STRUCTURAL AND MICROSTRUCTURAL COMPARATIVE ANALYSIS ON METALLIC ALLOYS OF COMPOSITION $Cu_{y\%}$-$Ni_{x\%}$-Me (Me = Sn, Cr, Al, Pt).

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ABSTRACT

This work presents a comparative study of microstructural and electrical properties of polycrystalline material Cu-Ni alloys synthesized by conventional and powder metallurgy. A sample of $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ was produced in electric furnace with voltaic arc and various samples containing Al, Sn and Cr as third element were produced by powder metallurgy. The microstructure of the samples was studied by optical microscopy, Vickers micro hardness and x rays powder diffraction. Their electrical conductivity was measured with a milliohmeter Agilent (HP) 4338B. Refinements of the crystalline structure of the samples were performed by the Rietveld method, using the refinement program GSAS. The refinement results and Fourier differences calculations indicate that the copper matrix structure presents not significant distortions by the used amounts of the other metal atoms. The refinement of non structural parameters allowed the micro-structural characterization. The dependence of the micro-structure with thermal and mechanical treatments is studied.

Keywords: copper-nickel alloys, powder metallurgy, microstructure, Rietveld Method, electrical properties, mechanical properties.

Introduction

Microstructural characteristics such as the size, type, form and regular distribution of precipitations determine the mechanical resistance in metallic alloys. This distribution is also fundamental to maintain a high electrical conductivity I the case of the copper alloys. It is also well known that in disordered solid solutions, the resistivity of metals and alloys is strongly influenced by the atomic displacements, vacancies and interstitials. In this work, were produced samples of alloys of Cu-Ni-Pt, Cu-Ni-Al, Cu-Ni-Sn and Cu-Ni-Cr from high purity precursors, to perform a comparative study of the microstructures and physical properties obtained by conventional and powder metallurgy [1-16].

The alloy elements are added to copper with purpose to improve its resistance, ductility and thermal stability, without causing considerable costs on its form, electric and thermal conductivity and its resistance to the corrosion, typical characteristic aspects of pure copper [14-20].

Products based on copper alloys such as porous material filters, electric friction equipments, contacts and structural parts can be manufactured through the process of powder metallurgy, which have the advantages of making fine grained homogenous structures, forming complicated shapes with close dimensional tolerances and the ability to produce parts with a superior surface finishing [1-13].

These advantages reduce or eliminate costly machining processes and allow less scrap loss, compared to other forming methods. To increase the strength, ductility and formability keeping good electric conductivity of these alloys, there have been used special thermal treatments, as well as variations in the chemical composition.

Experimental Procedure

A Sample of the alloy $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ was produced from high purity precursors, using an electric furnace with voltaic arc in vacuum. The sample was treated at 1073 K during 10 hours. For the preparation of $Cu_{98\%}Ni_{1\%}Al_{1\%}$, $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ and $Cu_{98\%}Ni_{1\%}Cr_{1\%}$ high purity powders of copper, nickel and the third element were mixed for a suitable time and then compacted under 1000 kPa in a cold uniaxial pressing.

Afterwards, the specimens were sintered at 800^{o}C in a high vacuum Carbolite furnace that had a hot zone of about 150 mm under vacuum. At last, the samples were homogenized at 550^{o}C under vacuum for 8 hours. For the metallographic and hardness characterization all samples were cold mounted and the compacts were grinding SiC papers followed by fine wet wheel polishing with diamond paste. Vickers hardness of the polished specimens was measured on a HXD 1000TM (Pantec) hardness tester with a load of 100g. Acidic $FeCl_3$ was used as the etchant.

The microstructures of the etched samples were observed in an optical microscope. X rays powder diffraction data were collected with a conventional Rigaku MultiFlex diffractometer with a fixed monocromator. The experimental conditions were: 40 kV, 20 mA, $10^{o} \leq 2\theta \leq 100^{o}$, $\Delta 2\theta = 0.02^{o}$, $\lambda_{CuK\alpha}$, divergence slit = 0.5^{o},

reception slit = 0.3 mm and step time 5 s. The electrical conductivity was measured using an Agilent 4338B milliohmmeter.

