

temperature. There exists little scientific literature on this system and hence there is scope to develop this field. It has been found from the existing studies that an equiatomic refractory alloy has broadly a BCC structure with some compositional variation in the as-cast structure. In many cases ordering phenomena was not evident from X-Ray powder diffraction data, but was found through HRTEM electron diffraction in Al-Co-Cr-Fe-Ni HEA.

As the above-mentioned refractory materials have melting point of nearly 3000°C, the equiatomic WMoNbTa alloy was prepared through arc melting in argon atmosphere. The starting metal powders all had purity above 99.95 percent. First a 5-gram pellet was made from the well-mixed powders by hydraulic press. Later the pellet was melted under arc five times each for 2 minutes. Each time the sample was melted, it was turned upside down for even better mixing of elements. This was probably a better method than a previous report where metal chips and powder were melted together in the arc-melting furnace, which might remove some small chips when the arc strikes the mixture. After this the samples were wrapped into tantalum foils and sealed inside tantalum ampules. The inside of the ampule had Argon atmosphere and it was annealed at 1800°C for a week. The grain size distribution provides us with 50 micron grains that could be studied for diffuse scattering experiments.

[1] J. W. Yeh, Y. L. Chen, et al. *Adv. Struct. Mater* **2007**, III 560, 1-9.

**Keywords:** high-entropy alloy, coloring problem, refractory alloy

## MS30.P24

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**Structural analysis of metal nano-particles prepared by leaching** Reiko Murao,<sup>a</sup> Kazumasa Sugiyama,<sup>a</sup> Satoshi Kameoka,<sup>b</sup> An-Pang Tsai,<sup>b</sup> <sup>a</sup>Institute for Materials Research, Tohoku University, Sendai (Japan). <sup>b</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai (Japan). E-mail: r\_murao@imr.tohoku.ac.jp

Catalytic fine particles can be obtained by the leaching of a variety of alloy powders using alkali or acid solutions [1]. During the leaching process, the structure of a parent alloy sample is decomposed and the X-ray diffraction pattern of resultant fine particles is usually very broad and diffuse. These features could be generally attributed to the small size of crystallite and the highly disordered structure [2]. To clarify structural features of such fine particles, the analysis of atomic pair distribution function (PDF), calculated from the total X-ray scattering measured by high-energy X-ray source, is suggested to be one of effective methods. However, high resolution PDF is not enough to discuss the structure around a specific element in the case of multi-component alloy system. In this context, the anomalous X-ray scattering (AXS) method [3] is a powerful tool to provide environmental structural information around a target element, not only in nearest neighbor but also in middle range region. Present paper demonstrates some examples of structural analysis for fine particles by anomalous X-ray scattering.

Structures of Raney Ru(Ni) fine particles prepared from Al<sub>13</sub>(Ru,Ni)<sub>4</sub> alloy powder by alkali-leaching (NaOH) were investigated by the high-energy X-ray scattering and AXS measurement at the Ni-K absorption edge. Ordinary PDF for Raney Ru indicates atomic correlation similar to that for fcc-Ru. However, a correlation peak at about 0.2 nm, which could not be described by the atomic arrangement in the fcc-typed structure, is developed as a function of the Ni content. Additionally this interesting correlation could be clearly observed in the environmental PDF around Ni. These experimental results support the partial oxidation of Ni so as to realize the Ni-O pair in the observed

PDFs. In middle range region of the environmental PDF, Ni-Ni(Ru) pairs with respect to the hcp-typed structure could be identified. These results suggest that the atomic rearrangement of Ni toward hcp-typed structure together with the partial oxidization was realized during the leaching process.

Structure of Pt/Cu fine particles prepared from a Cu<sub>3</sub>Pt alloy powder by acid-leaching (HNO<sub>3</sub>) was also studied by anomalous X-ray scattering. The ICP analysis indicates the Pt/Cu ratio of the obtained fine particles is about 85/15. Although the overall features observed in PDF is rather similar to that of fcc-Pt, the environmental RDF around Pt shows a correlation of the Pt-O pair at around 0.2 nm. Therefore, partial oxidation of Pt in the fine Pt/Cu alloy particles is readily suggested.

