Decomposition of Supersaturated Solid Solution in Fast-Quenched Al-Co-Zr and Al-Fe-Co-Zr Alloys

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Abstract. Aluminum-based alloys are the most popular structural materials. Strength and refactororiness can be improved by doping with transition metals; this effect can be amplified by fast quenching from liquid state, which will expand the solid-solution regions and disperse the intermediate phases in transition metal-aluminum alloys. The decomposition of supersaturated solid solutions (SSS) under special conditions releases the fine-dispersed hardening intermetallic phases, which boosts the strength of the alloy. The way fast-quenched Al-Co-Zr and Al-Fe-Co-Zr alloys change their microhardness after isothermic annealing at 470, 570, or 670 K indicates dispersion hardening. Durometer testing points to a considerable hardening of fast-quenched Al-Co-Zr and Al-Fe-Co-Zr alloys, which is caused by the decomposition of supersaturated solid solutions. Staging the decomposition of Co, Zr, or Fe SSS in aluminum helps predict how the doping additives as well as the temperature and timing of subsequent thermal treatment affect the strength of aluminum alloys.

1. Various SSS Decomposition Pathways
The application of hardening fast-quenched aluminum alloys is related to their resilience to heating. Analyzing the decomposition of the supersaturated solid solutions of doping additives in aluminum helps adjust the temperature and timing of subsequent thermal treatment. A supersaturated solid solution (SSS) is thermodynamically unstable, and any changes therein decrease free energy. In general, the process releases a phase that differs from the matrix in its chemical composition and structure. There are two fundamentally different pathways of this decomposition: it is either spinodal or occurs due to the emergence and growth of nucleation sites.

Spinodal decomposition was first theorized upon by Gibbs in the 19th century applicable to liquid solutions. Spinodal decomposition has drawn greater interest in recent decades, as it can be used to distributed the dispersed decomposition products evenly in the alloy. Unlike spinodal decomposition, which continuously decreases free energy, the emergence and growth of nucleation sites first causes a rise, then a fall in such energy. Thus, there exists a thermodynamic barrier that prevents large sites of a new phase from emerging; altering a solid solution therefore requires considerable energy for activation. At low temperatures, direct transition of a solid solution to an equilibristic structure might be impossible as the multiplier exp(-Ea/kt) is too low. In the case under consideration, nucleation sites are necessary for decomposition to begin and run spontaneously while decreasing free energy. Such sites can emerge if the system has locally altered structures.

2. Decomposition of Co, Fe, Zr SSS In Al
Durometric, X-ray diffraction, and microstructural analysis show that the decomposition of supersaturated Co and Zr; Fe, Co, and Zr solid solutions in Al can be either continuous or non-continuous. Ear-
lier studies revealed continuous (spinodal) release of the intermetallic phase caused by low-dose doping of binary aluminum alloys with zirconium, molybdenum, and tungsten [3]. The process is characterized by a single-phase structure, from which a fine-dispersed phase is released and is then distributed evenly in the alloy.

The microstructure of the tested fast-quenched Al-Co-Zr and Al-Fe-Co-Zr alloys doped at low dosage (Co 0.06;0.08at.%, Zr 0.03;0.08at.% in Al-Co-Zr, or Fe 0.014;0.07at.%, Co 0.006;0.02at.%, Zr 0.01; 0.03at.% in Al-Fe-Co-Zr) has the same traits as described in [3]. A characteristic shape of the TTT diagrams indirectly confirms the systems undergo spinodal decomposition. As shown in Figure 1, the curve of transition from the single-phase region ($\text{Al}_{\text{dep}}\text{Co,Zr}$ or $\text{Al}_{\text{dep}}\text{Fe,Co,Zr}$) to the two-phase region ($\text{Al}_{\text{dep}}\text{(Zr)}+\text{Co}_2\text{Al}_9$ или $\text{Al}_{\text{dep}}\text{(Fe,Zr)}+\text{Co}_2\text{Al}_9$) is nearly parallel to the Y-axis, whereas the transition region itself is very narrow. The modeled low activation energy [4] is consistent with the curves in TTT diagrams, i.e. a small region where cobalt aluminide is released from the Co and Zr SSS is associated with low activation energy of about ~10 kJ.

![Figure 1. TTT diagram for FQAs:](image)

(a) Al 99.00 at.%, Co 0.67 at.%, Zr 0.33 at.% ; (b) Al 99.10 at.%, Fe 0.4 at.%, Co 0.2 at.%, Zr 0.3 at.%.

Experimental data suggest supersaturated solid solution in a triple or quadruple FQA with a high concentration of doping additives will undergo two-phase decomposition. Intermetallic phase nucleates in samples containing Co 0.67at.%, 2.00at.%; Zr 0.33at.%, 1.00at.%, and Fe 0.08at.%, Co 0.04at.%, Zr 0.06at.% ) when subjected to short-term thermal treatment (0.3 h): ZrAl$_3$ or FeAl$_3$ in a triple alloy or a quadruple alloy, respectively. The presence of primary large inclusions of the second phase will accelerate the decomposition of supersaturated solid solutions. The way fast-quenched Al-Co-Zr and Al-Fe-Co-Zr alloys change their microhardness after isothermic treatment at 470, 570, or 670 K indicates dispersion hardening. Durometer testing reveals considerable hardening in Al-Co-Zr FQA.

Stronger diffusion of Co and Fe atoms in SSS renders such solutions in alloys non-resilient to heat. However, the morphological changes associated with the decomposition of Co and Zr, Fe, Co, and Zr SSS in Al are favorable. In many cases, FQA hardening is associated with lesser plasticity, which is due to localized release and rapid coagulation of phases. The suggested spinodal decomposition of fast-quenched low-alloyed Al-Co-Zr and Al-Fe-Co-Zr alloys partially addresses localized phase release characteristic of FQA, which helps retain plasticity. Decomposition as such is mainly affected by intermetallics ($\text{Co}_2\text{Al}_9$, $\text{FeAl}_3$, $\text{ZrAl}_3$) released by the isothermal annealing of the doping additive.
Figure 2. Dispersion hardening curves for triple alloys of aluminum and transition metals:
1) Al-Zr [7]; 2) Al-Co-Zr [7]; 3) Al Mo-Zr [8]; 4) Al-Nb-Zr [9]; 5) Al-Co-Zr; 6) Al-Fe-Co-Zr.

Crystallization produces solid solutions saturated with transition metals, and the greater the saturation, the stronger will be its effect on the kinetics of decomposition the SSS of doping additives undergo. Intermetallic phases released from the SSS retain their fine-dispersed structure for 12 hours at 470 to 670K.

3. Conclusions

Al-Co-Zr alloys are prone to retaining their plasticity, as cobalt additives improve plasticity as such [10] whereas the continuous release of the intermetallic phase reduces embrittlement caused by the localized release of phases from supersaturated solid solutions.

Analysis of the crystallization and decomposition of supersaturated solid solutions in fast-quenched Al-Co-Zr and Al-Fe-Co-Zr alloys is fundamental to developing a super-strong aluminum alloy technology.

4. References

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