Results and discussion

As showed in the optical micrographs of $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ (Fig. 1) precipitates are fine and bulk distributed. This influences an increasing of hardness (in relation to pure copper), which resulted in 815.00 ± 0.01 MPa. Pt is 100% soluble and increases 0,635 □□cm for each 1% of mass increasing. For this sample the measured conductivity was 57 % IACS. The Rietveld refinement results for $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ indicate that the amount of Ni and Pt for this alloy produced no detectable anisotropic strain or crystallite size effects, as well as no detectable preferred orientation.

Otherwise a very slightly broadening of peaks as well as preferential orientation was detected in the $Cu_{98\%}Ni_{1\%}Al_{1\%}$, with GW an order of magnitude greater and a texture index of 1.0062. The asymmetry of the profile function at low angles in both cases is instrumental conditioned. In Tables 1 and 2 are presented the refinement results and profile parameters obtained for $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ and $Cu_{98\%}Ni_{1\%}Al_{1\%}$, using function 4 of GSAS.

The samples $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ and $Cu_{98\%}Ni_{1\%}Cr_{1\%}$ show different characteristic although the composition of the last is similar to that of $Cu_{98\%}Ni_{1\%}Al_{1\%}$. Both samples were inevitably exposed to oxidation, which is almost not visible in the Sn-sample but more than 20% in the Cr-sample. Only the Sn-sample shows a detectable amount of Ni, although almost no detectable amount of Sn, probably due to the thermal treatments. The refinement results for both samples using profile function 4 of GSAS are showed in Tables 3 and 4.

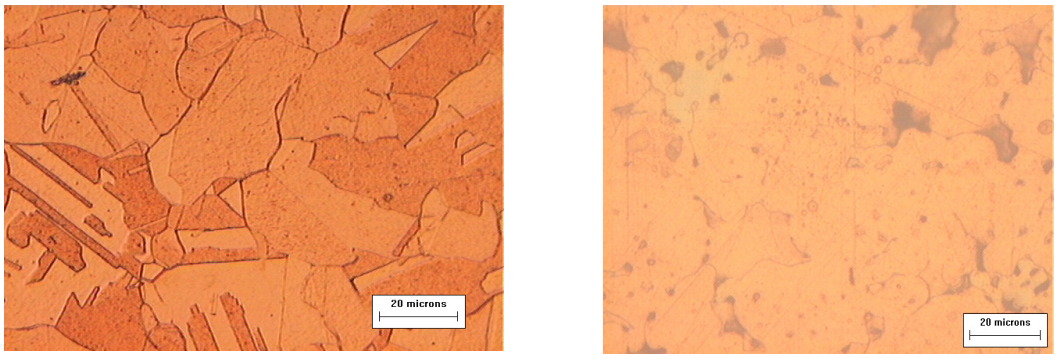

Figure 1: Microstructure of $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ (left) and $Cu_{98\%}Ni_{1\%}Al_{1\%}$ (right).

Table 1: Rietveld refinement results for $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ and $Cu_{98\%}Ni_{1\%}Al_{1\%}$.

$Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$	**$Cu_{98\%}Ni_{1\%}Al_{1\%}$**
Cu atomic positions x, y, z:	0.0 0.0 0.0
Thermal U_{iso} = 0.00957(15) ($Å^2$)	Thermal U_{iso} = 0.00348(32) ($Å^2$)
Cell Parameter: a = 3.6169(2) Å	Cell Parameter: a = 3.6174 (7) Å
R_{wp} = 6.92% R_p = 5.20%	R_{wp} = 11.01% R_p = 8.23%
□^{2} = 1.708% R_{Bragg} = 3.27%	□^{2} = 2.532% R_{Bragg} = 5.37%

The adjustments of both diffractograms are showed in Figures 2 e 3 and the more detailed Figure 4 shows the instrumental conditioned asymmetry of the profile function at low angles, which influenced the profile parameters, due to the higher intensity of reflection (111) in all samples.

