Escola Tècnica Superior
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Doctoral Thesis

Constitutive Relations to Model the Hot Flow of Commercial Purity Copper

By

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About the Cover

The painting, presently at the Prado Museum, is The Forge of Vulcan (1577) by Jacopo Bassano. Several versions of this original exist, at least one in the Louvre and another in the Prado Museum, painted by the sons of Jacopo, Francesco and Leandro. The oil on canvas painting (250 X 407cm) entered the royal collection inventory in 1666, however in time became lost and was found again hanging in the Sala de Juntes of the Universitat de Barcelona. Jacopo had little regard for the expressive potential or erotic undertones that classical culture could give to his paintings [1]. On The Forge of Vulcan, which is one of the few works of Jacopo illustrating mythological nature, only Cupid denotes an immortal character of the painting. The theme instead shows Jacopo's ability to represent a light source, the forge, and how his light can modify the textures and surfaces on which it shines; human bodies, earthenware objects, glass, steel or copper. The painting by Jacopo was chosen because, unlike other Forges of Vulcan by other artists, Jacopo's interpretation depicts the instant when Vulcan is hot forming a metal, which could be copper, the material studied on this doctoral thesis. The painting also conveys the ancient and classical character copper has. However the enlarged reproduction of Vulcan's arm while forging emphasizes the subject of the thesis, which is a more scientific perspective of the forging conditions that made Vulcan popular among the gods. The background corresponds to a micrograph of a copper after being compressed at 650ºC and $0.01s^{-1}$ to a true strain of 0.8. Polarized light was used to view the microstructure, which allowed a multicolor image. The micrograph shows the effect of incomplete dynamic recrystallization (incomplete forging) where smaller grains coexist with larger, however already recrystallized, grains. The initial grain size was much larger than any of the grains appearing on the micrograph (compare figures 3.33 and 3.36d for copper A on the results chapter).

Reference

[1] Falomir Faus Miguel, Los Bassano en la España del Siglo de Oro, (march 29-may 27, 2001), Museo Nacional del Prado, ISBN: 84-8480-006-7, Gráficas Varona, Salamanca, pp. 1-268.

Acknowledgments

First I thank God for in His design allowed me to stumble, but also allowed me to find wonderful people whose help in one manner or another contributed to produce the present work. Secondly I owe much of the opportunities in life to my father and mother, J. Víctor García P. and Aida Fernández Barrera, and also to my uncle and aunt, Royce R. Waters and Lila Waters, thank you for giving yourselves to me.

The Agencia Española de Cooperación Internacional (AECI) and the Universitat Politècnica de Catalunya (UPC) provided the financial support in Spain. A cooperation accord between the UPC and Tertub Tubo Técnico Europeo gave rise to this study. And Tertub is to be thanked for kindly providing the coppers studied.

I wish to thank Professor J.M. Prado and Dr. J. M Cabrera because upon my arrival to Barcelona they welcomed me into their research group at the Department of Materials Science. Thanks to them I had the means to reveal a new insight on the hot flow of copper and also thanks to them I was able to share the new knowledge in conferences abroad.

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Another group of people deserve my gratitude for making my stay away from home more bearable. I shall fall into the mistake of mentioning their names even though I run the risk of inadvertently omitting someone, however their friendship kept me going and this is the place to remember them. My only sister, Claudia, never forgot my absence and constantly kept me on her writing list. I also owe thanks to my first friend in Barcelona, E. A. Torres. We at the BPC club spent several wonderful moments together, thank you to all (E. Vergés, L. Acosta, K. Langohr, Y. Balagué, J. Bofill, M. Albareda, A. Alla, Y. Piedra, D. Fernández, J. Cano, J.A. Diaz, L. Zarate, A. Zazueta, M. Peyrard, C. Fernández and Olga). I wish to thank M. J. Laborda and her family for showing the hospitality of Catalunya to me. The guys who have shared my home away from home need a special mention; thank you J. Ribes, J. V. Catalá, J. Torrent, A. Llorach and D. Cardador. Another sporadic, however long time friend, is N. Noguerón who will remain in my memories. Lately I have felt most welcomed by another family of friends (S. Saravia, V. Guerra, P. Giraldo, D. Peña, L. Siemancas, B. Moya, A. L. Cruz, Nelson and L. F. García). I wish to thank again S. Saravia for filling my social agenda with enjoyable and interesting ideas, despite my lonesome character. The support given to me by our Metals Technology Group deserves recognition (E. Vaqué, A. Boulajaaj, J. Calvo, C. Merizalde, and N. Lugo). Gratitude also goes to a large

