

激光选区熔化成形 S-130 钢热处理工艺研究

高飘¹, 兰新强¹, 周亚雄², 王云², 杨欢庆², 王泽敏^{1*}¹华中科技大学武汉光电国家研究中心, 湖北 武汉 430074;²西安航天发动机有限公司, 陕西 西安 710100

摘要 采用激光选区熔化(SLM)技术成形 S-130 马氏体时效不锈钢,研究了热处理前后 S-130 试样的物相、显微组织以及力学性能,并对比分析了五步热处理和三步热处理工艺对组织和性能的影响。结果表明:SLM 成形 S-130 试样主要由大量马氏体和少量残余奥氏体组成,显微组织呈胞状枝晶结构,透射电子显微镜(TEM)观察到大量含有高密度位错的板条马氏体。经过两种热处理后,逆转变奥氏体的形成使得奥氏体的含量增加,大量的纳米级析出物在板条马氏体上弥散分布,同时残余/逆转变奥氏体在马氏体板条间析出。SLM 沉积态试样经过两种热处理后显微硬度和拉伸强度得到明显提升,且延伸率没有降低。相较于五步热处理,三步热处理后的试样具有更高含量的奥氏体以及更细小的板条马氏体和析出物,且在保证延伸率的情况下具有更高的显微硬度和拉伸强度。SLM 成形 S-130 马氏体时效不锈钢优化的热处理制度为三步热处理(固溶+冷处理+时效)。

关键词 激光技术;激光选区熔化;S-130 马氏体时效不锈钢;热处理;显微组织;力学性能

中图分类号 TN249

文献标志码 A

doi: 10.3788/CJL202249.0202003

1 引言

马氏体时效不锈钢是由低碳马氏体相变强化和时效强化两种强化效应叠加的高强度不锈钢,用马氏体时效不锈钢逐步代替沉淀硬化不锈钢是高强度不锈钢发展的重要趋势^[1]。Fe-Cr-Ni-Co-Mo 体系是一种新型的能兼顾高强度和良好韧性的马氏体时效不锈钢,可用于制造重型液氧煤油发动机氧泵壳体和液氧主阀壳体的液氧路承压部件等^[2]。传统加工方法如铸造、锻造等难以制备这些结构复杂的精密金属构件^[3]。作为近年来发展迅速的增材制造技术(3D 打印技术)之一,激光选区熔化(selective laser melting, SLM)技术以高能束激光为热源,能够实现复杂精密金属构件的整体成形,加工周期短,材料利用率高,成本低^[4-8]。因此,利用 SLM 技术成形 Fe-Cr-Ni-Co-Mo 马氏体时效不锈钢具有广阔的应用前景,市场价值巨大。

2007 年, Liu 等^[9]研究了铸态 FeCrNiCoMo 马氏体时效不锈钢[其化学成分(质量分数)为

15.0%~16.5% Cr, 6.0%~7.5% Ni, 9.5%~11.0% Co, 6.5%~7.5% Mo, 余下为 Fe]的组织 and 性能,并探究出优化的热处理工艺(1050 °C 固溶 1 h + 73 °C 冷处理 8 h + 540 °C 时效 4 h)。Tarasenko 等^[10]研究了淬火+时效热处理对铸态 FeCrNiCoMo 马氏体时效不锈钢[其化学成分(质量分数)为 9.6% Cr, 9% Ni, 5.9% Co, 2.9% Mo, 余下为 Fe]物相和性能的影响,并获得了优化的淬火温度(750 °C)和时效温度(500 °C)。2012 年,葛鹏等^[11]研究了不同固溶+时效处理对锻造 FeCrNiCoMo 马氏体时效不锈钢[其化学成分(质量分数)为 10.5%~12.0% Cr, 6.0%~8.5% Ni, 5.0%~7.0% Co, 2.0%~3.0% Mo, 余下为 Fe]组织和性能的影响,在优化的热处理条件下试样的屈服强度达到 1300 MPa,抗拉强度达到 1350 MPa。2014 年,苏文文等^[12-13]通过铸造工艺制备了 FeCrNiCoMo 马氏体时效不锈钢[其化学成分(质量分数)为 10.5%~12.0% Cr, 7.0%~8.5% Ni, 4.5%~6.0% Co, 2.5%~3.5% Mo, 余下为 Fe],

收稿日期: 2021-04-06; 修回日期: 2021-04-29; 录用日期: 2021-05-11

基金项目: 国防科技工业局民用航天技术预先研究项目(D010502)

通信作者: *zmwang@hust.edu.cn

经过 1130 °C × 5 h 均质化处理 + 975 °C × 1 h 晶粒细化处理 + 750 °C × 1 h 固溶处理 + -73 °C × 2 h 冷处理 + 500 °C × 3 h 时效处理后, 试样的抗拉强度、屈服强度和延伸率分别达到 1278 MPa、1207 MPa 和 13%。综上所述, 目前有关 Fe-Cr-Ni-Co-Mo 马氏体时效不锈钢的研究主要集中在传统铸造/锻造加工工艺及后续热处理上, 而采用 SLM 技术成形该不锈钢的研究还很少见。此外, SLM 沉积态以及后续热处理条件下 Fe-Cr-Ni-Co-Mo 马氏体时效不锈钢的组织 and 性能还有待探究。

基于上述背景, 本文采用 SLM 技术成形 S-130 马氏体时效不锈钢[其化学成分(质量分数)为 10.5%~12.0% Cr, 6.0%~9.0% Ni, 3.0%~

表 1 S-130 钢粉末的化学成分

Table 1 Chemical compositions of S-130 steel powder

Element	Cr	Ni	Co	Mo	C	Si	Mn	S	P	Fe
Mass fraction /%	10.5-12.0	6.0-9.0	3.0-7.0	1.5-3.5	≤0.03	≤0.50	≤0.70	≤0.015	≤0.015	Bal.

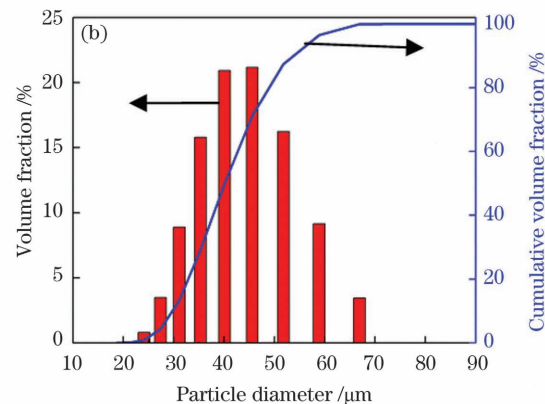
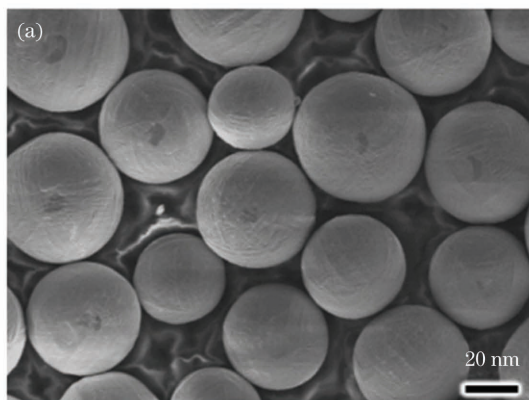