Table 2: Refined profile parameters for $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ and $Cu_{98\%}Ni_{1\%}Al_{1\%}$ using function 4 of GSAS.

Par.	**$Cu_{99,33\%}Ni_{0,23\%}Pt_{0,43\%}$**	**$Cu_{98\%}Ni_{1\%}Al_{1\%}$**
GU	6.29411E+02	1.181E+03
GV	-7.20612E+02	-7.967E+02
GW	2.20778E+02	1.879E+02
GP	0	1.769E+02
LX	0.860743	0
ptec	0.417544	0
trns	-7.21046	9.658E-02
shft	1.64172E+01	3.336E-01

Par.	**$Cu_{99,33\%}Ni_{0,23\%}Pt_{0,43\%}$**	**$Cu_{98\%}Ni_{1\%}Al_{1\%}$**
Sfec	0	0
S/L	3.49220E-02	4.257E-02
H/L	1.89520E-02	1.727E-02
ETA	1	0
S400	0.175904	0
S220	-0.15659	-1.591

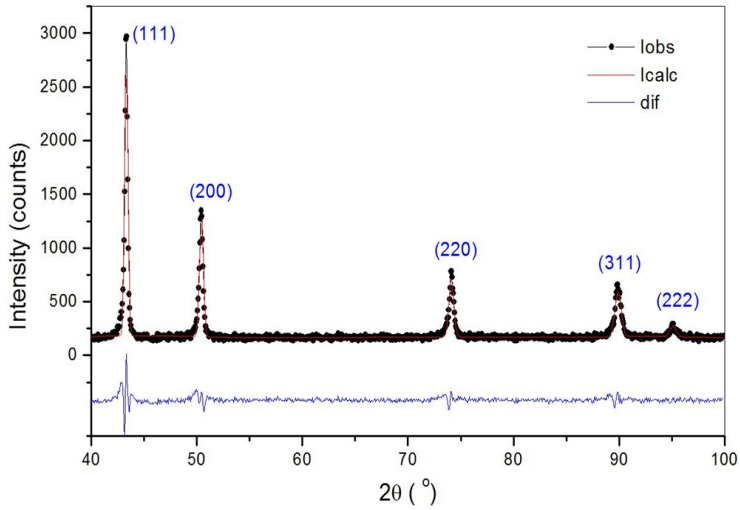

Figure 2: Adjustment of diffractogram for $Cu_{99.33\%}$ $Ni_{0.23\%}$ $Pt_{0.43\%}$