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Víctor G. García F.
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Abstract

A study was conducted to observe the differences in hot flow behavior of fire-refined 99.9% pure coppers, which allowed proposing models to predict the stress-strain curve and the dynamically recrystallized grain size. Fire-refined 99.9% pure coppers are characterized for having a residual composition of several other elements, up to 1000ppm in some cases. On coppers of at least 99.9% purity, which have few residual elements present, the hot flow differences had been attributed to solute atom interactions with dislocations, specifically by interstitial oxygen. On Electrolytic Tough Pitch coppers, which contain mainly high oxygen amounts, the hot flow differences are attributed to increasing amounts of Cu_2O particles. The present work instead demonstrates that the stress differences observed on 99.9% pure fire-refined coppers are due to the residual oxygen amount, which forms fine precipitates at intermediate temperatures that strengthen the metal matrix. Despite the low oxygen levels in the coppers studied (26-62ppm) Cu_2O precipitates were characterized and a theoretical analysis using precipitation-strengthening theories indicated that Cu_2O precipitates were the cause for the increase in strength. Oxygen atom interactions with dislocations are unlikely to cause an added back stress at temperatures above 600ºC, where this study was conducted. Three coppers with 26, 46 and 62ppm of oxygen were hot compressed at true strain rates of $0.3s^{-1}$, $0.1s^{-1}$, $0.03s^{-1}$, $0.01s^{-1}$, $0.003s^{-1}$ and $0.001s^{-1}$, and at eight different temperatures from 600ºC to 950ºC in 50º intervals. Evidence is presented of how the low oxygen levels in 99.9% pure coppers can affect the stress-strain behavior and the dynamically recrystallized grain size.

Besides finding the element and mechanism responsible for an added back stress, a mathematical algorithm to study and predict the stress oscillations during multiple peak dynamic recrystallization is also presented. Earlier attempts using Monte Carlo Computerized Models, Cellular Automata Models or Mathematical DRX Models did not predict the stress oscillations of real materials and their computational time made them unviable for industrial simulation processes. The new Damped Cosine Avrami Model for DRX is capable of predicting the transition from single peak DRX to multiple peak DRX. Also the new model defines the steady state stress without having to choose a value from an experimental curve that might not have reached a steady state yet. Another contribution of the new model is that demonstrates that the oscillations are completely predictable in terms of strain rate and temperature, a feature that had been said to be improvable before. The new model for DRX along with a modified Voce-Kocks restoration model was successfully applied to predict the hot flow curve.

In addition to the latter contributions this work also reports the relationship the dynamically recrystallized grain size has with temperature and strain rate. Coppers of 99.9% purity, like the ones studied, are expected to tend to a steady state grain size, which when at room temperature will determine the mechanical properties of the forged product.

Resumen

Se ha llevado a cabo un estudio con el fin de observar diferencias en el comportamiento de fluencia en caliente de los cobres refinados al fuego con una pureza de 99.9%, dicho estudio ha permitido proponer modelos para predecir la curva esfuerzo-deformación y para predecir el tamaño de grano recristalizado dinámicamente. Los cobres refinados al fuego con una pureza de 99.9% se caracterizan por tener una composición residual de varios otros elementos, en algunos casos hasta 1000ppm. En los cobres con por lo menos 99.9% de pureza que tengan pocos elementos residuales, las diferencias observadas durante la fluencia en caliente se atribuyen a las interacciones entre átomos disueltos y dislocaciones, específicamente las interacciones con oxígeno intersticial. En el cobre electrolítico, el cual contiene principalmente altos contenidos de oxigeno, las diferencias de fluencia se atribuyen a cantidades cada vez mayores de partículas de Cu_2O. Este trabajo más bien demuestra que las diferencias de esfuerzo encontradas en cobres refinados al fuego con una pureza de 99.9% son debidas a la cantidad de oxígeno residual, el cual forma finos precipitados a temperaturas intermedias que refuerzan la matriz metálica. A pesar del bajo contenido en oxígeno en los cobres estudiados (26-62ppm) se han caracterizado precipitados de Cu_2O y se han utilizado teorías del endurecimiento por precipitación que han indicado que los precipitados de Cu_2O eran los responsables del incremento en resistencia. Las interacciones entre átomos de oxígeno y dislocaciones son poco probables que causen un retro esfuerzo adicional a temperaturas superiores a los 600º C, en donde se ha llevado a cabo este trabajo. Se han comprimido tres cobres con 26, 46 y 62ppm de oxígeno a unas velocidades de deformación de $0.3s^{-1}$, $0.1s^{-1}$, $0.03s^{-1}$, $0.01s^{-1}$, $0.003s^{-1}$ y $0.001s^{-1}$ y a unas temperaturas desde 600º C hasta 950º C en intervalos de 50º. En este trabajo se presenta evidencia de cómo bajos contenidos de oxígeno en cobres 99.9% puros pueden afectar el comportamiento esfuerzo-deformación y el tamaño de grano recristalizado dinámicamente.