图 1 S-130 钢粉末。(a)形貌;(b)粒径分布

Fig. 1 S-130 steel powder. (a) Morphology; (b) particle size distribution

SLM 实验在自主研发的 LSNF-2 型设备上进行, 该设备配有 500 W 单模光纤激光器作为能量源^[14]。采用 SLM 技术成形了一系列 S-130 不锈钢块体试样(尺寸为 10 mm × 10 mm × 5 mm)和拉伸试样, 所使用的工艺参数为: 激光功率 360 W, 扫描速度 800 mm/s, 扫描间距 0.1 mm, 铺粉厚度 0.04 mm, 相位角 90°。SLM 沉积态 S-130 试样的致密度达到 99.9%。采用 KSL-1400X-A2 箱式电阻炉对 SLM 沉积态试样进行后续热处理, 其最高加热温度为 1400 °C, 加热速率为 10 °C/min。参考已有马氏体时效不锈钢的热处理工艺研究^[9-13], 对 SLM 成形的 S-130 试样分别进行两种热处理: 1) 均质化(1150 °C × 3 h, 空冷) + 晶粒细化(950 °C × 1 h, 空冷) + 固溶(800 °C × 1 h, 空冷) + 冷处理

7.0% Co, 1.5%~3.5% Mo, 余下为 Fe]。为了进一步提升沉积态试样的强度和硬度, 分别采用五步热处理(均质化 + 晶粒细化 + 固溶 + 冷处理 + 时效处理)以及三步热处理(固溶 + 冷处理 + 时效处理)对 SLM 沉积态试样进行后处理, 并对比分析了两种热处理工艺对 S-130 沉积态试样组织和性能的影响, 以期获得优化的热处理工艺。

2 实验材料、设备与方法

实验所用原材料是由西安欧中材料科技有限公司提供的 S-130 不锈钢粉末, 其化学成分如表 1 所示。S-130 粉末的形貌和粒径分布如图 1 所示。观察可知, 粉末呈球形, 平均粒径为 45.6 μm。

(-73 °C × 2 h, 空气中回复) + 时效(500 °C × 3 h, 空冷)(简称五步热处理); 2) 固溶(800 °C × 1 h, 空冷) + 冷处理(-73 °C × 2 h, 空气中回复) + 时效(500 °C × 3 h, 空冷)(简称三步热处理)。两种热处理的工艺流程如图 2 所示, 其中 RT 表示室温。

采用标准金相技术制备金相试样, 并采用王水(盐酸和硝酸的体积比为 3:1)对试样进行腐蚀。采用 XPert PRO 型 X 射线衍射仪(XRD)分析试样的物相组成。采用 Gemini SEM300 场发射扫描电子显微镜(SEM)对 SLM 成形态及热处理态试样的显微组织进行观察。采用 FEI TecnaiG2-F30 透射电子显微镜(TEM)对组织和物相进行深入分析。透射试样的制备步骤如下: 首先对尺寸为 10 mm × 10 mm × 2.5 mm 的薄片试样进行机械研磨, 使薄

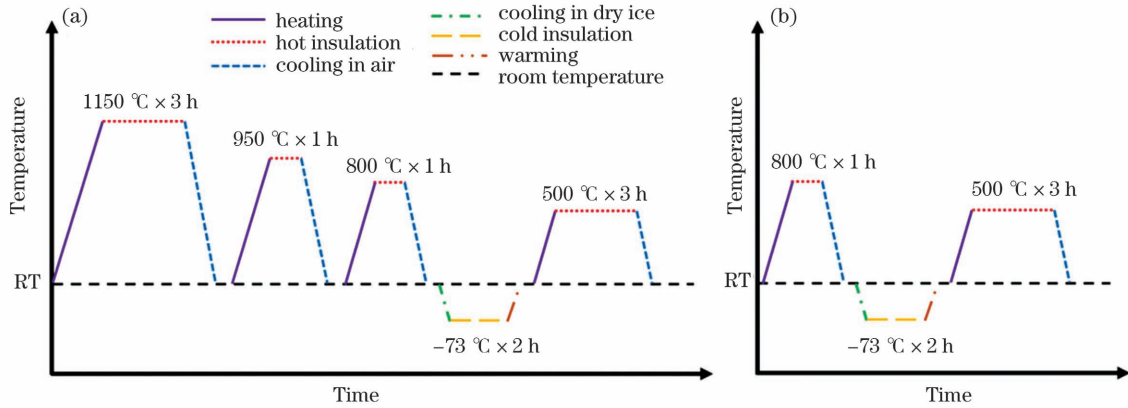


图 2 两种热处理工艺的流程。(a) 五步热处理; (b) 三步热处理

Fig. 2 Flow charts of two heat-treatment processes. (a) Five-step heat treatment; (b) three-step heat treatment

片的厚度小于 $50 \mu\text{m}$; 然后将薄片冲压成直径为 3 mm 的圆片; 最后采用 Gatan-695 型号的离子减薄仪对圆片进行进一步的减薄。采用 DHV-1000Z 型显微硬度计测量试样的显微硬度, 测试时在 2.94 N 载荷下保压 20 s , 每个试样至少测量 20 个点。采用 AG-IC100 型材料高温持久性能试验机进行室温拉伸实验, 每个参数下测试三根拉伸试样, 并采用 SEM 对拉伸试样的断口形貌进行观察。

3 分析与讨论

3.1 物相分析

图 3 显示的是 SLM 沉积态和热处理态 S-130 试样的 XRD 图谱, 可以观察到相对强度较大的马氏体相(α)衍射峰和相对强度较弱的奥氏体相(γ)衍射峰。SLM 成形的 S-130 试样主要由大量马氏体及少量残余奥氏体组成。经过两种热处理后, $(200)\gamma$, $(111)\gamma$ 和 $(220)\gamma$ 对应峰的相对强度得到明显增强, 表明奥氏体的含量增多。根据 Li 等^[15]和 Song 等^[16]的研究, 基于 XRD 谱图, 奥氏体和马氏体的相对含量为

$$V_{\gamma} + V_{\alpha} = 1, \quad (1)$$

$$V_{\gamma} = \frac{1.4I_{\gamma}}{I_{\alpha} + 1.4I_{\gamma}}, \quad (2)$$

式中: V_{γ} 和 V_{α} 分别是奥氏体和马氏体的体积分数; I_{γ} 和 I_{α} 分别是奥氏体和马氏体在 XRD 图谱中对应主峰的相对强度。结合图 3 所示的 XRD 图谱以及(1)、(2)式, 可以计算得出 SLM 沉积态试样的奥氏体含量(体积分数, 全文同)为 6.12% , 经过五步热处理和三步热处理后, 奥氏体的含量分别为 8.52% 和 11.31% 。热处理后奥氏体含量的增多主要是由于逆转变奥氏体的形成。已有马氏体时效不锈钢的热处理研究^[17-19]表明, 时效过程中非扩散

