Production of High-Strength Aluminum Alloys Reinforced by Nanosize Quasicrystalline Particles

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Quasicrystals are new perspective materials, in which

♦ the translational long-range is absent;
♦ there is a rotational symmetry with 5-, 8-, 10- or 12-fold axes (that is forbidden in crystalline materials), there is orientation long range ordering;
♦ high hardness (up to 10 GPa), brittleness while standard testing and plasticity at local loading are observed.

It was shown in previous works of authors that the plasticity at local loading is a result of the phase transition to a crystalline structure. It is proved by:

- serrated yielding during nano-hardness measurement;
- extrusions of ductile phase around the indent;
- special shape of the indents.
Overview of amorphous, nanocrystalline and quasicrystalline alloys

- High strength, hardness
- High corrosion resistance
- High accumulated elastic energy

Short range ordering in small regions. No long range ordering

- High strength and decreased ductility,
- High wear resistance,
- High fatigue limit
- Superplasticity after heating and annealing

High fraction of intergranular boundaries and triple junctions

- High strength, hardness
- High thermal stability
- Low friction coefficient
- Local ductility
- Low thermoconductivity

No translation symmetry, 5-, 8-, 10-, 12-fold symmetry of atomic structure

prospective for application as the structural materials and coatings
Packing Atoms in QC

4 atoms are packed in tetrahedron and 20 tetrahedrons are packed in icosahedron.

Icosahedron has six 5-fold axes.
Penrous Mosaic gives good description of QC atomic structure

decagons have identical orientations – long range ordering exists, but translation symmetry is absent

5 systems of quasiplanes are shown. They give 5-fold symmetry diffraction patterns
Mechanical Properties of QC

- High hardness (HV to 8-10 GPa) at temperatures to 600 K;
- High elasticity modulus (100-200 GPa);
- Macroscopic brittleness at $T < 0.8T_m$ and high ductility ($\varepsilon_{pl}$ to 130 % for AlCuFe and to 87 % for AlPdMn) at $T > 0.85T_m$ with strain softening;
- Strain softening is typical for QC

$Al_{63}Cu_{25}Fe_{12}$, polycrystal
[Bresson & Gratias, 1993]

$Al_{70}Pd_{21}Mn_9$, single quasicrystal
[M. Wollgarten et al., 1993]

$T_m = 870$ °C

$T = 750$ °C

Stress-strain curves for compression test in vacuum
Deformation of QC has dislocation character, but Burgers vector

\[ \mathbf{b} = \mathbf{b}_{\text{phon}} + \mathbf{b}_{\text{phas}} \]

\( \mathbf{b}_{\text{phon}} \) is the usual translation component;

\( \mathbf{b}_{\text{phas}} \) is the component typical for QC only and leads to formation of phason defects, which are local distortions of QC structure.

**Yield stress of QC**

\[ \tau = \tau^* + \tau_d + \tau_i \]

\( \tau^* \) is the Peierls stress – is large as in covalent crystals;

\( \tau_d \) is the dragging stress of phason defects, arising at dislocation motion;

\( \tau_i \) is the stress for overcoming other dislocations.

At a considerable concentration of phason defects a local lowering of the height of Peierls barriers and their widening occurs and softening stage begins.
Stress-strain curves at room temperature were obtained by indentation technique [Milman et al., 2000]

Plastic deformation decreases yield stress $\sigma_s$, but annealing increases $\sigma_s$.

High hardness in QC keeps up to 300 °C.
Isothermal section at 680 °C of the Al - Cu - Fe phase diagram in the vicinity of the icosahedral phase (≈ Al$_{63}$Cu$_{25}$Fe$_{12}$)

**Hume-Rothery rule:**

\[ e/a \approx 1.75 \text{ in Al-Cu-TM, Al-Pd-TM}; \ e/a \approx 2.1 \text{ in Al-Li-Cu} \]
Low-temperature microplasticity in QC (Al-Pd-Mn) is the result of phase transition during indentation: QC → approximant crystalline phase

indentation at 473 K, \( P = 2.34 \) N

Steps in nanoindentation curves of QC (Al\(_{65}\)Cu\(_{23}\)Fe\(_{12}\)) and extrusions around indentation can be interpreted as phase transition during indentation: QC → approximant crystalline phase
Nanoquasicrystalline Materials (NQC)

QC with nanosize grain (NQC) is the separate class of materials

In crystals dislocation energy \( E \sim \ln d \), in QC \( E \sim d \)

For this reason NQC differ essentially from QC and from NC.

