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等离子熔覆γ/Cr_7C_3复合材料涂层组织与耐磨性研究

刘秀波[1,2]，虞 钢[1]，郭 建[2]，张振国[2]，商全义[2]，谷亦杰[3]，崔洪芝[3]
(1. 中国科学院力学研究所，北京 100080；2. 中原工学院材料与化学工程学院，河南 郑州 450007；
3. 山东科技大学材料科学与工程学院，山东 青岛 266510)

摘 要：为探索提高工程机械易损零部件服役寿命的新技术，采用等离子熔覆工艺，以Ni-Cr-C混合合金粉末为添加材料，在易损零部件用钢Q235表面形成了以初生块状金属陶瓷Cr_7C_3为硬质耐磨相，以强韧性良好的γ/Cr_7C_3共晶为基体的复合材料冶金涂层，分析了涂层的显微组织和硬度，在室温干滑动磨损条件下测试了其耐磨性。研究结果表明：涂层组织致密，硬度较高，与基体之间为完全的冶金结合，在干滑动磨损条件下具有良好的耐磨性。

关键词：等离子熔覆； 涂层； 组织； 耐磨性
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工程机械、建筑机械和矿山机械中的许多零部件，在服役过程中都承受着持续的、强力的、恶劣的磨损，存在着严重的粘着磨损、磨粒磨损和冲蚀磨损等多种复合磨损，要求零部件具有良好的耐磨性、耐冲击性和一定的耐蚀性。同时，上述零部件还应具有一定的可焊接性能和可加工性等，以利于修补和法兰联结等[1]。为此，上述零部件一般都采用锻造和焊接性能良好的高强度低碳低合金结构钢制造，如Q235、16Mn钢等，但这类钢经热处理后的硬度及耐磨性能较低，导致其服役寿命大大降低，更换频繁。为了提高该类零部件的使用寿命，目前国内外普遍采用的防护方法一般为热喷涂、耐磨堆焊及镶嵌硬质合金，还有采用激光熔覆技术等。但热喷涂技术只能获得界面成分与性能突变的呈机械结合的涂层，耐磨损和抗冲击性能无法满足上述零部件的恶劣工况要求；堆焊工艺虽然对提高零件表面的硬度和耐磨性有一定作用，但其缺点也是明显的：手弧焊各处熔深和稀释率不一致导致硬度和结合力不均匀，尤其在边角处堆焊层容易与本体剥离，受焊丝及本体稀释率的影响，硬度及耐磨性提高有限，堆焊的操作环境恶劣，堆焊层内气孔夹杂和裂纹难以避免，使用效果不理想；国内外对高性能高结合力涂层都采用激光熔覆方法，由于成本高，仅限于航空发动机等少量高附加值产品和发电机组等特殊领域[2]，在普通机械制造领域并未广泛应用。所以，有必要继续寻求提高上述易损零部件服役寿命和性能价格比的的新工艺与新技术。

1 涂层组织设计

等离子束与激光束和电子束同为高能束，且可在常压下发生，不需真空环境，用于金属表面处理不需任何前处理，工艺过程简单，设备成本低，工件变形小，可望在金属表面防护中发挥重要作用。等离子熔覆技术是在程序控制的高稳定性直流压缩电弧等离子束流作用下，在上述零部件材料表面顺序快速形成熔池，同时向熔池中送入所需要的耐磨耐冲击合金成分，在熔池中迅速熔化扩散反应并凝固，形成十分牢固的高耐磨耐冲击冶金涂层的新技术[3]。

为保证所制备的涂层具有良好的耐磨性能，涂层组织中应含有较高体积分数的高硬度的耐磨相；同时，为充分发挥耐磨相的耐磨性能，耐磨相之间必须有起粘结和强有力支撑作用的基体连续相存在，该连续相应具有优良的韧性等特点，这是因为优良的韧性一方面可以防止涂层在服役过程中的开裂或剥落，另一方面可有效地减缓制备工艺过程中的热应力。所以，为满足上述低碳钢零部件的服役性能要求，涂层应为多相复合材料组织。金属碳化物Cr_7C_3因其良好的硬度和稳定性，可选择充当涂层的耐磨相，而γ镍基固溶体因为具有优异的高温和常温力学性能、紧

