Journal of Thermal Analysis, Vol. 54 (1998) 803-814

THE EFFECTS OF VARIOUS HEAT TREATING PARAMETERS ON THE HARDNESS AND MICROSTRUCTURES OF THE EXPERIMENTAL 18% NICKEL MARAGING STEELS

I. Pektaş[1] *and H. Atala*[2]

[1]Tübitak, 06100, Kavaklidere, Ankara
[2]Middle East Technical University, Metallurgical Engineering Department, 06531 Ankara
Turkey

(Received April 23, 1997, in revised form February 24, 1998)

Abstract

The effect of the parameters of heat treatment on the experimental 18% maraging steels was studied using hardness tester, optical, scanning electron and transmission electron microscopy and X-ray metallography techniques. The specimens were solution treated at 815, 900, 1000, 1060°C for periods between 1 and 4 h. After air-cooling to room temperature, a bcc martensitic structure was obtained. The higher temperature (1060°C) and longer time (4 h) of the solution treatment caused essentially homogeneous, massive martensitic structure. The aging of the steels was studied between 240 and 480°C from 1 to 41 h. As indicated by the results, the hardness *vs.* aging time curves show a rapid rate of hardening at 480°C while the response at 240 to 320°C is slower. The time required to reach peak hardness increases with decreasing temperature. The increase in hardness during aging can be explained by the precipitation of hardening phases. So, it is necessary to use a high temperature solution treatment to obtain a better alloy distribution and a tough martensitic structure, and an aging treatment at 480 °C between 4 and 10 h to achieve the desired properties.

Keywords: heat treatment, nickel maraging steels

Introduction

Aerospace design requirements are making increasing demands for better performance and greater efficiency in the use of high-strength structural materials. Indeed, the continued development of high-performance aerospace and missile systems require better combinations of high strength with high toughness levels. Because of the high strength and toughness combinations achievable in the maraging steels, these materials have come under intensive study in recent years [1–7]. This is particularly true of the important iron-based, 18% nickel, co-

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

balt, molybdenum alloys, additionally hardened with titanium and aluminium. These alloys have a martensitic structure that is very ductile in annealed condition. After aging of martensite, they can produce a high yield strength; up to 2200 Mpa, reduction of area of 60%, notch-tensile strength/tensile strength ration over 1.4 and Charpy impact resistance up to 26 ft-lb. They require a simple heat treatment and are strengthened by the precipitation of intermetallic compounds at temperatures of about 480°C [1].

The production of high strength and toughness levels requires a closely controlled aging process. The parameters which control the strength level are size, shape and distribution of precipitate particles, as well as the inherent properties of the matrix and of the precipitating phase [8, 9].

The main objectives of this investigation on the experimental 18% Ni maraging steels have been the following:

1) To review the development of commercial, precipitation strengthened iron-nickel maraging alloys.
2) To study the effects of various parameters of heat treatment on the hardness properties and microstructures.
3) To develop maximum response heat treatment cycles for the studied compositions.

Microstructural changes were observed by optical (OM), scanning electron (SEM) and transmission electron (TEM) microscopy. Hardness measurement tests were performed to obtain information about the effect of the various heat treatments on the properties of the steel.

Experimental

Materials

The charge materials used were master pure iron, nickel and cobalt. Molybdenum was supplied from ferro-molybdenum. Pure aluminium and ferro-titanium were then added, respectively. The charge material compositions are given in Table 1.

Preparation of samples

All test materials were 800 g master alloys which were vacuum induction melted under argon atmosphere using magnesia crucibles and cast under vacuum. Analysis of the steels was performed by means of chemical methods and spectral analysis.

Two alloys whose composition are given in Table 2 were investigated.

The alloys were poured at 1580 to 1600°C into dry sand mold under vacuum. The steel ingots produced were cut into four pieces, 40 mm long, by a Buehler abrasimet metal-cutting saw. Their outer surfaces were turned to 10 mm diameter in a lathe, and then heat treatment was applied. After solution treatment, slices 1 mm thick were obtained using a Buehler isomet low speed saw and then these slices were cut into four parts. These specimens were ready for aging treatments.