$\alpha \rightarrow \gamma$ 转变的发生会导致逆转变奥氏体的形成。需要说明的是, XRD 测试不能区分开残余奥氏体和逆转变奥氏体, 这是由于它们具有相同的面心立方(FCC)晶格结构。因此, 热处理后 S-130 试样的物相主要包含马氏体和残余/逆转变奥氏体。

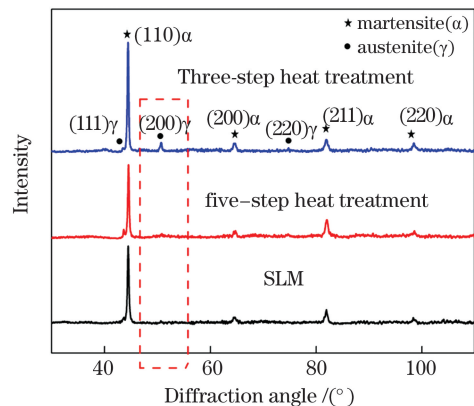


图 3 SLM 沉积态和热处理态 S-130 试样的 XRD 图谱

Fig. 3 XRD patterns of SLM as-deposited and heat-treated S-130 samples

此外, 相较于五步热处理后奥氏体的含量 (8.52%), 三步热处理后奥氏体的含量更高 (11.31%)。这主要是由于 SLM 沉积态试样经过均质化($1150 \text{ °C} \times 3 \text{ h}$, 空冷)和晶粒细化($950 \text{ °C} \times 1 \text{ h}$, 空冷)处理, 应力得到释放, 在后续三步热处理过程中, $\alpha \rightarrow \gamma$ 相转变的驱动力降低。相比之下, SLM 沉积态试样直接进行三步热处理, 较大的残余应力为 $\alpha \rightarrow \gamma$ 相转变提供了更大的驱动力, 进而形成更多的逆转变奥氏体。

3.2 显微组织

图 4 显示的是 SLM 沉积态 S-130 试样横截面和纵截面的显微组织特征。对横截面的组织进行观察, 如图 4(a)~(c) 所示。从图 4(a) 所示的低倍 SEM 图中可以观察到由 90° 相位角导致的“棋盘格”

结构。进一步,从图 4(c)所示的高倍 SEM 图中可以观察到胞状枝晶结构。对图 4(d)~(f)所示的纵截面组织进行观察,可以发现,低倍组织呈现典型的熔池形貌,高倍组织呈现胞状枝晶结构,枝晶的生长方向与熔池边界近似垂直,并沿熔池中心对称。类似的胞状枝晶结构在 SLM 成形的 SS CX 不锈钢中也可以观察到^[20]。为了进一步观察 S-130 沉积态试样的马氏体特征,对试样进行了 TEM 分析,如图 5 所示。从图 5(a)所示的明场 TEM 图中可以明

显观察到大量含有高密度位错的板条马氏体。对应的选区电子衍射(SAED)结果[图 5(b)]表明,马氏体具有典型的体心立方(BCC)结构。需要说明的是,SLM 沉积态试样中残余奥氏体的含量较少,在 TEM 测试中没有被观察到。此外,SLM 沉积态 S-130 试样中大量板条马氏体的形成主要是由于 SLM 过程中较快的冷却速率($10^3 \sim 10^8$ K/s)远高于马氏体转变所需的冷却速率^[21-22],奥氏体向马氏体的转变得以促进。

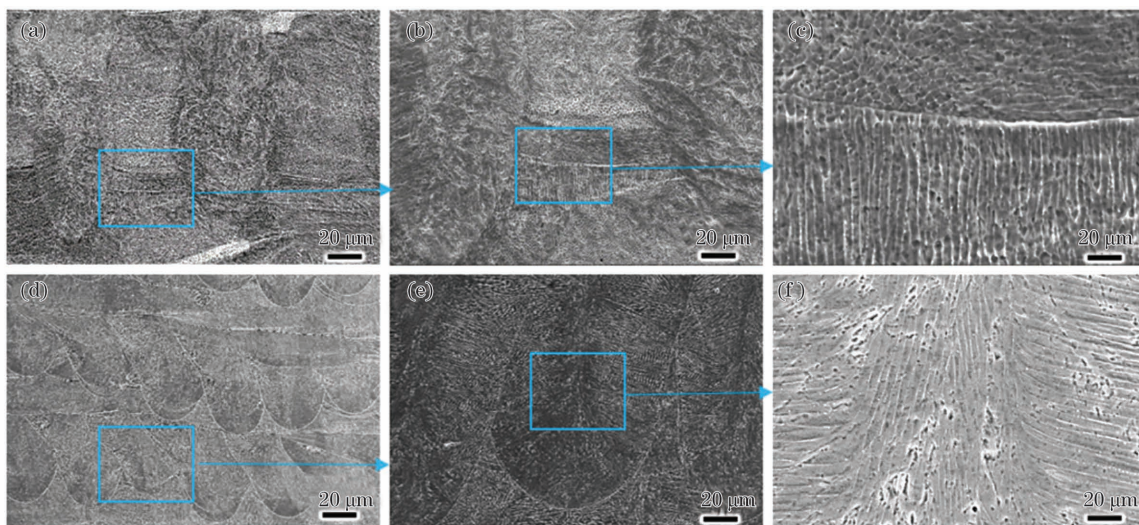


图 4 SLM 沉积态 S-130 试样横截面和纵截面在不同放大倍数下的显微组织。(a)~(c)横截面;(d)~(f)纵截面

Fig. 4 Microstructures of SLM as-deposited S-130 sample on cross and longitudinal sections under different magnifications. (a)~(c) Cross section; (d)~(f) longitudinal section

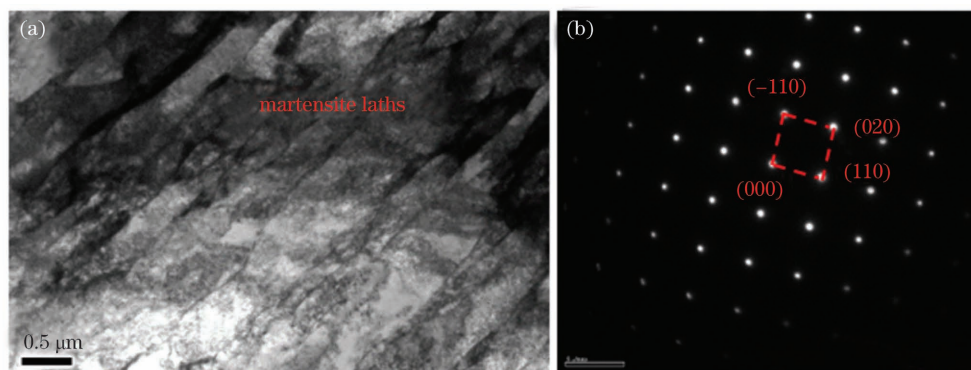


图 5 SLM 沉积态 S-130 试样的 TEM 分析。(a)明场 TEM 图;(b)对应的选区电子衍射图

Fig. 5 TEM analysis of SLM as-deposited S-130 sample. (a) Bright-field TEM micrograph; (b) corresponding SAED pattern

