JOURNAL OF MATERIALS SCIENCE 16 (1981) 3398–3404

Effect of quenching on the magnetic behaviour of some Ni-rich NiAl alloys

J. A. KILNER,* I. R. HARRIS
Department of Physical Metallurgy and Science of Materials, University of Birmingham, Birmingham, UK

The effects of quenching from 1443 K on the magnetic properties of NiAl alloys in the composition range 32.0 to 40.0 at% Al have been studied. Changes were observed in the magnetic properties of all the alloys and, in particular, large changes were observed for the 35 at% Al alloy when heated from an "as-quenched" state. These magnetic changes were also accompanied by a sample weight loss. The magnetic susceptibility and weight loss effects have been attributed to the absorption of hydrogen when the alloys were quenched into water from a high temperature and to its subsequent evolution when the samples were reheated under vacuum. The changes in the field dependence are thought to have a different origin and have been attributed to the diffusion of Ni antistructure atoms to form Ni clusters large enough to exhibit ferromagnetism. The composition dependence of the susceptibility at room temperature and the large changes seen in the susceptibility of the 35 at% Al alloy on heating both suggest that the Fermi energy of this composition lies on or close to a subsidiary peak in the electronic density of states curve. This observation has been correlated with the theoretical density of states curve for NiAl.

1. Introduction

The physical properties of the β'-phase NiAl have been extensively studied over a period of many years, but unfortunately there has been much disagreement over many of these physical properties including the nature of the intrinsic magnetic behaviour of this material. It now seems clear that many of the inconsistencies in the magnetic behaviour, especially in the Ni-rich alloys, were due to the presence of transition-metal impurities such as iron [1–5]. No magnetic data exists for compositions of less than 40 at% Al where, according to the most recent phase diagram [6], the β'-phase is only stable at high temperatures. Alloys in the composition range 38 to 32 at% Al inclusively, quenched from high temperature in order to retain the single phase condition, undergo a martensitic transformation to a face-centred tetragonal phase on cooling to room temperature. This transformation has been observed by several methods including metallography [7, 8], thermal arrest data [9], dilatometry [8] and resistivity measurements [9]. From these studies, transformation (M_s) temperatures have been reported which exhibit a linear composition dependence but disagreement exists over the absolute values of these transformation temperatures.

This study was undertaken in order to extend the previous magnetic susceptibility data [5, 11] to the Ni-rich, high temperature phase field of NiAl and to use susceptibility measurements to follow phase stability in these alloys.

2. Experimental procedure

2.1. Alloy preparation

Several alloys in the composition range 32 to 40 at% Al inclusively, were prepared by melting previously determined weights of high purity Ni† and Al† (both 99.998%) in an electric arc furnace under an atmosphere of oxygen free argon. Great

---

*Present address: Department of Metallurgy and Materials Science, Imperial College of Science and Technology, London, SW7 2BP, UK.

†Materials obtained from Koch-Light Laboratories Ltd.

0022–2461/81/123398–07$02.70/0

care was taken during the preparation of these alloys to avoid any contamination with transition metal elements such as iron which can have such a large influence on the magnetic susceptibility [5, 11]. After an initial melt the alloys were inverted and remelted and, after cooling to room temperature, the alloys were then heated to a temperature of 1443 K and held at this temperature for several hours to ensure homogeneity. The alloys were then quenched into a bath of brine at 273 K. All these operations were performed under an atmosphere of oxygen free argon. The quenched alloys were then sectioned into two pieces using a new diamond wheel. One half was retained for metallographic examination, the other half was used to determine the magnetic susceptibility.

2.2. Metallography

The metallographic examination of the quenched specimens showed three main features. Alloys of composition 38 and 37 at % Al were single phase in character and did not show any martensitic-like features. However, needle-like structures, typical of martensite, were observed in both a 36 at % Al and a 34 at % Al alloy whereas a 32 at % Al alloy showed a two-phase structure with colonies of martensite within the grains and precipitates of a second phase, both within the grains and at the grain boundaries.

2.3. Magnetic susceptibility

A magnetic balance based on the Faraday method was used in the measurement of the magnetic susceptibility of these alloys; this apparatus has been described elsewhere [10]. The method of Honda [12] and Owen [13] was used to check for the presence of small amounts of ferromagnetic contaminants. In this method the magnetic susceptibility is measured at several magnetic fields and by extrapolating these values to infinite field a susceptibility for the matrix is obtained. This method is very sensitive and can be used to detect very small amounts of ferromagnetic contaminant.

