Recrystallization of L 605 Cobalt Superalloy During Hot-Working Process

著者	FAVRE JULIEN JEAN GABRIEL
号	57
学位授与機関	Tohoku University
学位授与番号	工博第4723号
URL	http://hdl.handle.net/10097/61490

ふあべる　じゅりあん　じぇーん　がぶりえる
氏　　　　　名　FAVRE JULIEN JEAN GABRIEL
授 与 学 位　博士（工学）
学位授与年月日　平成２４年９月２５日
学位授与の根拠法規　学位規則第４条第１項
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）　材料システム工学専攻
学 位 論 文 題 目　Recrystallization of L 605 Cobalt Superalloy During Hot-Working Process(熱間加工によるＬ６０５コバルト基超合金の再結晶)
指 導 教 員　東北大学教授　千葉　晶彦
論 文 審 査 委 員　主査　東北大学教授　千葉　晶彦　東北大学教授　今野豊彦
東北大学教授　古原　忠　教授 Eric Maire (INSA-Lyon 大学)
准教授　Damien Fabregue INSA-Lyon 大学)

論文内容要旨

Co-20Cr-15W-10Ni alloy (L-605) is a cobalt-based superalloy combining high strength with keeping high ductility, biocompatible and corrosion resistant. It has been used successfully for heart valves for its chemical inertia, and this alloy is a good candidate for stent elaboration. Control of grain size distribution can lead to significant improvement of mechanical properties: in one hand grain refinement enhance the material strength, and on the other hand large grains provide the ductility necessary to avoid the rupture in use. Therefore, tailoring the grain size distribution is a promising way to adapt the mechanical properties to the targeted applications. The grain size can be properly controlled by dynamic recrystallization during the forging process. Therefore, the comprehension of the recrystallization mechanism and its dependence on forging parameters is a key point of microstructure design approach. The optimal conditions for the occurrence of dynamic recrystallization are determined, and correlation between microstructure evolution and mechanical behavior is investigated.

Compression tests are carried out at high-temperature on Thermecmaster Z and Gleeble forging devices, followed by gas or water quench (Figure 1a). Mechanical behavior of the material at high temperature is analyzed in detail, and innovative methods are proposed to determine the metallurgical mechanisms at stake during the deformation process. L-605 alloy follows a usual viscoplastic deformation behavior at high temperature: stress increases with strain rate and decreases with temperature. Compression curves exhibit a peak stress followed by flow softening, and then stabilizes to a plateau at the steady-state. Flow softening is attributed to the occurrence of dynamic recrystallization at large strain. Fits of experimental data provide the normalized hardening rat and the extrapolated steady-state stress. Normalized hardening rate increases

at low temperature and intermediate strain rate, and this effect is attributed to the operation of dynamic strain aging. From these two fundamental parameters, the constitutive equation of the material is determined by the Kocks-Mecking method. Flow stress is properly described by the Kocks-Mecking model (Figure 1b), and the estimations remain correct even for complex deformation situations such as speed jump tests.