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作者简介：刘秀波(1968—)，男，博士，高级工程师，E-mail：liuxiubo@imech.ac.cn。

密的面心立方结构、无固态相变、具有良好的稳定性和优异的韧性,可作为涂层的连续相(基体),具有这种多相组织特征的复合陶瓷涂层材料无疑会具有良好的耐磨和抗冲击性能,可望能成为提高上述低碳钢零部件服役寿命的涂层候选材料[4-6]。

本文采用等离子熔覆技术,以 Ni-Cr-C 混合合金粉末为添加原料,希望在普通 Q235 钢基体表面制得以 Cr_7C_3 为耐磨增强相、以 γ 镍基固溶体为基体的、十分牢固的高耐磨碳化物 - 金属复合材料冶金涂层,分析了涂层的显微组织、硬度及耐磨性,以期为提高工程机械易损零部件的服役寿命提供有益参考。

2　试验方法

以厚 10mm 的 Q235 钢板为基材,熔覆添加材料为 Ni30-Cr61-C9 (wt. %),粉末颗粒度 70 - 140μm,采用自动送粉装置,送粉量 9ml/min,在自行研制的等离子扫描设备上进行单道扫描,以免各道之间产生热影响,单道扫描宽度 5mm,工作电流 120A,工作电压 45V,Ar 气作为保护及电离气体,输出等离子束功率 10kW,等离子束斑尺寸为 10mm ×1mm,扫描速度 500mm/min。物相分析采用日本理学 D/max-3c 自动 X 射线衍射仪,用 MM-6 金相显微镜观察涂层组织,用 MH-6 型显微硬度计测试涂层的显微硬度,载荷 100 g,加载时间 15 s,磨损实验在 MM-200 环 - 块式滑动磨损实验机上进行,对磨钢环为经淬火处理的 45 钢 (HRC55),法向载荷为 20 kgf,对磨时间为 60min,在感量为 10^{-5} g 的分析天平上称取磨损失重,并以磨损失重来评价原始 Q235 钢和所制备涂层的耐磨性能。

3　结果与讨论

在等离子束流热源的直接作用下,大部分添加的 Ni-Cr-C 混合合金粉末和原始 Q235 钢表面一薄层快速熔化形成熔池,在基体的快速热传导和向外界空气的辐射传热作用下快速凝固成一层组织细小、成分相对均匀的冶金涂层。涂层的 X 射线衍射分析结果表明,通过等离子束流的处理,在 Q235 钢表面得到了由镍基固溶体 γ 和碳化物增强相 Cr_7C_3 组成的复合材料涂层,最终涂层厚度约 1.7mm。

图 1 为等离子熔覆耐磨复合材料涂层的典型金相组织照片。由图 1 (a) 可见,涂层中上部为灰白色不规则块状初生相大致均匀地分布在灰黑色连续相之上,X 射线衍射分析结合能谱分析证实,灰白色不规则块状相为初生的 Cr_7C_3 相,灰黑色连续相为镍基固溶体 γ 和 Cr_7C_3 的共晶组织。分析认为,合金熔池的主要成分为添加的 Ni、Cr、C 及基材熔入的少量的 Fe,随着合金熔池的快速冷却,熔点最高 (1838 K)、相形成自由能最负的 Cr_7C_3 相首先凝固析出,其周围的合金熔液则通过共晶反应并依附于初生 Cr_7C_3 相长大,最终形成 γ/Cr_7C_3 共晶。图 1 (b) 为涂层与基材结合区的显微组织情形,可见,由于这里的温度梯度很高且基材表面浅层熔化,涂层呈明显的柱状晶生长特性,涂层与基材之间形成了良好的冶金结合。

