MICROSTRUCTURAL STUDY OF SINGLE CRYSTALS OF ORDERED COMPOUNDS Ni_3Al

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INTRODUCTION

In nickel base alloy systems, the major phase or matrix is known as (γ), a Ni-base, austenitic, fcc phase that usually contains high percentages of Co, Cr, Mo, or W, and solid-solution strengthening elements such as Ti, Hf, Zr, V or Ta. An intermetallic phase, known as (γ'), is generally presented by an A_3B formula, in which A is typically Ni, Co or Fe and B is Al, Ti or Nb.

This γ'-phase has been identified as the major strengthening precipitate within the γ-matrix, and hence, can be considered the backbone of the system. The compatibility between both, (γ) and (γ') crystal structures, allows the nucleation and growth of a precipitate with low surface energy and long-term stability. The Ni-Al binary phase diagram reveals Ni_3Al as an example of γ'-phase which exists in the composition range of 23 to 27.5 %atm. Al at room temperature. It presents an $L1_2$ crystallographic structure, according to the Strukturbericht notation, consisting of four interpenetrated simple-cubic sublattices where one of which is occupied by Al atoms and the remaining three by Ni atoms, and conserves the cubic symmetry (space group cP4). Several intermetallic compounds with the $L1_2$ ordered structure exhibit an anomalous increase of flow stress with the temperature till a peak, called anomalous flow stress peak. Such a characteristic confers to the material containing these phases suitability for high temperature applications such as in superalloy blades for gas turbines. [1-4]

EXPERIMENTAL PROCEDURE

The two materials used in the present work are single crystalline bars composed uniquely by γ'-phase with $L1_2$ ordered structure, presenting the following compositions: $Ni_{74.3}Al_{24.7}Ta_1$, hereafter referred to as **Ni_3AlTa**, and $Ni_{76.6}Al_{24.3}$ (binary alloy), hereafter referred to as **Ni_3Al** simply. Both materials were provided by Professor D.P. Pope from the University of Pennsylvania.

Both single crystalline bars had parallelepipedic shape and growing direction, determined by use of Laue method, along a <001>-type axis. The bars of Ni_3AlTa and Ni_3Al had cross sections of $50x15mm^2$ and $50x7mm^2$, respectively, both having about 150mm in length.

Two samples of each specimen were cut by electrodischarge machine (**EM**), mounted in resin and mechanically polished until mirror quality. In order to reveal their solidification structure both samples were chemically etched using a solution containing 20ml HCl (concentrated), 20ml of H_2O, 30ml of ethanol and 1.5g of $CuCl_2$, and observed by means of Optical Microscope (**OM**) and Scanning Electron Microscope equipped by an EDS analyzer (**SEM-EDS**).

In order to prepare samples for observations by Transmission Electron Microscope (**TEM**) slices of 0.5mm thick were sectioned by **EM** from each bar, resulting in plates having normal direction parallel to a <110>-type axis. Still by, EM several discs of 3.0mm diameter were extracted from each plate and subsequently thinned by hand grinding using emery paper. The final thinning was done in an standard double jet polisher using a solution of 10% vol. $HClO_4$ in methanol (PA) at

-10°C and 20V. The TEM observations were carried out on a JEOL microscope (model JEM 200C) operating at 200KV using double-tilt specimen holder. The dislocation densities were measured by the Ham and Sharpe method [5].

RESULTS AND DISCUSSION

In order to investigate the presence or absence of other phases than the ordered intermetallic, both specimens were investigated by OM and their solidification macrostructures are shown in fig.-1. One can observe in Ni_3Al larger interdendritic arms space, and then larger dendrite arms, than in Ni_3AlTa specimens. No interdendritic segregation was detected by SEM-EDS analysis of both specimens.