The magnetic susceptibility as a function of temperature was measured for each alloy. The specimens were initially in the "as-quenched" state and the temperature of measurement was gradually increased. The results of these experiments showed many similar trends, but the 35 at % Al alloy showed an extremely large effect and for this reason we have limited most of our discussion to this alloy.

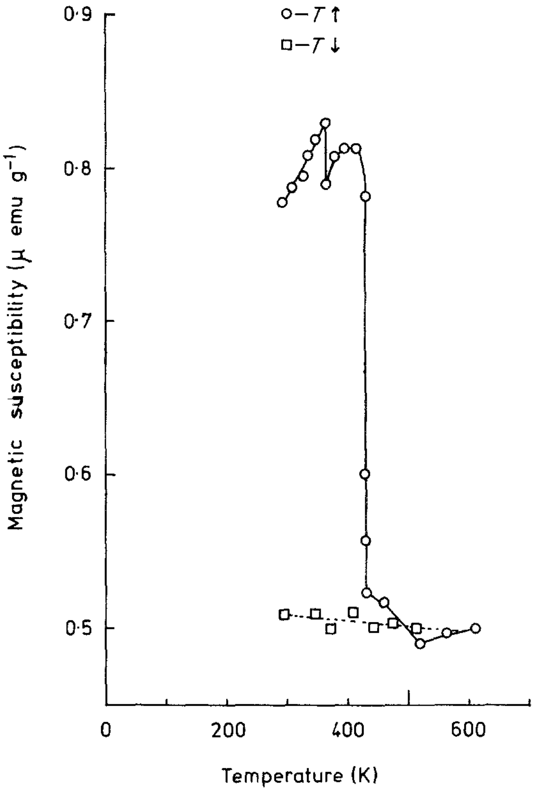

Figure 1 The variation of the magnetic susceptibility with temperature for a 35 at% Al alloy after quenching from 1443 K.

At room temperature it was found that, for most of the alloys including the 35 at % Al alloy, only a small field dependence was observed. As this alloy was heated from room temperature its susceptibility increased with very little change in the field dependence. At a temperature of 365 K the specimen was left for a period of ~ 1 h and following this treatment there was a small drop in the susceptibility coupled with a small weight loss (Fig. 1). As the temperature increased to ~ 430 K, the susceptibility gradually increased until at 430 K the susceptibility became time dependent, decreasing with time. This effect was accompanied by three other changes:

(1) a large specimen weight loss;

(2) an increase in the field dependence of the susceptibility; and

(3) a measurable deterioration of the vacuum in the magnetic balance.

Clearly, the specimen was losing a volatile component which appeared to be changing the susceptibility of the sample. The change in field dependence of this sample over this range of temperature

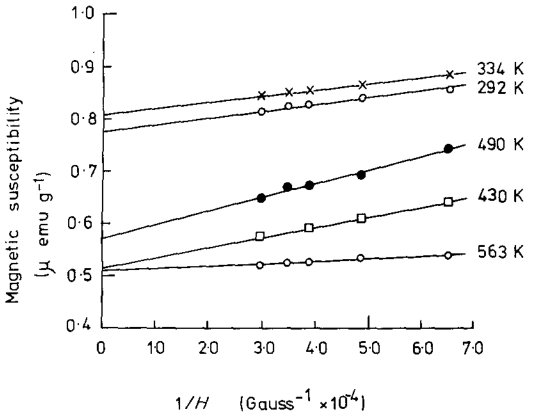

Figure 2 The variation of the field dependence of the susceptibility for the 35 at% Al on heating from room temperature.

is shown in Fig. 2 and the changes in both weight and susceptibility at 430 K are shown in Fig. 3.

The specimen was then heated to ~ 600 K and left to de-gas for 12 h under a high vacuum. At this temperature no field dependence of the susceptibility was apparent but on cooling the sample there was a large increase in the field dependence of the susceptibility, which increased with decreasing temperature, these data are shown in Fig. 4.

In order to verify that these effects were due to the quench from high temperatures into the brine, the experiment was repeated using the same sample and conditions. The susceptibility, weight loss and field dependence data were all reproducible.