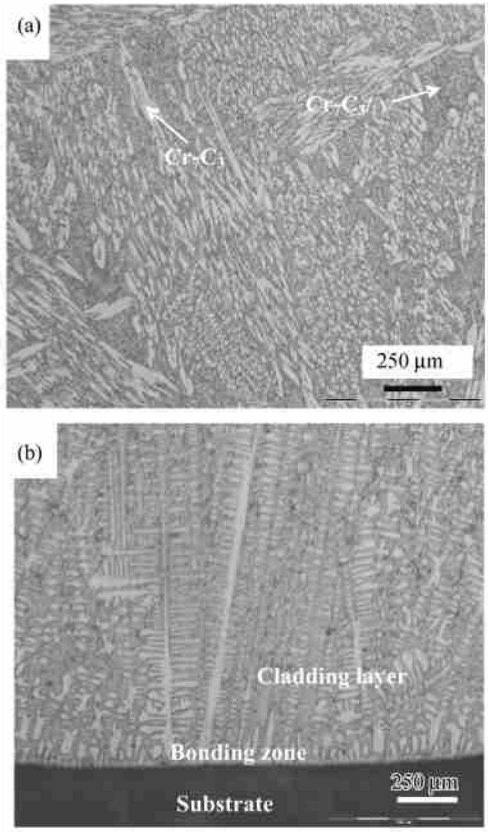

图 1　等离子熔覆耐磨复合材料涂层的典型组织
(a) 涂层中部典型组织;(b) 涂层与基材结合区组织
Fig. 1　Typical microstructure of plasma cladding wear-resistant composite coating
(a) microstructure of the central region of the coating;
(b) bonding region between the coating and substrate

图 2 为 Q235 钢等离子熔覆耐磨复合材料涂层沿层深方向显微硬度分布。由于熔覆涂层中大量高硬度的 Cr_7C_3 碳化物增强相的析出,一部分熔化的基材元素 Fe 也由于等离子高能束照射产生的非平衡条件也扩展固溶在 Cr_7C_3 碳化物中而最后得到 $(Cr,Fe)_7C_3$ 型混合碳化物;同时,快速凝固得到的组织细

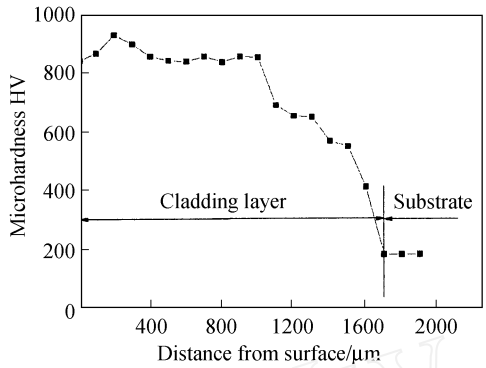

图2 等离子熔覆复合材料耐磨涂层沿层深方向的显微硬度分布曲线

Fig. 2 Microhardness profile of the plasma jet clad composite coatings prepared with Ni-Cr-C precursor mixed powders

小且分布比较均匀,所以,涂层具有较高的硬度及较合理的硬度分布。

涂层和原始Q235钢的室温干滑动磨损试验结果表明(见表1),涂层的磨损量大大小于基材的磨损量,这意味着涂层的滑动磨损耐磨性有明显提高,磨损失重数据表明其耐磨性能提高约7倍。

表1 干滑动磨损失重测试结果(g)

Table 1 Weight loss result of the dry sliding wear test (g)

Specimen No.		Weight loss of the composite coating	Weight loss of the untreated Q235 carbon steel
Before test	A	9.7342	11.1243
	B	8.7284	9.8370
After test	A	9.7144	10.9853
	B	8.7095	9.8370
The weight loss	A	0.0198	0.1390
	B	0.0189	0.1320
Result (average)		0.0194	0.1355

等离子熔覆所制备涂层和原始Q235钢的室温干滑动磨损表面形貌如图3所示。原始Q235钢表面有明显的塑性变形和严重的犁沟痕迹,其表面发生一定氧化(如图3(b)),显示出原始钢发生了严重的粘着磨损、磨粒磨损和一定的氧化磨损;与之形成鲜明对比的是,如图3(a)所示,涂层的磨损表面既没有明显的塑性变形,也没有犁沟,并可见其表面初生块状碳化物的分布。

