RAPPORT D'EXPERIENCE
EXPERIMENTAL REPORT

TITRE DU PROJET : *PROJECT TITLE* :

Competition between ordering and phase separation in model superalloys
Ni X Cr (X=Al,Fe,Ti)

HC-590

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DATE DE DEMARRAGE : 03/95

NOMBRE DE SESSIONS EFFECTUEES : 9+12 in SAXS : 12+9 in 7C

LIGNE : D2AM

INSTRUMENT :

		EXAFS	GM	UHV	IF
SAXS	*	*			
7 CERCLES	*				
BIO-CRISTALLOGRAPHIE	☐				☐ ☐

RAPPORT D'EXPERIENCE

The purpose of this project was to quantify ordering and unmixing in a model ternary superalloy NiCrAl, during the phase change process. Anomalous scattering has been used near the Cr and Ni edges. Experiments were done as well at small angles (ASAXS), to measure the composition variations for the three elements between precipitates and matrix [1], as at wide angles on superstructure lines (AWAXS), to measure long-range order parameters [2]. Those two sets of measurements must be done on the same samples, for different heat treatments.

The first ASAXS and AWAXS measurements were presented in 95's experimental report: ASAXS results were scarce, due to detector problems; AWAXS results concerned rather late stages of precipitation (sizes from 4 to 20nm where coarsening is the dominating evolution process). This first experiments confirmed that the experimental methodologies and set-up were appropriate. Both measurements were improved to give quantitative results on fairly early stages of unmixing/ordering during the four "campagnes" (24-27/11/95 and 12-15/04/96 for ASAXS; 14-17/12/95 and 29/04-1/05/96 for AWAXS).

This report will be divided in three parts (each including technical aspects and results):

- **Precipitation kinetics** (including the choice of the alloys and of thermal treatments and emphazising the full consistancy of the results of standard SAXS or WAXS on the <u>same samples</u>)
- **ASAXS results:** by recording several ASAXS patterns near both Cr and Ni edges, we have been able to extract partial structure factors and to show that the phase separation behaves like in a pseudobinary system.
- **AWAXS results:** from the integrated intensities of superstructure lines, we deduced the occupancy ratio for the three elements on the ordering sites of the L12 precipitates.For the earliest stages at 600°C recorded in powder mode, we reach the limits due to sample signal/noise; further informations can only be obtained using single crystals, with preliminary experiments performed mid of May.

1 PRECIPITATION KINETICS:

Superalloy (Ni Al X Y ...) qualities are based on the decomposition of a high temperature disordered fcc solid-solution after quench and aging into the two phase region of the phase diagram. The equilibrium phases are coherent "precipitates" γ' of the ordered superstructure L12 (as Ni3Al), embedded in a remaining solid solution γ. In the ternary system Ni Cr Al, the compositions have been selected in order to retain as close as possible the high temperature disordered state after water quench from a relatively low temperature (850-920°C). The two compositions Ni0.76Cr0.18Al0.055 (alloy A) and Ni0.75Cr0.16Al0.09 (alloy B) are on the same equilibrium tie-line near 600°C; ie a decomposition with Al enrichment in γ' with the corresponding rejection of Cr, but with different volume fractions respectively of the order of 10 and 40%.
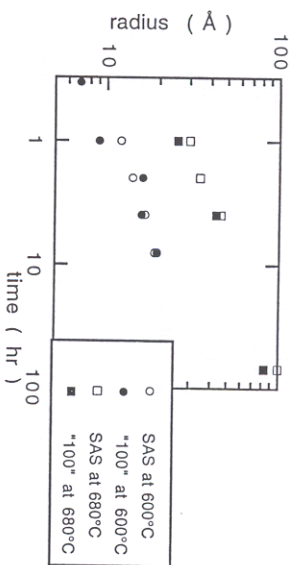
Standard SAXS and WAXS data give the same results for the sizes of precipitates (see Fig 1). The kinetics results will then be described independently of the technique.