In addition to the changes described above, a change in the colour of the sample was also observed. Before the quenching treatment, the sample had a yellow orange colour similar to copper and this changed immediately after quenching to a dull silver colour, similar to the other NiAl samples. The copper colour reappeared after the sample had been heated under vacuum to ~ 650 K.

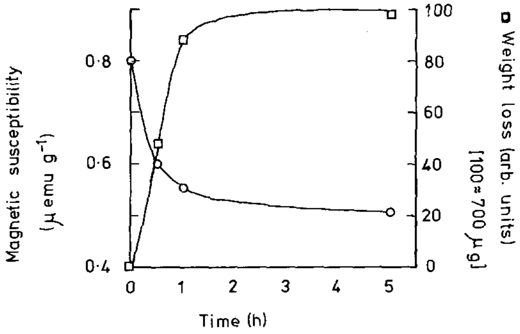

Figure 3 The time dependence of the weight loss (□) and susceptibility (○) for the 35 at% Al alloy at 430 K.

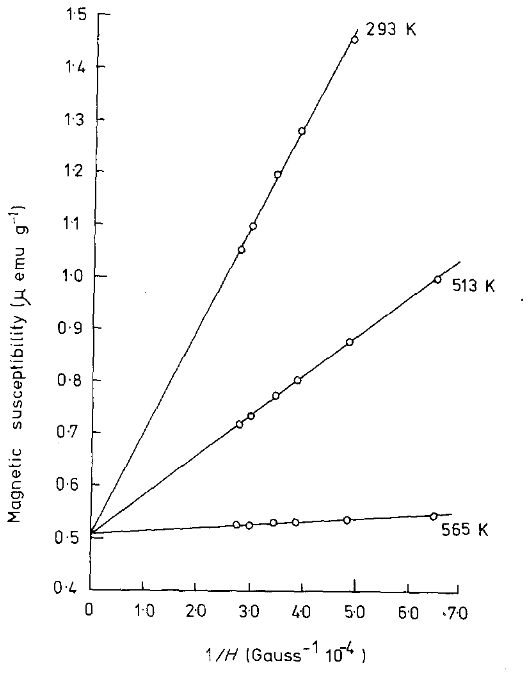

Figure 4 The field dependence of the susceptibility on cooling the 35 at% Al alloy from 650 K.

The effects outlined above were apparent to a lesser extent in many of the other alloys but no changes were seen when a 44 at % Al alloy was quenched under the same conditions.

The large field dependences seen in the alloys could be removed by annealing at temperatures of ~ 1100 K but in some cases this produced a permanent change in the value of the susceptibility which was probably due to the precipitation of another phase (such as Ni_3Al).

3. Discussion

Because of the complexity of the observed phenomena the discussion of the effects of quenching have been divided into four parts:

(1) The proposed nature and origin of the volatile component;

(2) The proposed nature and origin of the ferromagnetic component;

(3) A critical investigation of the mechanisms invoked in (1) and (2);

(4) A discussion of the effects of these two components on the measured susceptibility.

3.1. The proposed nature and origin of the volatile component

The probable volatile contaminants, given the experimental conditions, are O_2, H_2 or H_2O. Of these, hydrogen is the only contaminant likely to have an appreciable solubility in NiAl and to have any effect on the susceptibility. Unfortunately, from the limited experiments performed so far, this component has not been positively identified; however, hydrogen does seem to be the only reasonable candidate. As to the origins of the hydrogen, two mechanisms for its production seem feasible:

(1) a simple chemical reaction between the alloy surface and the water, i.e.

$$2\mathrm{NiAl} + 3\mathrm{H_2O} \rightarrow 2\mathrm{Ni} + 3\mathrm{H_2} + \mathrm{Al_2O_3} \quad (1)$$

or

(2) the catalytic dissociation of water at the surface of the alloy when the alloy is at high temperature, and subsequent dissolution of the hydrogen component into the NiAl at the high temperature.

3.2. The proposed nature and origin of the ferromagnetic component

The nature of this component is a little easier to resolve. In all the experiments the field dependence of the susceptibility became undetectable upon heating the samples to temperatures in the region 600 to 650 K. This reappears on cooling suggesting that the ferromagnetic Curie temperature of the contaminant lies in this temperature range. We therefore propose that this ferromagnetic component is nickel, one of the main components of the alloys, which has a Curie temperature of 631 K. The detailed variation of $C\sigma_s$ (the slope of the Honda–Owen plot) against temperature is shown in Fig. 5 and this indicates a Curie temperature close to that of nickel.

