

Cr含量对低Cu/Mg比Al-Cu-Mg-Ag合金微观组织和力学性能的影响^①

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摘要: 研究了Cr含量(质量分数)对低Cu/Mg比Al-Cu-Mg-Ag合金微观组织和力学性能的影响。结果表明:在低Cu/Mg比Al-Cu-Mg-Ag合金中添加Cr,合金中形成了Al-Cr相和Al_{1.6}TiCr_{0.4}相;Cr含量由0.17%提高到0.22%,合金的抗拉强度由463 MPa提高到484 MPa,提升了4.5%;屈服强度由288 MPa提高到319 MPa,提升了10.8%。合金力学性能的提升主要来源于Cr的固溶强化和S'相的析出强化。

关键词: 微合金化; Cu/Mg比; 固溶强化; 析出强化; Cr; Al-Cu-Mg-Ag合金; 析出相; 欠时效; 力学性能

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Effect of Cr Content on Microstructure and Mechanical Properties of Al-Cu-Mg-Ag Alloy with a Low Cu/Mg Ratio

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Abstract: The effect of Cr content in mass fraction on the microstructure and mechanical properties of Al-Cu-Mg-Ag alloy with a low Cu/Mg ratio was investigated. Results indicate that after an addition of Cr to the Al-Cu-Mg-Ag alloy with low Cu/Mg ratio, phases of Al-Cr and Al_{1.6}TiCr_{0.4} are generated in the alloy; with Cr content from 0.17% up to 0.22%, the alloy has its tensile strength improved from 463 MPa to 484 MPa (a 4.5% increase), and its yield strength enhanced from 288 MPa to 319 MPa (a 10.8% increase). The enhancement in mechanical properties is attributed to solid solution strengthening by Cr and precipitation strengthening by S' phases.

Key words: microalloying; Cu/Mg ratio; solid solution strengthening; precipitation strengthening; Cr; Al-Cu-Mg-Ag alloy; precipitate; under-aging; mechanical property

Al-Cu-Mg-Ag合金因其优良的耐热性能和抗蠕变性能,广泛应用于航空航天领域和石油工业,但该合金存在热稳定性和耐腐蚀性较差的缺点^[1-2]。学者们利用微合金化和优化热处理工艺等改善其性能。目前对Al-Cu-Mg-Ag合金力学性能的研究主要集中在高Cu/Mg比Al-Cu-Mg-Ag合金的主要析出相 θ' 相和 Ω 相^[3-7],而对低Cu/Mg比Al-Cu-Mg-Ag合金的主要析出相S(Al₂CuMg)相的研究很少。Cr作为铝合金常用的微合金化元素,广泛添加在Al-Zn-Mg-Cu合金中^[8-10]。郭帅^[11]研究了Cr的微合金化对低Cu/Mg比Al-Cu-Mg合金的性能影响,但由于其Cr添加量较少,

合金中未发现含Cr相。本文在此基础上,继续增加Cr添加量,研究Cr在低Cu/Mg比Al-Cu-Mg-Ag合金中的存在形式,并研究增加Cr添加量对低Cu/Mg比Al-Cu-Mg-Ag合金微观组织和力学性能的影响,以期促进含Cr的Al-Cu-Mg-Ag合金在石油和航天工业方面的应用。

1 实验方法

实验原料主要为工业高纯铝、纯镁、纯银和Al-50Cu(元素前数据表示该元素的质量分数,下同)、Al-10Mn、Al-4Cr、Al-6Ti、Al-4Zr中间合金,通过熔炼、铸造,制备

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了Cr添加量分别为0.17%和0.22%的2种合金,分别命名为A合金和B合金,其化学成分见表1。

表1 Al-Cu-Mg-Ag合金化学成分(质量分数)
Table 1 Chemical composition of Al-Cu-Mg-Ag alloy %

合金	Cu	Mg	Ag	Mn	Ti	Zr	Cr	Fe	Si	Al
A	3.08	1.81	0.51	0.60	0.15	0.13	0.17	0.04	0.03	余量
B	3.13	1.84	0.53	0.61	0.14	0.13	0.22	0.04	0.03	余量

对A、B合金铸锭进行双级均匀化处理:420℃/24h+480℃/48h,空冷至室温;然后在空气炉内将铸锭加热至410℃并保温2h,立即轧制成厚约2.5mm的薄板;对A、B合金薄板样品进行500℃/1h固溶处理和170℃/3h欠时效处理,所得样品分别命名为UA、UB。