Table 1 Composition of charge material (% mass)

Charge material	Ni	Co	Mo	Ti	Al	Cu	Si	C	S	P	Fe
Pure iron	–	–	–	–	–	–	–	0.02	–	–	remainder
Cobalt	–	99.6	–	–	–	–	–	–	–	–	–
Nickel	99.9	–	–	–	–	–	–	–	–	–	–
Fe-Mo	–	–	72	–	–	0.43	0.78	0.03	0.05	0.05	remainder
Fe-Ti	–	–	–	40	–	0.12	0.34	0.02	0.03	0.04	remainder
Aluminium	–	–	–	–	99.9	–	–	–	–	–	–

Table 2 Composition of the experimental maraging alloys (% mass)

Element	Ni	Co	Mo	Ti	Al	C	Si	Mn	S	P
Steel A	17.9	9.3	4.20	0.24	0.45*	0.027	0.17*	0.17*	0.030	0.017
Steel B	16.59	10.23	5.09	0.11	0.30*	0.028	0.18*	0.17*	0.035	0.017

*Spectral analysis
Other wet analysis method

Apparatus and procedure

The melting and pouring procedures were performed using a Balzers VSG 02 laboratory vacuum induction furnace with a working volume of max. 170 cm^3 (corresponding to 1.2 kg steel). A Hereaus resistance laboratory furnace with a maximum temperature of 1200°C was employed to austenitize and age the specimens. Solution treatment lasting from 1 to 4 h between 815 and 1060°C was applied to steel A, and for steel B 1060°C/4 h. After air-cooling, maraging was applied in the temperature range 240–480°C between 1 and 24 h (steel A) and between 1 and 41 h (steel B). The metallographic procedures were then applied to the specimens. After cleaning, the specimens were dried, and then fry etchant was applied for 10–20 s to the specimens. The vickers hardness measurements were performed at room temperature under a load of 100 g for 25 s. Separate specimens were used for each point on the hardness curves and the average of ten vickers readings was taken for each point on the curve. Slices with 250 μm thickness were then obtained from the bar samples with 3 mm diameter and these slices were then rolled to 100 μm thickness. After cleaning and drying, jet electropolishing was carried out in a 10:1 mixture of glacial acetic and perchloric acid, in the range 10–25 V d-c. The best condition was 12 V. The electrolytic thinning experiments were performed between 15–20°C and it was necessary to keep this solution well stirred and water cooled to prevent etching. These foils were used for TEM observations.

Result and discussion

Solution treatment time and temperature effect on hardness

The temperature/time parameters of the solution treatment have a pronounced effect on both the air cooled and aged microstructure, and hardness drops slightly for the solution treatment above 1000°C and long times. The microstructure becomes also progressively coarser with increasing temperature and holding time. Since the minimum and maximum temperatures to eliminate the reversion of austenite have been given as approximately 732 and 1093°C by previous investigators [1, 2] and air cooling of maraging steel for temperatures ranging from 815 to 1093°C does not generally result in retained austenite, solution treatment temperatures of 815, 900, 1000 and 1060°C between 1 and 4 h were selected as heat treatment parameters of experimental maraging steels in this study. The experimental maraging steels in the prescribed composition range were tested after being solution treated at temperatures between 815 and 1060°C for 1 to 4 h. Lowering the solution treatment temperature below 1000°C for steel A generally resulted in a lowering of hardness. The effect of solution treatment temperature on the hardness (alloy A) is shown in Figs 1 and 2.

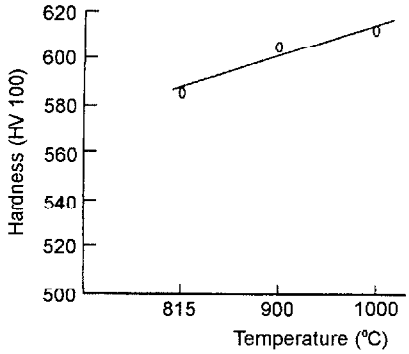

Fig. 1 The effect of solution treatment temperature (1 h) on alloy A subsequently aged 3 h at 480°C

The treatment for 1 h below 1000°C has not completely homogenized the structure. However, for the solution treatment at 1000 and 1060°C/4 h, the microstructure was essentially homogeneous. Figures 3 and 4 show the matrix distribution of the alloying elements in steels solution treated with different heat treatments.

Removal of segregation has a major influence manifested in the higher ductility and toughness of the experimental maraging steels. Although the toughness and tensile tests could not be performed in this study, the results obtained from solution treatment above 1000°C and aging at 480°C were much better than the results obtained from the treatment below 1000°C and aging at 480°C. Further increase in time and temperature of solution treatment resulted in a coarse martensitic structure and lowered the hardness values slightly as compared with the steels solution treated at lower temperatures and for shorter time for the same aging procedure.

