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## 铸造、快凝及增材耐热铝合金的研究进展

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**摘要:**近年来, 航空航天领域对 300~500 °C中温区间具有出色高温抗氧化、抗蠕变能力的轻质耐热铝合金材料, 需求愈加旺盛。然而, 铝合金的高温软化问题一直是制约中温区间零件结构设计和服役安全的关键短板。要克服该短板, 应针对不同应用场景的综合需求(性能、成本、效率), 考虑不同制备工艺的特性, 对不同体系合金进行外加或合金化原位自生的方式在合金基体内均匀分布足够数量的热稳定纳米相, 以此钉扎晶界并抑制晶界运动和位错滑移。本文从铸造、快速凝固、增材制造三方面归纳了耐热铝合金的研究进展和应用, 并展开分析了不同体系耐热铝合金组织性能的调控手段, 总结了耐热铝合金研究的最新成果, 同时对耐热铝合金未来的研究方向进行了展望。

**关键词:**耐热铝合金; 制备工艺; 成分优化; 组织调控; 服役性能

**中图分类号:** TG146.2      **文献标志码:** A

航空航天工业是国家战略产业的发展重点, 在满足结构强度和服役性能的前提下, 应尽可能节约能耗和降低运载成本。因此, 构件轻量化一直是其追求的重要目标<sup>[1-3]</sup>。铝合金材料因其轻质、高强、耐磨耐蚀等优势特性, 在航空航天领域具有广泛应用<sup>[4-5]</sup>。虽然大部分铝合金材料在室温条件下都有较好的综合力学性能, 但是铝合金高温软化问题一直是制约其中高温区间零件结构设计和服役安全的关键短板<sup>[4, 6-9]</sup>。比如具有代表性的 7075 铝合金, 在 200 °C和 300 °C条件下, 合金的抗拉强度只有室温的 30 %和 10 %<sup>[10]</sup>。因此, 对于航空航天领域最为关心的 300~500 °C温度区间, 行业更倾向于使用更重、更贵的钛合金<sup>[11-12]</sup>。若能提升铝合金的中温强度, 使其在>300 °C条件下服役, 则可取代部分昂贵的钛合金材料, 实现“以铝代钛”, 以满足构件轻量化与经济效益的双重需求<sup>[13-14]</sup>。

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耐热铝合金是指在 150~350 °C服役环境下具有足够的抗氧化性，并且在热-力耦合的长时间作用下，具备一定抗蠕变性以及力学性能的合金<sup>[15]</sup>。该类合金在航空航天、交通运输、高压输电、石油钻探等行业得到了广泛应用，例如飞机轮毂和航空尾翼、发动机活塞和缸体、高压输电导线及石油钻杆等，如图 1 所示<sup>[16-17]</sup>。随着航空工业、轨道交通及石油化工的不断发展，上述行业对耐热铝合金的综合性能（高温强度、耐热性能、抗疲劳性能等）提出了更高的要求。然而，大部分高强铝合金内部析出相(Al<sub>2</sub>Cu、Mg<sub>2</sub>Si、Mg<sub>2</sub>Zn 等)在 200 °C以上会迅速粗化<sup>[15]</sup>，造成铝合金强度急剧下降。因此，开发具备高耐热、高强韧的新型耐热铝合金材料已成为当前的研究热点。

铝合金的高温力学性能主要由两个因素决定，室温强度和高温强度的衰减率<sup>[7]</sup>，因此需同时保证室温强化效果和高温微观组织稳定性。目前，在成熟的高强铝合金研究基础上，提升耐热性能的主要策略是在基体内部形成高体积分数的热稳定强化相，以利用强化相对位错、晶界的有效钉扎作用来提升合金的高温综合性能。以此为研究目的，科研工作主要从三个方面入手：优化合金成分、改善制备工艺以及适配热处理工艺，来综合促使基体内部形成更高体积分数且弥散分布的热稳定强化相，从而提升铝合金的耐热性能。针对不同的应用场景和性能需求，需选择适合的耐热铝合金成分和制备方法。本文以传统铸造法、快速凝固技术以及激光增材制造三种制备工艺为大方向，聚焦于耐热铝合金成分-制备工艺-服役性能三者之间的关系，探讨三种制备方法优势与不足，展开分析不同体系耐热铝合金组织性能的调控手段，以期耐热铝合金的制备提供参考依据，并推动铝合金构件的应用和国家航空工业的发展。



图 1 耐热铝合金的应用领域分类<sup>[16-17]</sup>

Fig. 1 The classification of heat-resistant aluminum alloy based on their application area<sup>[16-17]</sup>

# 1 铸造耐热铝合金

对于耐热铝合金而言, 铸造工艺发展多年且较为成熟, 在汽车、航空航天, 船舶等行业均得到了广泛应用。在制造领域, 例如 A319、A380、ZL702A 等合金已成功商用化并用于汽车发动机的生产制造<sup>[11, 18-19]</sup>。铸造耐热铝合金的加工成形简单、制造成本低, 但其工艺特性导致元素固溶度较低, 难以在铝合金基体内形成足够体积分数的析出相<sup>[21-22]</sup>, 并且在使役温度超过 200 °C 以上时, 其内部的  $Mg_2Si$ 、 $Al_2Cu$ 、 $Al_2CuMg$  等强化相会逐渐粗化, 造成力学性能下降, 铸造耐热铝合金高温性能提升接近瓶颈<sup>[21-22]</sup>。

在汽车发动机不断追求轻量化和高功率的需求之下, 研究人员通过对常用 Al-Si 系和 Al-Cu 系铸造耐热铝合金, 进行调控合金成分、探索新型高温强化机理和改进铸造工艺来不断提高铸造耐热铝合金的高温性能。

## 1.1 Al-Si 系铸造耐热铝合金

Al-Si 系铸造铝合金是目前使用最广泛的铸造铝合金, 其生产总量高达铸造铝合金的 90 % 以上<sup>[23-24]</sup>, 常用于制造汽车轮毂<sup>[25-26]</sup>和发动机活塞<sup>[27]</sup>。为了在基体内形成足够数量的析出相来强化 Al-Si 合金, 常添加 Mg、Cu 元素来提高其室温力学性能, 再添加微量 Zr<sup>[28-29]</sup>, Sc<sup>[29-30]</sup>, Ni<sup>[31-32]</sup>, Ti<sup>[22]</sup> 等元素细化晶粒尺寸。以上元素形成的强化相具备良好的热稳定性, 且与铝基体存在一定的位向关系, 通过析出相在合金内的钉扎作用提升其高温力学性能<sup>[33-34]</sup>。

### 1.1.1 Al-Si-Mg 铸造耐热铝合金

Al-Si-Mg 铸造铝合金拥有良好的机械性能、铸造性能和疲劳性能, 被广泛应用于航空航天和汽车等领域<sup>[35-41]</sup>。Al-Si-Mg 铸造铝合金的主要强化相  $Mg_2Si$ , 经过固溶处理和人工时效可使其以强化颗粒  $\beta''$  ( $Mg_5Si_6$ ) 和预  $\beta''$  相混合均匀分布于 Al 基体中, 可获得较好的力学性能<sup>[42-43]</sup>, 然而当其使用温度高于 180 °C 时强化相尺寸会快速粗化或溶解, 失去对 Al 基体的钉扎效果, 导致机械性能快速下降<sup>[43-44]</sup>, 从而很大程度上限制了 Al-Si-Mg 合金的使用范围。

微合金化是目前提高 Al-Si-Mg 系铸造铝合金高温适应性的有效方法, 在室温下增强合金的力学性能并改善其微观组织, 在高温下减缓合金力学性能的衰退<sup>[45-50]</sup>。研究发现 Er、Sc、Zr 元素可以细化晶粒尺寸并改性共晶 Si, 从而可提高合金的强度和塑性。其中稀土元素 Er 添加在 Al-7Si-0.4Mg 合金中, 可促使共晶 Si 破碎和球化、降低二次枝晶臂间距、细化组织并生成抗粗化的含 Er 金属间化合物; 经过热处理后, Al-Si-Mg-Er 合金室温和 200 °C 抗拉强度分别提升为 165.8 MPa、115.7 MPa (未添加 Er 时为 119.3 MPa、95.6 MPa), 同时提高了合金高温暴露后的峰值硬度和抗过时效性能, 如图 2(a) 所示<sup>[46]</sup>。湖南大学 Yi<sup>[47]</sup> 得到了相似的结果, 相比 A356 合金 A356-Er 合金硬度随着人工时效时间延长表现更加稳定, 可见 Er 微合

金化的 A356 合金具有更佳的抗过时效能力和耐热性能, 见图 2(b) (蓝线为两者硬度差值)。在此基础上, Colombo 等<sup>[48]</sup>发现 Zr 元素在 A356-Er 合金中可再进一步提高合金组织的稳定性以及力学性能, 室温和 200 °C 抗拉强度可达 181.1 MPa 和 123.3 MPa, 并且合金抗过时效性能也得到一定的提升, 见图 2(c)。除了微合金化, 研究发现 Al-Si-Mg 合金在热处理过程中会逐渐球化 Si 颗粒, 削弱其与 Al 基体的应力集中, 并且在固溶和时效处理后强化相弥散均匀分布于基体中, 进而显著提高 Al-Si-Mg 合金的力学性能<sup>[51]</sup>。在高压铸造 Al-Si-Mg 合金的固溶处理过程中, 铸件内部的气孔会导致气泡的产生。韩国 Kang 等<sup>[52]</sup>研究发现在最佳固溶处理(520 °C+1.5 h)下可有效抑制气泡的产生, 且增大共晶硅和镁硅颗粒的面积和球度, 抗拉强度和屈服强度达到最高(296 MPa, 240 MPa)。

