**07.2–15** RAPIDLY SOLIDIFIED (MELT-SPUN) ALUMINIUM ALLOYS: MORPHOLOGY, TEXTURE AND EXCESS VACANCIES. By P. van Mourik, M. van Rooijen, N.M. van der Pers, Th.H. de Keijser and E.J. Mittemeijer, Laboratory of Metallurgy, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands.

The morphology and texture of melt-spun AlMg (0-16.45 at% Mg) and AlSi (0-20.23 at% Si) ribbons (25-50 μm thick) were investigated by light microscopy (phase and interference contrast, conical illumination) and X-ray diffraction (Schulz method). After melt-spinning (cooling rate $10^6$–$10^7$ $K.s^{-1}$) it was found by X-ray diffraction that the AlMg alloys were single phase, whereas in the AlSi alloys both a Si-rich phase and an Al-rich phase were found. Generally three zones can be discerned; i.e. starting from the wheel side:
(i) A chill zone. In the AlSi alloys this zone was featureless. In the AlMg alloys the grain boundaries in this zone were oriented more or less perpendicular to the wheel side and for alloys containing less than 5 at% Mg this zone could not be distinguished.
(ii) A zone containing relatively long, columnar crystals. These crystals were inclined forward (the angle between the columns and the spinning direction was less than 90°).
(iii) A zone of small equiaxed grains. With increasing Si and Mg content an increase of thickness of this zone was observed.

The textures from wheel and upper sides are symmetrical with respect to the longitudinal section of the ribbon, but in general they are not fibre textures. As compared to AlSi alloys, AlMg alloys show sharper textures. The sharpness of the textures decreased in both cases with increasing content of alloying element. At the wheel side (chill zone) a general tendency was found for (111) planes to be aligned parallel to the wheel side. The texture of the intermediate zone was such that simple crystallographic directions (like <100>, <110>, <111>) were tilted with respect to the spinning direction. This may be related to the inclination of the columnar crystals. The zone of equiaxed crystals was found to possess no texture at all.

The uni-directional heat flow condition in the puddle at the wheel side is believed to be responsible for the columnar structure, while outside the puddle at the top side the different cooling conditions in combination with convection in the liquid metal result in the equiaxed solidification structure.

Rapidly solidified metals generally possess larger amounts of excess vacancies than conventionally quenched metals. As the volume of a vacancy is smaller than that of an atom, annihilation of excess vacancies induces an increase of the average lattice parameter. In all cases the value of the lattice parameters showed a sudden increase on ageing. This increase of the lattice parameter cannot be attributed to precipitation. For the AlSi alloys this follows from precipitation experiments. For the AlMg alloys precipitation results in a *decrease* of the lattice parameter. Furthermore, no diffraction evidence for precipitation was found in the present experiments. Such sudden increase of the lattice parameter did not occur in additional experiments with conventionally quenched AlSi alloys. Therefore we arrive at the following conclusions:
(i) The increase of the lattice parameter at the start of ageing is caused by excess vacancy annihilation.
(ii) The amount of excess vacancies strongly increases with the concentration of the alloying element in solid solution.

These results may contribute to the understanding of the precipitation kinetics in rapidly quenched aluminium alloys. Excess vacancy annihilation results in the formation of vacancy loops. These loops may facilitate nucleation and may serve as a source of vacancies to promote precipitation and/or to accommodate misfit between matrix and precipitate.

**07.2–16** MAGNETIC AND CRYSTALLINE STRUCTURE OF A COATED $CoFe_2O_4$ COLLOIDAL PARTICLE. By A.C. Nunes, Physics Dept., University of Rhode Island, Kingston, RI 02881 USA; C.F. Majkrzak, Physics Dept., Brookhaven National Laboratory, Upton, NY 11973 USA; and A.E. Berkowitz, G.E. Corporate Research Laboratory, Schenectady, NY 12301 USA.