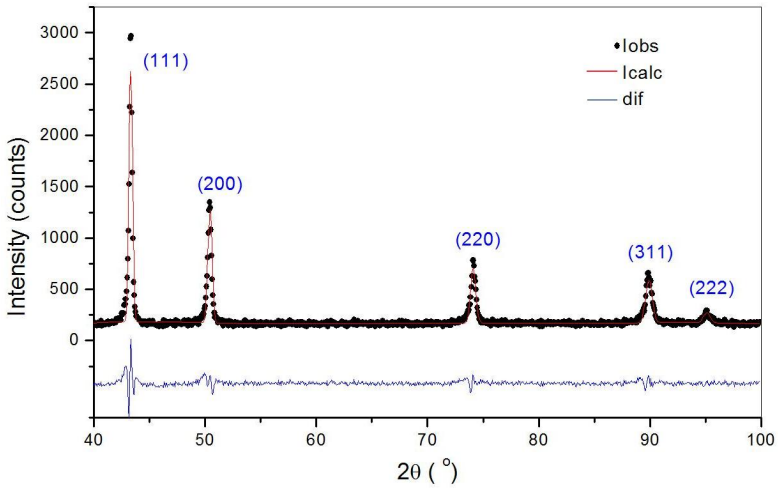

Figure 3: Adjustment of diffractogram for $Cu_{98\%}Ni_{1\%}Al_{1\%}$

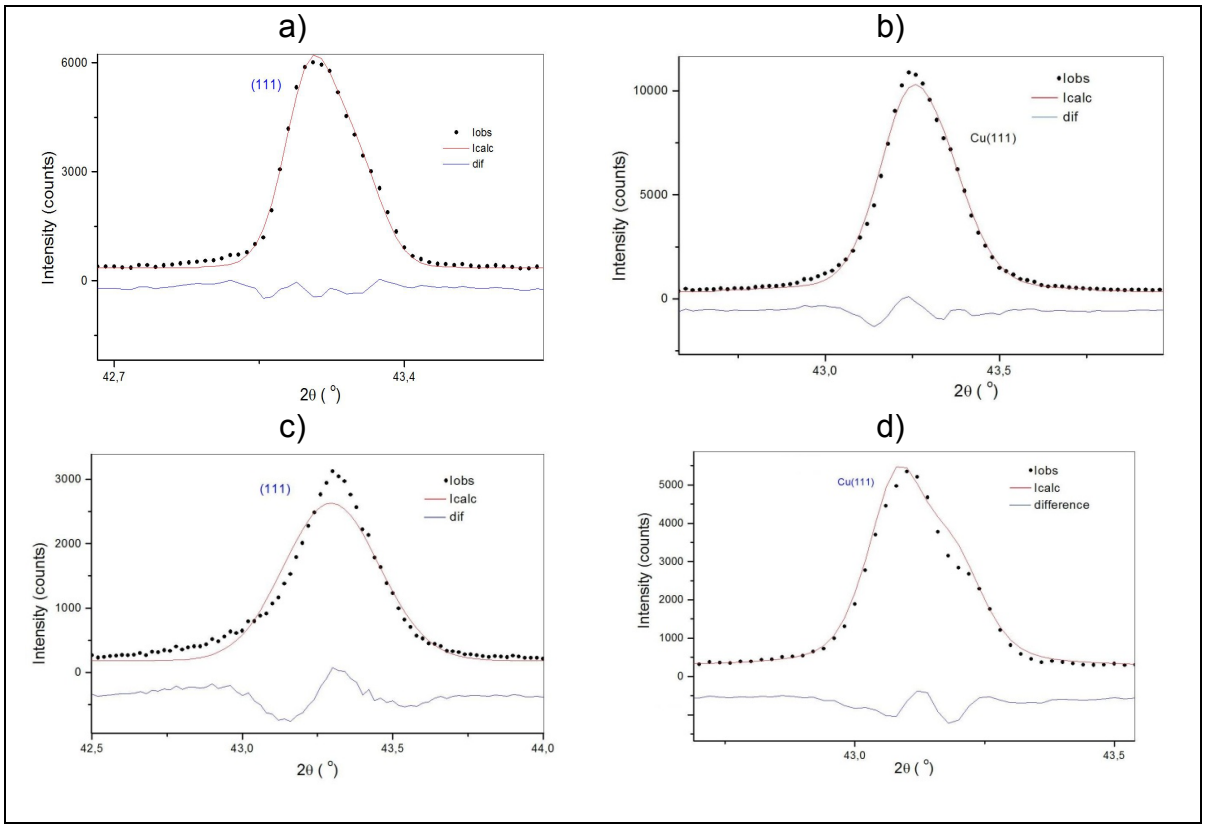

Figure 4: Asymmetric low angle peak profile of Cu (111) reflection of a) $Cu_{99,33\%}$ $Ni_{0,23\%}$ $Pt_{0,43\%}$ b) $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ c) $Cu_{98\%}Ni_{1\%}Al_{1\%}$ and d) $Cu_{98\%}Ni_{1\%}Cr_{1\%}$

Table 3: Rietveld refinement results for $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ and $Cu_{98\%}Ni_{1\%}Cr_{1\%}$.