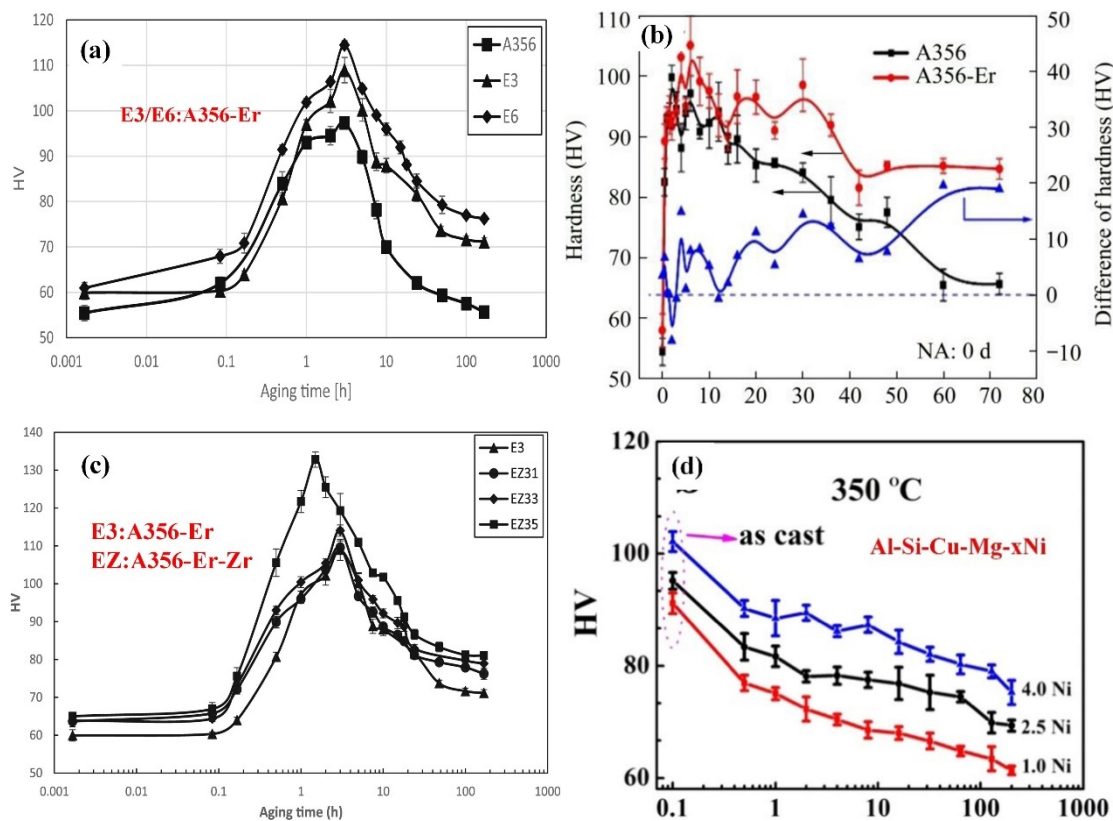


图2 Al-Si 系合金在时效过程中的硬度演变<sup>[46-48, 78]</sup>

Fig. 2 Evolution of hardness during aging: (a) A356, E3 and E6 at 200 °C<sup>[46]</sup>, (b) A356 and A356-Er at 180 °C without natural aging<sup>[47]</sup> (c) E3 and EZ series at 200 °C<sup>[48]</sup>, (d) Al-12Si-0.9Cu-0.8Mg alloys with the Ni contents from 1.0 % to 4.0 %<sup>[78]</sup>

### 1.1.2 Al-Si-Cu 铸造耐热铝合金

Al-Si-Cu 系合金是一种常用的耐热铝合金材料, 其主要强化相  $Al_2Cu$  的热稳定温度约为 225 °C, 在 200 °C 左右工况下可稳定使用<sup>[53-54]</sup>。但在高于 250 °C 环境温度下时, 商用 Al-Si-Cu 合金(A319)因时效过程形成的  $\theta'$  相 Ostwald 熟化, 导致其力学性能会显著下降, 抗拉强度和延伸率只有 70 MPa 和 7.0 %<sup>[55-56]</sup>。目前科研人员主要从减小二次枝晶臂间距(SDAS)<sup>[57]</sup>, 生成稳定金属间化合物<sup>[58]</sup>、降低孔隙率<sup>[59]</sup>和优化热处理<sup>[60]</sup>等

方式, 来提升 A319 合金的常温和高温力学性能。除此之外, 当合金中的杂质 Fe 含量高于 0.5 wt.%时, 会生成硬而脆的  $\beta\text{-Fe}(\text{Al}_3\text{FeSi})$ , 对合金的力学性能产生有害影响; 可通过优化 Fe 和 Mn 的含量, 使  $\beta\text{-Fe}(\text{Al}_3\text{FeSi})$  相转化为呈块状和树枝状的  $\alpha\text{-Fe}(\text{Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2)$  相, 并促进 Cu 元素的均匀分布, 使  $\text{Al}_2\text{Cu}$  强化相弥散分布于  $\alpha\text{-Fe}$  枝晶或  $\alpha\text{-Al}$  晶界, 热处理后以  $\theta''$  或者  $\theta'$  相存在。归因于微观组织变化, 新型共晶 Al-Si-Cu-Fe-Mn 合金在室温和 300 °C 下的抗拉强度分别为 336 MPa 和 144.3 MPa<sup>[61]</sup>。在此基础上, 东南大学 Liao 等<sup>[62]</sup>对 Al-12Si-4Cu-1.2Mn 合金进行热处理调控, 发现在最佳固溶温度和时间(510 °C-5 h)下, 其组织内部析出细小弥散相  $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$  和  $\text{Al}_{15}\text{Mn}_3\text{Si}_2$ , 使合金高温强度得到显著提升, 250 °C 抗拉强度可达 191.9 MPa。

Al-Si-Cu-Mg 合金是一种用途最广的典型合金, 约占汽车部件铝合金 85~90%<sup>[63-64]</sup>, 然而维持室温强度的  $\beta''$  和  $\theta''$  强化相在高温下会逐渐粗化。科研人员研究得出提高合金中 Cu、Mg 元素含量占比<sup>[65-67]</sup>、加快铸造过程的凝固速度<sup>[65, 68]</sup>、优化热处理<sup>[68]</sup>以及多级固溶处理<sup>[69]</sup>, 可以有效提高合金的力学性能。除此之外, Zr 微合金化 Al-Si-Cu-Mg 合金, 可明显细化晶粒且形成了低扩散系数的含 Zr 析出相( $\text{Al-Si-Zr-Ti}$ )和含 Cu 析出相( $\theta'$  和  $Q'$ ), 使合金在 200 °C 时的强度获得显著提升, 屈服强度和抗拉强度相比于原始合金分别提高了 26.5 % 和 32.3 % (224 MPa 和 246 MPa)<sup>[70]</sup>。过渡族元素 Cr、Ti、V、Zr 在 Al-Si-Cu-Mg 合金中可形成不同形貌的 Cr/Ti/V/Zr 弥散相, 其中  $\text{Al}_{10.7}\text{SiTi}_{3.6}$ 、 $\text{Al}_{21.4}\text{Si}_{3.4}\text{Ti}_{4.7}\text{VZr}_{1.8}$  等相在 T6 热处理后仍稳定, 促使微合金化后的合金室温下屈服强度和抗拉强度分别提高 30 % 和 5 %, 200 °C 下屈服强度和抗拉强度分别提高 12.8 % 和 4.9 %, 300 °C 下屈服强度和抗拉强度可保持在 184 MPa 和 196 MPa<sup>[71]</sup>。

Al-Si-Mg 系和 Al-Si-Cu 系铸造铝合金高温稳定性能有限, 一般只能在 225 °C 以下服役<sup>[72]</sup>。研究表明含 Ni 相在较高温度下仍能保持稳定, 因此 Al-Si-Cu-Ni-Mg 铸造铝合金被广泛应用于大多数汽车发动机的缸体和活塞, 也被称为活塞合金<sup>[73-74]</sup>。随着发动机功率的不断提高, 活塞的工作环境变得更加复杂和苛刻, 要求 Al-Si-Cu-Ni-Mg 活塞合金具有更加优异的抗蠕变性能、耐热性能以及抗疲劳性能。控制含 Ni 相的演变促使其形成热稳定性能更好的弥散相, 是 Al-Si-Cu-Ni-Mg 铸造铝合金的研究重点。Yang 等<sup>[75]</sup>发现在 Al-12.5Si-XCu-2Ni-1Mg(wt.%)合金中, Cu 含量的增加会促使  $\text{Al}_3\text{Ni}$  相( $\epsilon$  相)结合 Cu 元素逐渐转变为热稳定性能更好的  $\text{Al}_7\text{Cu}_4\text{Ni}$  相( $\gamma$  相), 合金室温抗拉强度从 263.8 MPa 提高到 278.9 MPa, 350 °C 高温下强度也由 78.1 MPa 升高到 93.5 MPa。Sui 等<sup>[76]</sup>发现向 Al-12Si-4Cu-2Ni-0.8Mg 合金中添加 Gd 元素, 可使  $\text{Al}_3\text{CuNi}$  相的形貌由针状转变为小块状, 二次枝晶间距(SDAS)也由 23  $\mu\text{m}$  降低至 16  $\mu\text{m}$ 。在合金中添加 0.1 %Gd 可以较好地改善 200 °C 以下的力学性能, 相比原始合金室温抗拉强度提高 30 % (260.3 MPa), 200 °C 抗拉强度提高 9.1 % (206.8 MPa); 添加 0.2 %Gd 的合金在 350 °C 下表现更佳, 抗拉强度提高 8.9 % (76.1 MPa)。Gao 等<sup>[77]</sup>对 Al-13.5Si-3.8Cu-2Ni-Mg 进行 Zr 微合金化处理, 发现添加 0.25 %Zr 元素之后, 基体内形成了块状  $\text{ZrAlSi}$  金属间化合物, 降低了初生 Si 的含量, 合金 350 °C 下的抗拉强度和延伸率分别提高了 15.8 %、13 %。Feng 等<sup>[78]</sup>研究了  $\epsilon\text{-Al}_3\text{Ni}$  相对 Al-Si-Cu-Mg-xNi 合金的组织 and 性能的影响, 发现  $\epsilon\text{-Al}_3\text{Ni}$  相可有效提高合金

在 350 °C 下的高温力学性能和显微硬度，如图 2(d)。对比 350 °C 热暴露 200 h 前后显微组织变化，如图 3 所示，可见  $\epsilon$ -Al<sub>3</sub>Ni 相具有优异的抗粗化能力和热稳定性。

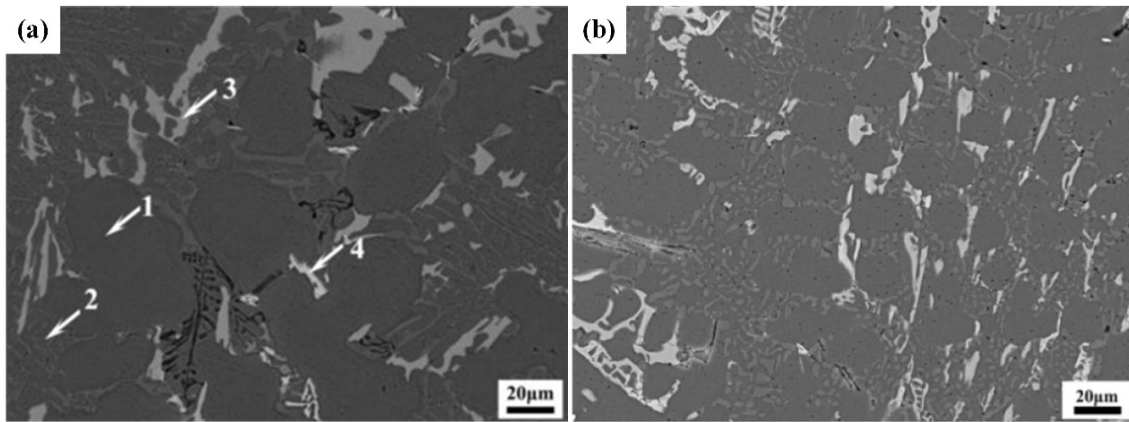


图 3 Al-12Si-2.5Ni-0.9Cu-0.8Mg 合金在 350 °C 热暴露 200 h 前后的微观组织<sup>[78]</sup>

Fig. 3 Microstructure of the Al-12Si-2.5Ni-0.9Cu-0.8Mg alloys: (a) as-fabricated, (b) after thermal exposure at 350 °C for 200 h<sup>[78]</sup>