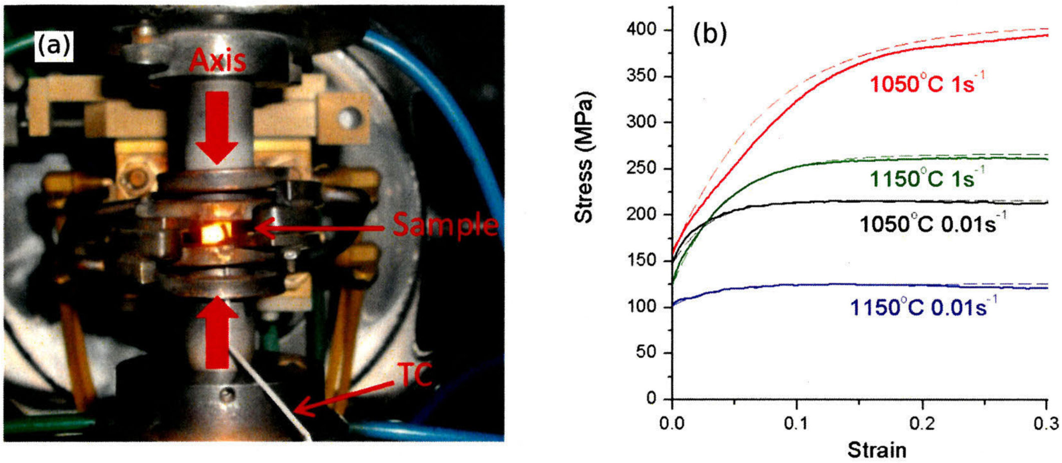

Figure 1: (a) Experimental device for hot compression – (b) Compression stress-strain curves (plain lines) and calculated curves by Kocks-Mecking model (dashed lines)

Deformation behavior is determined by applying the Dynamic Materials Model, and by construction of processing maps. Flow is stable at strain rate lower than $0.1s^{-1}$, and unstable at large strain rate. However the agreement with experimental data is partial only and this method provides little information on the effective deformation mechanisms at stake. Another method to study the mechanical behavior is developed based on the analysis of Kocks-Mecking: fractional flow softening is calculated at large strain and plotted into a 2D map, similarly to processing map. The agreement with experimental data is correct, and provides some predictive information on the microstructure changes. This parameter is considered as an indicator of the recrystallization process in the current case, and may also be used to follow some other structural changes such as shear bands or cracks formation.

Precipitation behavior of L-605 alloy during ageing treatment is investigated. Precipitates form at a temperature below 1100°C for several minutes to several hours holding time. Precipitates are M_6C carbides and form a network along the grain boundaries. It is concluded that the hot working process of L-605 might involve the precipitation of carbides for 1000°C and very low strain rate (strain rate=$0.001s^{-1}$). For higher strain rate, the precipitation is not expected due to the short processing time. For higher temperature, precipitation is sluggish and is not expected during the hot deformation process.

The grain growth kinetics of L-605 alloy is determined, and experimental results are compared with the static recrystallization process. Grain growth kinetics is very fast for temperature above 1100°C (>0.78 T_f), and produces a coarse microstructure after several minutes annealing only at 1200°C. The coarsening of the microstructure leads to a loss of strength and an improvement of ductility. The gain in ductility may be a serious advantage for stent manufacture, and despite the slight strength loss, it may be worth to apply an annealing treatment after forging to ensure to fulfill the maximal elongation requirement. The occurrence of abnormal grain growth was detected at intermediate annealing time, and produces an interesting bimodal grain size distribution. Grain growth can be properly estimated with the Hillert growth model by considering the grain boundary surface energy as the main driving force for boundaries migration.

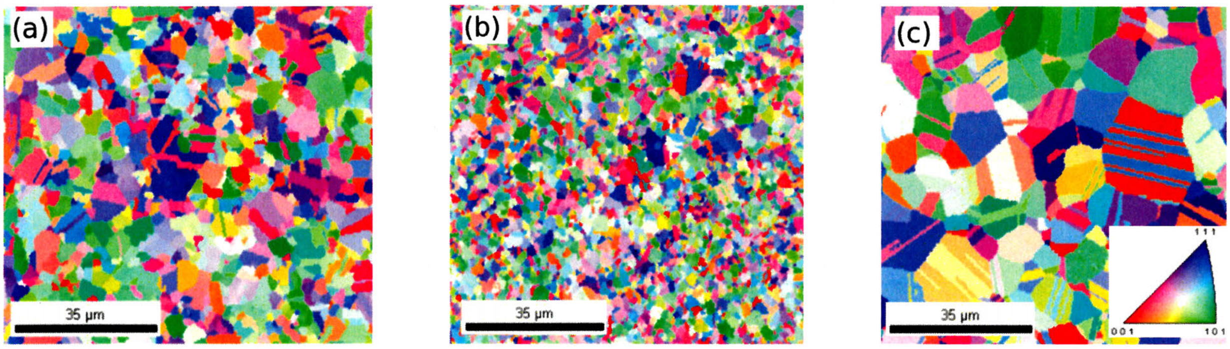

Figure 2: (a) Initial L-605 microstructure observed by EBSD– (b) Microstructure after cold-rolling and 1 second annealing at 1000°C – (c) Microstructure after cold-rolling and 1 second annealing at 1200°C