NQC have high hardness as QC and more and some plasticity at room temperature

NQC is the best material for dispersion hardening of metals
Stress-strain curves of Al-Cu-Fe quasicrystals, obtained by indentation

SMQC – submicron quasicrystal material
NQC – nanoquasicrystal
CGQ – coarse grain quasicrystal

At indentation of NQC cracks are ABSENT!

[Milman, Yefimov, Ulshin, Ustinov et al., 2006]
A. Inoue has shown that Al alloys with disperse strengthening by metastable intermetallic phases with a quasicrystalline structure can be produced by rapid solidification.

The present work is devoted to Al-Fe-Cr alloys, obtained by rapid solidification technique (water atomization and melt-spun ribbons)

*Powder consolidation was made by* isothermal pressing and extrusion of pressed billets in hermetic capsules or by vacuum forging and extrusion of forged billets.
The chemical composition of some investigated alloys are given in the table

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition, at %</th>
<th>Composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Al}<em>{94}\text{Fe}</em>{3.5}\text{Cr}_{2.5}$</td>
<td>$\text{Al-6.88Fe-4.54Cr}$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Al}<em>{94}\text{Fe}</em>{2.5}\text{Cr}_{2.5}\text{Ti}_1$</td>
<td>$\text{Al-4.89Fe-4.55Cr-1.68Ti}$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Al}<em>{94}\text{Fe}</em>{2.5}\text{Cr}<em>{2.5}\text{Ti}</em>{0.5}\text{Zr}_{0.5}$</td>
<td>$\text{Al-4.86Fe-4.52Cr-0.83Ti-1.59Zr}$</td>
</tr>
</tbody>
</table>
Schematic representation of the Al-alloys Water Atomization Unit
Production of Melt-Spun Ribbons
Characteristic particle shape in water atomized POWDERS of Al-Fe-Cr-(Ti, Zr) alloys (a) and quasicrystalline participates in section of powder particles (SEM) (b)
Microstructure of RIBBON Al$_{92.8}$Fe$_3$Ti$_2$Cr$_2$Sc$_{0.2}$, TEM investigation

Nanostructural Al matrix (200-300 nm) and are reinforced by nanosize (50-100 nm) quasicrystalline particles
NEW DIRECTION in POWDER METALLURGY:
producing powders by the technique of rapid crystallization of the melt with the formation of non-equilibrium metastable structures (the solidification rate to $10^6$ °C/s)

*Techniques of producing powders:*

- manufacturing powders by atomizing the melt with high-pressure water or by gas atomization;
- manufacturing flakes and ribbons by spinning on a rapidly turning metallic wheel.

*Techniques of powder consolidation:*

- isothermal pressing and extrusion of pressed billets in hermetic capsules;
- vacuum forging and extrusion of forged billets.

**Powder consolidation is carried out by means of severe plastic deformation without sintering process**

*Advantages:*

- a possibility of increasing the concentration of alloying elements, lowering the grain size, eliminating the liquation → improving mechanical properties;
- dissolution of harmful admixtures in the solid solution (e.g., Fe in Al that allows to use the recycled Al for producing high-strength Al alloys);
- creating new structural states: amorphous and quasicrystalline phases.
Structure, dark field image (a) and electron diffraction pattern of 5-fold symmetry (b) of an i-phase PARTICLE in RIBBON Al$_{84.2}$Fe$_7$Cr$_{6.3}$Ti$_{2.5}$
Evaluation of phonon and phason distortions in Al-Fe-Ti-Cr quasicrystalline phase

\[ B^2 = AG_{II}^2 + CG_{\perp}^2 + D \]  