## 1.2 其他铸造耐热铝合金

### 1.2.1 Al-Cu 系铸造耐热铝合金

相较于 Al-Si 系铸造耐热铝合金，Al-Cu 系合金因 Cu 元素的存在，具有更佳的耐热性能<sup>[79]</sup>和抗疲劳性能<sup>[80-81]</sup>，但因缺少 Si 元素的存在，其铸造性能较差，成形窗口较小，易产生铸造缺陷<sup>[82]</sup>。目前该合金常用于简单形状零件的制备，例如发动机气缸头和缸盖等。Samuel 等<sup>[83]</sup>采用铸造后放入冰水混合物提高凝固速度的方法制备了新型 Al-27Cu-5Si 三元共晶合金，合金组织由不同长度尺度的二元和三元共晶组成，且合金内具有更高的  $\theta$ -Al<sub>2</sub>Cu 强化相体积分，造成合金硬度显著提升(224 HV)。相比 A319 合金，Al-27Cu-5Si 合金 200 °C 抗拉强度提高了 54 % (347.1 MPa)，300 °C 抗拉强度提高 139 % (217 MPa)。Chen 等<sup>[84]</sup>对 Al-5Cu-1Mn 进行 Ni 合金化，发现时效处理后基体内析出了细小析出相( $\theta''$ )，该相可显著提升合金在 300 °C 的力学性能，相较于原合金的抗拉强度提高 21.6 %。

### 1.2.2 Al-Mg 系铸造耐热铝合金

Al-Mg 系铸造铝合金具备良好的焊接性能、加工性能及耐腐蚀性能，也被称为耐蚀铝合金<sup>[85]</sup>。Al-Mg 系铸造耐热铝合金相较于 Al-Si 系合金缺少共晶 Si 的强化，室温强度较低；相比于 Al-Cu 系合金缺少热稳定富铜相的强化，中高温强度也相对较低。Choi 等<sup>[86]</sup>制备了以 Co-Ni 基相强化的 Al-Mg-Si-Co-Ni 合金，Co-Ni 相在 Al 基体中以 Al<sub>3</sub>(Ni, Co) 存在，该相在 450 °C 高温仍对基体具备较好的强化作用，促使合金 450 °C 时的抗拉强度可达 205.4 MPa，相比室温抗拉强度只下降了 50 MPa，表现出了优异的高温力学性能。

表 1 铸造耐热铝合金室温及高温力学性能

Table 1 Mechanical properties of cast heat-resistant aluminum alloys at room-temperature and high-temperature

Material	HT	Room temperature			Elevated temperature			Ref:	
		UTS (MPa)	YS (MPa)	TE (%)	T (°C)	UTS (MPa)	YS (MPa)		TE (%)
Al-7Si-0.4Mg(A356)	T6	119.3	108.6	3.7	200	95.6	80.3	7.4	[46]
Al-7Si-0.4Mg-0.22Er	T6	165.8	139.2	5.6	200	115.7	104	12.7	[46]
Al-7Si-0.4Mg-0.25Er-0.59Zr	T6	181.1	160	7.4	200	139.9	123.3	16.9	[48]
Al-.8.6Si-3.8Cu(A319)	cast	211	155.7	2.0	300	93.5	82.1	8.5	[87]
Al-13Si-5Cu-0.6Fe-0.6Mn	T6	336	280	0.82	300	144.3	130	7.2	[61]
Al-12Si-4Cu-2Mn	T6	245		3.61	350	96		9.28	[88]
Al-12Si-3.5Cu-2Mn-1Cr	T6	279		3.3	350	106		8.8	[89]
Al-7Si-0.5Cu-0.3Mg	T6	282	261	2.74	200	224	177	3.39	[70]
Al-7Si-2Cu-0.3Mg-0.2Zr	T6	355	291	1.77	200	246	186	3.8	[70]
Al-7Si-Cu-0.5Mg	T6	301.3	230.7	6.2	200	217.6	198.4	1.7	[71]
Al-7Si-Cu-0.5Mg-0.5Cr-0.4Ti-0.4V-0.25Zr	T6	313	300	2.7	300	197.4	184	12.3	[71]
Al-12Si-4Cu-2Ni-0.8Mg(M142)	T6	240	225	<1.0	350	90		8	[14]
Al-12Si-0.9Cu-4Ni-0.8Mg	-				350	116		2.0	[78]
Al-12.3Si-0.9Cu-4Ni-0.8Mg		208	172.9	0.52	250	187	141.3	0.73	[90]
Al-12.9Si-5.5Cu-1.8Ni-1Mg	T6	278.9			350	93.5			[75]
Al-12Si-4Cu-2Ni-0.8Mg	cast	200.3	174.6	0.72	350	69.9	53	13.5	[76]
Al-12Si-4Cu-2Ni-0.8Mg-0.2Gd	cast	247.2	192.9	0.91	350	76.1	61.8	9.75	[76]
Al-13.5Si-3.8Cu-2Ni-Mg-2.5Zr	T6				350	86.8	82.8	4.5	[77]
Al-12.5Si-5Cu-2Ni-0.84Mg-0.5Fe	T6				350	94.3		8.6	[91]
Al-12Si-4Cu-2.7Ni-Mg-0.6Fe	-				350	106	93	5.4	[92]
Al-13Si-3.7Cu-3.2Ni-1.1Mg-0.8Fe-0.5Cr	T6				350	98.6			[93]
Al-Si-Ti-Zr-Cr-V-Ni		252	104	6.8	250	192		8.0	[28]
Al-27.4Cu-5.4Si	-				300	218.4	164.7	27.4	[83]
Al-5Cu-1Mn-0.5Ni	T6				300	141	117	4.7	[84]
Al-5Cu-0.8Mg-0.3Ag	-	516	482	9.5	350	99	89	18.2	[94]
Al-5Cu-0.8Mg-0.3Ag-0.2Ce	-	562	528	7.3	350	156	154	16.3	[94]
Al-1Mg-1.1Si-0.8CoNi	-	255.8	240.3	16	450	205.3	195.1	20.5	[86]

### 1.3 铸造耐热铝合金的使役性能

汽车发动机的缸体和活塞承受着热-力耦合循环载荷的长时间作用下,可能导致零件某位置疲劳裂纹的萌生和扩展甚至完全断裂,最终造成汽车发动机的失效<sup>[95]</sup>。为了评估铸造耐热铝合金在中高温下长期工作的寿命,研究疲劳性能对于耐热铝合金的发展具有重要意义。铸造耐热铝合金的疲劳研究主要集中在疲劳裂纹扩展<sup>[96-97]</sup>、铸造缺陷<sup>[98-101]</sup>、加载频率<sup>[105]</sup>、应力应变比<sup>[106-107]</sup>、合金化元素含量优化(Cu、Fe)<sup>[78, 102, 104]</sup>和热处理<sup>[108]</sup>等工艺和性能参数对疲劳性能的影响。Feng等<sup>[78]</sup>研究了 $\epsilon$ -Al<sub>3</sub>Ni相对Al-12Si-0.9Cu-0.8Mg-xNi铝合金350℃低周疲劳性能的影响,发现 $\epsilon$ -Al<sub>3</sub>Ni可有效提高合金的疲劳寿命。但当Ni含量为4%时,因 $\epsilon$ -Al<sub>3</sub>Ni相的粗化,在最小的峰值位移的前提下合金的疲劳寿命最短;含2.5%Ni合金具有最优异的低周疲劳性能,在350℃温度下低周疲劳强度系数为198.3MPa,疲劳强度指数为-0.1295。Wu等<sup>[109]</sup>研究了

$\alpha$ -Al<sub>15</sub>Mn<sub>3</sub>Si<sub>2</sub>相在室温和350 °C下对Al-12Si-4Cu-1.2Mn铸造铝合金高周疲劳性能的影响,发现 $\alpha$ -Al<sub>15</sub>Mn<sub>3</sub>Si<sub>2</sub>相比 $\alpha$ -Al对抗疲劳的贡献更大,在室温和350 °C下高周疲劳强度分别为125.0 MPa和47.5 MPa,表现出优异的抗疲劳性能。

汽车发动机需长时间在高温复杂环境下稳定工作,其中热暴露实验是最能代表其真实工作环境的实验,可见热暴露特性也应作为铝合金耐热性的考察指标。而且,铝合金在热暴露后显微组织将会发生变化,比如可能新相形成、晶界无析出带(PFZ)发展、析出相和金属间化合物粗化以及位错和微裂纹变化,进而将影响铝合金的力学性能<sup>[110-111]</sup>。近几年对铸造耐热铝合金热暴露性能的研究发现,热暴露性能的提升主要是因Al<sub>3</sub>Sc相和纳米Si(syn)相<sup>[112]</sup>、弥散分布的Al<sub>3</sub>Zr析出物<sup>[113]</sup>、 $\epsilon$ -Al<sub>3</sub>Ni相<sup>[78]</sup>、条状的 $\delta$ -Al<sub>3</sub>CuNi相<sup>[114]</sup>、Al<sub>20</sub>Cu<sub>2</sub>Mn<sub>3</sub>相<sup>[118]</sup>、纳米Al<sub>11</sub>Cu<sub>5</sub>Mn<sub>3</sub>相<sup>[115]</sup>、块状和树枝状的 $\alpha$ -Fe(Al<sub>15</sub>(Fe, Mn)<sub>3</sub>Si<sub>2</sub>)富铁相<sup>[61, 118]</sup>、 $\alpha$ -Al(Mn, Fe)Si弥散相<sup>[116]</sup>、汉字状Al<sub>20</sub>Cu<sub>2</sub>Mn<sub>3</sub>和Al<sub>15</sub>Mn<sub>3</sub>Si<sub>2</sub>富锰弥散相<sup>[62]</sup>、Al<sub>15</sub>Mn<sub>3</sub>Si<sub>2</sub>共晶富锰相<sup>[117]</sup>的存在。Lin等<sup>[122]</sup>对不同Cu、Ti含量的Al-Si-Cu-Mn-Fe合金进行300 °C热暴露100 h实验,发现热暴露后的高温力学性能随着Cu、Ni元素含量的增加而提高,在热暴露0.5 h后因 $\theta$ (Al<sub>2</sub>Cu)强化相的存在强度下降不多;在热暴露10 h后 $\theta$ (Al<sub>2</sub>Cu)强化相的逐渐粗化导致力学性能迅速下降45.9%;在继续热暴露到100 h时,因为热稳定性能优异的Al<sub>20</sub>Cu<sub>2</sub>Mn<sub>3</sub>相和 $\alpha$ -Fe(Al<sub>15</sub>(Fe, Mn)<sub>3</sub>Si<sub>2</sub>)相的存在,强度只下降了4.3%。