Static recrystallization is observed during the annealing of cold rolled 23% L-605 alloy. This phenomenon is very brief and results into the high instability of deformed ultrafine microstructure at high temperature. Figure 2 illustrates the very extreme brevity of the recrystallization phenomenon: only a couple of seconds annealing is enough to achieve grain refinement or coarsening, depending on annealing temperature. Hillert grain growth model is shown to be inadequate to predict microstructure evolution during static recrystallization, because the nucleation is not considered. Moreover the driving force for recrystallization is the dislocation density and not any more the grain boundary surface energy. This example illustrates that simple models do not hold any more in the case of recrystallization. As a consequence, the grain growth law and the nucleation process must be thoroughly determined by modeling to predict the microstructure change in the specific case of recrystallization.

Microstructures after hot deformation are evaluated using SEM-EBSD and TEM. The occurrence of dynamic recrystallization is observed for all the deformation conditions tested, and leads to significant grain refinement. For temperature higher than 1100°C and strain rate lower than $0.1s^{-1}$ or higher than $1s^{-1}$ (Figure 3), dynamic recrystallization leads to an homogeneous equiaxial microstructure with a grain size about 10 μm. Deformation at T<1100°C and strain rate in the range $0.1\text{-}1s^{-1}$ results in an heterogeneous microstructure with grain size lower than 1 μm. Dynamic recrystallization operates following a discontinuous mechanism by bulging from grain boundaries. A second nucleation mechanism involving annealing twins was highlighted for T>1100°C. In the first step, Σ3 annealing twins rotate from 60° to 55°, and then in a second step bulging can operate. The recrystallized fraction was shown to evolve inversely with dynamic recrystallized grain size and misorientation parameter.

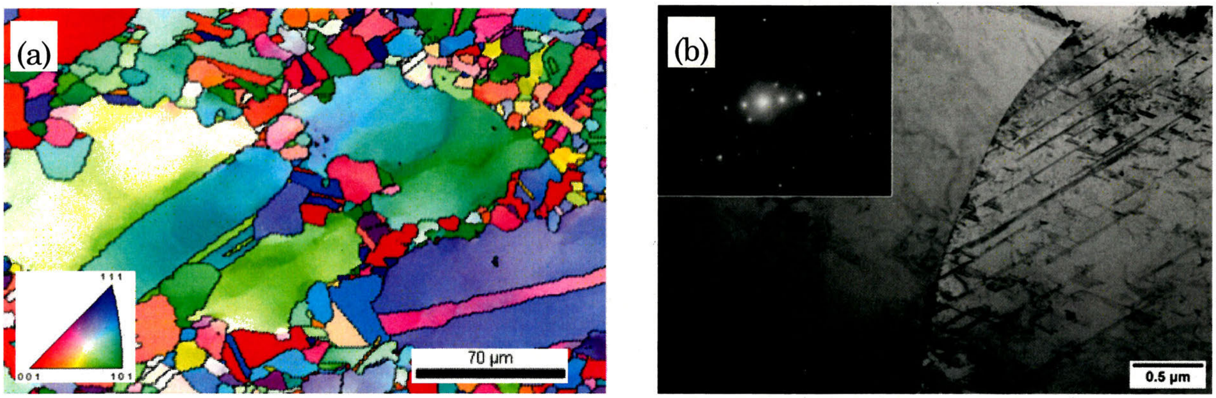

Figure 3: (a) Microstructure of L-605 deformed at strain $\varepsilon=0.36$ and 1100°C $0.001s^{-1}$ observed by EBSD – (b) Microstructure for the same deformation condition observed by TEM

