ESRF	**Experiment title:** Atomic diffusion in the noble metal binary alloys	**Experiment number:** HS-4228
Beamline: ID10A	**Date of experiment:** from: 03.11.2010 to: 09.11.2010	**Date of report:** October 17, 2012
Shifts: 18	**Local contact(s):** Federico Zontone	*Received at ESRF:*

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Report:

Applying X-ray Photon Correlation Spectroscopy for large scattering angles ($|\vec{q}| \approx 0.2 - 2$Å) has shown promise as a method for studying diffusion on its fundamental scale [1, 2]. Here we report on an atomic-scale XPCS study of the diffusion in a binary alloy composed of nickel and platinum. Our goal was to study the influence of short-rage order (SRO) on atomic mobility and to evaluate the usability of polycrystalline samples for aXPCS experiments.

The behavior of a low concentration of platinum solute atoms in a nickel matrix, in particular $Ni_{97}Pt_3$, was studied in single- and in polycrystalline samples. The results will be published in [3]. As it is difficult and for some materials even impossible to get single crystalline samples, it was our goal to evaluate the information gained from the polycrystalline sample. Showing that results of polycrystals are comparable to single crystals would open a wider field of materials examinable with aXPCS. A $Ni_{60}Pt_{40}$ and a $Ni_{75}Pd_{25}$ sample were also measured, but the results were inconclusive.

The experiment was performed with a beam energy of 8 keV. Slits of $8 \times 8\,\mu m^2$ defined the beam size and the beam was focused with the compound refractive lenses-system. We mounted the samples in our specially designed vacuum furnace in order to perform measurements at different temperatures. Between the furnace and the CCD camera a movable evacuated flight-tube of 0.5 m length was placed to reduce air scattering effects. A number of frames with an exposure time of 10 s was collected for different temperatures and at different scattering angles for both the polycrystalline and the single-crystalline sample. While for the polycrystal all azimuthal angle positions of the CCD camera are equivalent, for the single-crystalline sample an additional azimuthal scan was carried out.

The atomistic mechanism of diffusion in Ni-Pt is the exchange of a nickel or platinum atom with a vacancy. An atomistic jump model is defined by the jump probabilities (P_n) to the nearest- (n=1), next-nearest- (n=2) and further neighbor shells. Because of the low concentration of Pt atoms in $Ni_{97}Pt_3$ we used the probabilities calculated in frame of the so called encounter model for self diffusion [4]. Renormalization of these jump probabilities, neglecting exchanges with a vacancy that do not lead to an effective jump, gives $P_1 = 92.6$ %, $P_2 = 2.4$ %, $P_3 = 3.9$ % and $P_4 = 0.8$ % (neglecting probabilities for further jumps which sum up to n $P_{n\geq 5} = 0.3$ %). As we have shown theoretically [5], short-range ordering has an influence on the mechanism of diffusion. We made a comparison between two models for short-range order (SRO) in this system. For the first model we assumed that the concentration of Pt atoms was small enough to neglect SRO effects all together. As there is a weak tendency towards $L1_2$ ordering for $Ni_{1-x}Pt_x$ with x = 0.2 [6], a second model with strong Pt-Pt repulsion was used. Although in case of small concentrations of x=0.03 one can not speak of the formation of $L1_2$ structure, the effects on SRO are still significant.

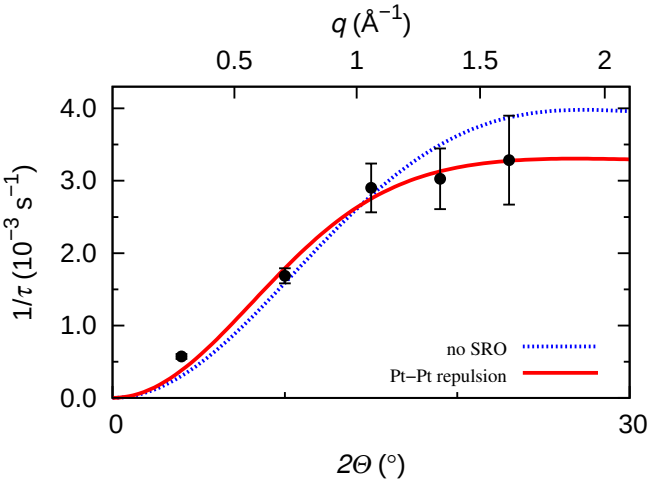

Figure 1: Correlation times measured for different scattering angles compared to models of atomic jumps according to the encounter model with no SRO (blue) and corrected for SRO resulting from Pt-Pt repulsion (red).

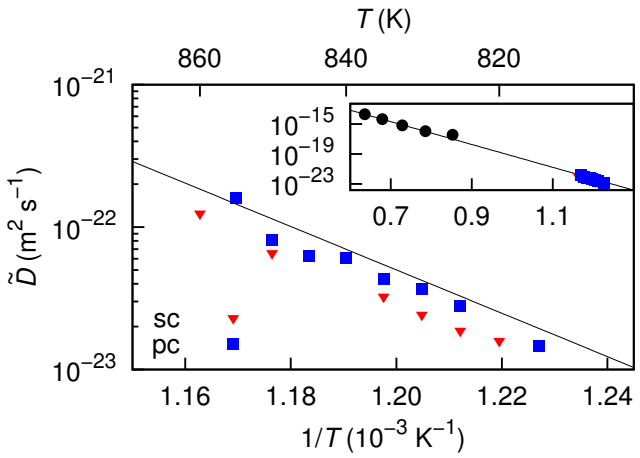

Figure 2: Diffusivities for single-crystalline (sc, triangles) and polycrystalline (pc, squares) $Ni_{97}Pt_3$ measured at different temperatures in comparison to data from tracer experiments (black).

Using a Metropolis Monte Carlo algorithm we calculated the SRO configuration for $Ni_{97}Pt_3$ and gained Warren-Cowley parameters of α_1 = -0.0309, α_2 = 0.0042 and α_3 = 0.0018. Figure 1 shows both models and the data measured for the single crystalline sample with its ⟨110⟩ axis oriented parallel to the incoming X-ray beam.

As the model with SRO correction for strong Pt-Pt repulsion agrees well with our experimental data, this model was used to calculate the diffusivities from correlation times at different temperatures. The results for the single crystalline, as well as for the polycrystalline sample agree well with diffusivities measured at higher temperatures with the tracer technique [7] extrapolated to lower temperatures using the Arrhenius law as shown in figure 2. This data was also used to calculate an activation enthalpy of 2.93(10) eV for single-, and 2.97(18) eV for the polycrystalline sample. Additional to interaction effects between atoms, which are accounted for by SRO, it was our goal to investigate the effects of interactions between vacancies and atoms on the diffusion mechanism. Unfortunately the statistics of our data was not good enough to allow for sound conclusions.

We conclude that aXPCS allows to draw conclusions about the atomistic jump mechanisms and determine diffusivities and the activation enthalpy. Further we have shown the importance of SRO in a system measured with a coherent method like aXPCS. Although single crystalline samples yield more information, we demonstrated that aXPCS experiments on polycrystalline samples are possible.

This research was funded by the Austrian Science Fund (FWF) contract P-22402.

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