分别采用扫描电镜、透射电镜观察合金的微观组织和沉淀颗粒;在HV-10B型仪器上测试合金显微硬度,载荷5kg,加载时间10s;在WOW-50E型试验机上进行室温拉伸试验,拉伸速率2mm/min。

2 实验结果与讨论

2.1 合金时效硬化行为

经500℃/1h固溶处理后,170℃下不同Cr含量(质量分数,下同)Al-Cu-Mg-Ag合金时效硬化曲线如图1所示。随着时效时间增加,A、B合金硬度都呈现先增加后降低的趋势,并且各时效时间下B合金的硬度均高于A合金的硬度。固溶处理后A合金的硬度值为84.2HV,B合金的硬度值为97HV,B合金表现出更强的固溶强化效应。时效8h,A、B合金的硬度均到达时效峰值硬度,分别为140HV、150HV。继续延长时效时间,2种合金的硬度总体呈下降趋势。可以看出,增加Cr添加量可以使合金时效硬度提高,这归因于Cr的固溶强化效应。

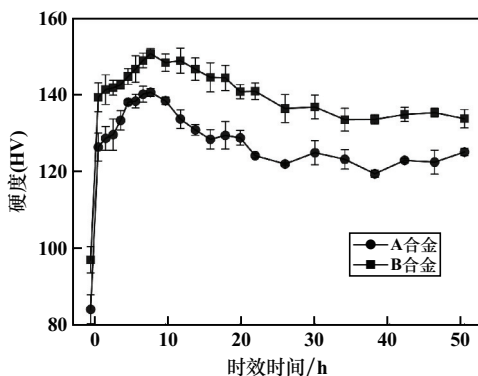


图1 170℃下不同Cr含量Al-Cu-Mg-Ag合金的时效硬化曲线
Fig.1 Age-hardening curves of Al-Cu-Mg-Ag alloys with different Cr contents at 170℃

2.2 合金拉伸性能

欠时效态下不同Cr含量Al-Cu-Mg-Ag合金室温拉伸性能如图2所示。随着Cr含量从0.17%增加到0.22%,合金抗拉强度从463MPa提高到484MPa,提高了4.5%;屈服强度从288MPa提高到319MPa,提高了10.8%;延伸率也有所提升。由此可见,随着微合金化程度提高,合金拉伸性能提高。

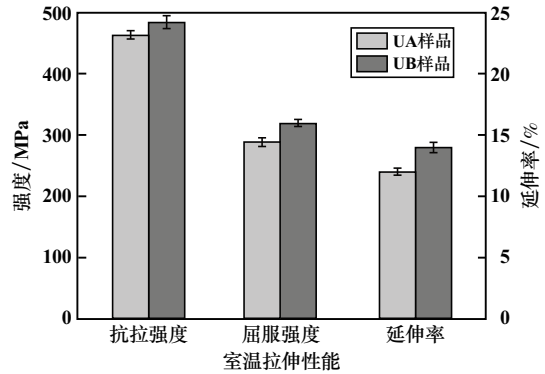


图2 欠时效态下不同Cr含量Al-Cu-Mg-Ag合金的室温拉伸性能

Fig.2 Tensile properties of under-aged Al-Cu-Mg-Ag alloys with different Cr contents at room temperature

2.3 合金物相分析

欠时效态下不同Cr含量Al-Cu-Mg-Ag合金的XRD图谱如图3所示。从图3可知,UA、UB样品相组成几乎没有区别,都由于Cr的加入而形成了 $Al_{1.6}TiCr_{0.4}$ 相和Al-Cr相。另外,合金中还有 Al_2CuMg 、 Al_3Ti 存在。

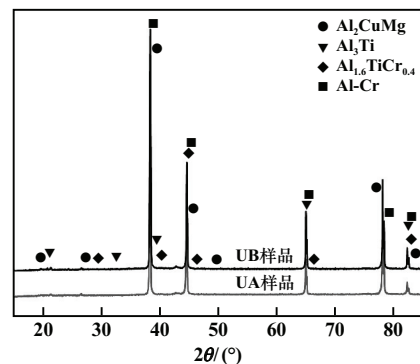
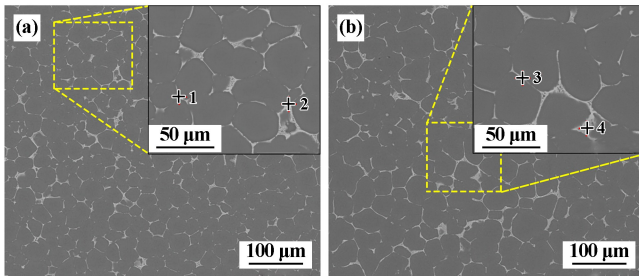