图 6 显示的是两种热处理态试样纵截面的显微组织特征。从图 6(a)、(d)所示的低倍 SEM 图中可以观察到沉积态的熔池形貌消失,同时出现了明显的板条马氏体结构。从图 6(c)、(f)所示的高倍 SEM 图中可以观察到板条马氏体上弥散分布的纳米级析出物。析出物的尺寸较小,在之前的 XRD 测试中没有被检测到。采用 TEM 进一步观察热处理态试样的物相和组织特征,如图 7 所示。从

图 7(a)所示的明场 TEM 图中可以观察到马氏体板条间析出的薄片状奥氏体以及纳米级析出物。图 7(b)所示的选区电子衍射图表明马氏体(BCC 结构)和奥氏体(FCC 结构)的取向关系为 $[001]_{\alpha}$ 平行于 $[011]_{\gamma}$,这与经典的 Nishiyama-Wassermann (N-W)关系相一致^[9,23]。众所周知,板条马氏体强化和析出物强化是马氏体时效不锈钢重要的两种强化机制^[9,24]。一方面,具有高位错密度的板条马氏

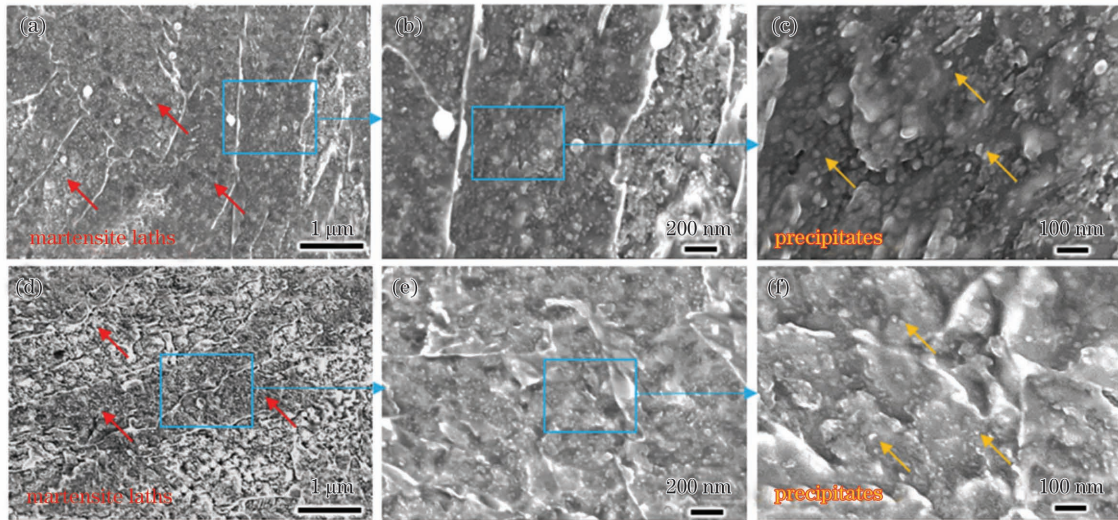


图 6 两种热处理态 S-130 试样纵截面在不同放大倍数下的显微组织。(a)~(c) 五步热处理；(d)~(f) 三步热处理
Fig. 6 Microstructures of two heat-treated S-130 samples on longitudinal sections under different magnifications.

(a)–(c) Five-step heat treatment; (d)–(f) three-step heat treatment

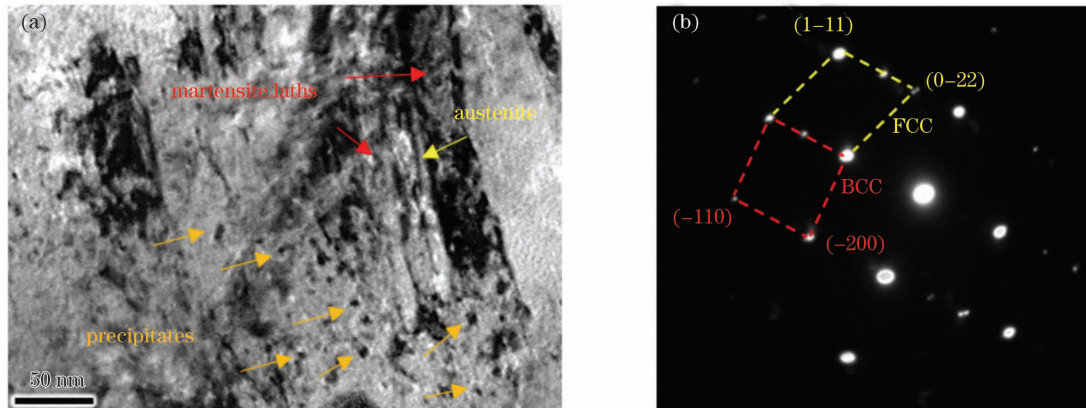


图 7 热处理态 S-130 试样的 TEM 分析。(a) 明场 TEM 图；(b) 对应的选区电子衍射图

Fig. 7 TEM analysis of heat-treated S-130 sample. (a) Bright-field TEM micrograph; (b) corresponding SAED pattern

体保证了基体的高强度。另一方面,弥散分布的细小析出物与位错的交互作用阻碍了位错的运动,从而进一步提高了钢的强度。之前已有 Fe-Cr-Ni-Co-Mo 马氏体时效不锈钢的研究^[9,10,23]表明,热处理后形成的析出物主要包含碳化物($M_{23}C_6$ 及 M_6C)、 Ni_3Mo 、 Fe_2Mo 和 R 相[成分为 $Mo_mCr_p(Fe, Co, Ni)_n$]。本研究团队前期通过 FEI TecnaiG2-F30 透射电子显微镜附带的能谱分析仪(EDS)对热处理后纳米级析出物的成分进行了确定^[25]。结果表明,析出物主要为 CrMoC 碳化物。这是由于在固溶+冷处理或均质化+晶粒细化+固溶+冷处理过程中获得了全马氏体组织(过饱和固溶体),而在随后的时效处理过程中,具有较高位错密度的马氏体促进了合金元素的扩散,在马氏体基体上析出了纳米级金属间化合物和碳化物。