## 2 快凝耐热铝合金

时效强化是目前标准系列铝合金的常见策略,然而大多数的析出相在高温下会逐渐粗化并失去对铝基体的钉扎作用。随着快速凝固技术的逐渐成熟,为弥散强化型耐热铝合金的研制提供了一种新的解决思路<sup>[119-120]</sup>。快速凝固技术相比传统铸造工艺极大地提高了合金的凝固速度以及合金元素在铝基体中的过饱和固溶度,促使形成更高体积分数和热稳定的细小弥散相,进而有效提高合金的强度与耐热性能<sup>[121-122]</sup>。比如Wang等<sup>[123]</sup>采用喷射沉积技术制备了由Cu、Mg、Fe合金化的过共晶Al-Si合金,归因于快速凝固技术较高的冷却速率,铝基体中均匀分布着颗粒状Si弥散体和片状金属间化合物( $\delta$ -Al<sub>4</sub>FeSi<sub>2</sub>和 $\beta$ -Al<sub>3</sub>FeSi相),相比粉末冶金的Al-20Si-3Cu-1Mg合金<sup>[124]</sup>具有更优异的高温强度。

### 2.1 快凝耐热铝合金的制备工艺

目前快凝耐热铝合金的传统制备工艺主要包括:平面流铸造法<sup>[125]</sup>、气雾化法<sup>[126]</sup>和喷射沉积法<sup>[127]</sup>。三种工艺均具备较大冷却速度,其中平面流铸造法冷却速度为10<sup>5</sup>~10<sup>6</sup> K/s,气雾化法冷却速度为10<sup>3</sup>~10<sup>4</sup> K/s,喷射沉积法冷却速度最低,约10<sup>3</sup> K/s左右。以上工艺可总结为使用不同的方法使熔融金属分解为薄带或液滴状,以增大冷却速度实现快速凝固,各有其特色与优势。快速凝固技术作为新材料制备技术的典型代

表, 过程稳定可控, 在成形耐热铝合金方面占据着重要地位。

平面流铸造法(planar flow casting, PFC)由美国公司 Allied-Signal 于 1979 年最先提出<sup>[128]</sup>, 如图 4(a)所示<sup>[125]</sup>, 其基本原理为: 熔融金属从金属坩埚压注入到高速旋转的铜辊(或钼辊)上, 由表面张力将熔融金属保持为稳定的液桥, 并在辊面形成液膜, 接触到辊面后受到急速冷却作用而凝固成连续薄带, 所得薄带的宽带和厚度由辊轮的转速来控制。平面流铸造法冷却速度可达  $10^5$  K/s, 合金疲劳强度和断裂韧性较高。然而, 制备为薄带合金后, 还需粉碎、粉末筛选、粉末冶金等后续复杂工艺, 生产成本低<sup>[129]</sup>。

雾化法中最常用的是美国麻省理工 Grant 教授的超声雾化法和 Pratt-Whitney 公司研发的离心雾化法, 如图 4(b)所示<sup>[130]</sup>。其基本原理为: 在高速高频的脉动气流或者高速转盘产生的离心力作用下, 熔融合金被外力分割为均匀细小的液滴, 再通过惰性气体强制对流等方式传导散热而迅速冷却成粉末<sup>[131-134]</sup>。这种方法典型特征是冷却速度可达  $10^3\sim 10^4$  K/s, 粉末球形度高, 尺寸更为细小并且适合小部件的制备<sup>[135-137]</sup>。

喷射沉积技术最早由 1968 年英国 Singer 教授提出, 后由英国 Osprey 公司实现工业化<sup>[138]</sup>, 如图 4(c)所示<sup>[139]</sup>, 其基本原理为: 经真空感应熔化处理后的液态金属, 通过 Osprey 装置雾化为细小的液滴后, 喷射在金属基底上。依靠基底的急速热传导使液滴迅速凝固而沉积, 便逐渐形成具有一定致密度和结合强度的预制坯料, 再经过变形加工等方式得到所需产品。喷射沉积技术是在雾化法的基础上发展而来, 其更大优势是可将雾化制粉和固化成形无间断完成, 进而更有效控制氧含量、减少粉末污染; 还可直接制备较大尺寸的致密金属实体, 从而缩短工艺流程、降低成本<sup>[140-141]</sup>。但是, 喷射沉积技术冷却速度较低, 导致零件性能低于其他快凝技术。

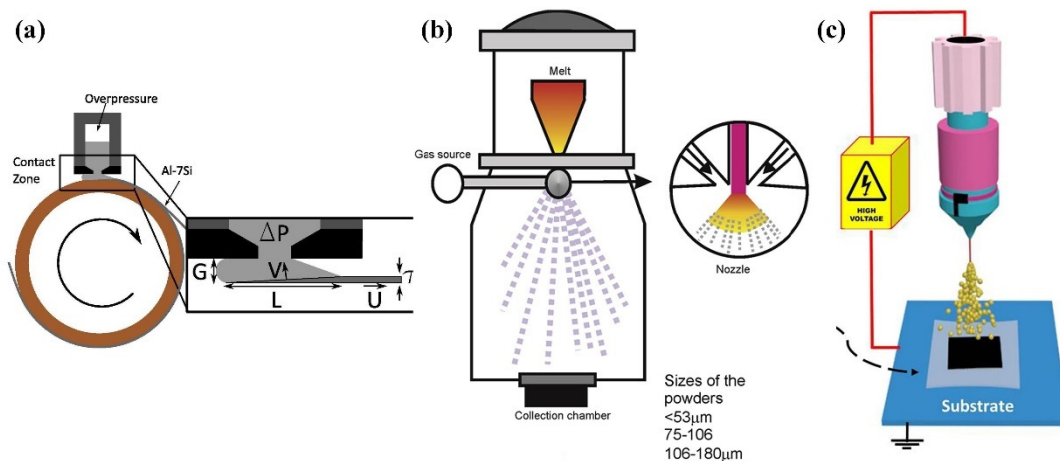


图 4 平面流铸造、雾化法、喷射沉积原理示意图<sup>[125, 130, 139]</sup>

Fig. 4 Schematic diagram of (a) planar flow casting<sup>[125]</sup>, (b) as atomization<sup>[130]</sup>, (c) spray deposition<sup>[139]</sup>

## 2.2 Al-Fe 系快凝耐热铝合金

快速凝固技术为 Al-Fe 系合金制备开辟了一条新的途径。在过去铸造工艺过程中, 铁元素常被认为是一种有害的杂质, 因为其在铝基合金中的溶解度非常有限而且在缓慢冷却下常生成粗大且脆性的金属间化

合物,例如  $\text{Al}_{13}\text{Fe}_4(\theta)^{[142]}$ 。然而现在,铁元素被发现在热稳定性上有不错的增强潜力,因为铁元素在铝基合金中的扩散系数比其他典型合金元素(Si、Cu和Mg)低好几个数量级。在借助快速凝固技术提高Fe元素在铝基体中的固溶度下,可以形成热稳定性不错的金属间化合物。目前由快速凝固技术和粉末冶金制备的Al-Fe系快凝耐热铝合金在高温下有不错的力学性能表现,甚至可与航天用钛合金相比<sup>[132, 142-143]</sup>。

### 2.2.1 Al-Fe-V-Si 快凝耐热铝合金

由美国联合信号公司(Allied Signal)研发的经典快凝耐热铝合金Al-Fe-V-Si,因其断裂韧性高、比刚度大、室温和高温强度优异等优点,被寄望于成为航空航天领域钛合金的替代品<sup>[144-146]</sup>。同样,Al-Fe-V-Si合金优异的力学性能与凝固速率有很大的关系,提高冷速可抑制合金内针状 $\text{Al}_{13}\text{Fe}_4$ 相的生成,而形成热稳定的 $\text{Al}_{12}(\text{Fe}, \text{V})_3\text{Si}$ 强化相,从而有效提高合金的耐热性,可见利用快速凝固技术制备Al-Fe-V-Si耐热铝合金的必要性<sup>[147]</sup>。

Al-8.5Fe-1.3V-1.7Si(AA8009)作为采用快速凝固技术/粉末冶金技术(RS/PM)的制备工艺开发出最具代表的快凝耐热铝合金,合金中含有体积分数约24%的 $\text{Al}_{12}(\text{Fe}, \text{V})_3\text{Si}$ 耐热强化相,相比铸造耐热铝合金具有更佳的高温力学性能<sup>[148]</sup>。例如AA8009在室温和250℃下抗拉强度可达400 MPa和300 MPa,而铸造活塞合金Al-12.3Si-0.9Cu-4Ni-0.8Mg(M142)在室温和250℃下抗拉强度只有208 MPa和187 MPa<sup>[90]</sup>。Wang等<sup>[149]</sup>通过喷射沉积技术制备了Al-8.5Fe-1.1V-1.9Si耐热铝合金,发现喷射沉积技术可抑制低凝固速率形成的粗大且脆性的初晶硅晶体和枝晶间共晶相,并且在铝基体上弥散分布着热稳定良好的细小球状 $\text{Al}_{12}(\text{Fe}, \text{V})_3\text{Si}$ 颗粒,如图5(a-b),从而使其具有优异的室温和高温力学性能,室温和300℃下抗拉强度可达445 MPa和229 MPa。

### 2.2.2 Al-Fe-Ni及Al-Fe-Ce快凝耐热铝合金

Průša等<sup>[150]</sup>用离心雾化技术制备出片状颗粒粉末,再结合粉末冶金工艺和热挤压制备出Al-12Fe和Al-7Fe-5Ni合金。对比相应铸造合金显微组织,快凝合金虽未发现新亚稳相的生成,但其显微组织更加细化,没有铸造合金中粗大且细长的金属间化合物,而是以细小共晶的金属间化合物( $\text{Al}_{13}\text{Fe}_4$ 和 $\text{Al}_9\text{FeNi}$ )均匀弥散分布在铝基体中,如图5(c-f)。对比铸造Al-12Si-1Cu-1Mg-1Ni合金,快凝Al-Fe合金经300℃和400℃退火100 h后硬度和压缩屈服强度几乎无变化,而铸造合金下降到退火前的50%;快凝Al-7Fe-5Ni合金在300℃温度和120 MPa压力的压缩蠕变实验中总蠕变应变只有15%,而铸造合金高温抗蠕变性能最差,总蠕变应变是Al-7Fe-5Ni三倍多(50%)。事实证明,通过离心雾化法和粉末冶金热挤压制备的Al-12Fe和Al-7Fe-5Ni合金相比铸造合金具有优异的热稳定性。

同济大学王嘉婧等<sup>[151]</sup>采用平面流铸造法制备了Al-7Fe-4Ce合金薄带,并研究了退火处理对合金物相及力学性能的影响。初始状态下,薄带内析出相主要有初生相 $\text{Al}_3\text{Fe}$ 、亚稳相 $\text{Al}_6\text{Fe}$ 和 $\text{Al}_{10}\text{Fe}_2\text{Ce}$ 。在340℃退火处理后,合金显微组织保持稳定并且其物相几乎无变化( $\text{Al}_6\text{Fe}$ 不转变、 $\text{Al}_3\text{Fe}$ 不粗化),可说明合金在