A new insight of the modeling of dynamic recrystallization taking as a starting point the experimental data is proposed. By combining the results from the mechanical behavior study and microstructure observation, the recrystallization at steady-state is thoroughly analyzed, and provides a quantitative estimation of grain boundaries mobility in L-605 alloy. In parallel, data extracted from the literature is analyzed and provides the mobility of pure copper and pure cobalt grain boundaries. Mobility increases with temperature, in agreement with the Turnbull estimation. By comparing the results on L-605 alloy and pure cobalt, it is deduced that solute elements decrease the grain boundary mobility. Solute-drag effect explains the relatively low boundary motion in L-605, and can be described by the theory of Cahn. However, for the sake of simplicity the Turnbull estimation is used in the successive steps as it provides exactly the same estimated values as the Cahn theory with more simplicity.

The nucleation criterion for the bulging from grain boundaries is reformulated to a more general expression accounting for the effect of the pre-existing boundaries, and suitable for any initial grain size. The new criterion makes the continuous transition between recrystallization and grain growth process, and is applicable even in the case of ultrafine grain materials. Nucleation frequency can be deduced from experimental data at steady-state through modeling, and is extrapolated to any deformation condition based on a new semi-empirical formula. From this point, both grain growth and nucleation are completely determined in a quantitative way, and the basis for a complete model is settled.

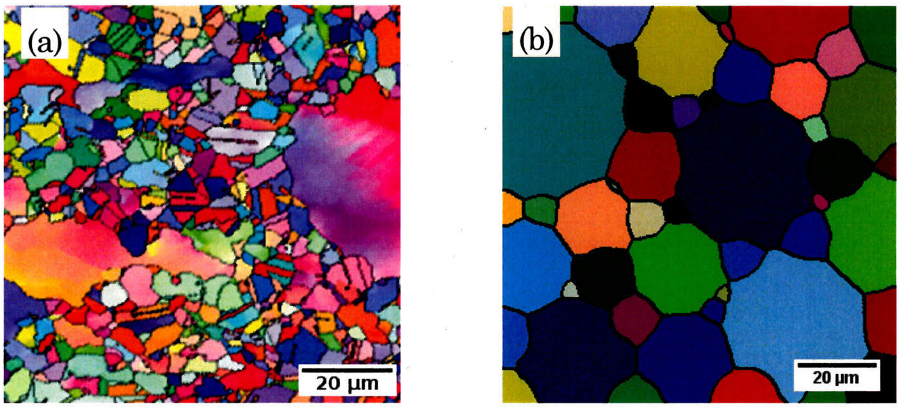

Figure 4: (a) Microstructure after deformation at strain $\varepsilon=0.8$ and 1200°C $1s^{-1}$ – (b) Computed microstructure obtained from analytical modeling for the same deformation conditions

The mobility of boundaries and the nucleation frequency are injected in a class model to calculate the grain size evolution during the dynamic recrystallization process. In addition, modeled microstructure are numerically computed and plotted into 2D metallographic cut images (Figure 4). The model reproduces very well the mechanical behavior at high temperature, and provides a fair estimation of the grain size distribution. However the model does not predict the minimum of grain size and recrystallized fraction for intermediate strain rate at low temperature. Meta-dynamic recrystallization and adiabatic heating at high strain rate may be responsible of the formation of this minimum. Therefore the model does not reproduce exactly the experimental data as it does not account for this phenomenon. A possible interaction between dynamic strain aging and recrystallization is also suggested as an interpretation of the grain size observed, but requires further investigation to be confirmed and fully understood.