Alloy A:
After quench, we did not detect a signal due to an eventual precipitation. The volume fraction increases by a factor of 10 after an isothermal aging at 600°C from 0.33h to 8h. Precipitates with sharp interfaces appear to grow

slowly. We are therefore observing an early stage of precipitation, for a composition off-centered with respect to the miscibility gap. In this regime, there is nucleation and growth but also simultaneously coarsening. On the other hand, the isothermal aging at 680°C corresponds to a later stage where the coarsening dominates the kinetics: the size growth is in t1/3 with an almost constant volume fraction; it corresponds to the evaporation-condensation mechanism described by Lifshitz-Slyozov and Wagner.
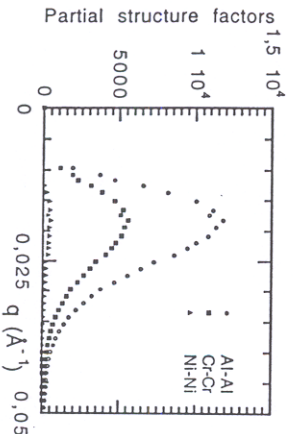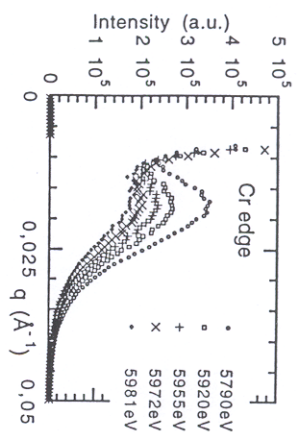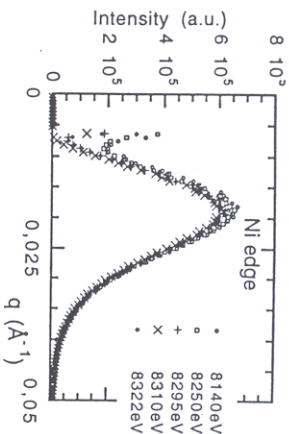
Alloy B:
Precipitation is already present after quench; moreover, together with small homogeneous precipitates, there are big (intergranular) precipitates. After partial reversion, the already present precipitates coarsen, but we should achieve proper homogeneisation and quench before any discussion on the kinetics.

radius (Å)

○	SAS at 600°C
●	"100" at 600°C
□	SAS at 680°C
■	"100" at 680°C

time (hr)

2 ASAXS RESULTS:

Although the methodology developed with O. Lyon at LURE is also well adaped to D2AM-SAXS instrument, measurements need to overcome more severe (contradictory) constrains. First, it appears a strong tail at small angles which superimposes to the signal of interest, rather weak (fig.2). This tail (classically observed inSAXS on alloys or metallic glasses) can be fitted to a q^{-n} power law and substracted correctly if the measured q range goes down to sufficiently low angles (qmin ≈ 0.01Å^{-1}). On the other hand, the Cr fluorescence, when probing the Ni edge, gives a flat signal which can be determined on the large q side of the SAXS pattern.

As a first compromise, we choose a long geometry (1600mm between sample and detector), to the detriment of the counting rate. This analysis shows that data is quantitative and can be well corrected for the three elements except for the very small scattering tail, and the corresponding Partial Structure Factors: the relative amplitude of the PSFs are very close from the one deduced from the two phase model, confirming the existence of well-defined γ' precipitates.

[1] J.P. Simon & O. Lyon, *ASAXS in Materials science*, in "Resonant Anomalous Scattering" by G. Materlik, C.J. Sparks & K. Fischer (North-Holland 94)

[2] A. Marty, M. Bessiere, F. Bley, Y. Calvayrac & S. Letèvre, *Determination of long range order in Ni-base ternary alloys by X-ray anomalous diffraction using synchrotron radiation*. Acta metall. mater. 38 (1990) 345-350

Figures (top):

Intensity (a.u.) vs q (Å⁻¹) — Ni edge; legend: 8140eV, 8250eV, 8295eV, 8310eV, 8322eV

Intensity (a.u.) vs q (Å⁻¹) — Cr edge; legend: 5790eV, 5920eV, 5955eV, 5972eV, 5981eV

Partial structure factors vs q (Å⁻¹); legend: Al-Al, Cr-Cr, Ni-Ni

They show γ' enrichment in Al, with the corresponding depletion in Cr while the whole sample is almost homogeneous in Ni. This holds for the three (1, 4 and 69h) aging at 680°C: in this coarsening stage close to equilibrium, precipitation follows the tie-line.