The mechanism for the production of this ferromagnetic nickel is not clear; however, two explanations seem plausible. Firstly there is the direct chemical reaction mechanism discussed previously. This is clearly attractive because it accounts for both the suggested contaminants. Secondly there is the possibility of the formation of large clusters of Ni antistructure atoms, (the intrinsic defect of these compositions), which may attain a sufficient size to achieve ferromagnetism. Thus, we can propose the following mechanism; at high temperatures these antistructure atoms will most likely be arranged at random over the available sites, and this configuration should be frozen into the alloy on quenching. However, when the alloys are subsequently heated these Ni atoms can diffuse together and form clusters, perhaps as the precursor to the formation of a second phase precipitate. Large concentrations of Ni atoms have recently been observed in Ni-rich alloys by Mukerjee *et al.* [14], which consist of extra planes of Ni thought to re-arrange to give a local f c c stacking.

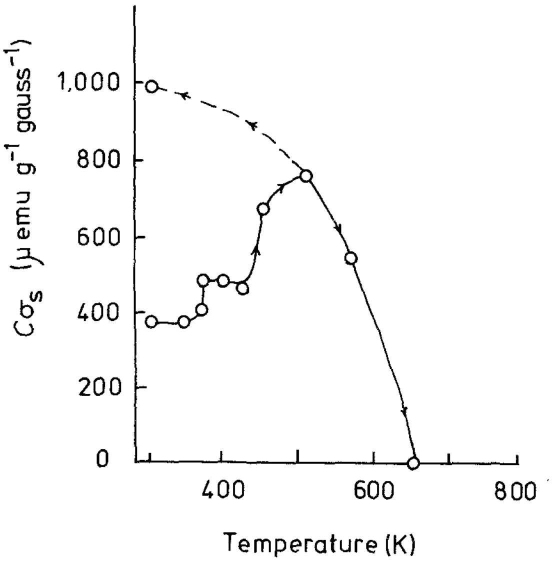

Figure 5 The variation of the slopes ($C\sigma_s$) of the Honda–Owen plots on initially heating and then cooling the quenched 35 at% Al alloy. The arrows indicate heating and cooling.

3.3. A critical investigation of the mechanisms involved in Sections 3.1 and 3.2

Of the mechanisms mentioned above for the production of hydrogen and the ferromagnetic Ni, the most simple is the suggested chemical reaction. To test this hypothesis more thoroughly, susceptibility measurements were carried out on a 38 at% Al alloy, which was quenched from 1443 K into liquid nitrogen. This alloy showed a low field dependence at room temperature and a peak in field dependence at ~ 570 K, similar to the behaviour when quenched in brine. However, none of the phenomena associated with the loss of a volatile component were observed. As in the previous studies, the field dependence on cooling to room temperature was higher than that in the as-quenched state. This would suggest that the production of the ferromagnetic Ni is independent of the hydrogen production. Further evidence to support this hypothesis was obtained on cleaning the surface of the 35 at% Al alloy which exhibited a large field dependence after quenching into brine. Only a slight reduction in the field dependence was apparent suggesting that the ferromagnetic Ni is distributed throughout the bulk, and is not purely a surface layer as might be expected from the proposed chemical reaction.

The evidence therefore favours the suggestion that the two contaminants are produced independently, the hydrogen by the catalytic cracking of water and the ferromagnetic Ni by the diffusion of Ni antistructure atoms.

An analysis of the 293K Honda–Owen plot shown in Fig. 4 indicates a concentration of 1 Ni atom in $\sim 10^5$ giving rise to this effect if it is assumed that the atoms have the saturation moment of pure nickel ($0.6\,\mu_B$).

3.4. The effects of the contaminants on the susceptibility

3.4.1. *Proposed sequence of events*

The proposed sequence of events when the alloys are quenched into an aqueous medium is as follows. At the high temperatures, prior to quenching, the material exists in the CsCl structure with the Ni antistructure atoms distributed at random over the available sites. This randomness is "frozen-in" upon quenching. In addition, upon quenching, hydrogen is produced which dissolves into the lattice at high temperatures and because NiAl is an endothermic absorber the hydrogen is metastably retained in solution at room temperature, perhaps as a result of a low diffusion rate or a surface energy barrier, or a combination of both factors. The dissolved H atoms have the effect of changing the Fermi energy of the host lattice and the nature of this change, i.e. whether it is an increase or a decrease in susceptibility will depend both upon the nature of the dissolved hydrogen and upon the local shape of the electronic density of states curve. We shall assume that the hydrogen forms some solid solution with the lattice and donates its electron to the conduction band.