$Cu_{90\%}Ni_{5\%}Sn_{5\%}$	**$Cu_{98\%}Ni_{1\%}Cr_{1\%}$**
Cu atomic positions x, y, z: 0.0 0.0 0.0	
Thermal U_{iso} = 0.00849(34) (Å^2)	Thermal U_{iso} = 0.00187(25) (Å^2)
Cell Parameter: a = 3.6196(4) Å	Cell Parameter: a = 3.6194(3) Å
R_{wp} = 7.81% R_p = 6.00%	R_{wp} = 8.04 % R_p = 6.21%
□^{2} = 2.435 R_{Bragg} = 4.61%	□^{2} = 1.973% R_{Bragg} = 8.94%

Table 4: Profile parameters using function 4 of GSAS for $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ and $Cu_{98\%}Ni_{1\%}Cr_{1\%}$

Par.	$Cu_{90\%}Ni_{5\%}Sn_{5\%}$	$Cu_{98\%}Ni_{1\%}Cr_{1\%}$
GU	6.29411E+02	3.10940E+01
GV	1.43165E+03	-4.71315E+01
GW	-4.56742E+02	2.49522E+01
GP	0	7.89818
LX	5.55342	4.64857
ptec	0	1.08093
trns	-1.36640E+01	-1.23072E+01
shft	1.09341E+01	2.68649E+01
Sfec	0	0
S/L	2.39199E-02	3.16859E-02
H/L	4.78531E-03	4.78284E-03
ETA	0.75	0.75
S400	0	0
S220	0	-0.531359E-01

The adjustment of diffractogram for sample $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ is shown in Fig. 5, where appear visibly the nickel (111) and (200) reflections and no detectable intensities for Sn and copper oxides. Otherwise, Fig. 5 shows the adjustment for $Cu_{98\%}Ni_{1\%}Cr_{1\%}$ with Cu_2O and no detectable quantity of nickel or chromium.

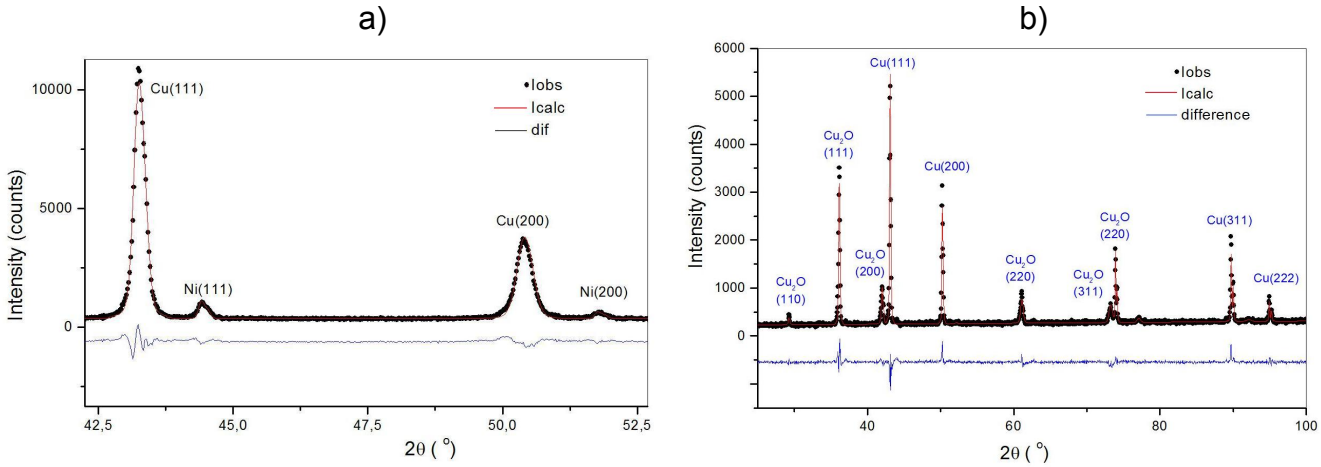

Figure 5: Adjustment of diffractogram for a) $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ with Cu and Ni reflections; b) $Cu_{98\%}Ni_{1\%}Cr_{1\%}$ with Cu_2O Bragg reflections.

Conclusions

The obtained microstructure and first-rate mechanical strength (370 MPa) and electrical conductivity (30 %IACS) values for $Cu_{98\%}Ni_{1\%}Al_{1\%}$ and $Cu_{90\%}Ni_{5\%}Sn_{5\%}$ could justify a good quality employment for these alloys using powder metallurgy instead conventional metallurgy processing. However, fine grained homogenous

structures and precise final compositions should be still achieved with further homogenization, using different temperatures for each alloy.

