dimensions during operation is the decomposition of the metastable austenite phase at elevated temperatures. The austenite face-centred cubic (fcc) structure transforms into the bainite body-centred cubic structure, together with the appearance of very fine nm-sized precipitates.

The combined use of the high-energy X-rays available at the ESRF and our dedicated micro-tensile stage with heating capabilities has allowed us to monitor in-situ the austenite decomposition in the bulk microstructure as a function of time for different combinations of temperature and applied tensile stress. The measurements were performed by continuously recording the diffraction patterns on a two-dimensional detector placed behind the sample as a function of time at selected temperatures in the range of 476-504 K for an applied tensile stress of: $\sigma = 0$ and $\sigma = 295$ MPa. This combination of temperature and stress mimics the operating conditions of the bearings during its lifetime. The available optics at the ID15A beam line of the ESRF permits to reduce the beam dimensions down to $5 \times 25 \mu\text{m}^2$. This has allowed us to study both the average behaviour of the metastable austenite phase and the transformation kinetics of individual austenite grains. The observed transformation behavior has been correlated to the change in sample dimensions that are recorded simultaneously during the in-situ diffraction experiment. The Rietveld analysis of the powder diffraction data reveals that the time to completely transform the metastable austenite reduces from 6 to 3 hours when increasing the temperature from 476 to 489 K. The presence of the applied tensile stress of 295 MPa reduces the activation energy from 138 to 104 kJ/mol. We have also observed a continuous decrease in the austenite lattice parameter while keeping the sample at a constant temperature. This effect is ascribed to the depletion in carbon of the remaining austenite grains resulting from the formation of iron carbides. The results of our in-situ diffraction study constitute a key input to control the austenite stability in high-carbon steels during the industrial processing of the material, in order to keep the changes in the bearing dimensions within the required limits during its lifetime.

Keywords: steel, creep, diffraction

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A multidisciplinary study of the resolution of hydratropic acid by ephedrine

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Following the introduction of regulatory guidelines for the production of stereoisomeric drugs in 1992, the number of drugs marketed as single enantiomers has increased considerably [1]. Classical resolution is often used to obtain enantiopure compounds by the pharmaceutical industry. However, despite its importance, the choice of chiral acid/base to use as a resolving agent is still mostly made on a trial and error basis. An understanding of the relationship between the crystal structure of the diastereomeric salt pairs, their relative energies and crystallization behaviour, would lead to improvements in the separation process.

In the present study we have performed an experimental and

computational investigation of the relationship between the resolution efficiency of ephedrine (E) as a resolving agent for 2-phenylpropionic (hydratropic) acid (PP) and the physical properties of the diastereomeric salt pairs ERPP and ESPP. The crystal structure of the least soluble salt (ERPP) and a polymorph of the most soluble salt (ESPP form IV) have been determined by low temperature single crystal X-ray diffraction and ESPP form II by powder X-ray diffraction (PXRD). Two further polymorphs and a hydrate of ESPP have been identified by infrared spectroscopy and PXRD. Differential scanning calorimetry with thermogravimetric analysis was used to determine the relative stability of the salt pairs and polymorphs. HPLC and solubility measurements have been used to measure the resolution efficiency of ERPP and the most stable polymorph (form I) of ESPP.

The experimental crystal structures reveal that the resolution efficiency is affected by the competition between intra- and intermolecular interactions, as in the most stable salt (ERPP), the ephedrine forms an intramolecular N-H...O interaction, in addition to having different intermolecular hydrogen bonding motif to both ESPP polymorphs. CrystalOptimizer [2] has been used to calculate the lattice energy, $E_{\text{latt}} = U_{\text{inter}} + \Delta E_{\text{intra}}$, the balance between the intramolecular energy penalty, ΔE_{intra} , for distortions of the ions within the crystal, and the intermolecular lattice energy, U_{inter} . The experimental work on this system shows both the challenges to, and potential benefits of, computational assessment of resolving agents.