340 °C时可保持较好的热稳定性。

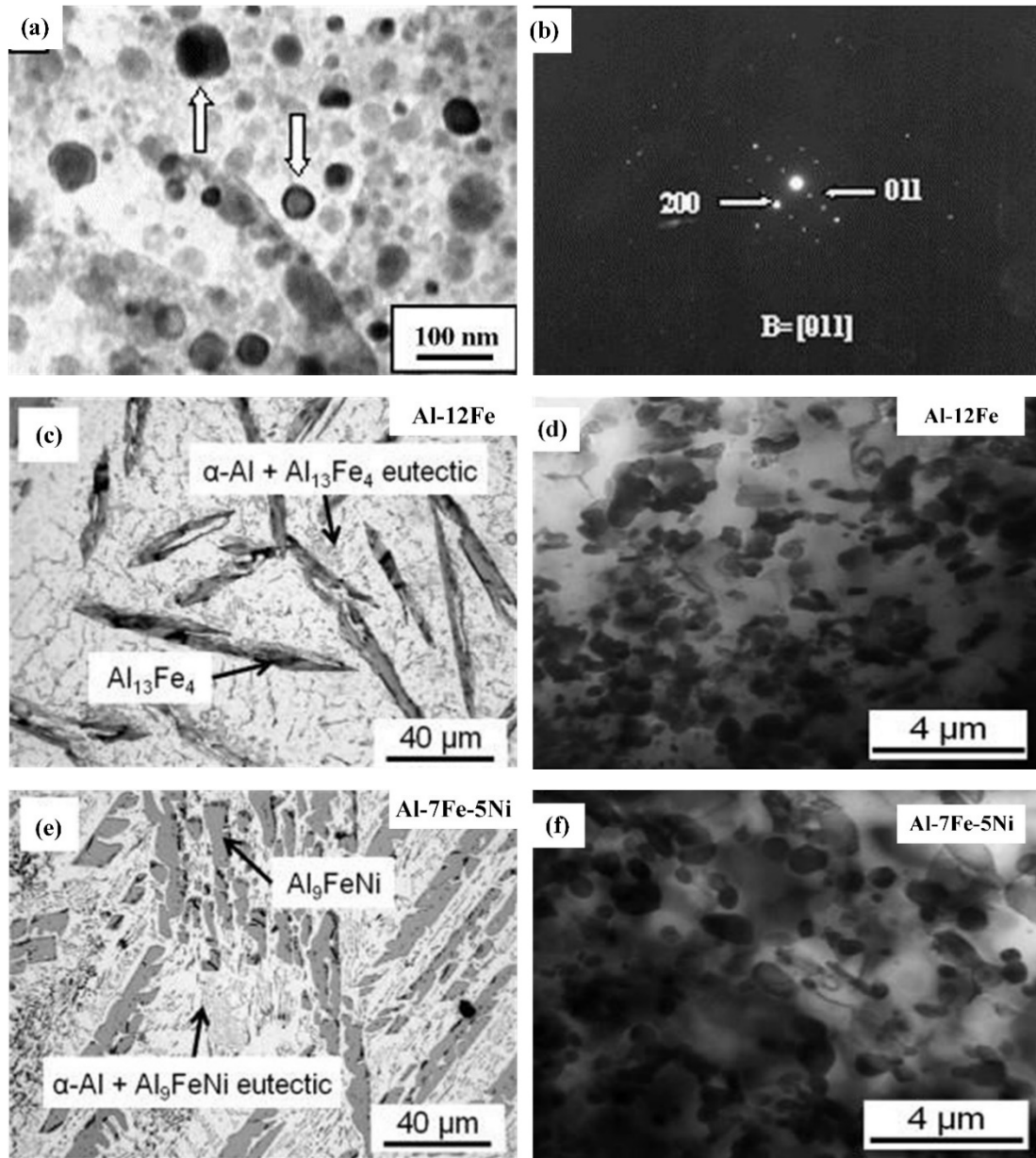


图5 颗粒状  $\text{Al}_{15}(\text{Fe}, \text{V})_3\text{Si}$  化合物电子显微镜照片, 铸造和快凝制备的 Al-12Fe 及 Al-7Fe-5Ni 显微组织<sup>[140, 150]</sup>

Fig. 5 TEM micrograph showing particle-like phases of the  $\text{Al}_{15}(\text{Fe}, \text{V})_3\text{Si}$  compound: (a) Bright-field image; (b) selected area diffraction pattern,  $B=[0\ 1\ 1]$ <sup>[150]</sup>; Microstructures of the slowly solidified alloys: (c) Al-12Fe; (d) Al-7Fe-5Ni; TEM brightfield

micrographs of the PM alloys: (e) Al-12Fe; (f) Al-7Fe-5Ni<sup>[140]</sup>

### 3 增材制造耐热铝合金

近年来, 金属增材制造(additive manufacturing, AM)因其能够制备尺寸精度高且机械性能良好的高致密

复杂构件,同时缩短生产周期和减少材料浪费的优势,逐渐成为国内外制备航空零部件的关键技术<sup>[152-155]</sup>。此外,最具有发展前景的选区激光熔化(selective laser melting, SLM)技术为耐热铝合金力学性能的提升带来了新的技术突破<sup>[156-158]</sup>。相比快速凝固技术,SLM过程中熔池的冷却速率至少高出1~2个数量级( $\sim 10^7$  K/s)<sup>[159-161]</sup>,从而获得更加细小的微观组织并且析出更高浓度的强化相,显著提高铝合金的高温性能<sup>[162]</sup>。然而,在SLM复杂热循环的过程中,因铝合金粉末反射率高、热导率高、凝固范围大且流动性较差的特性,铝合金部件易形成气孔和热裂缺陷<sup>[163-165]</sup>,比如Al7075<sup>[166]</sup>、AA8009<sup>[167]</sup>、Al2618<sup>[168]</sup>、Al2124<sup>[169]</sup>和Al2024<sup>[170]</sup>。因此,目前铝合金的增材制造一直局限于共晶或近共晶Al-Si合金,如AlSi12<sup>[171-172]</sup>、AlSi10Mg<sup>[173-174]</sup>和AlSi7Mg<sup>[175]</sup>等。原因在于Al-Si合金具有较窄的凝固区间,在SLM快速凝固过程中具有良好的流动性和较低的热裂倾向<sup>[176-177]</sup>。然而,由于高温下其微观组织表现不稳定(富硅晶界断裂)<sup>[178-179]</sup>,Al-Si合金在200℃下的抗拉强度却只有室温的50%左右,且高于此温度时几乎无塑性<sup>[119]</sup>,如图9所示。

综上所述,开发适用于选区激光熔化的新型高强耐热铝合金成分是十分必要的<sup>[180-181]</sup>。要求其在尽量减少气孔、裂纹等缺陷的前提下,在室温下具有足够的强化机制,并且在中高温(250℃以上)下仍能保留很高的强度(在**高强与耐热**两个特性之间取得平衡)<sup>[182]</sup>。因此,需要在基体内形成热稳定性更佳的强化相来提升其耐热性能。耐热强化相可大体分为三大类:热稳定的共晶相、低粗化率的析出相和超高熔点的陶瓷相<sup>[183-184]</sup>。以此为目的,提高铝合金耐热性主要有三条策略:1)引入过渡金属元素(transition metal, TM),形成高体积分数的共晶相;2)添加稀土元素或过渡金属元素(如Sc、Er、Zr)微合金化,再通过时效处理析出粗化率低的析出相;3)添加陶瓷颗粒为增强相。三种策略互相并不排斥,合金设计可能采用其中一种或者多种策略进行耐热性能协同增强。

### 3.1 Al-TM 耐热共晶铝合金

含过渡金属的铝合金是借助快速凝固/粉末冶金技术应运而生的,在300~350℃内具有广阔的应用前景<sup>[164, 185-187]</sup>。其微观组织设计思路大体为添加扩散系数较低的过渡金属元素TM(如Mn、Cr、Fe、Ni和Ce等),并借助快速凝固技术或SLM技术的非平衡凝固特性,在铝基体内形成高体积分数( $> \sim 20\%$ )的热稳定 $Al_xTM_y$ 共晶相。通常,Al-TM合金是基于共晶或者近共晶成分,是因为较小的凝固区间可以大大减少热裂倾向,形成细晶组织,例如Al-Fe-V-Si<sup>[167, 187]</sup>、Al-Fe-Ni<sup>[188-189]</sup>、Al-Ni<sup>[158, 190]</sup>和Al-Ce<sup>[182, 191]</sup>合金。

#### 3.1.1 Al-Fe系耐热共晶铝合金

据报道,Al-Fe合金在铸造慢速凝固过程中容易形成粗大、片状或者针状的 $\theta$ -Al<sub>13</sub>Fe<sub>4</sub>和 $\beta$ -Al<sub>5</sub>FeSi金属间化合物,大大降低合金韧性和力学性能<sup>[192-193]</sup>。借助SLM技术独特的局部熔化和快速凝固过程,Fe元素在铝合金以Fe-Si-Ni颗粒的形式分散,有效提高合金在300℃下的抗拉强度和延展性(185 MPa, 24%)<sup>[194]</sup>。SLM制备的近共晶Al-2.5Fe合金<sup>[195]</sup>和过共晶Al-15Fe合金<sup>[196]</sup>,都具有多个熔池组成的独特显微组织和弥散分布的细小亚稳态Al<sub>6</sub>Fe金属间化合物,如图6所示。相比传统铸造,合金强度和塑性得到了有效提升,

近共晶 Al-2.5Fe 合金硬度相比含有粗大、片状  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> 相的铸造合金提高了一倍多<sup>[195]</sup>; 过共晶 Al-15Fe 合金细化的组织在 300 °C 下表现稳定, 且维氏硬度在时效 100 h 后仍能稳定在 165 HV<sup>[192]</sup>。