Q235钢表面等离子熔覆γ/Cr_7C_3复合材料涂层具有优良的耐磨性,与原始Q235钢相比提高了近7倍。涂层具有良好滑动磨损耐磨性的主要原因是:第一,等离子熔覆γ/Cr_7C_3耐磨复合材料涂层中的初生相Cr_7C_3具有硬度高、耐磨性好的特点,在摩损过程中起到了抗磨骨干作用;第二,作为涂层基体的γ/Cr_7C_3共晶组织具有较好的韧性和一定的塑性,在磨损过程中可对耐磨增强相Cr_7C_3起到强有力的支撑和联接作用,最大限度地发挥了耐磨增强相Cr_7C_3的抗磨骨干作用;第三,等离子熔覆复合材料涂层的主要组织组成相为Cr_7C_3金属陶瓷相,其结合键除具有金属键之外,还有较强的共价键成分,其键合性质与45钢对磨环的键合性质差别很大,很难与之产生粘着,因而粘着磨损抗力很高;第四,等离子熔覆γ/Cr_7C_3复合材料涂层组织细小均匀,赋予该涂层以优良的强、韧性结合,使涂层材料在磨损过程中不致于产生开裂和显微剥落现象,特别是可防止其产生整体脱落[7,8]。综上所述,等离子熔覆γ/Cr_7C_3复合材料涂

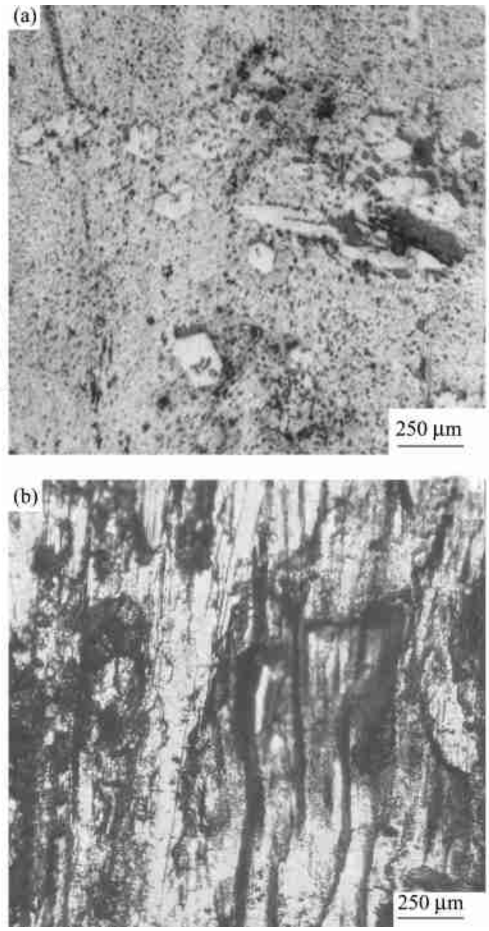

图3 等离子熔覆耐磨复合材料涂层和原始钢滑动磨损后的表面形貌

(a)涂层的表面磨损形貌;(b)原始Q235钢的表面磨损形貌

Fig. 3 Worn morphology of (a) the plasma clad composite coating and (b) the untreated Q235 carbon steel

层表现出优异的耐磨性能。

4　结论

采用等离子熔覆新工艺,以 Ni30-Cr61-C9(wt. %)混合合金粉末为原料,在 Q235 钢表面获得了以高硬度耐磨金属陶瓷碳化物 Cr_7C_3 为增强相,以强韧性良好的 γ/Cr_7C_3 共晶组织为基体的复合材料冶金涂层,涂层在室温干滑动磨损试验条件下具有优良的耐磨性能。等离子熔覆 γ/Cr_7C_3 复合材料耐磨涂层可望大幅提高工程机械易损零部件的服役寿命。

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0.042 %, the decrease of strength and toughness results from the increase of inclusions in the steel. The mechanism of effects of RE on microstructure of GDL-1 steel is analyzed on the basis of sympathetic nucleation-ledgwise growth model.

Key words: rare earth; bainite steel; strength and toughness; microstructure

Study on the grain refinement mechanism of low carbon micro-alloyed steels for line-pipe applications

ZHANG Hong-mei[1,2], WANG Hong-bin[1], LIU Zhen-yu[2], LIU Xiang-hua[2], WANG Guo-dong[2] (1. University of Science and Technology Liaoning, Anshan 114044, China; 2. The State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang 110006, China)

Trans Mater Heat Treat, 2006, 27(6): 99～102, figs 3, tabs 1, refs 11.

