JOURNAL OF MATERIALS SCIENCE 31 (1996) 3259–3262

The stability of $LaNi_5$ in a Cu matrix

D. MORENO
NRCN, Beer-Sheva POB 9001, Israel

C. A. F. MANWARING, I. R. HARRIS
School of Metallurgy and Materials, University of Birmingham, B15 2TT, UK

The reaction of $LaNi_5$ with Cu powder during sintering at high temperature was examined in order to obtain better conductivity and ductility. Pressurized and forged copper–$LaNi_5$ pellets were investigated by optical metallography, DTA, XRD and TEM. The need for heat treatment after pressing and/or forging is vital to obtain good diffusion bonding between the copper particles and to improve the material strength. No interaction between La, Ni and Cu were observed after heating at 1173 K but a very stable La_2O_3 phase was created around the $LaNi_5$ particle. Rolling up to 85% reduction showed good ductility.

1. Introduction

Absorption and desorption of hydrogen in $LaNi_5$ based alloys, either in a gaseous environment as a hydrogen store or in an alkaline solution as a reversible hydrogen battery electrode has been the subject of new research in the last few years [1–3].

Certain changes occur by exposure of $LaNi_5$ to hydrogen. The α/β transition by hydrogen absorption, causes a 24% volume expansion which leads to decrepitation of the metal into powder with a particle size around 4–20 μm [1]. Many of the rechargeable metal hydrides become fine powder after relatively few hydrogen absorption–desorption cycles. The accumulation of internal stresses and defects in $LaNi_5$ seem to be more marked in block samples than in pulverized samples [4]. Fine powder reaction beds have poor heat and mass transfer characteristics in addition to unstable and incoherent structures. Great improvement in the thermal conductivity of metal hydride powder has been achieved when metal matrices such as aluminium or nickel foam and copper nets hold the powder hydride [5–7]. Proper processing can combine the useful properties of $LaNi_5$ metal compound with a surrounding matrix into one system due to the improvement of the formability of such a metal compound. However, powder metallurgy processes are not in thermodynamic equilibrium during initial fabrication of the powder, during production of the compound and during sintering. Interdiffusion and reaction processes can create interface reactions which seriously affect the $LaNi_5$ properties. These reactions can be beneficial or detrimental. A freshly fractured surface of $LaNi_5$ during pulverization causes La enrichment on the surface which acts to decrease the surface energy. La is very reactive with oxygen. This reaction leads to surface segregation, selective oxidation of La, and formation of a surface Ni precipitate which surrounds the $LaNi_5$ particles [8].

In this study, the reaction of $LaNi_5$ with Cu powder during sintering at high temperature was examined.

2. Experimental details

The $LaNi_5$ supplied by Rare Earth Products Ltd. (batch BM669) was sifted to 45 μm and mechanically mixed with 75 μm electrolytic copper powder to 10, 30 and 50% $LaNi_5$ composition. X-ray diffraction (XRD) analysis of the $LaNi_5$ sifted powder showed the presence of a certain amount of La_2O_3. The copper–$LaNi_5$ mixed powder was subjected to 2×10^5 Pa hydrogenation at room temperature for a few hours, then heated at 513 K for 3 h, to reduce the copper oxide by hydrogen reaction and to recover the copper powder. The mixed powder as cold pressed at 1000 MPa into pellets of cylindrical shapes approximately 12.7 mm diameter × 5.5 mm. Some of the pellets were forged at high energy for high density and were reduced to coins, approximately 22 mm diameter × 1.6 mm. Samples were cut from the coins for different experiments. The forged and pressurized samples were heat treated at 1173 K for sintering.

In the present study, the samples were investigated by optical metallography, differential thermal analysis (DTA), XRD, and transmission electron microscopy (TEM).