論文審査結果の要旨

本研究は生体用金属材料、特に循環器系疾病治療器具（血管閉塞治療器具）であるステント用合金とし使用されているL605合金：Co-20Cr-15W-10Ni合金（以後CCWN合金と称する）の最適加工方法の確立を目指し、当該合金の高温変形挙動を調べたものである。

第1章では各種のステント応用に必要な合金の力学特性、ステント加工に必要な各種塑性加工技術について述べている。さらに、ステント用合金として使用可能な各種Co基合金の組織、力学特性、高温変形挙動について従来の研究成果について整理して述べている。

第2章は本研究の実験方法について述べている。CCWN合金の組成、初期組織と力学特性について、さらに、熱間加工シミュレーターを用いたCCWN合金の高温変形挙動の評価方法、組織解析方法について説明している。

第3章ではCCWN合金の高温変形挙動について調べた結果について述べている。まず、高温変形挙動を動的材料モデル（Dynamic Material Model:DMM）による定量化を行い、歪速度、加工温度などの熱間加工パラメータによる高温変形挙動を予測する方法（Processing map）を構築している。さらに、様々な加工温度、歪速度における高温変形から得られる応力と歪の関係を、Kocks-Meckingモデルにより記述して、応力-歪応答の実験曲線を記述する構成式を示している。また、動的再結晶による加工軟化量から動的再結晶の発現する高温変形条件を加工温度、歪速度、ひずみ量と間で成立する関係の定量化を行っている。これらの方法により、CCWN合金に現れる動的再結晶が発現する変形条件、微細組織の変化と高温変形条件との関係について定量的な理解が可能になった。本研究では、以上のようにCCWN合金の熱間鍛造による結晶粒微細化のための組織制御法について、各種Processing mapの構築を行い、熱間鍛造による組織微細化などをもたらす熱間鍛造加工の最適化の方法について示しており、学術的にも、実用の面でも貴重な知見を与えている。

第4章ではCCWN合金の高温変形の際に現れる微細組織変化について調べている。高温変形により出現する析出相の形成条件についてTTT曲線を作成して示し、計算状態図により析出が予測される各種Co-W系化合物、各種炭化物相の析出挙動について明確にした。これらの成果は、熱間鍛造などの高温変形による組織制御を行う際に析出物を出さない高温加工条件（組織制御法）の確立を可能にし、ステント用の合金素材としての最適加工法の開発に貢献するものであり、実用上重要な知見である。さらに、高温加工後に形成される動的再結晶粒の結晶粒径制御法の確立に必要な熱処理による結晶粒界移動挙動について詳細に検討を行い、粒成長挙動のモデル化（HillertモデルとTurnbullモデルの適用）を試み、実験観察結果を記述し、学術的にも重要な成果が得られている。

第5章ではCCWN合金の静的再結晶挙動および動的再結晶挙動について詳細に調べている。熱間加工後に現れる動的再結晶組織は結晶粒界に沿った“ネックレス”状の再結晶粒が形成され、bulging機構による動的再結晶挙動であることを明確にし、高速変形、低温の加工条件では異常な組織を示すことを見出している。これらの異常は高速変形の際の断熱変形による温度上昇とmeta-動的再結晶挙動に対応する挙動であり、第3章で構築したprocessing mapで示唆される組織形成予測の不一致の原因がこれらの機構によることをしめした。これらの知見はprocessing mapの構築とこれによる最適熱間鍛造条件の予測技術の高精度化確化に貢献するものであり実用的にも重要な知見である。

第 6 章は CCWN 合金に現れる動的再結晶挙動について実験結果を記述する材料モデルの構築を行っている。

以上、得られた知見を総合して評価すると、本研究により得られた成果は生体用 CCWN 合金の高温変形挙動を詳細な組織解析を行うことに明らかにしている。さらに材料組織学的モデルの構築により CCWN 合金の高温変形挙動を定量的に理解する上で重要な知見を与えるものと評価できる。また、これらの成果はステント加工技術の最適化に有用であり、実用の面において重要である。

よって、本論文は博士(工学)の学位論文として合格と認める。