进一步对两种热处理条件下板条马氏体和析出

物的尺寸进行测量,结果如图 8 所示。观察可知,经过五步热处理后,马氏体板条的宽度为 $(823.65 \pm 30.05)nm$,析出物的尺寸为 $(15.22 \pm 2.83)nm$ 。相较于五步热处理,三步热处理后获得的马氏体板条的宽度 $(562.59 \pm 20.06)nm$ 更小,析出物的尺寸 $(8.58 \pm 2.13)nm$ 也更小。未经过均质化($1150\text{ }^\circ\text{C} \times 3\text{ h}$,空冷)和晶粒细化($950\text{ }^\circ\text{C} \times 1\text{ h}$,空冷)处理的 SLM 试样中具有更大的残余应力,在后续固溶+冷处理过程中为马氏体转变提供了更大的驱动力,促进了更细小板条马氏体的形成,同时在后续时效过程中为 $\alpha \rightarrow \gamma$ 相转变以及第二相粒子的析出提供了更大的驱动力,进而获得了更高含量的逆转变奥氏体以及更多细小的析出物。Chen 等^[26]在 SLM 成形 5CrNi4Mo 工具钢的研究中发现,沉积态试样内部的残余应力为后续热处理过程中的相变以及晶粒形核的长大提供了驱动力,有利于获得细小的组织。

本研究团队同样发现, SLM 成形 Ti-40Al-9V-0.5Y 合金中较大的残余热应力为后续时效处理过程中的相变(α_2 -Ti₃Al \rightarrow γ -TiAl 和 B₂-TiAl \rightarrow γ -TiAl) 提供了更大的驱动力, 促进形成了更多的 γ -TiAl 相并获得了更细小的组织^[27]。

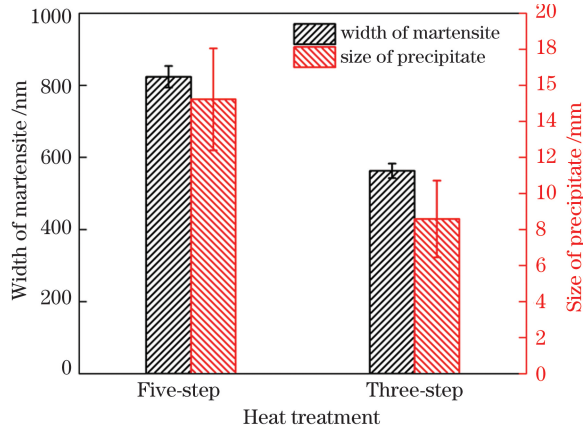


图 8 两种热处理条件下 S-130 试样马氏体的宽度和析出物的尺寸

Fig. 8 Martensite widths and precipitate sizes of two heat-treated S-130 samples

3.3 力学性能

图 9 显示的是 SLM 沉积态和两种热处理条件下 S-130 试样的显微硬度。观察可知, SLM 沉积态试样的显微硬度为 (351.51 ± 11.16) HV。相较于 SLM 沉积态试样, 经过两种热处理后, 试样的显微硬度明显提升, 增幅超过 8.98%。同时, 相较于五步热处理条件下试样的显微硬度 $[(383.08 \pm 11.06)$ HV], 三步热处理条件下试样的显微硬度更高 $[(404.94 \pm 10.32)$ HV]。

图 10 显示的是 SLM 沉积态和两种热处理条件下 S-130 试样的拉伸性能。观察可知, SLM 沉

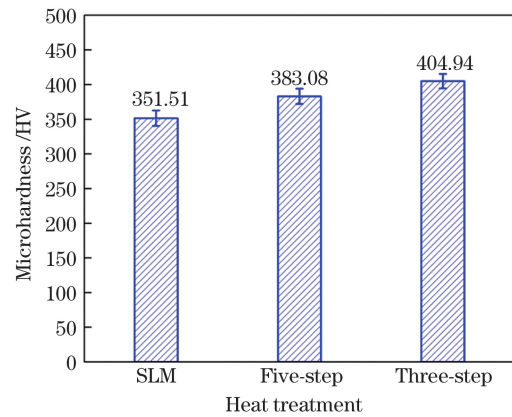


图 9 SLM 沉积态和热处理态 S-130 试样的显微硬度

Fig. 9 Microhardness of SLM as-deposited and heat-treated S-130 samples

积态试样的屈服强度和抗拉强度分别为 (852.6 ± 40.86) MPa 和 (1072.89 ± 2.96) MPa。相较于 SLM 沉积态试样, 经过两种热处理后, 试样的屈服强度和抗拉强度得到明显提升, 增幅分别超过 33.92% 和 14.99%。同时相较于五步热处理条件下试样的屈服强度 $[(1141.82 \pm 56.09)$ MPa] 和抗拉强度 $[(1233.7 \pm 9.56)$ MPa], 三步热处理条件下试样的屈服强度 $[(1235.76 \pm 6.17)$ MPa] 和抗拉强度 $[(1266.97 \pm 6.62)$ MPa] 也更高。此外, 两种热处理态试样的延伸率 [分别为 $(17.69 \pm 0.23)\%$ 和 $(17.47 \pm 0.15)\%$] 与沉积态试样 $[(17.66 \pm 0.11)\%$] 相当。进一步对 SLM 沉积态和两种热处理条件下拉伸试样的断口进行 SEM 观察, 如图 11 所示。可以看出, 所有试样的拉伸断口均由大量韧窝构成, 属于典型的韧性断裂。这也表明热处理前后 S-130 试样的断裂模式均是韧性断裂。

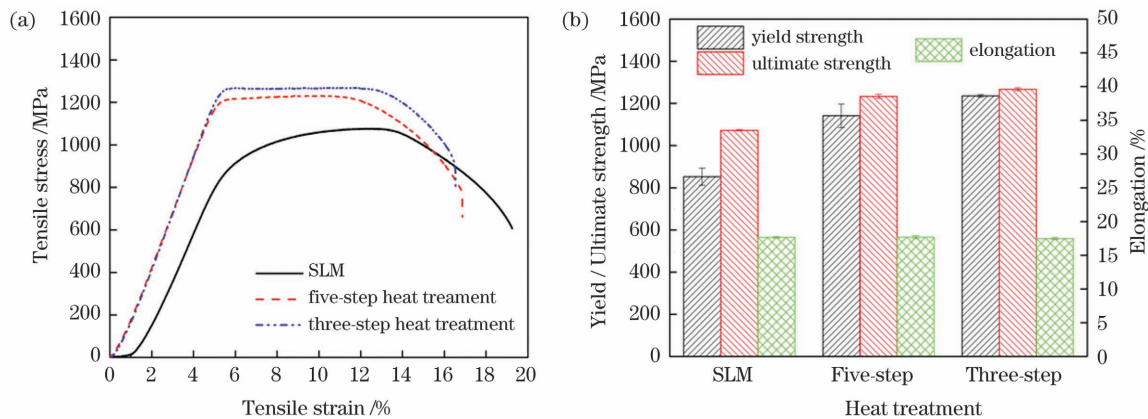


图 10 SLM 沉积态和热处理态 S-130 试样的拉伸性能。(a) 应力-应变曲线; (b) 屈服强度、抗拉强度和延伸率

Fig. 10 Tensile properties of SLM as-deposited and heat-treated S-130 samples. (a) Tensile stress-strain curves; (b) yield strength, ultimate strength, and elongation