3. Results and discussion

Whereas the 30% and 50% $LaNi_5$ containing samples partially disintegrated during forging, the pressurized and forged copper–10% $LaNi_5$ pellet was obtained with good integrity and without cracks. Hydrogen absorption in the copper–10% $LaNi_5$ pellet was carried out at 10×10^5 Pa and the capacity was examined by means of pressure changes in a calibrated volume chamber. The absorption obtained as shown in Fig. 1, was about 80% of the calculated capacity of the

0022–2461

$LaNi_5$. The experiment was carried out for three consecutive cycles and most of the pellets were pulverized. The low amount of 10% $LaNi_5$ in the copper matrix minimized the intensity of the $LaNi_5$ XRD peaks, and no obvious change was observed in the XRD trace of the mixed powder before and after the experiment.

The disintegration of the pellet by hydrogen absorption is attributed to the expansion of the $LaNi_5$ during the reaction. These particles are localized around the copper grains as we will see later. The stresses developed around the $LaNi_5$ particles by expansion are introduced into the copper grains and create discontinuities in the pellet. The integration of the pellets was done by mechanical pressing and forging only. In order to improve the cohesivity of the copper grains by thermal diffusion, the samples were heated to 1173 K. This temperature was selected by

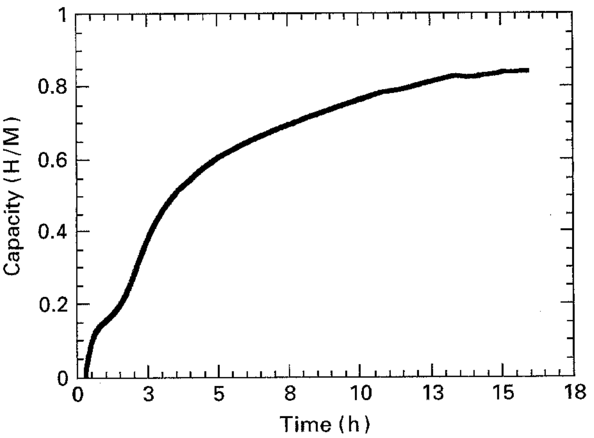

Figure 1 Hydrogen absorption in the copper–10% $LaNi_5$ pellet carried out at 10×10^5 Pa without heat-treatment. The capacity was examined by means of pressure changes in a calibrated volume chamber.

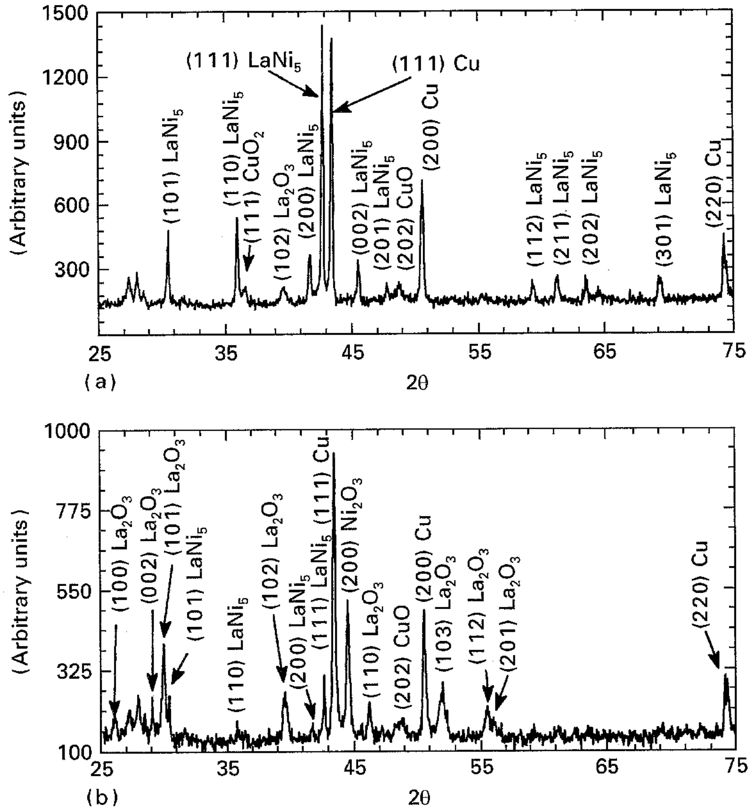

Figure 2 A comparison of the XRD traces for the copper–50% $LaNi_5$ pellet (a) before and (b) after heating to 1173 K.