(1)

\[ B \] – X-ray line broadening,
\[ A \] and \[ C \] – measures of phonon and phason disordering respectively,
\[ D \] is the quantity reciprocal to the squared size of coherent region \( D_{eff} \).

\[ G_{II} = \frac{1}{a_6} \sqrt{\frac{N + M\tau}{2(1 + \tau^2)}} \]
\[ G_{\perp} = \frac{1}{a_6} \sqrt{\frac{\tau(N\tau - M)}{2(1 + \tau^2)}} \]  

(2)

\( G_{II} \) and \( G_{\perp} \) – components of the reciprocal lattice vector,
\[ N/M \] – Cahn indices of reflections from icosahedral phase,
\( \tau = (1 + \sqrt{5})/2 \) – the golden section,

\[ a_6 = d \frac{\sqrt{N + M\tau}}{2\sqrt{2 + \tau}} \]

– the parameter of the elementary cell of the i-phase in the 6-dimensional space,

\[ d \] – the interplanar distance defined from the line position in XRDP (\( 2d\sin\theta = \lambda \))
Angular dependence of X-ray line broadening for rapidly quenched Al-Fe-Cr-Ti ribbons

Factors characterizing the values of phonon (A) and phason (C) distortions in the Al-Fe-Cr-Ti i-phase

Ribbon structure and composition | $A_i$ phonon distortion | $C_i$ phason distortion
--- | --- | ---
QC particles in Al matrix | $Al_{84.2}Fe_7Cr_{6.3}Ti_{2.5}$ | $5 \times 10^{-5}$ | $1.2 \times 10^{-2}$
 | $Al_{93}Fe_3Ti_{2}Cr_2$ | $130 \times 10^{-5}$ | $4.5 \times 10^{-2}$
QC phase in X-ray diffraction patterns of POWDERS

Al_{94}Fe_{2.5}Cr_{2.5}

Al_{94}Fe_{2.5}Cr_{2.5}Ti_{0.5}Zr_{0.5}

Al_{94}Fe_{2.5}Cr_{2.5}Zr_{1}
Sections of X-ray diffraction patterns of RODS of alloys $\text{Al}_{94}\text{Fe}_{3.5}\text{Cr}_{2.5}$, $\lambda = 12.8$:

a) $T_{\text{extrusion}} = 400^\circ \text{C}$;  
b) $T_{\text{extrusion}} = 350^\circ \text{C}$
# Mechanical properties of RODS from Al-Fe-Cr alloys

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Test temperature</th>
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<tbody>
<tr>
<td></td>
<td>20 °C</td>
</tr>
<tr>
<td></td>
<td>YS, MPa</td>
</tr>
<tr>
<td>Al-Fe-Cr</td>
<td>485</td>
</tr>
<tr>
<td>Al-Fe-Cr-Ti</td>
<td>546</td>
</tr>
<tr>
<td>Al-Fe-Cr-Ti-Zr</td>
<td>648</td>
</tr>
</tbody>
</table>
Change of hardness of PM extruded RODS after isochronous annealing at various temperatures, holding time of 100 h
Conclusion

The process of water atomization may be used for production of powder of Al-Fe-Cr alloys containing i-phase. Compaction of these powders must be made by severe plastic deformation without sintering.

The elevated temperature aluminum alloys obtained by the optimum regimes had a nanostructural Al matrix (200-300 nm) and are reinforced by nanosize (50-100 nm) quasicrystalline particles.

The best compositions of Al-Fe-Cr-Ti and Al-Fe-Cr-Ti-Zr had tensile strength at 300 °C on the level of 300 MPa and higher together with the residual elongation at ambient temperature of about 8 % and Young modulus close to 89 GPa. The produced alloys had a good thermal stability of strength properties at 300 °C.

According to X-ray diffraction analysis, only the quasicrystalline i-phase as a strengthening one is present in the structure of the rods of alloys manufactured by optimum regimes.

THANK YOU FOR ATTENTION!