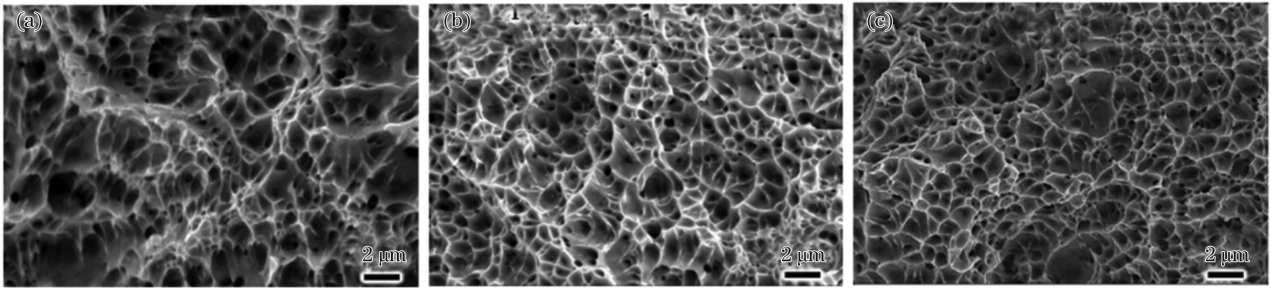


图 11 SLM 沉积态和热处理态 S-130 拉伸试样的断口形貌。(a)SLM 沉积态;(b)五步热处理;(c)三步热处理

Fig. 11 Fracture morphologies of SLM as-deposited and heat-treated S-130 tensile samples. (a) SLM as-deposited state; (b) five-step heat treatment; (c) three-step heat treatment

表 2 列出了 SLM 沉积态试样经两种热加工工艺后的力学性能与同类铸造试样的对比结果。观察可知,相较于铸造十五步热处理试样,SLM 试样经五步热处理后,屈服强度和抗拉强度更低,而 SLM 试样经三步热处理后,屈服强度和抗拉强度与之相

当。此外,SLM 试样经两种热处理后,延伸率均较铸造十五步热处理试样更高。总体而言,SLM 试样经三步热处理后的拉伸性能较铸造试样经五步热处理后的更优异。

表 2 SLM 沉积态试样经不同工艺处理后的力学性能

Table 2 Mechanical properties of SLM as-deposited samples after treatment with different processes

Technique	Yield strength /MPa	Ultimate strength /MPa	Elongation /%
As cast+five-step heat-treatment ^[12]	1207	1278	13
SLM+five-step heat-treatment	1141.82±56.09	1233.7±9.56	17.69±0.23
SLM+three-step heat-treatment	1235.76±6.17	1266.97±6.62	17.47±0.15

根据上述研究结果,我们可以得出,在保证延伸率的情况下,三步热处理相较于五步热处理具有更好的强化效果。一般而言,奥氏体的强度和硬度较马氏体低^[10,13]。相较于五步热处理,试样经过三步热处理后奥氏体含量增多,但显微硬度和拉伸强度得到明显提高,这主要是由于宽度更细的板条马氏体和尺寸更小的析出物造成的强化作用更显著。根据霍尔-佩奇公式^[23-24,27-28]可知,晶粒尺寸越小,晶界面积越大,位错运动的阻力越大,硬度和屈服强度越高。一方面,马氏体尺寸越小,位错运动受到马氏体相界面的阻力越大,马氏体的硬度和屈服强度越高。另一方面,弥散分布的细小析出物与位错的交互作用增强,位错运动的阻力增大,从而使得不锈钢的硬度和屈服强度得到进一步提高。此外,三步热处理后试样具有更高的奥氏体含量,使其仍保持较高的延伸率。综上所述,SLM 成形 S-130 马氏体时效不锈钢优化的热处理制度为三步热处理(固溶+冷处理+时效)。

4 结 论

采用 SLM 技术成形了 S-130 马氏体时效不锈钢,对比分析了五步热处理(均质化+晶粒细化+固

溶+冷处理+时效处理)和三步热处理(固溶+冷处理+时效处理)对沉积态试样组织和性能的影响。主要结论如下。

1) SLM 成形 S-130 试样主要由大量马氏体和少量残余奥氏体(~6.12%)组成。五步热处理和三步热处理过程中逆转变奥氏体的形成使得奥氏体的含量分别增至 8.52%和 11.31%。

2) SLM 成形 S-130 试样的显微组织呈胞状枝晶结构,枝晶生长方向与熔池边界呈近似垂直。TEM 观察到大量含有高密度位错的板条马氏体。经过两种热处理后,大量的纳米级析出物在板条马氏体上弥散分布,同时残余/逆转变奥氏体在马氏体板条间析出。

3) 未经过均质化(1150 °C×3 h,空冷)和晶粒细化(950 °C×1 h,空冷)处理的 SLM 试样具有更大的残余应力,为后续三步热处理过程中的相转变和沉淀物析出提供了更大的驱动力,三步热处理态试样相较于五步热处理态试样含有更高含量的奥氏体以及更细小的板条马氏体和析出物。

4) SLM 沉积态试样的显微硬度、屈服强度、抗拉强度和延伸率分别为(351.51±11.16)HV, (852.6±40.86)MPa, (1072.89±2.96)MPa 和

(17.66±0.11)%。经过两种热处理后,显微硬度、屈服强度和抗拉强度得到明显提升,且延伸率没有降低。相较于五步热处理,经过三步热处理后试样具有更高的显微硬度和拉伸强度。SLM 成形 S-130 马氏体时效不锈钢优化的热处理制度为三步热处理(固溶+冷处理+时效)。