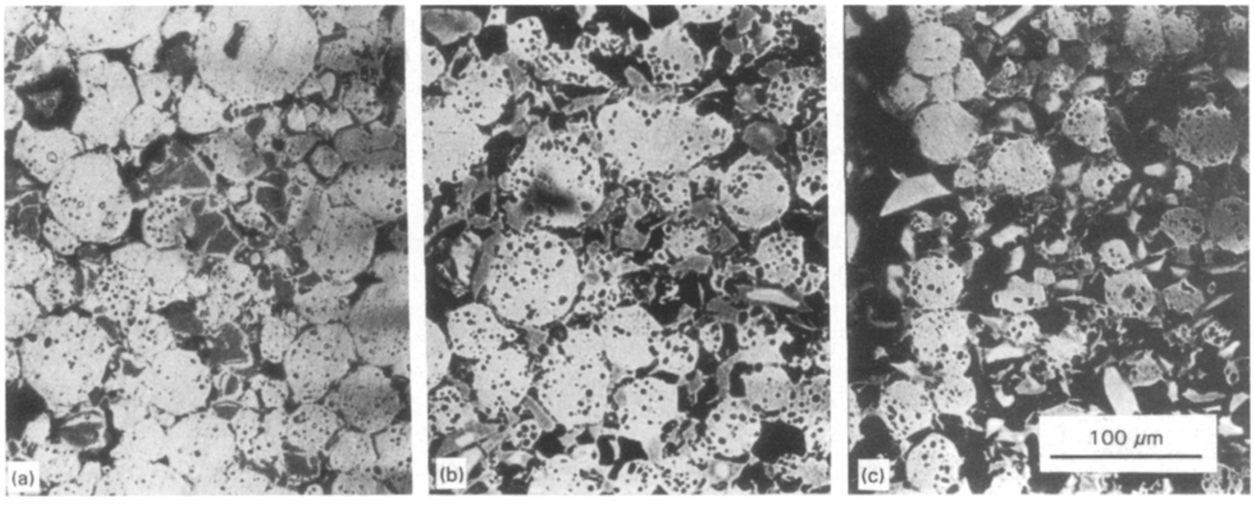

Figure 3 Cu–$LaNi_5$ sintered alloy, (a) 10%, (b) 30% and (c) 50% $LaNi_5$ after heating at 1173 K.