Además de haber encontrado el elemento y el mecanismo responsable del retro esfuerzo adicional también se presenta un algoritmo matemático para estudiar y predecir las oscilaciones de esfuerzo durante la recristalización dinámica de pico múltiple. Intentos anteriores utilizando Modelos Computarizados de Monte Carlo, Modelos de Autómatas Celulares o Modelos Matemáticos para la Recristalización Dinámica (DRX) no predicen las oscilaciones de esfuerzo de materiales reales y su tiempo de computo los hace inviables para procesos de simulación industrial. El nuevo Modelo de Avrami con Coseno Amortiguado para la DRX es capaz de predecir la transición de DRX de pico simple a DRX de pico múltiple. Además el nuevo modelo define el esfuerzo de estado estable sin tener que escoger un valor de una curva experimental que posiblemente no haya alcanzado un estado estable. Otra contribución del nuevo modelo es que demuestra que las oscilaciones son completamente predecibles en términos de la velocidad de deformación y la temperatura, una característica que antes se había dicho ser improbable. El nuevo modelo para la DRX junto con un modelo modificado de Voce-Kocks para la restauración dinámica han sido exitosamente implementados para predecir la fluencia en caliente.

Adicionalmente a las anteriores contribuciones este trabajo también da a conocer la relación que tiene el tamaño de grano recristalizado con la temperatura y la velocidad de deformación. Se asume que los cobres 99.9% puros, como los estudiados, tenderán a un tamaño de grano de estado estable el cual cuando esté a temperatura ambiente determinará las propiedades mecánicas del producto forjado.

Resum

Aquest estudi s'ha dut a terme amb la finalitat d'observar diferències en el comportament de fluència en calent de coures refinats al foc amb una puresa de 99,9%. L'esmentat estudi ha permès proposar uns models per predir la corba tensió-deformació i per predir la mida del gra recristal·litzat dinàmicament. Els coures refinats al foc amb una puresa de 99,9% es caracteritzen per tenir una composició residual de varis altres elements, en alguns casos fins a 1000ppm.

En els coures amb el menys 99,9% de puresa que, a més a més, tinguin pocs elements residuals, les diferències observades durant la fluència en calent s'atribueixen a les interaccions entre àtoms dissolts i dislocacions, específicament les interaccions amb oxigen intersticial.

En el coure electrolitic, el qual conté principalment alts continguts d'oxigen, les diferències de fluència s'atribueixen a quantitats cada vegada més grans de partícules de Cu_2O.

Aquest treball demostra que les diferències de tensió trobades en coures refinats al foc amb una puresa de 99,9% són degudes a la quantitat d'oxigen residual, el qual forma fins precipitats a temperatures mitjanes que reforcen la matriu metàl·lica. Malgrat el baix contingut d'oxigen en els coures estudiats (26-62ppm) s'han caracteritzat precipitats de Cu_2O i s'han utilitzat teories d'enduriment per precipitació que han indicat que els precipitats de Cu_2O eren els responsables de l'increment en resistència. Les interaccions entre àtoms d'oxigen i dislocacions són poc probables que causin una retro tensió addicional a temperatures superior als 600º C, on es s'ha dut a terme aquest treball. S'han comprimit tres coures amb 26, 46 i 62ppm d'oxigen a unes velocitats de deformació de $0.3s^{-1}$, $0.1s^{-1}$, $0.03s^{-1}$, $0.01s^{-1}$, $0.003s^{-1}$ i $0.001s^{-1}$ i a unes temperatures des de 600º C fins 950º C en intervals de 50º.