参 考 文 献

- [1] Jiang Y. Optimization of heat treatment technology of maraging stainless steel[J]. *Materials Science and Technology*, 2010, 18(4): 571-574.
姜越. 马氏体时效不锈钢热处理工艺优化[J]. *材料科学与工艺*, 2010, 18(4): 571-574.
- [2] Tian J L, Wang W, Yin L C, et al. Three dimensional atom probe and first-principles studies on spinodal decomposition of Cr in a Co-alloyed maraging stainless steel [J]. *Scripta Materialia*, 2016, 121: 37-41.
- [3] Liu Z W, Cheng X, Li J, et al. Heat-processing technology for laser additive manufacturing of 05Cr15Ni5Cu4Nb precipitation-hardening stainless steels[J]. *Chinese Journal of Lasers*, 2017, 44(6): 155-162.
刘正武, 程序, 李佳, 等. 激光增材制造 05Cr15Ni5Cu4Nb 沉淀硬化不锈钢的热处理工艺[J]. *中国激光*, 2017, 44(6): 155-162.
- [4] Gu D D, Zhang H M, Chen H Y, et al. Laser additive manufacturing of high-performance metallic aerospace components[J]. *Chinese Journal of Lasers*, 2020, 47(5): 0500002.
顾冬冬, 张红梅, 陈洪宇, 等. 航空航天高性能金属材料构件激光增材制造[J]. *中国激光*, 2020, 47(5): 0500002.
- [5] Yang C, Dong Z H, Chi C T, et al. Microstructure and mechanical properties of 24CrNiMo alloy steel formed by selective laser melting[J]. *Chinese Journal of Lasers*, 2020, 47(5): 0502008.
杨晨, 董志宏, 迟长泰, 等. 选区激光熔化成形 24CrNiMo 合金钢的组织结构与力学性能[J]. *中国激光*, 2020, 47(5): 0502008.
- [6] Chen S, Tao F H, Jia C Z. Microstructure and micro-hardness of 4Cr5MoSiV1 die steels fabricated by selective laser melting [J]. *Chinese Journal of Lasers*, 2019, 46(1): 0102007.
陈帅, 陶凤和, 贾长治. 选区激光熔化 4Cr5MoSiV1 模具钢显微组织及显微硬度研究[J]. *中国激光*, 2019, 46(1): 0102007.
- [7] Zong X W, Gao Q, Zhou H Z, et al. Effects of bulk laser energy density on anisotropy of selective laser sintered 316L stainless steel[J]. *Chinese Journal of Lasers*, 2019, 46(5): 0502003.
宗学文, 高倩, 周宏志, 等. 体激光能量密度对选区激光熔化 316L 不锈钢各向异性的影响[J]. *中国激光*, 2019, 46(5): 0502003.
- [8] Zhang J L, Li F L, Zhang H J. Research progress on preparation of metallic materials by selective laser melting [J]. *Laser & Optoelectronics Progress*, 2019, 56(10): 100003.
张家莲, 李发亮, 张海军. 选区激光熔化技术制备金属材料研究进展[J]. *激光与光电子学进展*, 2019, 56(10): 100003.
- [9] Liu K, Shan Y Y, Yang Z Y, et al. Effect of aging on microstructure and mechanical property of 1900 MPa grade maraging stainless steel[J]. *Journal of Materials Science & Technology*, 2007, 23(3): 312-318.
- [10] Tarasenko L V, Shal'kevich A B. Phase composition and hardening of steels of the Fe-Cr-Ni-Co-Mo system with martensite-austenite structure[J]. *Metal Science and Heat Treatment*, 2007, 49(3/4): 188-193.
- [11] Ge P, Yang Z Y, Ding Y L. Investigation on toughening of Fe-Cr-Ni-Co-Mo system high-strength stainless steel for cryogenic applications [J]. *Hot Working Technology*, 2012, 41(24): 227-229, 233.
葛鹏, 杨卓越, 丁雅莉. 低温用 Fe-Cr-Ni-Co-Mo 系高强不锈钢韧化工艺研究[J]. *热加工工艺*, 2012, 41(24): 227-229, 233.
- [12] Su W W, Yang Z Y, Ding Y L. Effect of repeat solution treatment on properties of cast maraging stainless steel for cryogenic applications [J]. *Heat Treatment of Metals*, 2014, 39(4): 15-18.
苏文文, 杨卓越, 丁雅莉. 重复固溶处理对超低温用铸造马氏体时效不锈钢性能的影响[J]. *金属热处理*, 2014, 39(4): 15-18.
- [13] Su W W, Yang Z Y, Ding Y L. Effects of strong carbide forming elements on low temperature properties of casting high-strength steel [J]. *Hot Working Technology*, 2014, 43(13): 41-43, 47.
苏文文, 杨卓越, 丁雅莉. 强碳化物形成元素对铸造高强度钢低温性能的影响[J]. *热加工工艺*, 2014, 43(13): 41-43, 47.
- [14] Yang J J, Han J, Yu H C, et al. Role of molten pool mode on formability, microstructure and mechanical properties of selective laser melted Ti-6Al-4V alloy [J]. *Materials & Design*, 2016, 110: 558-570.
- [15] Li Y C, Yan W, Cotton J D, et al. A new 1.9 GPa maraging stainless steel strengthened by multiple precipitating species[J]. *Materials & Design*, 2015, 82: 56-63.
- [16] Song Y Y, Li X Y, Rong L J, et al. The influence of

- tempering temperature on the reversed austenite formation and tensile properties in Fe-13%Cr-4%Ni-Mo low carbon martensite stainless steels [J]. *Materials Science and Engineering: A*, 2011, 528 (12): 4075-4079.
- [17] Sarkar S, Mukherjee S, Kumar C S, et al. Effects of heat treatment on microstructure, mechanical and corrosion properties of 15-5 PH stainless steel parts built by selective laser melting process[J]. *Journal of Manufacturing Processes*, 2020, 50: 279-294.
- [18] Song J, Tang Q, Feng Q X, et al. Effect of heat treatment on microstructure and mechanical behaviours of 18Ni-300 maraging steel manufactured by selective laser melting [J]. *Optics & Laser Technology*, 2019, 120: 105725.
- [19] Krasnikova S I, Vukelich S B, Drobot A V, et al. Dendritic inhomogeneity of stainless maraging steels [J]. *Metal Science and Heat Treatment*, 1985, 27 (10): 781-786.
- [20] Asgari H, Mohammadi M. Microstructure and mechanical properties of stainless steel CX manufactured by direct metal laser sintering [J]. *Materials Science and Engineering: A*, 2018, 709: 82-89.
- [21] Yadollahi A, Shamsaei N, Thompson S M, et al. Effects of building orientation and heat treatment on fatigue behavior of selective laser melted 17-4 PH stainless steel [J]. *International Journal of Fatigue*, 2017, 94: 218-235.
- [22] Bailey N S, Tan W D, Shin Y C. Predictive modeling and experimental results for residual stresses in laser hardening of AISI 4140 steel by a high power diode laser [J]. *Surface and Coatings Technology*, 2009, 203(14): 2003-2012.
- [23] Liu K, Shan Y Y, Yang Z Y, et al. Effect of heat treatment on prior grain size and mechanical property of a maraging stainless steel [J]. *Journal of Materials Science & Technology*, 2006, 22: 769-774.
- [24] Schnitzer R, Zinner S, Leitner H. Modeling of the yield strength of a stainless maraging steel [J]. *Scripta Materialia*, 2010, 62(5): 286-289.
- [25] Gao P, Jing G Y, Lan X Q, et al. Effect of heat treatment on microstructure and mechanical properties of Fe-Cr-Ni-Co-Mo maraging stainless steel produced by selective laser melting [J]. *Materials Science and Engineering: A*, 2021, 814: 141149.
- [26] Chen H Y, Gu D D, Dai D H, et al. Microstructure and composition homogeneity, tensile property, and underlying thermal physical mechanism of selective laser melting tool steel parts [J]. *Materials Science and Engineering: A*, 2017, 682: 279-289.
- [27] Gao P, Wang Z M. Tailored microstructure and enhanced comprehensive mechanical properties of selective laser melted Ti-40Al-9V-0.5Y alloy after aging treatment [J]. *Materials Science and Engineering: A*, 2020, 780: 139183.
- [28] Gao P, Huang W P, Yang H H, et al. Cracking behavior and control of β -solidifying Ti-40Al-9V-0.5Y alloy produced by selective laser melting [J]. *Journal of Materials Science & Technology*, 2020, 39: 144-154.