图3 欠时效态下不同Cr含量Al-Cu-Mg-Ag合金的XRD图谱
Fig.3 XRD patterns of under-aged Al-Cu-Mg-Ag alloys with different Cr contents

2.4 合金显微组织分析

不同Cr含量Al-Cu-Mg-Ag铸态合金的显微组织见图4。由图4可见,A、B铸态合金的晶粒尺寸并无明显差异,SEM形貌表现为典型的枝晶偏析特征,晶粒呈现等轴状。对图4中合金的第二相粒子进行了

EDS分析,结果如表2所示。由表2可知,第二相粒子主要为 $Al_x(Cu, Mn, Fe, Cr)$ 和 Al_2CuMg 相。 Fe, Cr, Mn 元素表现为互相聚集的状态,即Mn含量高的第二相其中 Fe 和 Cr 含量也相对较高。由于 Cr 的添加,A、B铸态合金中均形成了 $Al_x(Cu, Mn, Fe, Cr)$ 粒子,但晶粒大小并没有明显差异。



(a) A合金; (b) B合金

图4 不同Cr含量Al-Cu-Mg-Ag铸态合金的显微组织

Fig.4 Microstructure of as-cast Al-Cu-Mg-Ag alloys with different Cr contents

表2 图4中各点的EDS分析结果(质量分数)

Table 2 EDS analysis results of each point in Figure 4 %

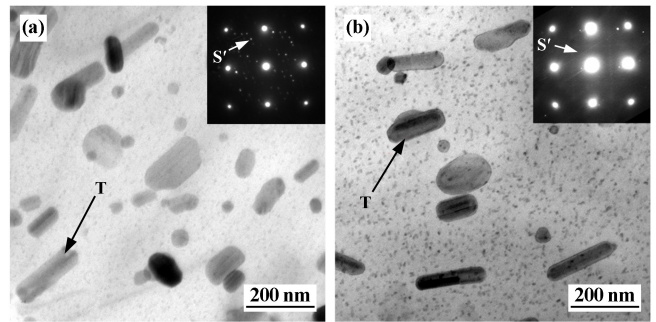
点号	Cu	Mg	Mn	Cr	Fe	Al
1	22.10	22.95	0.31	0.15	0.28	余量
2	5.50	3.64	3.41	0.68	2.27	余量
3	19.42	20.50	0.47	0.25	0.31	余量
4	6.77	1.23	7.40	1.33	3.11	余量

2.5 合金TEM分析

图5为UA、UB样品沿 $\langle 100 \rangle_\alpha$ 轴的明场图像和相应的选区电子衍射(SAED)图。可以看出,晶粒内部存在一些粗大的棒状T相($Al_{20}Cu_2Mn_3$)。在相应的SAED图中可以看见变体的S相(Al_2CuMg)衍射斑点,由于样品为欠时效状态,为了了解Cr的添加对低Cu/Mg比Al-Cu-Mg-Ag合金相关析出相的大小和分布的影响,对UA、UB试样进行了TEM分析,结果见图5。合金中可能有 S'' 和 S' 同时存在,本文暂不做区分,统一认为是 S' 相。未长大的短针状 S' 相大多为弥散分布,还有一些 S' 相在T相与Al基体的界面周围析出。对UA、UB样品沿 $\langle 100 \rangle_\alpha$ 轴的亮场图像中的短针状 S' 相(尺寸太小近乎看作球状)进行了面积分数和尺寸统计,结果如表3所示。UB样品中析出的 S' 相较UA样品析出的 S' 相的数量更多,尺寸更大。由此可以看出,提高Cr含量,可以使合金中 S' 析出相数量增加,从而提高合金性能。

2.6 讨论与分析

微合金化主要通过细化晶粒、影响强化相析出或



(a) UA样品; (b) UB样品

图5 UA、UB样品沿 $\langle 100 \rangle_\alpha$ 轴的明场图像和相应的选区电子衍射(SAED)图

Fig.5 Bright field images of UA and UB samples along $\langle 100 \rangle_\alpha$ axis and corresponding SAED pattern