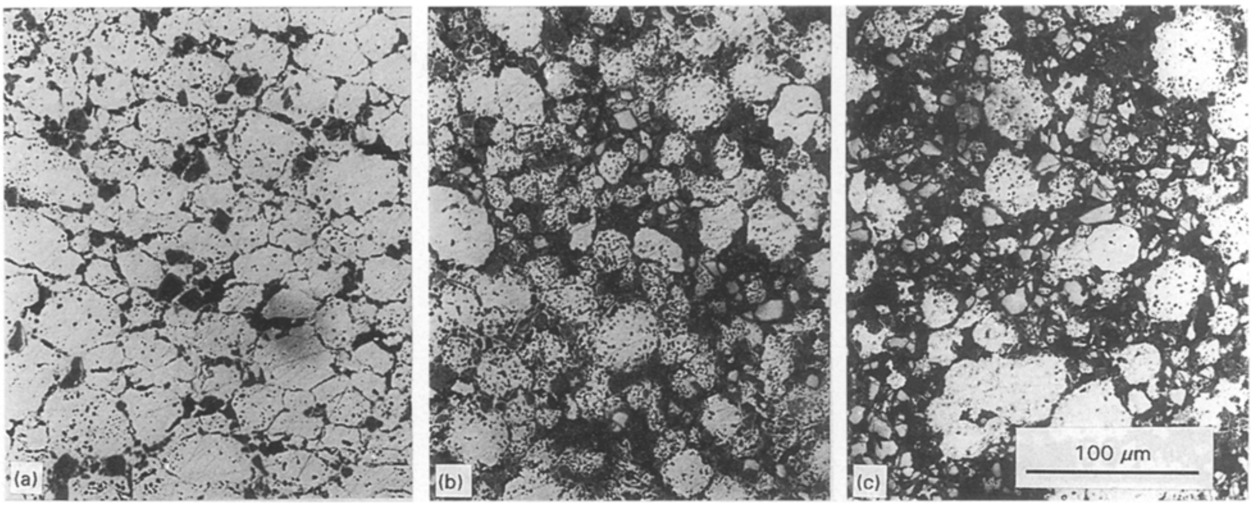

Figure 4 Cu–$LaNi_5$ Forged alloy, (a) 10%, (b) 30% and (c) 50% $LaNi_5$ after heating at 1173 K.

inspection of the component phase diagrams and after DTA of the samples in order to make sure that no new phases could be created prior to this temperature. Fig. 2 shows a comparison of the XRD traces for the copper–50% $LaNi_5$ pellet before and after the heating to 1173 K. No metallic phases were observed after heating. Mainly, the creation of La_2O_3 was observed. Figs. 3 and 4 show micrograph comparisons of the $LaNi_5$ particle location at different compositions for pressurized and forged samples, respectively. Whereas in the 50% copper matrix the particles are attached to the copper matrix by certain interfaces, the $LaNi_5$ particles in the 90% copper matrix are completely surrounded by the copper. Fig. 5b and d show the $LaNi_5$ particles surrounded by an oxide layer which was detected by XRD. This phase is not observed in Fig. 5a and c where the particles are surrounded by the copper matrix. The copper–10% $LaNi_5$, pressed and forged, was rolled to 85% reduction and TEM samples were prepared from the rolled foil by an electro-polishing jet technique. The TEM micrograph and the respective selected area diffraction (SAD) are shown in Fig. 6. The large plastic deformation of the copper matrix and the broken edges of the $LaNi_5$ particle caused by such deformation, probably causes the spread of the diffraction points of the copper reciprocal lattice and the random diffraction points

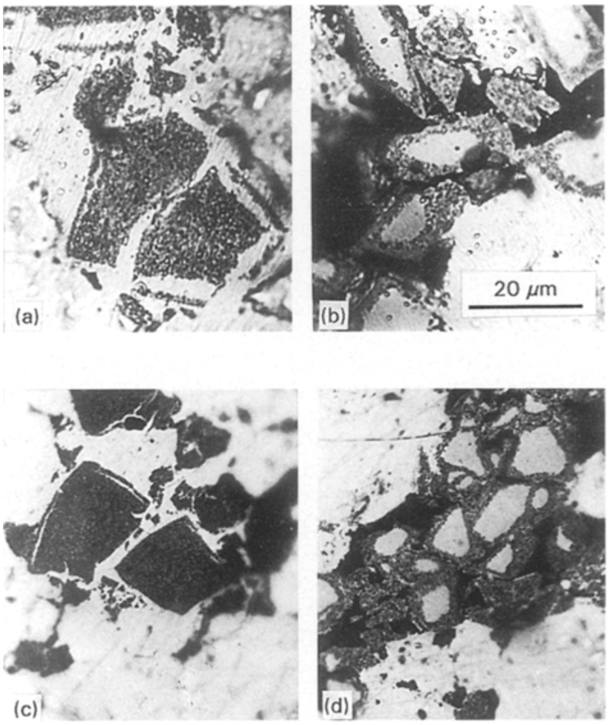

Figure 5 Cu–$LaNi_5$ alloy (a) 10%, and (b) 50% $LaNi_5$ pressurized and sintered at 1173 K. (c) 10% and (d) 50% $LaNi_5$ pressurized, forged and sintered at 1173 K.