Heat-Treatment Process of S-130 Steel Produced by Selective Laser Melting

Gao Piao¹, Lan Xinqiang¹, Zhou Yaxiong², Wang Yun², Yang Huanqing², Wang Zemin^{1*}

¹ Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China;

² Xi'an Space Engine Company Limited, Xi'an, Shaanxi 710100, China

Abstract

Objective The Fe-Cr-Ni-Co-Mo system is a new type of maraging stainless steel (MSS) possessing ultra-high strength and good toughness, which is considered as a potential structural material for fabricating landing gear parts, powertrain parts of vehicles, and liquid-oxygen kerosene engine components. It is difficult to fabricate these complex-structured precision metal components by traditional processing methods (e. g. casting and forging). As a fast-growing additive manufacturing technology, selective laser melting (SLM) can be used to fabricate complex-structured and high-performance parts with a short processing period, a high material utilization rate, and low production cost. However, few public reports on the fabrication of Fe-Cr-Ni-Co-Mo MSSs by SLM are available. Based on this, here an S-130 MSS is produced by SLM, whose chemical compositions (mass fractions) are Cr

(10.5%–12.0%), Ni(6.0%–9.0%), Co(3.0%–7.0%), Mo(1.5%–3.5%), and the rest is Fe. To obtain the optimal heat-treatment regime, the effects of five-step and three-step heat-treatments on microstructures and properties are compared and analyzed.

Methods The spherical gas atomized S-130 powder with an average size of $45.6 \mu\text{m}$ is the starting material. The SLM experiment is carried out on a self-developed machine. A series of S-130 cuboid samples and tensile test samples are deposited using the optimized SLM parameters: laser power of 360 W, scanning speed of 800 mm/s, hatch spacing of 0.1 mm, layer thickness of $40 \mu\text{m}$, and phase angle of 90° . Heat-treatments are conducted in a muffle furnace at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. The SLM as-deposited S-130 samples are heat-treated under two kinds of heat-treatment processes: 1) homogenization ($1150 \text{ }^\circ\text{C} \times 3 \text{ h}$, air cooling) + grain refinement ($950 \text{ }^\circ\text{C} \times 1 \text{ h}$, air cooling) + solution ($800 \text{ }^\circ\text{C} \times 1 \text{ h}$, air cooling) + cryogenic cooling ($-73 \text{ }^\circ\text{C} \times 2 \text{ h}$, warming in air) + aging ($500 \text{ }^\circ\text{C} \times 3 \text{ h}$, air cooling) (five-step heat treatment); 2) solution ($800 \text{ }^\circ\text{C} \times 1 \text{ h}$, air cooling) + cryogenic cooling ($-73 \text{ }^\circ\text{C} \times 2 \text{ h}$, warming in air) + aging ($500 \text{ }^\circ\text{C} \times 3 \text{ h}$, air cooling) (three-step heat treatment). Microstructure and phase characteristics are observed and identified by the means of X-ray diffractometer (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM). Microhardness and tensile properties are also evaluated.

Results and Discussions The phase compositions of the SLM as deposited S-130 samples consist of the dominant martensite and few retained austenite (volume fraction of 6.12%). The contents (volume fractions) of austenite are increased to 8.52% and 11.31% after the five-step and three-step heat-treatments, respectively (Fig. 3), which is mainly ascribed to the formation of reverted austenite. The SLM as-deposited S-130 samples present cellular dendrite structures (Fig. 4). The TEM results reveal a large number of martensite laths with a high density of dislocations (Fig. 5). After two kinds of heat treatments, the large quantity of nanosized spheroidal precipitates are generated and uniformly dispersed in the martensite laths, and the lamellar retained/reverted austenite are distributed among the martensite laths (Figs. 6 and 7). After the five-step heat treatment, the martensite width is $(823.65 \pm 30.05) \text{ nm}$ and the precipitate size is $(15.22 \pm 2.83) \text{ nm}$. Comparatively, the martensite width obtained after the three-step heat treatment [$(562.59 \pm 20.06) \text{ nm}$] is finer, and the precipitate size [$(8.58 \pm 2.13) \text{ nm}$] is smaller (Fig. 8). This is mainly due to the larger residual stress in the SLM samples without homogenization + grain refinement treatment, which provides a greater driving force for martensitic transformation and promotes the formation of finer lath martensite during the solution + cryogenic cooling. Meanwhile, it provides a greater driving force for the α - γ phase transformation and precipitation of the second phase particles during the subsequent aging, thus obtaining more fine precipitates. The average microhardness, yield strength, and ultimate strength of the SLM as-deposited S-130 sample are $(351.51 \pm 11.16) \text{ HV}$, $(852.6 \pm 40.86) \text{ MPa}$, and $(1072.89 \pm 2.96) \text{ MPa}$, respectively. After the five-step heat treatment, the average microhardness, yield strength, and ultimate strength increase to $(383.08 \pm 11.06) \text{ HV}$, $(1141.82 \pm 56.09) \text{ MPa}$, and $(1233.7 \pm 9.56) \text{ MPa}$, respectively. After the three-step heat treatment, the average microhardness, yield strength, and ultimate strength increase to $(404.94 \pm 10.32) \text{ HV}$, $(1235.76 \pm 6.17) \text{ MPa}$, and $(1266.97 \pm 6.62) \text{ MPa}$, respectively. The elongation for the two kinds of heat treatments [$(17.69 \pm 0.23)\%$ and $(17.47 \pm 0.15)\%$, respectively] is comparable to that of the SLM as-deposited sample [$(17.66 \pm 0.11)\%$] (Fig. 10). Compared with that after the five-step heat treatment, the sample after three-step heat treatment possesses high microhardness and tensile strength. According to the Hall-Petch formula, the smaller the martensite lath, the higher the resistance of the martensite phase interface to dislocation movement, and the higher the martensite hardness and yield strength. Besides, the interaction between the dispersed finer precipitates and dislocations is enhanced, the resistance to dislocation movement is increased, and thus the hardness and yield strength are further improved. In addition, the sample has a high austenite content after three-step heat treatment, which ensures a high elongation.

Conclusions In this paper, an S-130 MSS is successfully produced by SLM. For SLM as-deposited samples, the phase analysis reveals a large amount of martensite and a small amount of retained austenite, and the microstructure is characterized by the cellular dendrite structures and a large number of martensite laths. After the two kinds of heat treatments, the formation of reverted austenite increases the content of austenite, and a large number of nanosized precipitates are uniformly dispersed in the martensite laths. Meanwhile, the lamellar retained/reverted austenite is distributed among the martensite laths. Compared with those of the SLM as-deposited samples, the microhardness and tensile strength are significantly improved and the elongation is not reduced after two kinds of heat treatments. Moreover, in comparison to that after five-step heat treatment, the sample after three-step heat treatment possesses a high content of austenite and slenderer martensite laths as well as finer precipitate, which contributes to high

microhardness and tensile strength under the condition of ensuring elongation. The optimized heat-treatment regime for the SLM as-deposited S-130 MSS is three-step heat treatment (solution + cryogenic cooling + aging).

Key words laser technique; selective laser melting; S-130 maraging stainless steel; heat treatment; microstructure; mechanical properties