Thus, as the alloy is heated from room temperature two changes are thought to occur:

(1) Hydrogen is evolved from the material which gives rise to all the "volatile" phenomena observed, and the Pauli contribution to the susceptibility changes, due to a change in the population of the conduction band.

(2) The antistructure nickel atoms diffuse through the lattice and form clusters, some of which are large enough to display ferromagnetism. This leads to the growth of the field dependence.

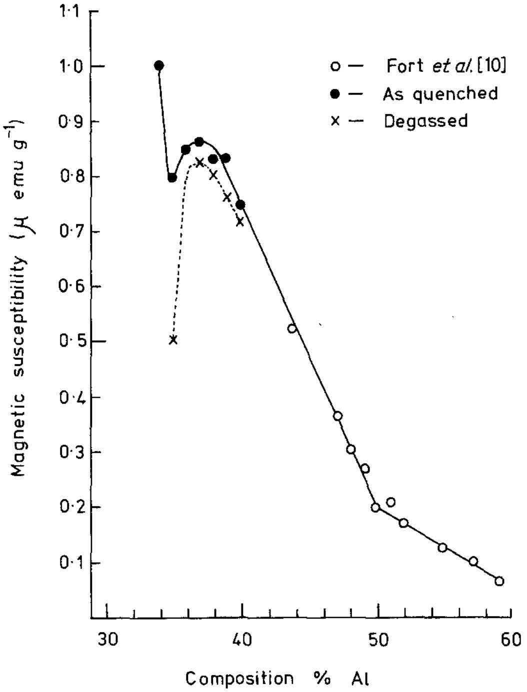

Figure 6 The room temperature composition dependence for alloys in the β'-phase field.

Whether the evolution of hydrogen and the diffusion of nickel are linked by a common mechanism is not apparent from the experimental data; however, the quench into liquid nitrogen would suggest that the two may be independent. The ferromagnetic component is retained on cooling to room temperature but it can be removed, with a consequent permanent change in the susceptibility, suggesting that the clusters are metastable and may perhaps be the precursor of the formation of some second phase such as Ni_3Al or Ni_2Al [15].

3.4.2. *The explanation of the large change of susceptibility in the 35 at% Al alloy*

Fig. 6 shows the room temperature susceptibility against composition curve for the as-quenched and de-gassed alloys including data for the more Al-rich alloys taken from Fort *et al.* [5]. The large effect seen in the 35 at% Al alloy on quenching is shown in this diagram as well as the peak in susceptibility values at a composition of 37 at% Al. This peak is most probably due to a maximum in the Pauli contribution caused by the Fermi energy changing with the composition of the alloys. The reason

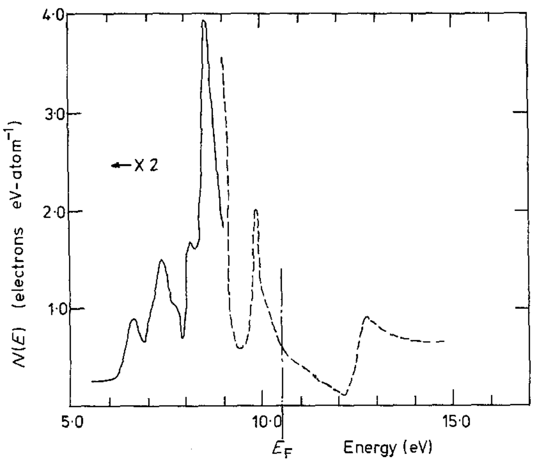

Figure 7 The electronic density of states for NiAl as calculated by Connolly and Johnson [16].

why this should occur is best explained with reference to Fig. 7 which shows the density of electronic states calculated by Connolly and Johnson [16]. There is a small subsidiary peak near to the Fermi energy of stoichiometric NiAl, consequently as the Fermi energy decreases with decreasing Al content the Fermi energy will pass through this peak, provided the behaviour can be approximated to that of a rigid band. The Pauli contribution will mirror this change in the density of states curve, and, provided that the Lamor and Landau contributions only change by a small amount over this limited composition range, the total susceptibility will therefore follow these changes. A similar behaviour has been observed in $(Ni_{1-x}Co_x)Al$ alloys by Prun *et al.* [17] and Begot *et al.* [18]. In these alloys the Co content determines the number of electrons in the conduction band and therefore the position of the Fermi level.