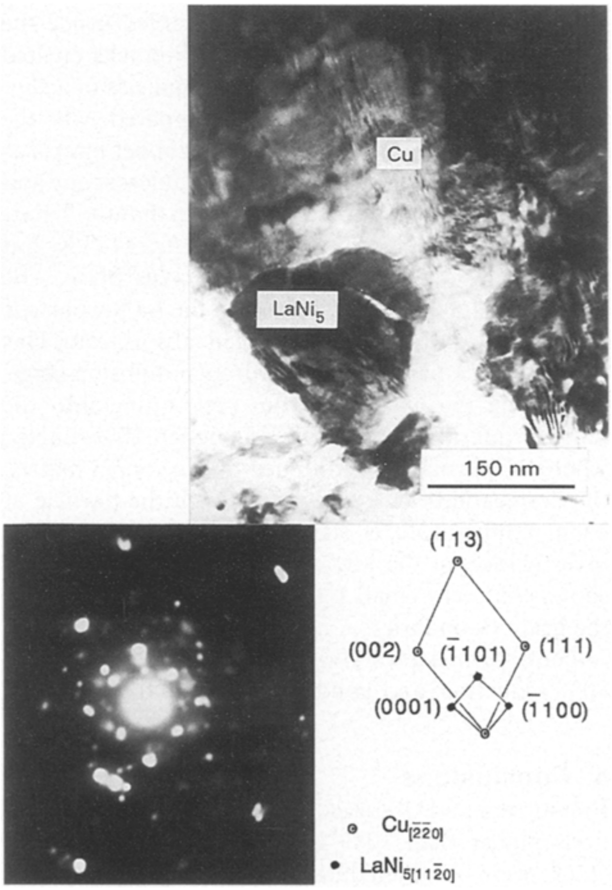

Figure 6 TEM micrograph and the SAD patterns of a rolled Cu–10% $LaNi_5$ foil.