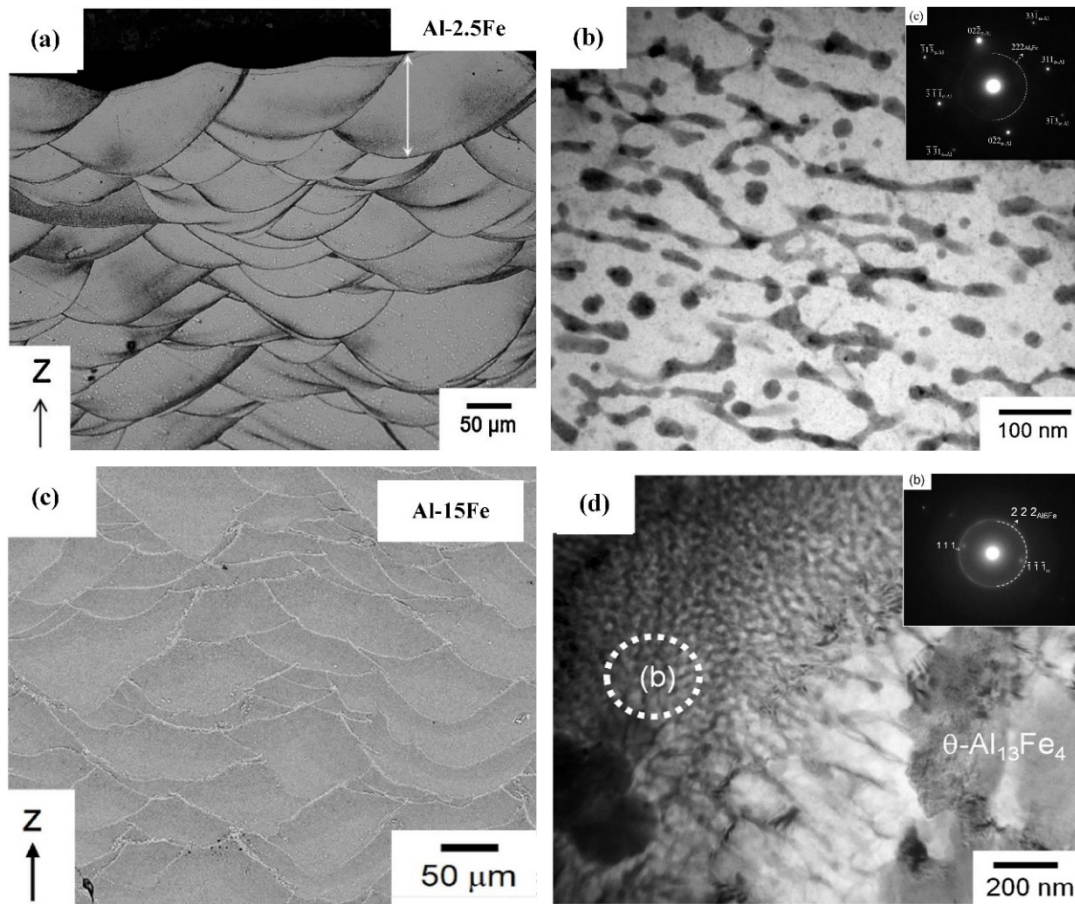


图6 Al-2.5Fe 与 Al-15Fe 合金的多熔池显微组织及亚稳态 Al<sub>6</sub>Fe 金属间化合物<sup>[192, 195]</sup>

Fig. 6 Optical microstructure (a, c) and metastable Al<sub>6</sub>Fe phases (b, d) in Al-2.5Fe(a, b)<sup>[195]</sup> and Al-15Fe (c, d)<sup>[192]</sup> alloys

由于 Fe 和 Ni 元素在铝中的扩散系数较低且快速凝固技术可抑制粗大的脆性初生相<sup>[139, 196]</sup>, SLM 技术制备候选 Al-Fe-Ni 耐热铝合金逐渐引起人们极大的兴趣。俄罗斯乌拉尔联邦大学 Loginova 等<sup>[191]</sup>和上海交通大学 Ding 等<sup>[158]</sup>都设计了一种适应 SLM 独特成形特性的新型耐热 Al-Fe-Ni 合金, 并对比研究了不同制备工艺(铸造和 SLM 技术)对 Al-Fe-Ni 合金显微组织和相的影响。发现在最佳的工艺参数下 SLM 技术的快速凝固可有效抑制初生 Al<sub>9</sub>FeNi 相的形成, 并促进组织的细化以及共晶 Al<sub>9</sub>FeNi 相的均匀分布。在力学性能方面, SLM 制备 Al-Fe-Ni 合金在室温下其硬度可达铸态合金的 2~3 倍; 在 300 °C 下, 棒状 Al<sub>9</sub>FeNi 金属间化合物具有良好的热稳定性如图 7 所示<sup>[189, 158]</sup>。

北京航空航天大学郑立静等<sup>[197-198]</sup>在 SLM 成形 Al-8.5Fe-1.3V-1.7Si(FVS0812)耐热铝合金方面开展了较多研究工作, 发现合金组织由  $\alpha$ -Al 基体、纳米级 Al<sub>12</sub>(Fe, V)<sub>3</sub>Si 相(20-70 nm)和少量 Al<sub>m</sub>Fe 相组成。发现优化工艺参数可消除因粗大 Al<sub>m</sub>Fe 相和热残余应力导致的周期性裂纹, 从而提升致密度至 99.3 %, 并显著提高合金的力学性能, 抗拉强度可达 454 MPa, 硬度可达 250 HV, 相较于平面流铸造法和喷射沉积法

(130-158 HV)有较大的提升。在热稳定方面, Al-8.5Fe-1.3V-1.7Si 合金在 400 °C退火 1 h 后在晶粒和晶界处析出细小  $\text{Al}_{12}(\text{Fe}, \text{V})_3\text{Si}$  弥散相, 且其硬度在退火后仍可保留 180 HV; 随后在 425 °C热暴露 500 h, 对比热暴露前后微观组织发现  $\text{Al}_m\text{Fe}$  和  $\text{Al}_{12}(\text{Fe}, \text{V})_3\text{Si}$  相的粗化可忽略不计, 如图 8 所示, 导致合金硬度在热暴露 10 h 后可一直稳定保持在 150 HV, 展示出 Al-8.5Fe-1.3V-1.7Si 合金优异的耐热性能。

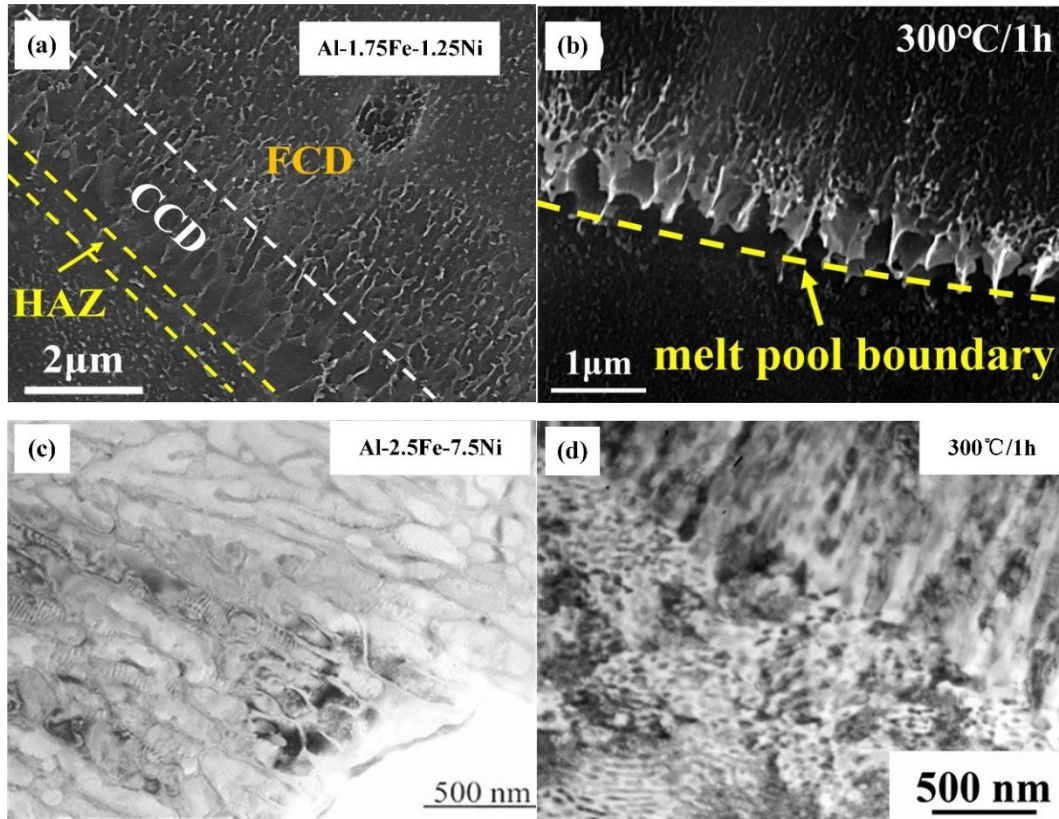


图 7 Al-Fe-Ni 合金在 300 °C退火 1 h 前后的显微组织<sup>[158, 189]</sup>

Fig. 7 SEM images of the microstructure: (a, c) as-fabricated, (b, d) annealed at 300 °C for 1 h in Al-1.75Fe-1.25Ni(a, b)<sup>[189]</sup> and Al-2.5Fe-7.5Ni (c, d)<sup>[158]</sup> alloys

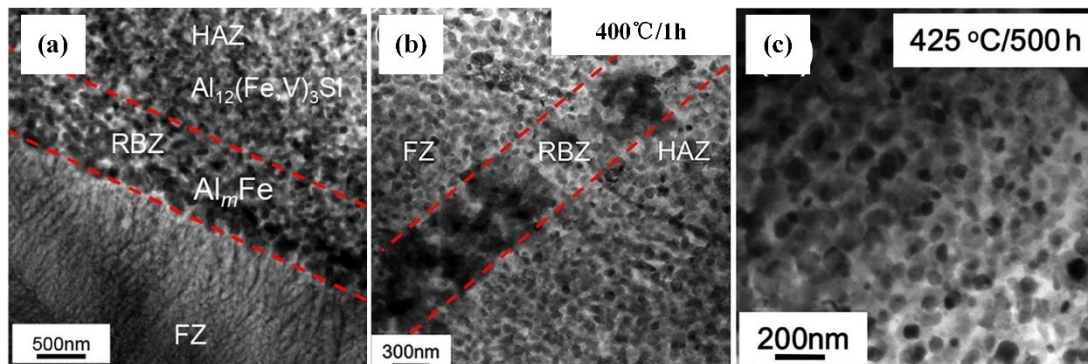


图 8 Al-8.5Fe-1.3V-1.7Si 合金在退火前后和热暴露的显微组织<sup>[198]</sup>

Fig. 8 SEM images of the microstructure (a) as-built, (b) after annealing at 400 °C for 1 h, (c) after thermal exposure at 425 °C for 500 h in Al-8.5Fe-1.3V-1.7Si alloys<sup>[198]</sup>

### 3.1.2 Al-Ni 及 Al-Ce 系耐热共晶铝合金

Al-Ni 及 Al-Ce 系共晶合金具有优异的热稳定性、流动性及抗热裂性能,有望取代 Al-Si 系合金<sup>[191, 199]</sup>。研究证实了 Al-Ni 共晶合金在 SLM 技术下可形成高致密度(99.83 %)的高强耐热合金零件<sup>[158]</sup>。在弥散分布的细小共晶相( $Al_3Ni$ )作用下,促使 Al-Ni 合金具有良好的力学性能,室温和 300 °C 下的抗拉强度分别可达 410 MPa 和 140 MPa,如图 9 所示。Chang 等<sup>[190, 199]</sup>研究了热处理对 SLM 制备 Al-Ni-Cu 和 Al-Ni-Cu-Fe-Zr-Sc 耐热铝合金组织演变和纳米沉淀的影响,发现常规热处理使  $Al_7Cu_{23}Ni$  相析出并聚集于 Al-Ni-Cu 合金熔池边界,提高了延伸率却削弱了抗拉强度,还使其具有了脆性疲劳断裂性能;而超高温固溶处理促使 Al-Ni-Cu-Fe-Zr-Sc 合金熔池边界的分解和细晶区的扩展,并在细晶区分布着  $Al_9Fe(Cu)Ni$  和  $Al_3(Sc, Zr)$  纳米强化相,有效提高合金强度,改善合金高温力学性能。