[1] T. Tanabe, S. Kamooka, A.P. Tsai, *Analysis Today*, **2006**, 111, 153-157.

[2] A.J. Smith, D.L. Trimm, *Annu. Rev. Mater. Res.* **2005**, 35, 127-142. [3] Y. Waseda, *Anomalous X-ray scattering for Materials Characterization*, Springer, Hidelberg **2002**.

**Keywords:** high-nergy X-ray scattering, anomalous X-ray scattering, nanocrystal

## MS30.P25

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**Low-temperature plasticity of magnesium alloy AZ31 with different microstructure**

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The feature of plastic deformation of magnesium alloy AZ-31 by tension in the temperature range 4.2-295 K are examined depending on microstructure after squeeze casting (SC) and severe plastic deformation (SPD) via hot rolling and equal channel angular pressing. The SPD processing results in decrease of grain size and formation of a texture for basal dislocation glide. The microstructure of the samples for tension that were cut from the initial SC and SPD materials were also monitored by X-ray diffraction. The ratio of the integrated intensities of the (10.0), (00.2) and (10.1) reflections along and perpendicular to the sample axis are ~1.1 and 1.4 for SC and SPD samples, respectively. The integrated intensity of the (00.2) reflection for a sample from the SPD material is greater by an order of magnitude than for a sample from the initial SC material. These ratios of the integrated intensities indicate that the flat sample for tension retained the texture of the initial material, and its longitudinal axis coincides with the direction of rolling and pressing. The coherent scattering regions for SC and SPD derived from the Hall plots for the basal plane are 150 and 0.2 μm, respectively. These estimates, as is customary in these cases, are lower than the average grain size obtained by transmission microscopy, but the relative change in the coherent scattering region in the SC and SPD samples correlates with significant reduction in the grain size owing to rolling and pressing of the material. It is found that in the temperature range 4.2-25 K the plastic deformation becomes unstable (serrated) with stress jumps in the SPD alloy greater than in the SC one. The temperature dependence of yield stress of this alloy is typical of thermally activation unpinning of dislocations from short range obstacles. Correlation of yield stresses for SPD and SC samples at given temperature is explained by hardening due to refinement of grain size and owing to favorable texture. The work hardening coefficient to alloy decreases a grain size but the ductility (strain to fracture) increases due to texture. The strain rate sensitivity of flow stress at T≤100 K does not

depend on alloy microstructure and is determined by intersection with forest dislocations. As the deformation temperature increases in the range 150-200 K, the strain rate sensitivity rises owing to activation of dynamic recovery and contribution of diffusion processes under plastic deformation of fine-grained materials.

**Keywords:** magnesium alloy, structure, low temperature.

### MS31.P01

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#### Coordinated productive and unproductive substrate binding in the COX-2 homodimer

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The cyclooxygenases (COX-1 and COX-2) are membrane-associated heme-containing homodimers that generate prostaglandin H<sub>2</sub> from arachidonic acid (AA) in the committed step of prostaglandin and thromboxane biogenesis and are the targets for nonsteroidal anti-inflammatory drugs. Both isoforms behave as heterodimers during catalysis, exhibiting half-of-sites reactivity. Although AA is the preferred substrate for both COX isoforms, these enzymes, with varying efficiencies, oxygenate other fatty acid and endocannabinoid substrates. To elucidate the atomic level interactions that are involved with binding and conformational positioning of substrates for catalysis, we determined the X-ray crystal structures of AA, eicosapentaenoic acid (EPA), and 1-arachidonoylglycerol (1-AG) bound to murine COX-2 to 2.10, 2.40, and 2.20 Å, respectively. AA, EPA, and 1-AG bind in different conformations in each monomer constituting the homodimer in their respective structures, such that one monomer exhibits productive binding and the other unproductive binding of the substrate in the cyclooxygenase channel. Comparison of the COX-2: substrate crystal structures revealed an alternate rotamer conformation of Leu-531 that allowed for these novel substrate conformations; but interestingly, mutagenesis of Leu-531 in COX-2 did not result in a significant decrease in  $V_{max}$  or  $K_m$ , in contrast to similar studies with COX-1. We conclude that the mobility of Leu-531 increases the accessible volume at the opening of the cyclooxygenase channel, and contributes to the observed ability of COX-2 to oxygenate a broader spectrum of substrates compared to COX-1. Furthermore, the alternate conformations of substrates bound to the COX-2 homodimer may be mechanistically associated with the observed half-of-sites reactivity.