In a Fe-18% Nickel steel, bcc martensitic transformation always occurs on cooling, even at very slow cooling rates and the crystallographic structure of

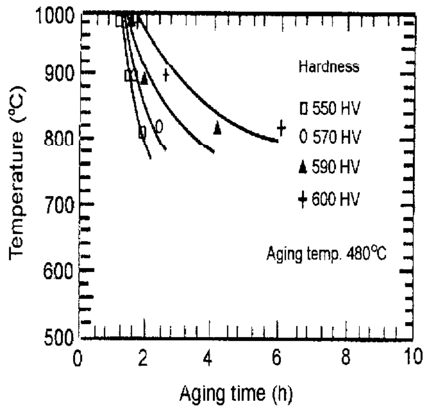

Fig. 2 The effect of solution treatment temperature (1 h) and aging time at 480°C on the hardness for alloy A

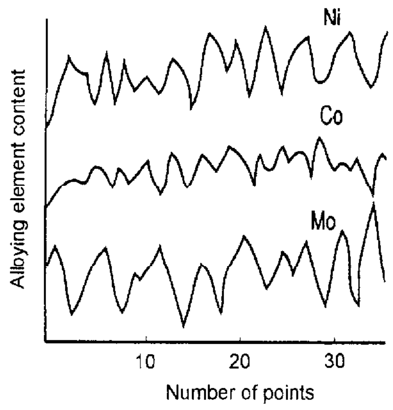

Fig. 3 Element analysis of the specimen solution treated at 815°C/1 h

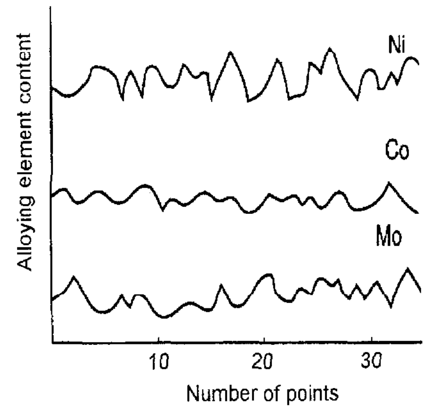

Fig. 4 Element analysis of the specimen solution treated at 1060°C/4 h

iron-nickel martensite is virtually the same as that of iron-nickel ferrite. The principal difference seems to be that the martensitic structure contains a high density of dislocations. In order to obtain a lath bcc martensitic structure, the percentage of nickel ranges between 12 and 20%, cobalt between 8 and 10% and a third element which is responsible for the hardening phenomenon, such as Mo, Ti or W are sufficient [10–12]. In fact, it can also be considered to be a massive type martensite, which is characterized by a high dislocation density and irregular blocky shaped grains having the appearance of ferrite. The higher temperature and longer time of solution treatment reveal the blocky appearance of the structure that is interpreted as massive martensitic transformation. Since the *Ms* temperature is primarily determined by the chemical composition, previous thermal and mechanical history, and increasing grain size raises the *Ms* temperature, a massive transformation will occur at higher transformation temperatures.

Aging responses

The hardening responses of the experimental maraging steels as a function of aging time and temperature are given in Figs 5 and 6. As indicated in Figs 5 and 6, steel A specimens (Fig. 5) were solution treated at 815°C for 1 h and steel B specimens at 1060°C for 4 h (Fig. 6) followed by air cooling. After this procedure, these steels were heated to moderate temperatures, but below the temperature range of rapid reversion to austenite. Their hardness value increased markedly with aging time. So, from a precipitate-free martensitic structure in the unaged condition, the structure changes within several hours to a finely dispersed mass of precipitates over the entire martensitic matrix. It appears that after some hours of aging 50% of the hardness of martensite results from the martensitic structure and 50% from the precipitate hardening produced in the maraging process.

All the steel matrixes display the same general behaviour in that a higher maximum hardness (H_{max}) is attained by an aging treatment at 480°C for short

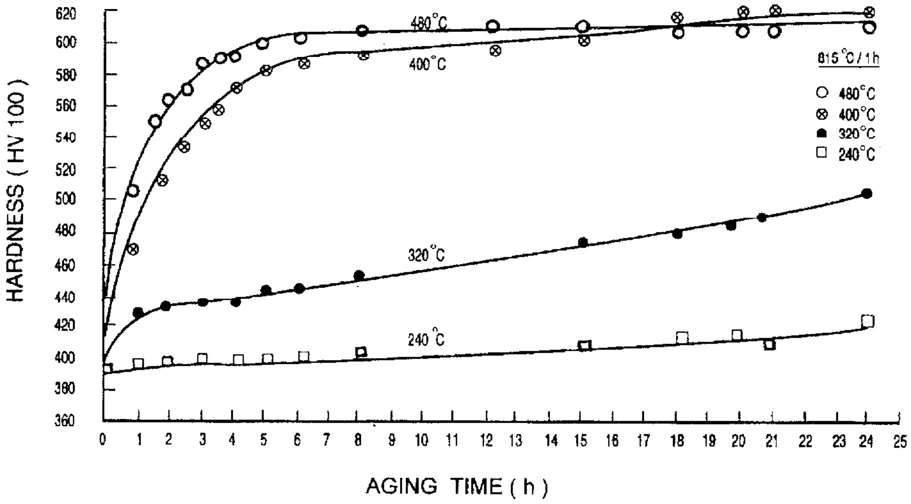

Fig. 5 The effect of aging temperature and time on the hardness of steel A solution treated at 815°C/1 h