Abstract: The effect of strain amount and cooling rate on phase transformation behavior and microstructure refinement were studied on a Gleeble 1500 thermomethanical simulator using a low carbon low alloy pipeline steel X70. It is found that increasing of strain amount or accelerating of cooling rate improve the formation and refinement of acicular ferrite. The typical features of the acicular ferrite is of very fine sub-structure, high dislocation density and ultra-fine grains in thin lath shape. Precipitating of small M/A islands and cementite on matrix of the laths was observed by TEM analysis. On the other hand, the precipitated phases are found at the boundary and inner of ferrite. The results show that the mechanism of grain refinement for low alloy steels is different from that of low carbon steel, it includes strain induced ferrite, ferrite recrystallization and growth of ferrite hindered by the precipitation of the second phase.

Key words: grain refinement; acicular ferrite; island microstructure; precipitate phase

Effect of the electropulsing on microstructure and mechanical properties of the cold-drawing copper wire

TIAN Shao-quan, XU Zhuo-hui, TANG Guo-yi (Advanced Materials Institute, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China)

Trans Mater Heat Treat, 2006, 27(6): 103～107, figs 6, tabs 0, refs 14.

Abstract: The effect of the treatment of electropulsing on microstructure and mechanical properties of cold-drawing copper during recrrystallization process were studied. In comparison with conventional treatment (i.e. in tube furnace), the treatment of electropusing can distinctly shorten recrystallization time by 90 %, reduce the recrystallization temperatures by 50 %, improve the tensile strength by 8 %, and enhance the elongation by 20 %. The mechanism of the treatment of electropusing can be attributed to the coupled actions of the thermal and athermal effects.

Key words: electropulsing; microstructure; recrystallization; thermal and athermal effects; critical temperature

Preparation of WC/Co powders by electroless plating and its coating on 2Cr13 stainless steel by laser cladding

WU Tao, ZHU Liu, LI Jian, YAO Ji-peng (College of Material and Chemical Engineering, Zhejiang University, Hangzhou 310027, China)

Trans Mater Heat Treat, 2006, 27(6): 108～110, figs 2, tabs 3, refs 10.

Abstract: WC/Co composite powders prepared by electroless plating were coated on 2Cr13 stainless steel by laser cladding. The composition, morphology, microstructure and performance of the WC/Co composite coating were studied. The results show that the WC/Co composite powders contain about 17.23wt % of Co. It is found that the composite coating is metallurgically bonded to the substrate. The coating consists of three zones: melting zone, bonding zone and heat affected zone of the substrate. The micro-hardness of the coating reaches $1200HV_{0.1}$.

Key words: WC/Co composite powder; laser cladding; microstructure; micro-hardness

Study on fabrication of Cr_3C_2-AlN-FeCr multiphase coatings by combustion synthesis

LI Wen-ge, ZHANG Guang-jun, LI Jun (College of Material Engineering, Shanghai University of Engineering Science, Shanghai 201600, China)

Trans Mater Heat Treat, 2006, 27(6): 111～113, figs 6, tabs 0, refs 11.

Abstract: A multiphase coating on carbon steel was fabricated by combustion synthesis method. In order to improve wettability between coating and substrate σ-(Fe, Cr) was selected as wetting component. The microstructure and phase composition of the sample show that the coating is a multiphase system consisting of chromium carbide, AlN and σ-FeCr. The cross section morphology of interface between the coating and substrate is observed and shows that the bond is metallurgy bonding. The result of thermal shock resistance is also shown that the coating had good bonding strength.

Key words: combustion synthesis; multiphase ceramics; coating

Study on microstructure and wear resistance of plasma jet clad γ/Cr_7C_3 composite coating

LIU Xiu-bo[1,2], YU Gang[1], GUO Jian[2], ZHANG Zhen-guo[2], SHANG Quan-yi[2], GU Yi-jie[3], CUI Hong-zhi[3] (1. Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China; 2. School of Materials and Chemical Engineering, Zhongyuan Institute of Technology, Zhengzhou 450007, China; 3. College of Materials Science & Engineering, Shandong University of Science and Technology, Qingdao 266510, China)

Trans Mater Heat Treat, 2006, 27(6): 114～117, figs 3, tabs 1, refs 8.