We describe an X-ray and polarized neutron powder diffraction study of finely divided $CoFe_2O_4$ particles (diameter approximately 100 Angstroms) coated with oleic acid and naked. Powder line shapes and electron microscopy indicate that a disordered layer approximately 25 Angstroms thick may be induced in the ferrite by the prescence of the surfactant. Line profiles of coated particles taken with polarized neutrons vary in width with the neutron polarization state suggesting that the magnetization density within a coated particle is attenuated in a surface layer thicker than the crystallographically disordered layer. This is not observed with the naked particles, which show neutron spin state independent line widths. Thes results are consistent with Mössbauer and magnetization experiments reported earlier (IEEE Trans. Magn. MAG-16 (1980)).

**07.2–17** IN-SITU ANNEALING X-RAY DIFFRACTION STUDIES OF METAL-METAL AND METAL-SEMICONDUCTOR THIN-FILM INTERFACE REACTIONS. By J. M. Vandenberg and R. A. Hamm, AT&T Bell Laboratories, Murray Hill, NJ 07974

Alloy formation and diffusion in polycrystalline thin-film couples is a field of intensive study because of increasing interest in both basic properties of thin films and practical device applications. In conventional studies the alloying procedure involves sequential deposition of two metals or a metal on a semiconductor followed by a vacuum annealing treatment at various temperatures. The interface reaction is then investigated on its structural properties. We have now designed a high-vacuum annealing system for in-situ X-ray diffraction studies. This system enables us to monitor the interface reaction as a function of time and temperature during in-situ annealing under vacuum in the temperature range 35° - 950°C. A small high-vacuum chamber was built with an adjustable Mo heating block to hold the thin-film sample and an aluminized mylar window was used for the incoming and diffracted X-ray beam. The chamber was mounted on a standard Huber-Guinier adjustment base; in this design we made use of glancing angle X-ray diffraction with the Seeman-Bohlin focusing geometry and monochromatic $CuK\alpha_1$ radiation using a 12 kW Cu rotating anode. A moving X-ray film cassette can be mounted on the base to provide time and temperature dependent photographic X-ray analysis. In-situ X-ray experiments were carried out to study the sequence of phase formation in Cu-Al, Au-Al and Ag-Al thin-film couples. While the temperature was slowly increased (~0.4°C/min) transient phases were found to grow in the thin-film interface. These phases could be identified as high-temperature or metastable phases such as $\beta_1$ - $Cu_3Al$ and some of them were found to be new phases (J. M. Vandenberg et al, Thin Solid Films (1982) 97, 313).

In a similar study on the growth of A15 materials in multilayer films a new Sn-rich phase with a phase transition was observed in the initial stage of the interface reaction.

For another practical application, gold contact metallization on InGaAsP layers was studied (J. M. Vandenberg et al, J. Appl. Phys. (1982) 53, 7385). A well-defined sequence of Au-In alloys with increasing In content was identified; as the composition changes from the binary InP to the ternary InGaAs the reaction temperatures of the alloys decrease. These observations could be explained in terms of the thermodynamics of solid state reactions and related to previously observed variations in contact resistance.

The moving X-ray film cassette can be exchanged with a Huber counter tube attachment; scans and data acquisition are computer controlled. In this mode the initial growth kinetics of the Cu-Al thin-film system were studied. The rate of reaction of $CuAl_2$, the first phase growing in the interface, was monitored via changes of integrated intensities. Similar studies were done using in-situ annealing Rutherford backscattering analysis. Good agreement was obtained between growth parameters of $CuAl_2$ determined for each technique. The X-ray technique appears to be the more advantageous method to simultaneously study the growth of more than one phase, since it allows exact phase identification and therefore each phase can be monitored individually. In the case of the Cu-Al system the in-situ X-ray scans indicated the growth of $Cu_9Al_4$ together with $CuAl_2$ and the growth parameters of $Cu_9Al_4$ could now for the first time be determined. These results indicated that in-situ annealing X-ray diffraction can be a valuable tool to study phase formation and growth kinetics of individual phases in thin-film interfaces.

07.2–18 IN SITU OBSERVATION OF TANTALUM THIN FILM OXIDATION. By S. Lugomer, M. Kerenović and M. Stipančić, Electronical Faculty, Banja Luka, Yugoslavia.