En aquest treball s'evidencia com poden afectar el comportament tensió-deformació i la mida del gra recristal·litzat dinàmicament els baixos continguts d'oxigen en coures 99,9% purs.

A més a més d'haver trobat l'element i el mecanisme responsable de la retro tensió addicional també es presenta un algorisme matemàtic per estudiar i predir les oscil·lacions de tensió durant la recristal·lització dinàmica de pic múltiple. Intents anteriors utilitzant Models Computaritzats de Monte Carlo, Models d'Autòmats Cel·lulars o Models Matemàtics per a la recristal·lització dinàmica (DRX) no prediuen les oscil·lacions de tensió de materials reals i el seu temps de càlcul els fa inviables per a processos de simulació industrial. El nou Model d'Avrami amb Cosinus Amortit per la DRX és capaç de predir la transició de DRX de pic simple a DRX de pics múltiples. A més a més el nou model defineix la tensió d'estat estable sense haver d'escollir un valor d'una corba experimental que possiblement no hagi assolit un estat estable. Un altra contribució del nou model és que demostra que les oscil·lacions són completament predeïbles en termes de la velocitat de deformació i la temperatura, una característica que abans s'havia dit ser improbable. El nou model per la DRX junt amb un model modificat de Voce-Kocks per a la restauració dinàmica van ser exitosament implementades per predir la fluència en calent.

Addicionalment a les anteriors contribucions aquest treball també dona a conèixer la relació que tenen la mida del gra recristal·litzat dinàmicament i la velocitat de deformació. S'assumeix que els coures 99,9% purs, com els estudiats, aniran a una mida de gra d'estat estable el qual quan estigui a temperatura ambient determinarà les propietats mecàniques del producte forjat.

About the Author

Víctor G. García F. started his journey into the materials world in 1994 as an undergraduate mechanical engineering student when he entered the Metallurgy Section of the Department of Physics in the National Autonomous University of Honduras. After obtaining his degree in 1996, he worked as Warranty Manager for several heavy-duty equipment manufacturers. His yearn for knowledge helped him to be a scholar of the Agencia Española de Cooperación Internacional, which allowed him to begin his post graduate studies at the Universitat Politècnica de Catalunya in Barcelona where he has been investigating several hot forming phenomena at the Metals Technology Group of the Materials Science and Metallurgical Engineering Department. At the Department he was elected Student Body Representative (2001-2002). He has continuously collaborated in teaching laboratory practices to undergraduates and has also collaborated on research projects for a local copper tubing manufacturer.

Quotes to Remember While Reading this Work

"A *theory* of work hardening is today as hopeless as ever; but a *model* of work hardening of pure fcc material we would consider now virtually available"

Kocks U.F., Mecking H., Progress in Materials Science 48 (2003) 171-273.

About work hardening "it was the first problem to be attempted by dislocation theory and may be the last to be solved"

Cottrell A.H., Dislocations and Plastic Flow in Crystals, Oxford University Press, 1953.

Lord Kelvin comments on Sir William Rowan Hamilton's work on quaternions, now called vectors, "although being notably ingenious, they have proven to be of misfortune to all who in some manner have studied them (as well as) vectors… have never been of the least remote usefulness to any existing creature".

Grossman Stanley I., Álgebra Lineal, 2da edición, Grupo Editorial Iberoamérica, 1988.

About equations used to describe dislocation cell structures "Theory discovers order, as embodied in the preceding equations, where the eye does not necessarily see it".

Kuhlmann-Wilsdorf D., Theory of Plastic Deformation, Mat. Sc. & Eng, A113, 1989.

"The ultimate goal has always been, and certainly must remain, the ability to predict the plastic properties of a material from a knowledge of its composition, grain size and the physical parameters of its phases. This goal appears now to be in sight, but it is certainly far from attained".

Kuhlmann-Wilsdorf D., Theory of Plastic Deformation, Mat. Sc. & Eng, A113, 1989.

About an extensively used relationship "Lacking any physical model, it must be considered fortuitous that any set of n' and α' can correctly describe the behaviour over a wide range of stresses. In spite of these reservations, we have found … a good description of the hot working data…".

Frost H.J., Ashby M.F., Deformation-Mechanism Maps, Pergamon Press, Oxford, 1982.

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