The second compromise was more adapted to early stages, and weak signals. The geometry was shortened to 800mm, and the photon flux was two order higher thanks to optics improvement. The flux allowed for the first time to test two ideas. First, the Cr fluorescence strongly degrades the signal/noise ratio near the Ni edge: since the Cr fluorescence is much softer than the elastic signal, ie absorbed much more efficiently, a copper filter is inserted between the sample and the detector; together with fluorescence attenuation, the filter avoids also the detector saturation. For data acquisition near the other (Cr) edge, arised the second following difficulty: the scattering tail nearby the beam-stop is much stronger, giving a local saturation of the linear gaz detector. This tail was attenuated by fixing a 10mm wide Cu filter on the beam stop. After this experiment we noticed that there has been a local deterioration of counting efficiency, unfortunately classical in case of overload in gaz detectors. We hope that the CCD detector under construction will be much robust and user friendly. Data have been recorded for the growth stage (from 0.33 to 8h at 600°C) in alloy A and for the as-quenched state of alloy B. If data are complete and seem tractable, the complete analysis will tell if they are quantitative

3 AWAXS RESULTS:

3-1 Experiments

The occupancy ratio for the three elements on the ordering sites of the L12 precipitates requires integrated intensities of superstructure lines. The same samples already measured by ASAXS, were studied in transmission with a rotation of the sample holder around the normal of the sample foil (to average the texture). The grain size is very small (several microns) so that we used a powder analysis. Furthermore, we check that there was no texture bias, since recorded patterns with and without omega oscillations can be superimposed. In order to put all measurements on the same scale, for the different X-ray energies and different heat treatments, integrated intensities of superstructure lines were compared to those of the corresponding fundamental lines. The superstructure intensities are about 0.01 of the fundamental ones.

For data acquisition near the Ni edge, it appears compulsory to use a Ge111 analysor, in order to suppress fluorescences and to reduce air scattering. For energies near the Cr edge, the X-ray flux is too small and a standard configuration was used (Dec 95); the ratios of integrated intensities 100/200 is compatible with the ones measured near the Ni edge although there is a systematic scaling factor of about 0.9. Under these conditions, superstructure reflexions, although giving small counting rates (several cps max) and widened (>1°) give a tractable signals, except for early stages at 600°C. Finally, in April 96, the analysis of December's data has shown that the anomalous intensities sufficiently vary near the Ni edge to extract occupancy ratios. Therefore, all acquisitions have been made with the analysor, with energies ranging from 10 to 8.1keV, saving realignment time. The dedicated spinner sample holder adapted to the Be box, was operational: the parasitic scattering of the line, including the evacuated Be box, was about 0.5 cps to be compared to noise of the detector without beam (0.07 cps) and an incident flux of several 10¹¹ ph/s. The limiting noise comes now from the sample itself (~2 cps). If analysis is not complete, we presume the effect of the tails of fundamental peaks (TDS on 111 varying in dq⁻²). Full anomalous quantitative analysis will then be very difficult for the early states at 600°C.

Therefore, we prepare single crystals of the same composition, with the same thermal treatments. During preparatory tests done in May, 100 superstructure lines were easily measured in reflection after an aging of 2h at 600°C and also measured after quench (local order or nucleus of γ'?). We cannot calibrate by the fundamental 200 peaks which intensity suffer dynamics effects. We therefore, made systematic tests of absolute intensity calibration using an Al powder. The analysis under progress actually reveals unconsistancies; They should be understood for the next experiment scheduled for end of July, mainly dedicated to single crystals.

3.2 Results:

The following figure show powder patterns of the 100 superstructure peak, recorded for 69h at 680°C. The upwards figure is under the Ni edge (8333eV), diamonds: -233eV, squares: -10eV; the downwards figure is under the Cr edge (5990eV), diamonds: -150eV, squares: -8eV.
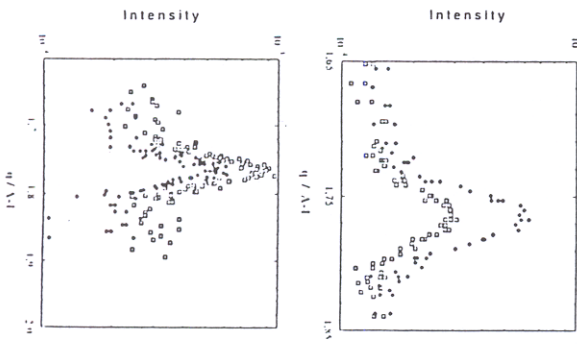
For the sample studied in Dec95 (1h, 4h, 69h at 680°C and 2 and 8h at 600°C), the analysis of the data gives the same results concerning ordering:
- when approaching the Ni edge, there is a drastic decrease of intensity (from 0.007 to 0.003)
- when approaching the Cr edge, there is a slight decrease of intensity around 0.017

The results are consistent with a small ordering of Cr on the Al sublattice.

Nevertheless the absolute order-parameters are larger than the volume fraction. It means that the intensity ratio superstructure/fundamental has been overevaluated: this is probably related to the difficulty of performing reliable Al calibration.

Figures (bottom): Intensity vs q / Å⁻¹ (two plots)