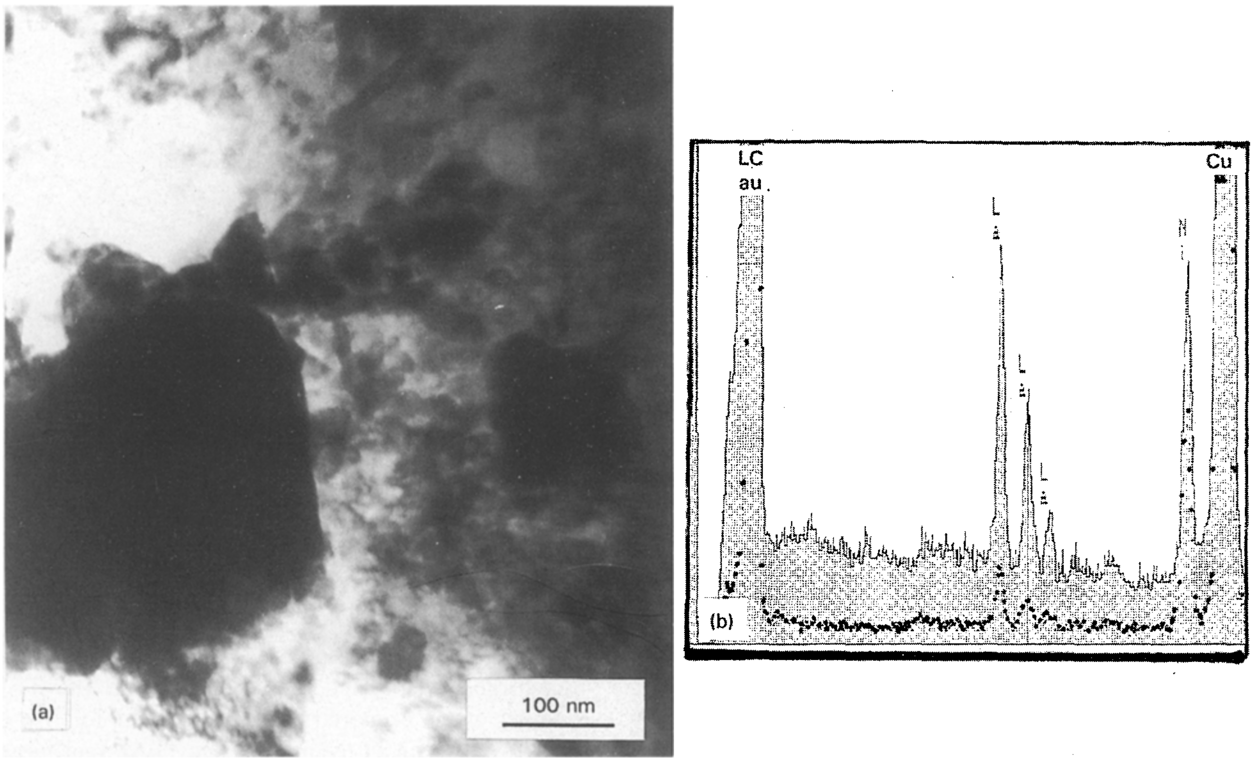

Figure 7 (a) TEM image of a $LaNi_5$ particle in a Cu matrix after heat treatment at 1173 K, and (b) a qualitative X-ray chemical analysis comparison between the particle (background) and the matrix (dots).

around the $LaNi_5$ particle pattern. The diffraction patterns indicate the hexagonal structure of the $LaNi_5$ and the cubic structure of the copper. The boundary between the particle and the matrix looks very sharp and no additional phases were observed. Some slip fringes and discontinuity can be observed inside the particle which can be correlated with cracks created under large stresses. X-ray chemical analysis of a similar $LaNi_5$ particle in Fig. 7a is compared with the chemical analysis of the surrounding copper matrix as shown in Fig. 7b. Results obtained by microscopy and XRD techniques lead to the conclusion that the $LaNi_5$ remains stable after heat treatment at 1173 K but some deterioration on the surface takes place. The creation of La_2O_3 on the surface of the $LaNi_5$ particle becomes a problem for hydrogen absorption. This oxide forms a barrier at the hydrogen diffusion stage, preventing the hydrogen from penetrating into the particle interior. In the case of copper–10% $LaNi_5$, where the particle is surrounded by the copper matrix, the permeability of hydrogen through the particle at room temperature is significantly low. Microprobe investigation in the low energy backscattering mode shows that very small $LaNi_5$ particles are located at the grain boundaries.

The copper–10% $LaNi_5$ pellet was rolled to 50 and 80% reduction, and good ductility was found.

4. Conclusions

Pressurized and/or forged Cu–$LaNi_5$ with concentrations higher than 10% $LaNi_5$, are very brittle and cracks were obtained during the forming process. The forged Cu–10% $LaNi_5$ disintegrated after a few cycles of hydrogen absorption. The need for heat treatment after pressing and/or forging is vital to obtain a good diffusion bond between the copper particles and to improve the material strength. No interaction of La, Ni and Cu was observed after heating at 1173 K but a very stable La_2O_3 phase was created around the $LaNi_5$ particle, especially in samples with content higher than 10% $LaNi_5$. Rolling up to 85% reduction showed good ductility.

References

1. E. H. KISI, C. E. BUCKLEY and E. M. GRAY, *J. Alloys Compounds* **185** (1992) 369.
2. T. SAKAI, K. OGURO, H. MIYAMURA, N. KIRIYAMA, A. KATO and H. ISHIKAWA, *J. Less-Common Metals* **161** (1990) 193.
3. T. SAKAI, H. MIYAMURA, N. KURIYAMA, A. KATO, K. OGURO and H. ISHIKAWA, *J. Electrochem. Soc.* **137** (1990) 795.
4. H. UCHIDA, A. HISANO, K. TERAO, N. SATO and A. NAGASHIMA, *J. Less-Common Metals* **172–174** (1991) 1018.
5. U. MAYER, G. GROLL and W. SUPPER, *ibid.* **131** (1987) 235.
6. M. NAGEL, Y. KOMAZAKI and S. SUDA, *ibid.* **120** (1986) 35.
7. M. RON, E. BERSHADSKY and J. JOSEPHY, *ibid.* **172–174** (1991) 1138.
8. L. SCHLAPBACH, "Topics in Applied Physics", Vol. 67, "Hydrogen in Intermetallic Compounds II, 2 Surface Properties and Activation 15–95" (Springer-Verlag, Berlin, Heidelberg, 1992).

Received 20 February
and accepted 25 October 1995