The presence of the subsidiary peak also explains the large difference in the as-quenched and de-gassed values of the susceptibility of the 35 at% Al alloy if it is assumed that the Fermi energy of this alloy lies in the minimum close to the very steep gradient on the low energy side of the peak. Normally the Pauli contribution for this alloy will be rather low but if it is assumed that, when hydrogen is dissolved into the lattice the Fermi energy is increased, then the Fermi level will traverse the steep gradient in the density of states curve thus giving rise to the large change in susceptibility. Clearly, the reverse is true as hydrogen is lost from the lattice. This peak also means that an increased number of electrons can be acommodated in the band for a small rise in Fermi energy which could account for the relatively large solubility of hydrogen for this composition.

This change in the density of states as hydrogen is dissolved into the lattice may also account for the reversible colour changes seen in this work.

4. Conclusions

The changes in magnetic behaviour of these alloys can be explained by two assumptions:

(a) On quenching, hydrogen is formed which dissolved into the NiAl lattice causing a change in the Fermi energy and consequently a change in the magnetic susceptibility.

(b) On heating these alloys, Ni antistructure atoms diffuse to form large clusters, some of which are large enough to be ferromagnetic.

The magnitude of the changes seen in the 35 at% Al alloy and the shape of the room temperature susceptibility against composition curve can be explained by the presence of a subsidiary peak in the density of states curve.

Acknowledgements

We are grateful to G. J. Small for the data on the liquid nitrogen quench.

References

1. J. R. WILLHITE, L. B. WELSH, T. YOSHITOMI and J. O. BRITTAIN, *Solid State Comm.* **13** (1973) 1907.
2. C. L. WILEY, L. B. WELSH, L. H. SCHWARTZ and J. O. BRITTAIN, *Phys. Lett.* **48A** (1974) 474.
3. K. IKEDA, *ibid.* **53A** (1975) 375.
4. D. E. ELLIS, G. A. BENESH and E. BYROM, *J. Appl. Phys.* **49** (1978) 1543.
5. D. FORT, J. A. KILNER and I. R. HARRIS, *Met. Sci. J.* **9** (1975) 305.
6. A. TAYLOR and N. J. DOYLE, *J. Appl. Cryst.* **5** (1972) 201.
7. Y. K. AU and C. M. WAYMAN, *Scripta Met.* **6** (1972) 1209.
8. V. S. LITVINOV, L. P. ZELENIN and R. SHKYLAR, *Fiz. Metal. Metalloved.* **31** (1971) 138.
9. J. L. SMIALEK and R. F. HEHEMANN, *Metall. Trans.* **4** (1973) 1571.
10. D. FORT, R. E. SMALLMAN and I. R. HARRIS, *J. Less-Common Met.* **31** (1972) 263.
11. J. A. KILNER, I. R. HARRIS and G. LONGWORTH, unpublished work (1980).
12. K. HONDA, *Ann. Phys. Lpz.* **32** (1910) 1048.
13. M. OWEN, *ibid.* **37** (1912) 657.
14. D. MUKERJEE, M. H. LORETTO and R. E. SMALLMAN, Proceedings of the 9th International Conference On Electron Microscopy, Toronto, August 1978 (1978) Vol. 1, p. 334.
15. F. REYNAUD, *J. Appl. Cryst.* **9** (1976) 263.
16. J. W. D. CONNOLLY and K. H. JOHNSON, NBS

3rd Materials Research Symposium on Electron Density of States, edited by L. H. Bennet, (National Bureau of Standards, Washington, D.C. 1971) p. 323.
17. A. F. PRUN, V. I. CHECHEMOKOV, V. I. NEDEL'KO, F. A. SIDORENKO and A. P. KOTOV, *Fiz. Metal. Metalloved.* 38 (1974) 431.
18. J. J. BEGOT, R. CAUDRON, P. FAIVRE, A. LASALMONIE and P. COSTA, *J. de Physique* 35 (1974) L-225.

Received 27 April and accepted 20 May 1981.