俄罗斯国立科技大学 Manca 等<sup>[191]</sup>对 Al-3Ce-7Cu 耐热铝合金 SLM 打印试样的组织和性能进行了系统研究。Al-3Ce-7Cu 合金内部为细小  $Al_{11}Ce_3$  和  $Al_{6.5}CeCu_{6.5}$  共晶相,在对其进行 400 °C-5 h 退火处理后, $Al_{6.5}CeCu_{6.5}$  相尺寸无显著变化且合金硬度只略有下降;在力学性能方面,合金在常温条件下抗拉强度为 459 MPa, 250 °C 抗拉强度为 197 MPa,并且热处理前后的力学性能几乎相同,Al-3Ce-7Cu 合金表现出良好的耐热性和高温力学性能。美国橡树岭国家实验室<sup>[182, 185]</sup>也开展了 SLM 制备 Al-12Ce 和 Al-10Ce-8Mn 合金的相关研究。结果发现,Al-12Ce 合金在 300 °C 退火 24 h 后没有表现出显微组织粗化,且硬度一直稳定在 85 HV; Al-10Ce-8Mn 合金通过 SLM 快速凝固过程可使组织细化,并在基体内部形成大量  $Al_{20}Mn_2Ce$  和  $Al_{11}Ce_3$  金属间化合物,借此 Al-10Ce-8Mn 合金在 300 °C 时的力学性能仍可保持较稳定,如图 9 所示。可见 Al-12Ce 和 Al-10Ce-8Mn 合金优异的耐热性能。

### 3.1.3 其他合金

Al-Si(-Mg)系列合金在高温下因蜂窝状共晶结构被破坏,没能表现出稳定的高强度<sup>[200]</sup>。向 Al-Si 合金添加不同的合金元素,可以提高合金材料的综合力学性能<sup>[201-202]</sup>。研究发现 Ni 可以减少针状沉淀 Al-Fe-Si 的尺寸,从而提高合金的机械性能<sup>[203]</sup>。Manca 等<sup>[204]</sup>向 Al-Si 合金中添加了扩散系数较低的 Ni 和 Fe 元素,并利用 SLM 技术制备了新型耐热 Al-Si-Ni-Fe 合金。在 Si、 $Al_5Fe(Ni, Cu)$ 和  $Al_3(Ni, Cu)$  纳米级析出相形成的精细结构下,Al-Si-Ni-Fe 合金硬度可达 186 HV,且在 200 °C 时合金具备 355 MPa 的高压缩强度,400 °C 仍可保留 125 MPa。Al-Ca-Ni-Mn 过共晶合金中  $Al_4Ca$  共晶相具备较高热稳定性,合金在 200-400 °C 区间显微硬度值未出现明显降低<sup>[205]</sup>。

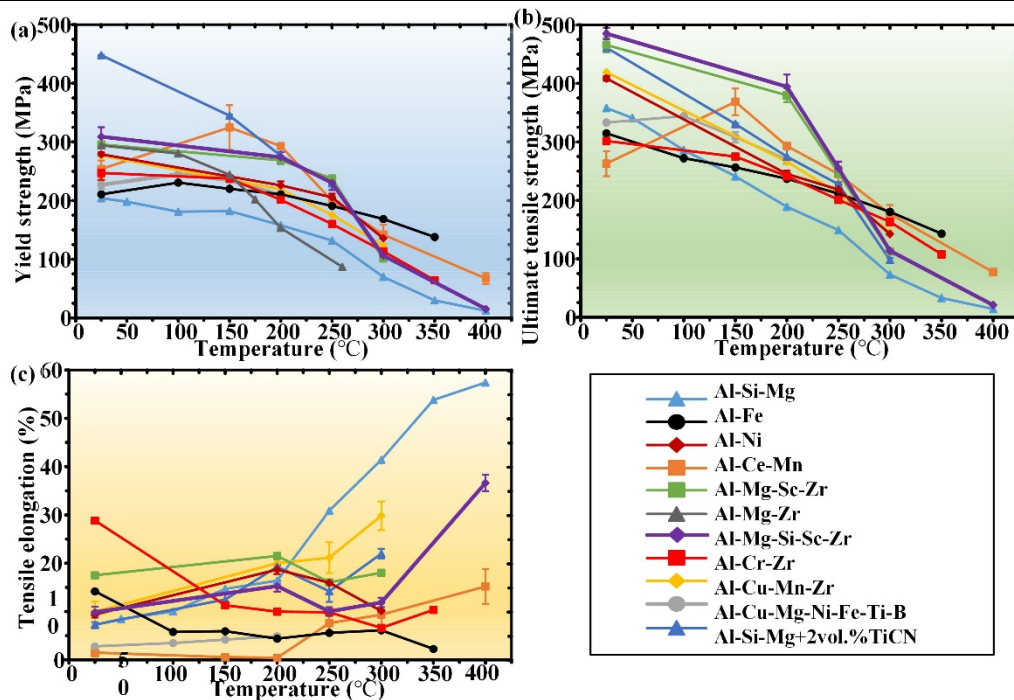


图9 增材制造耐热铝合金高温拉伸性能(YS、UTS和EL)随测试温度的变化<sup>[119, 156, 158, 182, 218, 224-225, 228-229, 244-245]</sup>

Fig. 9 High-temperature tensile properties ((a) yield stress, (b) Ultimate tensile stress, and (c) elongation at break) of Al-Si-Mg<sup>[119]</sup>, Al-Fe<sup>[156]</sup>, Al-Ni<sup>[158]</sup>, Al-Ce-Mn<sup>[182]</sup>, Al-Mg-Sc-Zr<sup>[218]</sup>, Al-Mg-Zr<sup>[244]</sup>, Al-Mg-Si-Sc-Zr<sup>[224]</sup>, Al-Sc-Zr<sup>[225]</sup>, Al-Cu-Mn-Zr<sup>[245]</sup>, Al-Cu-Mg-Ni-Fe-Ti-B<sup>[229]</sup> and Al-Si-Mg+2vol.%TiCN<sup>[228]</sup> samples as a function of testing temperatures.

### 3.2 沉淀强化耐热铝合金

由于常规商用的 2xxx、6xxx 或 7xxx 合金材料凝固区间较大, 在 SLM 复杂热循环的快速熔化再凝固过程中, 晶粒趋向于沿打印方向生长形成柱状晶组织或者形成更严重的裂纹或微裂纹缺陷<sup>[206-208]</sup>。美国加利福尼亚大学 Martin 等<sup>[209]</sup>在 Nature 发文指出, 通过静电吸附向铝合金粉末表面引入纳米 ZrH<sub>2</sub> 粒子, 利用 Al<sub>3</sub>Zr 的异质形核效果, 可实现了 7075 和 6061 铝合金的无裂纹细晶粒增材制造。研究人员总结发现通过向铝合金中添加 X 元素(X=Sc、Zr、Ti、Er 等), 均可与基体形成具有 L1<sub>2</sub> 型结构的 Al<sub>3</sub>X 相, 该相可作为异质形核质点促进晶粒细化<sup>[210-212]</sup>; 还可作为热稳定的析出相存在, 在 250~400 °C 温度区间内长时间保持与基体的位向关系, 钉扎晶界, 一方面阻碍位错滑移, 导致位错堆积, 另一方面抑制晶界运动, 提高塑性变形的抗力, 沉淀的钉扎效应如图 10 所示<sup>[213-214, 224]</sup>。

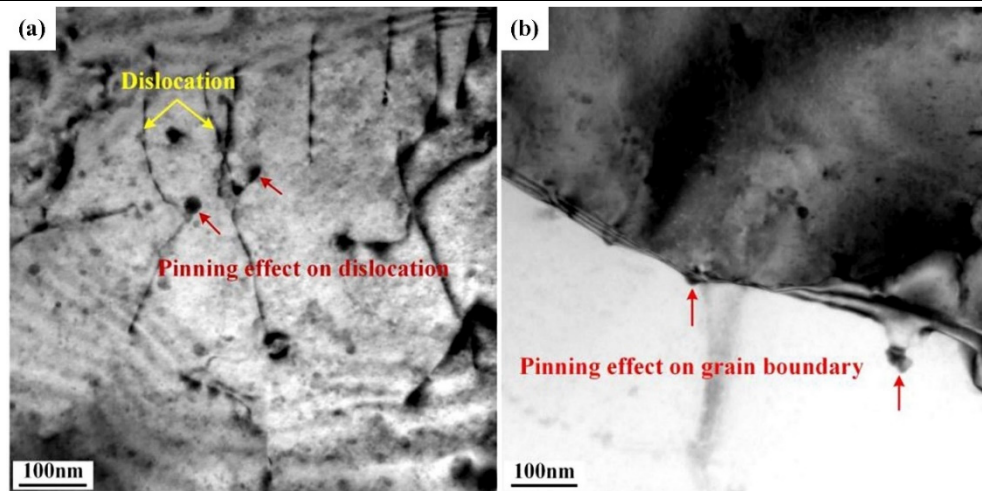


图 10 沉淀的钉扎效应: (a)位错, (b)晶界<sup>[224]</sup>

Fig. 10 Pinning effect of precipitation: (a) dislocation, (b) grain boundary.<sup>[224]</sup>

### 3.2.1 Al-Mg 沉淀强化耐热铝合金

由中客公司研发的新一代 Sc、Zr 微合金化 Al-Mg 合金(Scalmalloy®), 在 SLM 制备工艺下具有优异的力学性能<sup>[215-216]</sup>、热稳定性<sup>[216-218]</sup>和各向同性<sup>[216, 219]</sup>, 受到高强耐热铝合金研究人员的广泛关注。Spierings 等<sup>[215-216]</sup>对 SLM 成形 Al-Mg-Sc-Zr 合金的组织 and 性能进行了大量研究, 在超细晶组织和热稳定 Al<sub>3</sub>(Sc, Zr)析出相的钉扎作用下, 合金在 350 °C 保温 4 h 热处理后合金表现出优异的抗拉强度(500 MPa 以上)、延伸率(8.6 %以上)、硬度(137 HV)以及各向异性(5 %以下); 在耐热性能方面, 对比发现在 350 °C 热处理前后晶粒平均尺寸几乎无变化, 如图 11(a-c), 证明了 Al-Mg-Sc-Zr 合金可承受约 300 °C 高温。Bi 等<sup>[218]</sup>研究在长期时效下 Al-Mg-Sc-Zr 合金的耐热性能表现, 发现在 300 °C 长期时效 144 h 过程中晶粒形态基本保持不变, 如图 11(g-i), 在 200 °C 下抗拉强度高达 393.9 MPa, 如图 9 所示。该合金细小的晶粒组织以及具有核-壳结构、与 Al 基体保持着共格关系以及热稳定的 Al<sub>3</sub>(Sc, Zr)弥散析出相对其优异的耐热性能和高温力学性能做出了至关重要的贡献。