Preferential orientation could be a factor to take into account in some cases, as a result of mechanical processing of the powder samples. The small amounts of dopants in all samples caused no structural distortions that could be detectable by x rays powder diffraction.

The refinements indicate a very slightly effect in the microstructure of the powder metallurgy sample, possibly due to thermo mechanical processing. The asymmetric broadening of low angle peaks is due to instrumental effects.

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References

1. J. CRANE AND J. WINTER, Copper: Properties and alloying, Encyclopedia of Materials Science and Engineering, vol 2, Ed. MB Bewer, Pergamon Press and the MIT Press 1986, p. 848 – 855.

2. P. W. TAUBENBLAT, Copper Selection of high conductivity alloys, Encyclopedia of Materials Science and Engineering, vol 2, Ed. MB Bewer, Pergamon Press and the MIT Press 1986, p. 863-866.

3. ASM Specialty Handbook: Copper and Copper Alloys, Metal, chapter 1, section 1, ASM International, 2001.

4. C. R. BROOKS, "Heat Treatment, Structure and Properties of Nonferrous Alloys", ed. ASM, Metals Park, 1988, chapter 8.

5. A. BUTTS, "Copper, the Science and Technology of the Metal, its Alloys and Compounds", ed. Reinhold Publishing Corporation, New York, 1954, 3th printing 1960.

6. G. GOSH, J. KIYAKE and D M. E. FINE, JOM, March (1997), p. 56-60

7. A. ROTEM, D. SHECHTMAN, AND A. ROSEN, Metall. Trans. A .1988, vol. 19A, p. 2279-2285.

8. D. Steiner, R. Beddoe, V. Gerold, G. Kostorz and R. Schmelczer, Scripta Metall., 1983, vol. 17, p. 733-36

9. A. GUHA, ," Development of a high-strength, high-conductivity Cu-Ni-Be Alloy, high conductivity Copper and Aluminum Alloys, eds. E. Ling and P. Taubenblat W., TMS – AIME Publ. 1984, p. 133-145.

10. Y. SAKAI, K. INOUE, AND H. MAEDA, Acta Metall. Mater. 43 (1995), p. 1517.

11. W. A. MONTEIRO, Proceedings of IX CBECIMAT, Águas de São Pedro /SP, dez.90, p. 546-549.

12. W. A. MONTEIRO, M. A. G. SILVEIRA E O. JÚLIO Jr, Metalurgia & Materiais, v. 51, may 95, p. 440-444.

13. W. A. MONTEIRO, F. COSANDEY AND P. BANDARU, The Effect Of Thermomechanical Treatment On The Microstructure Of A Cu-Ni-Be Alloy, Proceedings of THERMEC'97, Wollongong, Australia, July 1997.

14. W. A. STADTLER, Production of Metallurgy Parts ASTM, Powder Metallurgy, Ohio, p.449-463, 1989.

15. GHADIRI M., FARHADPOUR, F.A., CLIFT R., SEVILLE, J. P. K. Particle characterization size and morphology, The Institute of Metals Series on Powder Metallurgy - An Overview. London, p.56-75, 1991.

16. THE INSTITUTE OF METALS, Powder metallurgy - An overview. 1. Ed. The Institute of Metals Series on Powder Metallurgy, London, Great Britain, 1991.

17. W. A. KAYSSER Solid State Sintering. The Institute of Metals Series on Powder Metallurgy - an overview. London, p45-53, 1991.

18. F. THÜMMLER ,& R. OBERACKER, Introduction to Powder Metallurgy, The Institute of Materials, 1993, ISBN 0-901716-26-X)

19. A.C. LARSON, R.B. VON DREELE, Los Alamos National Laboratory. Los Alamos, EUA. Copyright, 1985–2000, The Regents of the University of California, 2001.

20. W. A. MONTEIRO, F. COSANDEY, P. BANDARU, The effect of termomechanical treatment on the microstructure of a Ni-Cu-Be alloy, THERMEC`97, Australia, 1997.