[1] H. Caner, E. Groner, L. Levy, I. Agrat, *Drug Discovery Today*. **2004**, 9 (3), 105-110. [2] P.G. Karametzanis, S.L. Price, *J.Chem.Theor.Comp.* **2006**, 2 (4), 1184-1199.

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Microstructure evolution in MgF₂ and ZnO doped LAS Glass-Ceramics

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The microstructure evolution, including glassy phase separation, crystallization and phase transformation plays the most important role in practical mechanical property and application of lithium aluminosilicate (LAS) glass-ceramic materials. The main goal of this study is to demonstrate the correlations among phase development, microstructure, thermal expansion coefficient and mechanical strength associated with the content of MgF₂ and ZnO with commercial-like recipes. In this work, the result of flexural strength of LAS glass-ceramics strongly depends on the concentration of additives, MgF₂ and ZnO. When about 6% ZnO are added, the strength of a sample increases from about 62 MPa to 78 MPa. However, MgF₂ bearing samples accompany with a ~50% decreased in flexural strength. This is because the morphology, phase composition and transformation temperature are changed via doping. X-ray powder diffraction (XRD) results shows that the main phase follows the regular way, hexagonal β -quartz solid solution formed at lower temperature and transform to tetragonal β -spodumene solid solution at higher temperature. The transformation temperature of β -quartz solid solution to β -spodumene solid solution is lowered for several tens of degrees when the ZnO or MgF₂ is doped. It might be due to the weakening effect of silicate network by these additives. Also, various secondary phases, such as ZrTiO₄, and spinel of zinc and magnesium are usually precipitated at higher temperatures for samples with higher content of MgF₂. In addition, X-ray absorption

near edge structure (XANES) feature is also used to certify the existence of some minor phases and the structural role of the doped elements. The significant change in XANES features of Zn K-edge indicates that Zn ions are usually involved in the crystallization process for samples doped with > 1% ZnO. Zn²⁺ ions might substitute Li⁺ site in the main crystalline phase. This substitution phenomenon results in the formation of secondary phases. Thermal expansion mismatch from the microstructure non-uniformity is responsible for the strength drop of MgF₂ bearing samples.

Keywords: glass-ceramic, XANES, X-ray diffraction

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Evolution of the microstructure of bimetallic valves

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New our casting methods using heightened pressure of inert gas allow to obtain complex-form products from a variety of combination traditional and new high-temperature materials (G. Teterin at al. 1996). Distribution of the alloy components as well as phase composition across the valve section was obtained by means of energy-dispersive analysis and X-ray diffraction. The difference X-ray method has been used to investigate the evolution of the phase composition and microstructural characteristics of highly effective bimetallic engine valves. The head of the valves is made of Ti or Ti-Al, and the main rod is made of different materials. Bragg angle and the width of Bragg intensity profiles of reflection of high and low order for the phases were measured. The assessment of the change in the microstructure of the strain level at the predominant phase has been made on the basis of data of the angular dependence of the width of the Bragg reflection. As a reference standard of an instrument shape of reflections SRM 660 (LaB6) is used. Reliability and composition of the joining of head and stem was investigated by various method also. Hardness measurements were undertaken using 15-g, 50-g and 100-g loads using Micromet-2001 and PMT-3 testers. After casting the head of the valve it has a tetragonal gamma-phase and hexagonal alpha-phase; the ratio of the phases changes during the subsequent thermal treatment, and as a result the mechanical properties of the valve head become better. It should be noted that it is necessary to perform the control over the rod junction area because during some processing modes the martensitic beta-phase could appear, which can reduce the fracture toughness of the material and lead to a higher level of strain and as a result may appear some kind of micro-cracks in the junction of the valve. The exhaust valve were tested as a part of engine under the real-life condition of operation. It has been suggested the model described the processes

Keywords: strain-stress, phase composition, casting methods

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Analytical methodology for the quantification of respirable crystalline silica (RCS) in occupational environments using a CIP 10-R sampler

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