### 3.2.2 Al-Mg-Si 及 Al-Mn 沉淀强化耐热铝合金

除了 Al-Mg 合金外, Sc 和 Zr 微合金化有效提高力学性能和耐热性能的效果也成功应用在其他铝合金中<sup>[220-226]</sup>。Al-Mg-Si-Sc-Zr 合金在弥散分布的 Mg<sub>2</sub>Si 和 Al<sub>3</sub>(Sc, Zr)沉淀的钉扎效应下, 如图 10 所示, 室温抗拉强度高达 488 MPa, 200 °C 中温下任保持在 394 MPa, 如图 9 所示, 具有优异的高温力学性能<sup>[224]</sup>。Cr 和 Zr 合金化的铝合金(Al-4Cr-1.5Zr)在 400 °C/10 h 峰值时效下维氏硬度可有 130 HV 且具有抗过时效能力, 峰值时效后室温抗拉强度在 400 MPa 以上, 且相比 Al-Si-Mg 合金具有优异的高温强度, 如图 9 所示<sup>[225]</sup>。专为 SLM 设计的 Al-Mn-Sc 耐热铝合金, 合金最大强度可达 580 MPa, 在 350 °C 和 450 °C 等温时效 6 h 过程中, 热稳定的 Al<sub>6</sub>Mn 和 Al<sub>3</sub>Sc 颗粒对晶粒粗化有强烈的抑制作用, 进而保证合金组织和性能的稳定<sup>[226]</sup>, 如图 11(d-f)。

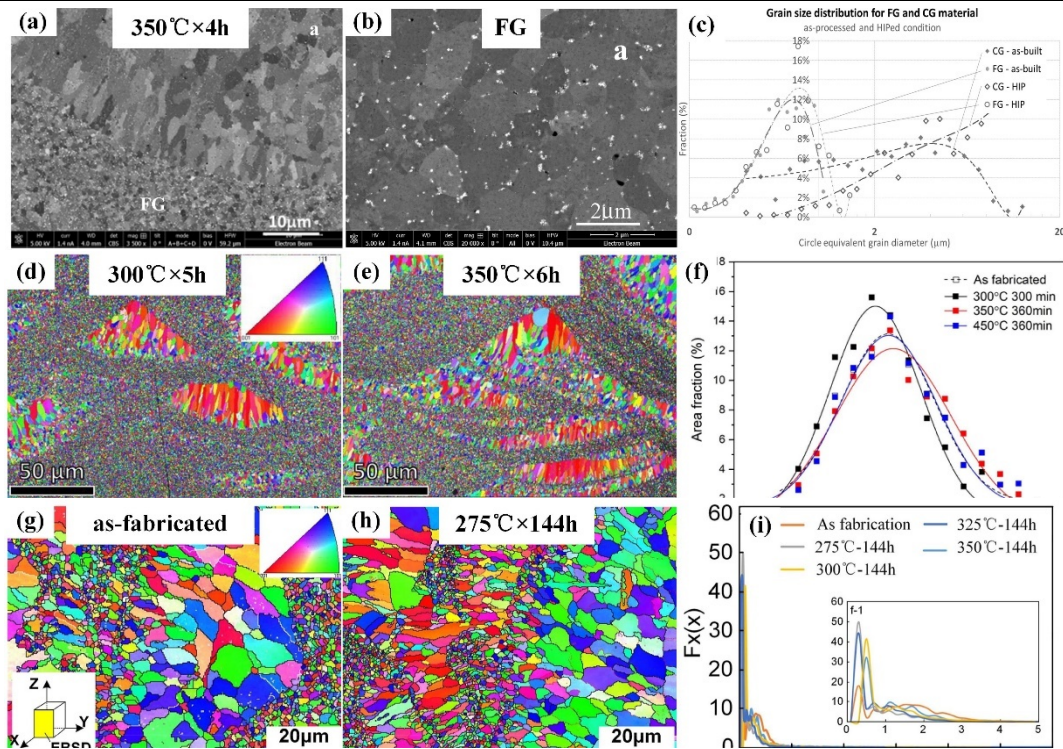


图 11 Al-Mg-Sc-Zr 和 Al-Mn-Sc 合金在不同时效条件下的微观组织和晶粒尺寸统计<sup>[215, 218, 226-227]</sup>

Fig. 11 Back scattered electron microscopy image of (a) heat treated (350 °C/4 h) Al-Mg-Sc-Zr, (b) magnification of Al-Mg-Sc-Zr in FG region<sup>[215]</sup>, EBSD images of the microstructure after different aging treatment conditions: (d) 300°C for 5 h, (e) 350°C for 6 h<sup>[226]</sup>, (g) as-fabricated<sup>[227]</sup>, (h) 275°C for 144 h<sup>[218]</sup> in the SLM-fabricated Al-Mg-Sc-Zr<sup>[218, 227]</sup> and Al-Mn-Sc<sup>[226]</sup> alloy samples, (c)(f)(i) Grain size distribution of the Al-Mg-Sc-Zr and Al-Mn-Sc alloy samples<sup>[215, 218, 226]</sup>

### 3.3 陶瓷颗粒增强耐热铝合金

与共晶和沉淀强化铝合金不同，陶瓷颗粒增强铝合金是向熔融铝基体中添加超高熔点(>1000 °C)且不可溶的纳米陶瓷颗粒(如 TiCN<sup>[228]</sup>、TiB<sub>2</sub><sup>[229-231]</sup>、SiC<sup>[232-233]</sup>、TiC<sup>[234-237]</sup>等)以钉扎晶界，限制晶粒生长和位错运动，这对提高铝合金的高温力学性能起着至关重要的作用。分散的纳米陶瓷颗粒不仅可用于增强合金耐热性，同时还可以促进晶粒的异质形核，进而细化晶粒和降低材料的热裂敏感性<sup>[228-229, 238-239]</sup>，使得铝合金可加工性和力学性能显著提高。

#### 3.3.1 Al-Si-(Mg)陶瓷颗粒增强耐热铝合金

目前，增材制造的陶瓷颗粒增强铝基复合材料公开研究主要集中在 Al-Si-(Mg)合金<sup>[183]</sup>，其中 TiC 陶瓷颗粒占有重要地位。因为 TiC 颗粒除了拥有许多优异的物理性能，而且相比 SiC 颗粒很少在铝基体中生成额外的脆性相，从而避免硅化钛可能产生的毒化效应<sup>[240-242]</sup>。并且 TiC 颗粒在 AlSi10Mg 合金的成形过程中诱导异质成核细化 Al-Si 双峰组织，并且在高温变形过程中有效钉扎晶界、阻碍位错运动；相比原合金，TiC 增强 AlSi10Mg 合金在任何温度下都具有更高的屈服强度并且在所有中高温下拥有更高的抗拉强度，

如图9所示<sup>[228]</sup>。

### 3.3.2 Al-Cu 陶瓷颗粒增强耐热铝合金

除了 Al-Si-(Mg)合金以外, 研究人员还对陶瓷颗粒增强商用纯铝和 Al-Cu 合金<sup>[183]</sup>进行了系列研究, 研究表明 TiC 颗粒在纯铝和 TiB<sub>2</sub> 颗粒在 Al-Cu 合金各有不错的表现。因为 TiC 陶瓷颗粒在铝基体中的化学稳定性高于 780 °C 并且与熔融铝有良好的润湿性, 作为纯铝的高密度分散纳米颗粒是不错选择<sup>[237, 243]</sup>。基于高体积分数 TiC 的 Orowan 强化、晶粒细化、载荷转移及强界面结合的强化机制下, Al-TiC(35 Vol.%) 纳米复合材料的微压缩试验中屈服强度高达 1011 MPa, 延伸率超过 10 %, 并且在 400 °C 微压缩试验仍可保留 243 MPa, 延伸率超过 15 %。TiB<sub>2</sub> 颗粒在 Al-Cu-Mg-Ni-Fe(EN AW 2618)合金中促进晶 α-Al 晶粒的异质形核和微观结构的细化, 从而解决了 2618 铝合金 SLM 难加工性和易开裂的问题; 在优化工艺条件下, TiB<sub>2</sub>/2618 复合材料在 T5 热处理下屈服强度可达 495 MPa, 并且相比锻造制备的 2618 合金具有更高的高温机械强度, 如图9所示<sup>[237]</sup>。

## 4 结语和展望

耐热铝合金材料因其出色的高温抗氧化、抗蠕变能力, 在航空航天和汽车领域具有广泛应用。其高温性能是决定零件结构设计和服役安全的关键, 由室温强度和高温强度的衰减率两个因素决定, 因此保证高温微观组织稳定性和强化效果是提升其耐热性能的主要手段。

当前耐热铝合金发展所面临的主要问题有:

1) 如何通过成分设计+快速凝固制备工艺获得兼顾细晶和弥散分布纳米相的组织形貌是制备耐热铝合金的首要问题;

2) 如何调控纳米析出相尺寸、含量、与基体位向关系, 使合金在兼具较高耐热性和较好的力学性能;

3) 除高温强度外, 耐热铝合金的蠕变性能, 热疲劳性能及热暴露性能等研究相对薄弱;

4) 耐热铝合金的强韧化机制与耐热机理仍需进一步深入研究。

综合耐热铝合金的研究现状及应用需求, 耐热铝合金未来发展主要集中在:

1) 通过热力学计算和计算相图法, 对合金成分进行设计, 获取适合于快速凝固工艺的合金成分, 探索新型的合金体系;

2) 研究高热稳定析出相与基体的关系, 系统研究合金高温综合性能, 并建立微观组织-综合性能的联系;

3) 深入了解耐热铝合金高温时的强韧化机制与耐热机理, 为其合金成分设计及制备奠定理论基础。

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# Research Progress of Casting, Rapid Solidified and Additive Manufactured Heat Resistant Aluminum Alloy

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**Abstract:** In recent years, the demand for lightweight heat-resistant aluminum alloy with excellent high temperature oxidation resistance and creep resistance in the medium temperature range of 300~500 °C has become more and more exuberant in the aerospace field. However, the high temperature softening problem of aluminum alloy has always been restricting the structural design and service safety of parts in the middle temperature range. To overcome this shortcoming, the characteristics of different preparation processes should be considered according to the comprehensive requirements (performance, cost, efficiency) of different application scenarios. A sufficient number of thermally stable nano-phases should be uniformly distributed in the alloy matrix by adding or alloying in-situ self-generation for different system alloys, so as to pin the grain boundary and inhibit the grain boundary movement and dislocation slip. In this paper, the research progress and application of heat-resistant aluminum alloys were summarized from three aspects of casting, rapid solidification and additive manufacturing. The control methods of microstructure and properties of heat-resistant aluminum alloys with different systems were analyzed, and the latest research results of heat-resistant aluminum alloys were summarized. At the same time, the future research direction of heat-resistant aluminum alloys was prospected.

**Key words:** heat-resistant aluminum alloy; preparation process; component optimization; microstructure regulation; service performance

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