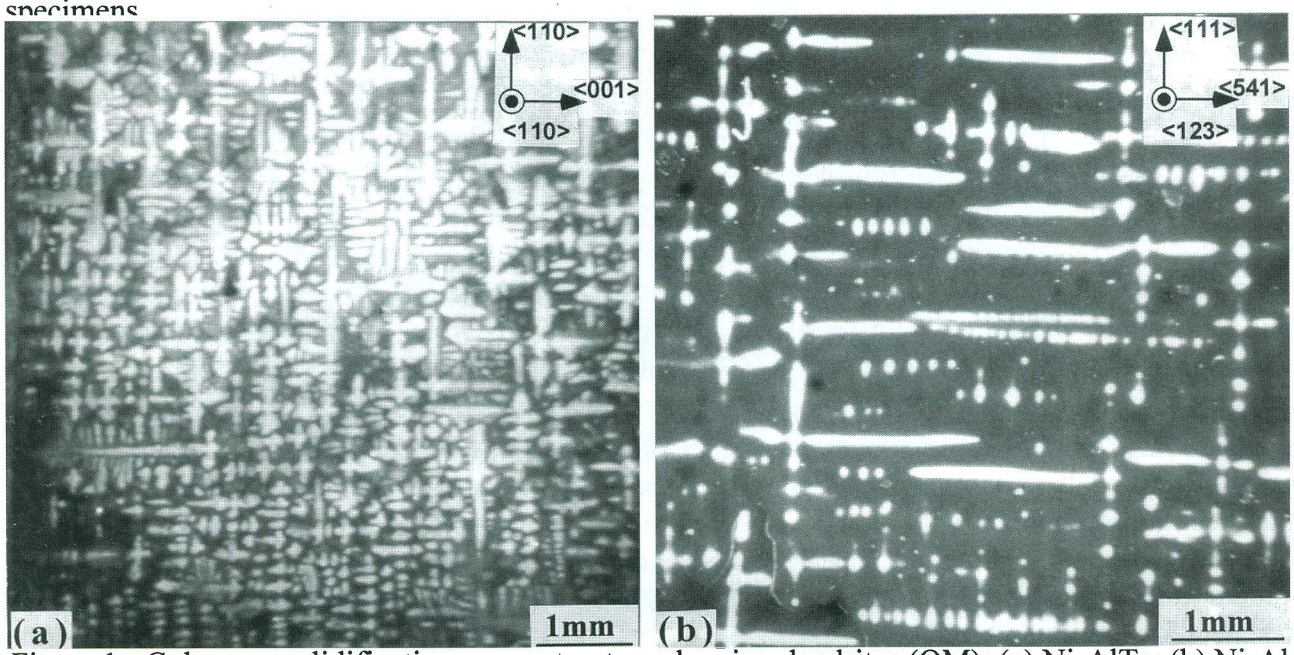

Figure 1.- Columnar solidification macrostructure showing dendrites (OM): (a) Ni_3AlTa; (b) Ni_3Al.

It could be expected larger interdendritic arms space in Ni_3AlTa specimen than in Ni_3Al since this second presents smaller cross-section than the first, resulting in a more rapid and more frequent deviation from the planar solid-liquid interface growth. Such a statement should be true if the herein study intermetallic bars were not solidified under controlled gradient of temperature and solidification speed.

The solidification parameters that form dendritic macrostructures are very well known and described in the literature. [6] It has been accepted that during an alloy solidification it could occurs substantial changes in the concentration ahead the solid/liquid interface affecting locally the solidification temperature of this liquid. This phenomenon is known as *metastable constitutional undercooled zone*. In alloys, this instability generates a protuberance at the solid/liquid interface that will contribute to a concentration gradient and then the local gradient of the liquidus temperature preserving this *region of constitutional supercooling*. Hence, the last interdendritic liquid to solidify can present different composition compared to that of the first crystals formed. Primary trunk spacing between dendrites is an important parameter for columnar macrostructures and is directly proportional to the gradient of temperature between liquid and solid, and inversely proportional to the solidification rate. Therefore, fine or coarse dendrites can be produced when these two parameters are controlled independently, such as in directional solidification where typical gradients of temperature are of about 10K/mm. Typical gradients of temperature for

solidification of single crystal turbine blades are on the order of 100 K/mm and solidification rate ranging from 1 to 5mm/s. [6]