Comparative study of isothermal (T=700K) and nonisothermal (T increased from 300K to 700K) thin Ta film oxidation in air, by in situ reflectivity and electrical resistivity measurements, has been performed.

Amorphous, very porous structure, consisting of $Ta_2O_5$, TaO and TaOx (x<1) solid mixture, was found.

An anomalous electrical resistivity peak was found in the incubation period. Nonisothermal oxidation kinetics curve $d=f(\tau)\,|\,\tau$=time, d=oxide thickness|, fit very well the interrupted kinetics; incubation period-to the temperature dependent Koofstad's equation:

$$d = \frac{RT}{Q} \ln(\tau+\tau_0)+C,$$

and period of extended oxidation - to the simple logarithmic equation:

$$d = 49 \log(\tau-46)+5.$$

Isothermal oxidation kinetics curve fit excellently the uninterrupted parabolic equation.

$$d = 21(\tau - 9)^{1/2} - 19.$$

|$\tau$ in minutes, d in nm|.

07.2–19 INFLUENCE OF CORRELATION AND ANISOTROPY ON THE CRYSTAL FACE MOLECULAR ROUGHNESS. BY Z.Matysina, A.Ovrutski, L.Chuprina, M.Milyan. Dniepropetrovsk State University, 320000 Dniepropetrovsk, USSR. The molecular roughness on the crystal surface bonding with melt has been investigated by the quasichemical method with taking into account the correlation of reciprocal atom situations and anisotropy of atomic interaction. The dependences of the interfacial free energy on concentration of condensed "solid" atoms were determined for different temperatures and interaction energies of atom pairs $V_{ss}$, $v_{ss}$, $V_{sl}$, $V_{ll}$ (s- "solid", l - "liquid", $V_{ss}$ and $v_{ss}$ are the energies of strong and weak s-s bonds). Both correlation and anisotropy reduce the free energy, the minimum of surface free energy becomes more deep for roughness surface. Temperature dependences of the face roughness (the energy of the surface relative to the energy of smooth face) were calculated and they were compared with the known results of other models. The coincidence of theory with the experimental data for Bi was received for $v_{ss}=0.9\ V_{ss}$ if $V_{sl} \leq 0.97 V_{ll}$. The model with limitations on the "solid" atoms surrounding was studied also.

07.2–20 ФАЗООБРАЗОВАНИЕ В ТОНКИХ ПЛЕНКАХ Tl – S. Ф.И.Алиев, И.В.Иванова, Д.И.Исмаилов и Р.Б.Шафизаде, Институт Физики Академии Наук Азербайджанской ССР, Баку, СССР.

Рассмотрены вопросы взаимодействия и фазообразования в системе Tl – S при вариации условий вакуумного осаждения компонентов. Проведен электронографический анализ образующегося конденсата. При одновременном осаждении Tl и S на свежие сколы NaCl, на которые предварительно был осажден углерод толщиной ~50Å, образуются 5 различных сульфидов таллия: 4 из них в аморфном состоянии и 1 в поликристаллическом. Кристаллизация аморфных пленок показала наличие соединений: $Tl_2S$, $Tl_4S_3$, TlS и $Tl_2S_5$, а кристаллическая фаза отнесена к составу $Tl_8S_{17}$ ( Васильев и др., Известия АН СССР, серия Неорганические материалы (1973) 9, №4, 553). Все фазы, кроме $Tl_2S$, текстурированы, ось текстуры – ось "c". Косые текстуры от $Tl_8S_{17}$ позволили однозначно определить период кубической решетки a = 10.60Å, пространственная группа характеризуется отсутствием погасаний. При последовательном осаждении компонентов (Tl на S и наоборот) на плоскости конденсации образуются лишь две аморфные фазы: $Tl_4S_3$ и TlS. Термообработка поверхности конденсации при T≈150°C в течение ~ 20 минут приводит к кристаллизации аморфных пленок, при этом помимо указанных двух фаз выявляется еще и фаза $Tl_2S$.