Abstract: In order to explore the new techniques for improving the service life of the easily damaged components of machines effectively, a wear resistant γ/Cr_7C_3 composite coating was fabricated on substrate of commercial Q235 plain carbon steel by plasma cladding using Ni-Cr-C elemental powder blends. The microstructure, microhardness and wear resistance of the coating were investigated and the wear mechanisms were analysed. The results show that the plasma clad composite coating has a compact and rapidly solidified microstructure consisting of primary coarse blocky carbide Cr_7C_3 and the inter-blocky tough γ/Cr_7C_3 eutectic matrix and is metallurgically bonded to the steel substrate. The composite coating possesses high hardness and excellent wear resistance under dry sliding wear test conditions.

Key words: plasma jet cladding; coating; microstructure; wear resistance

Effect of ceramic additive in lubricating oil on contact fatigue and wear performance of steel/steel friction pair

YUE Wen[1,2], WANG Cheng-biao[1], TIAN Bin[3], GU Yan-hong[4], LIU Jia-jun[5] (1. School of Engineering and Technology, China University of Geosciences (Beijing), Beijing 100083, China; 2. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China; 3. Anton Oilfield Services (Group) Ltd. Beijing 100102, China; 4. School of Mechanical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China; 5. Mechanical Engineering Department, Tsinghua University, Beijing 100084, China)

Trans Mater Heat Treat, 2006, 27(6): 118～123, figs 9, tabs 4, refs 10.

Abstract: The effect of a ceramic additive with the main composition of $Al_4[Si_4O_{10}](OH)_8$ in lubricating oil on the contact fatigue and wear performance of steel/steel friction pair was investigated on a ball-rod contact fatigue tester. The anti-fatigue mechanism of this additive was analyzed by means of scanning electron microscopy (SEM) and nano-indenter test. The results show that the ceramic additive can raise the contact fatigue life L_{10} to 1.3 times, and improves the friction performance of the steel significantly. The micro-cracks in pits and their edages formed during friction and wearing are covered by a bright substance with a quite high hardness of 14GPa. The anti-fatigue mechanism of the ceramic additive is mainly due to the new substance formed on the worn surface, which is beneficial to increase the contact fatigue life and improve the friction performance of the steel.

Key words: ceramic additive; contact fatigue; wear; SEM; nano-indenter test

Monte carlo simulation of the influence of trace impurities on the recrystallization of high purity Al

TANG Jian-guo[1,2], ZHANG Xin-ming[1], XIAO Ya-qing[1], DENG Yun-lai[1] (1. School of Materials Science and Engineering, Central-South University, Changsha 410083, China; 2. School of Mechanical Engineering, Hunan International Econmics University, Changsha 410205, China)

Trans Mater Heat Treat, 2006, 27(6): 124～128, figs 7, tabs 1, refs 16.

Abstract: The influence of trace impurities on the recrystallization was analyzed with the energy conversion model, in which the drag force of impurity atoms is converted into the free energy change during recrystallization. And the energy conversion model is implemented with the Monte Carlo numeric simulation method. The simulated results reveal that the fluctuation of trace impurity has strong influence on the recrystallization behavior. And the simulation results agree with the experimental result well.

Key words: trace impurities; recrystallization texture; high purity aluminum; energy conversion model; Monte Carlo simulation

Compressive behavior of spherical pore Al alloy foam and its theoretical model

WANG Zhan-guang[1], SHANG Jin-tang[2], HE Si-yuan[3], HE De-ping[2], SHAN Jian[1] (1. College of Civil Engineer, Southeast University, Nanjing 210096, China; 2. Department of Materials Science and Engineering, Southeast University, Nanjing 210096, China; 3. Department of Biomedical Engineering, Southeast University, Nanjing 210096, China)

Trans Mater Heat Treat, 2006, 27(6): 129～133, figs 7, tabs 1, refs 15.

Abstract: The stress versus strain curves, energy absorption capacity and energy absorption efficiency of spherical pore Al alloy foam ($Pr \leq 65\%$) under uniaxial compression were investigated. Compared with polygonal pore Al alloy foam, the mechanical properties of the foam with spherical pore is relatively higher. The relationship between yield stress and porosity is obtained with spherical self-consistent model. The prediction for yield stress of spherical pore Al alloy foam is in agreement with the experimental results.

Key words: spherical pore Al alloy foam; spherical self-consistent model; yield stress