As already mentioned, no other phases than the ordered intermetallic Ni_3Al were found and any segregation was detected, reinforcing the statement that strengthening elements (eg. Ti, Hf, Zr, V or Ta), in low concentrations, substitute Al positions in the lattice.[4] When single crystals of binary and single phase, of ordered intermetallic Ni_3Al are obtained they are not stoichiometric, since their stoichiometric single crystals are not feasible, and hence are generally slightly rich in Ni.

Crystallographic misorientations of about 5° and 2° were found along the polished surfaces, respectively of Ni_3AlTa and Ni_3Al specimens, when analyzed by Laue method. This fact does not mean that the herein-studied bars can not be considered single crystals. It has been stated that small crystallographic misorientations between dendrite arms of single crystals can be accommodated by the presence of a number of geometrically necessary dislocations. Higher misorientation can be accommodated by formation of subgrain boundaries.[6]

Observing the macrostructures of solidification of both single crystalline specimens, shown in fig.-1, one can see different interdendritic spacing between them. Taking into account the enormous difference of etching time (t_e) between the two specimens (t_e= 5min for Ni_3AlTa and t_e= 240min for Ni_3Al) and according to the Laue results above discussed, one can state that the difference on etching time is related to the misorientation between dendrite arms. In this case, Ni_3AlTa specimen were easily etched due to more significant misorientations between its dendrites arms that results in a surface able to better deflect a light beam of an OM than the Ni_3Al specimen. On the other hand, if the above statement is correct, the Ni_3AlTa specimen should have higher dislocation density than the binary Ni_3Al and it could also explain the difference of etching time between the specimens due to the fact that dislocations are sites more susceptible to chemical etchings, and then rising the contrast when OM observations are done.

In order to confirm the above statement several samples of each specimen were observed by TEM and a summary of the results obtained are shown in fig.- 2. In ordered intermetallic compound of Ni_3Al type the dislocations are named *superdislocations* and are generally found dissociated in two *superpartial dislocations* bordering an Anti-Phase Boundary (**APB**).[1-4] Observed by TEM the superpartial dislocations usually have appearance of two parallel lines. If the material did not suffer any plastic deformation the superdislocations will have appearance of two parallel and straight lines as presented in fig.-2(a). Hence, remembering that both specimens were cut by EM, which is a cutting process that minimizes plastic deformation of metals, it is possible to conclude that such dislocations were originary from the solidification. Using several pictures took sequentially over a region of each sample, it was possible to mount plates of each region and count the number of dislocation lines in an area. Such a counting must be corrected by a factor (depending on the diffraction vector **g** used) in order to account for the invisible dislocations. In spite of the fact that the herein used method be not too much precise, it is enough for a comparative study between the two specimens and revealed dislocation densities for Ni_3AlTa and Ni_3Al of about $1x10^9$ lines/cm^2 and $5x10^7$ lines/cm^2 respectively. Figure 2(b) exemplifies dislocation arrangements observed in both samples. These arrangements were more frequent in Ni_3AlTa than in Ni_3Al samples and are very probably located between dendrite arms.

According to the structure factor expression, and then the diffusion factors for Al and Ni for generic ***hkl*** planes it was expected no reflections for certain planes, but ordered intermetallic compounds generally exhibit these so called *forbidden reflections* (fig.-3(c)). These forbidden reflections will appear as less intense reflections in ordered alloys and their presence when analyzed by TEM have been used to identify when a compound is ordered or not.