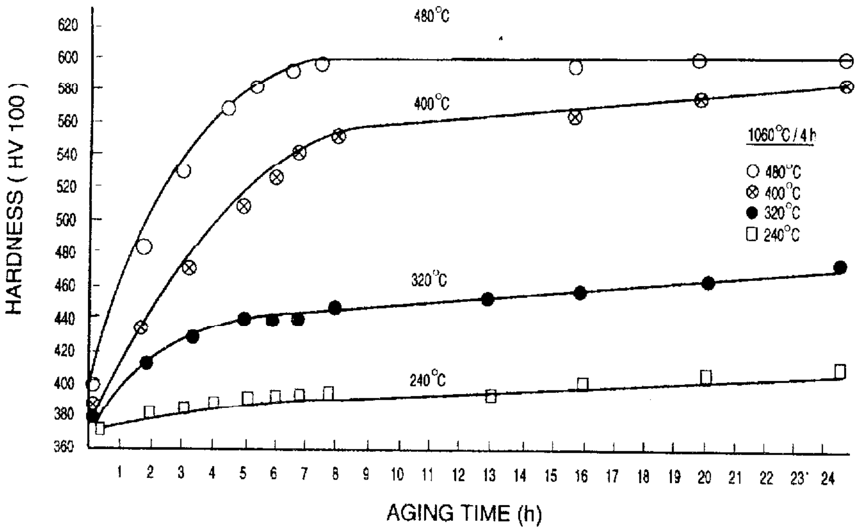

Fig. 6 The effect of aging temperature and time on the hardness of the steel B solution treated at 1060°C/4 h

duration and the time to reach H_{max} is longer at low temperatures (Figs 5 and 6). Analysis of these data indicates that 480°C is the optimum aging temperature and the hardness properties were evaluated at this temperature for various times. The aging of the experimental maraging steels studied here can be controlled by three different processes, as follows:

1) aging of martensite 2) precipitation of intermetallic compounds 3) austenite reversion.

In this study, maraging temperatures were planned as 240, 320, 400 and 480°C, aging times from 1 to 24 and 1 to 41 h were studied. Since the formation of austenite by reversion and coalescence of the particles have been reported by previous investigators at temperatures above 500°C [12, 13], the maximum aging temperature was selected as 480°C to avoid austenite reversion. The effect of maraging temperature and time on the hardness of the specimens shown in Figs 5 and 6 indicate that the optimum hardness response occurs for maraging between 4 and 10 h at 480°C. For practical and economical reasons, an aging treatment at 480°C for 4 h should be preferred. As observed in Figs 5 and 6, the curves show a rapid initial rate of hardening at 480°C, while the hardening response at 240 and 320°C is slower. As the hardness value of the air-cooled alloys was approximately 390 vickers, it has risen to 560–580 vickers and then gradually increased to 600 vickers over a total time period of 24 h at 480°C aging temperature. It is

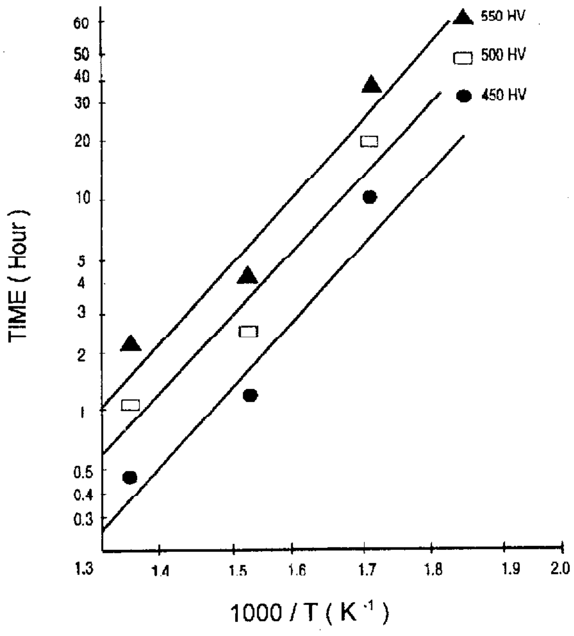

Fig. 7 Time to reach various hardness levels *vs.* reciprocal maraging temperature for steel A solution treated at 815°C/1 h