表3 UA、UB样品 S' 相的面积分数和尺寸统计

Table 3 Area fraction and size of S' phase in UA and UB samples

样品名称	面积分数/%	直径/nm
UA	11.8	8.8
UB	13.2	12.7

形成相关金属间化合物影响合金的力学性能^[12-17]。在微观组织结构上,Al合金中添加Cr元素会形成Al-Cr相(如 $Al_7Cr, Al_{11}Cr_2, Al_{45}Cr_7$ 等)和富含 Cr, Fe, Mn, Cu 的粒子^[13-18]。文献[19]在Al-Mg-Si合金中添加0.07%Cr,诱导形成了 $Al_{45}Cr_7$ 相,其作为 α -Al的异质形核点,细化了晶粒。文献[11]在低Cu/Mg比Al-Cu-Mg合金中进行Cr的微合金化,却未发现明显的晶粒细化现象。在低Cu/Mg比的Al-Cu-Mg-Ag合金中,本文将Cr添加量从0.17%提高到0.22%,Cr添加量的增加并未导致明显的晶粒细化(图4)。提高Cr含量可以使 S' 相含量增加、尺寸增大(图5和表3),这是由于Cr以弥散粒子的形式作为异质形核点,促进了 S' 相的形核析出,在相同时间的欠时效状态下,UB样品的 S' 相的含量更多、尺寸更大,进而使UB样品室温下的拉伸强度和屈服强度更优。

在力学性能上,UB样品的硬度、拉伸强度、屈服强度均优于UA样品。考虑Cr元素添加影响欠时效Al-Cu-Mg-Ag合金力学性能的强化机制,其理论屈服强度($\sigma_{0.2}^{cal}$)^[20-21]可估计为:

$$\sigma_{0.2}^{cal} = \sigma_0 + \Delta\sigma_{HP} + \Delta\sigma_{SS} + \Delta\sigma_P \quad (1)$$

式中: σ_0 为纯铝的晶格摩擦应力; $\Delta\sigma_{HP}$ 、 $\Delta\sigma_{SS}$ 、 $\Delta\sigma_P$ 分别为由晶界、固溶体原子和沉淀物引起的屈服强度增量。

细晶强化主要是晶粒尺寸差异引起的强度变化,由于两合金的晶粒大小基本没有差异,细晶强化对两

合金所做出的贡献并无差距,可视为 $\Delta\sigma_{\text{HP(UA)}} \approx \Delta\sigma_{\text{HP(UB)}}$ 。

固溶强化增量可由固溶强化屈服强度增量的方程^[21-22]来分析:

$$\Delta\sigma_{\text{SS}} = \sum k_i c_i^m \quad (2)$$

式中: c_i 为固溶体中溶质元素 i 的浓度,%; k_i 为相应的固溶体强化效率; m 为与合金相关的常数,对于 Al-Cu-Mg-Ag 合金, $m=1$ 。在本实验中两合金的固溶强化增量的差异主要由 Cr 含量决定。 $c_{\text{Cr(UA)}} < c_{\text{Cr(UB)}}$, 相对应的固溶体强化效率不变,则有 $\Delta\sigma_{\text{SS(UA)}} < \Delta\sigma_{\text{SS(UB)}}$ 。

合金中的 S' 相尺寸太小,近似看作很小的圆形,忽略尺寸因素的影响,沉淀强化增量的分析方程^[20]可表示为:

$$\Delta\sigma_{\text{P}} = M \frac{\Delta\mu}{4\pi\sqrt{2}} \sqrt{f_{\text{V}}} \quad (3)$$

式中 M 、 $\Delta\mu$ 和 f_{V} 分别为 Al 的泰勒因子、相与基体之间的剪切模量、颗粒的体积分数。本文以 S' 相的面积分数近似替代其体积分数,则有 $f_{\text{V(UA)}} < f_{\text{V(UB)}}$, 沉淀强化增量 $\Delta\sigma_{\text{P(UA)}} < \Delta\sigma_{\text{P(UB)}}$ 。

再将公式(2)、(3)所得结论代入公式(1)中,即可得: $\sigma_{0.2(\text{UA})}^{\text{cal}} < \sigma_{0.2(\text{UB})}^{\text{cal}}$, 这与实验结果吻合。

3 结论

1) 在低 Cu/Mg 比 Al-Cu-Mg-Ag 合金中添加 0.17%Cr 和 0.22%Cr, 都会形成 $\text{Al}_{1.6}\text{TiCr}_{0.4}$ 相和 Al-Cr 相,且两者晶粒尺寸相差不大;相对于含 0.17%Cr 的合金,相同时效状态下,含 0.22%Cr 的合金中析出数量更多、粒径更大的 S' 相,表现出更优的力学性能。

2) Cr 含量由 0.17% 提高到 0.22%, 合金抗拉强度由 463 MPa 提高到 484 MPa, 提升了 4.5%; 屈服强度由 288 MPa 提高到 319 MPa, 提升了 10.8%。合金强化机制是 Cr 元素的固溶强化效应和 S' (Al_2CuMg) 相的析出强化效应。

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