**Keywords:** substrate\_complex, bioactive\_lipid, enzyme\_allostery

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#### The role of crystallography in chemical kinetics and industrial processes

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Single crystal crystallography plays a very important part in understanding the mechanisms of chemical reactions, including catalytic reactions. The isolation and identification of intermediates and products provide the researcher with a clearer understanding of reaction routes and the effects of steric bulkiness and/or electronic effects of coordination compounds.

Transition metal-catalyzed ethylene oligomerisation typically produces a broad range of  $\alpha$ -olefins. The development of alpha-olefins is an ongoing process [1] and recently the selective tetramerisation of ethylene to 1-octene was reported [2]. The evaluation of a large number of diphosphinoamine (PNP) ligands with various substituents on both N and P ligands reported that the predominant factor in the catalytic selectivity is the steric bulk on the central nitrogen atom compared to the basicity of the phosphine [3-7].

This study reports the synthesis of a range of PNP ligands with varying catalytic activity and selectivity and with a systematic variation of electro-steric properties of the N-substituents. A range of crystal studies were completed to further evaluate any correlations [8-9]. A comparison of the crystallographic data of these PNP ligands with the catalytic behaviour was made in an attempt to further understand this process, but also to provide more information for further catalyst design [10].

[1] J.T. Dixon *et al.*, *J. Organomet. Chem.* **2004**, 689, 3641. [2] A. Bollman *et al. J. A.C.S.*, **2007**, 126, 14712-14723. [3] K. Blann *et al. J. Catal.*, **2007**, 249, 244. [4] M.J. Overett *et al. Chem. Comm.* **2005**, 622. [5] K. Blann *et al. Chem. Comm.*, **2005**, 620. [6] S. Kuhlmann *et al. J. Catal.*, **2007** 245, 277. [7] E. Killian *et al. J. Mol. Catal. Chem.* **2007**, 270, 214. [8] N. Cloete *et al. Acta Cryst.* **2008**, E64, o480. [9] N. Cloete *et al. Acta Cryst.* **2009**, E65, o3081. [10] N. Cloete *et al. Angewandte*, submitted for publication February **2011**.

**Keywords:** tetramerisation, catalysis, ligand design

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#### Structural properties of various Copper(II) catalysts for oxidation catalysis

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The aerobic oxidation of substituted phenols as a research topic plays an important role in synthesis and biological systems. The demand for value added derivatives of phenolic compounds is steadily growing in the world market, with benzoquinone derivatives constituting a key intermediate in the industrial production of Vitamin E<sup>1</sup>. The use of dioxygen as oxidant is environmentally friendly and available in bulk from the atmosphere. Dioxygen can be catalytically activated by first row transition metal complexes (Cu(II), Co(II) and Mn(IV))<sup>2</sup>. The addition of co-catalysts (LiCl or MgCl<sub>2</sub>) can significantly increase the reactivity of these catalysts during the oxidation cycle<sup>3</sup>.

In the current study, model catalyst precursors containing O<sub>2</sub>O bidentate ligand systems such as troplone and 2-methyl-3-hydroxy-4-pyrone derivatives, which forms five-membered chelates, have been synthesized and structurally characterized, and will be discussed. Different aspects of the dioxygen oxidation of selected organic substrates by these copper(II) catalysts, as well as a proposed mechanism for the process, will also be presented.

[1] H. Sun, K. Harms, J. Sundermeyer, *J. Am. Chem. Soc.*, **2004**, 126, 9550. [2] L.I. Simandi, *Catalytic Activation of Dioxygen by Metal Complexes, Catalysis by Metal Complexes*, **1992**, 13, 10. [3] W. Brenner, *German Patent Hoffman-La Roche*, **1972**, 2(221), 624

**Keywords:** copper, oxidation, catalysis