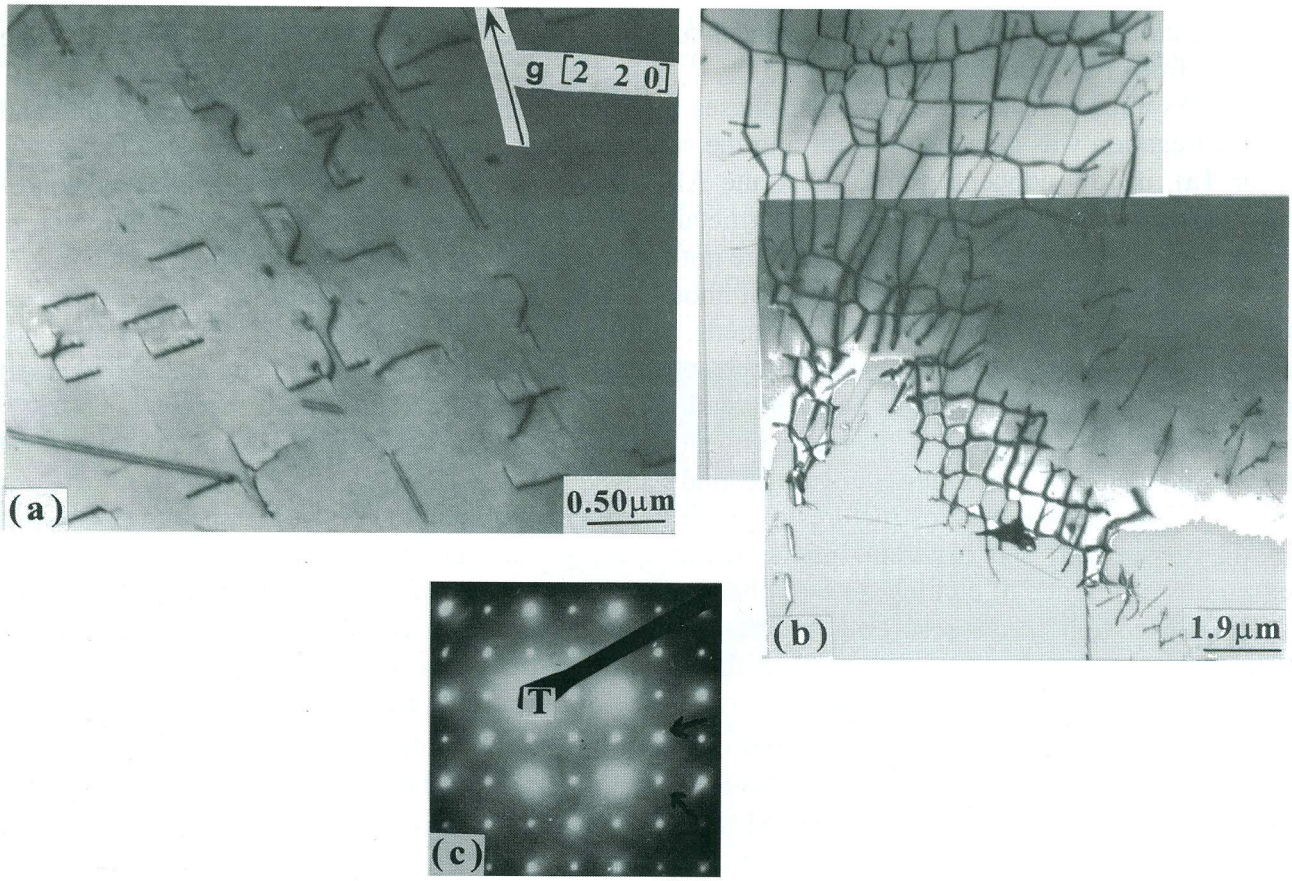

Figure 2.- TEM observations of Ni_3AlTa samples showing: (a) superdislocations present in the crystal, originally from solidification; (b) superdislocations arrangement; (c) typical diffraction pattern of a zone axis [001] of a thin foil whit normal direction parallel to [110].

CONCLUSIONS

In columnar (dendritic) solidification of single crystalline, ordered, intermetallic compounds Ni_3Al, small crystallographic misorientations between dendrite arms are accomodated by a number of geometrically necessary superdislocations.

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