also observed that the time required to reach maximum hardness increases with decreasing temperature. In Fig. 7 is shown the time to reach various hardness levels *vs.* the reciprocal maraging temperature for the specimens initially heat treated at 815°C. At aging temperatures lower than 480°C, little change occurs in the hardness unless the aging time is very extended. The high hardening rate of 18% Ni maraging steels at 480°C aging temperature can be associated with an increase in the rate of diffusion in the bcc martensite structure with an elevated dislocation density. However, in the martensite structure the rate of aging and increase of the hardness may also be driven by the supersaturation of the solid solution.

The increase in hardness of the steels with increasing aging temperature, suggests that the diffusion process is complex and involves the movement of several different solute elements at the same time. This complex behaviour comes from a combination of precipitation processes. The hardening response at the given aging temperatures is also conditioned by the presence of excess vacancies remaining in the martensite after transformation that will tend to associate with the solute atoms present [13, 14]. The vacancy controlled diffusion of the substitutional alloying elements is thought to be responsible for the hardening behaviour of the experimental maraging steel in this study. During the study, all microsctructures were observed by using metallographic techniques. Since the microstructure has a major importance in the control of the properties of all materials, it is necessary to identify and control the microstructure to obtain the desired properties. Therefore, metallographic studies were an important part of the microstructure examinations for identification of phases, their amounts and effects in this investigation. All microstructural studies were performed on the specimens solution treated at 815, 900 and 1000°C for 1 h and 1000°C for 4 h. The martensitic structures are slightly different from their as-aircooled structure due to the aging of martensite and the precipitates. Figure 8 shows a relatively uniform distribution of dislocations which are nucleation sites for further stages.

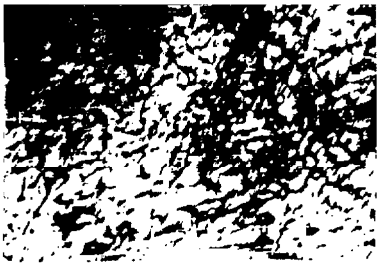

Fig. 8 The micrograph of the specimen solution treated at 1000°C/4 h and aged 1 h at 480°C

Figures 9 and 10 show the diffraction pattern with the zone axis $[1, 3, \bar{5}]$ for the steel solution treated at 900°C and aged 3 h at 480°C. Here, weak spots come

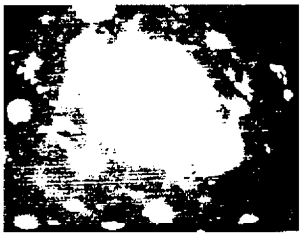

Fig. 9 Diffraction pattern of the steel solution treated at 900°C and aged 3 h at 480°C

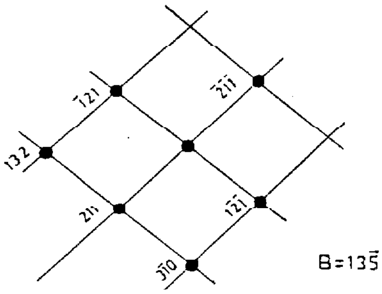

Fig. 10 Same diffraction pattern

from the precipitates and the lines observed are arising from a strain between matrix and precipitates. The precipitate particles of two different morphologies seen in the dark field micrographs were also widely observed by previous investigators [12]. The relatively uniform distribution of spherical particles is attributed to homogeneous nucleation whereas the occurrence of the rod/plate like particles in an arrangement similar to that of the initial dislocation structure suggest a dislocation-nucleated precipitation. However, in this work it has not been possible to verify this point, although the precipitates observed were very similar to those observed in the literature [12, 14]. The dark field micrograph (Fig. 11) corresponding to the reflections shows that the needle-shaped particles approximately 100 Å long are quite visible. The uniform arrangement of these particles suggests that they are coherent.

Peak hardness was attained in steel A after aging for 14 h and in steel B after aging 8 h at 480°C. In comparing the martensitic structures of the steel A aged between 1 and 30 h, it is apparent that some visible differences in martensite plates exist to account for the measured difference in their hardness, since the duration of aging affects the martensite plates and precipitates present. After a 34 h aging treatment, the hardness begins to drop. This can be explained as overaging suggesting that it is due to austenite reversion. The microstructural examinations which were conducted on the steel solution treated at 1060°C for 4 h and air-cooled, indicate massive type martensite. Peak hardness was attained in this

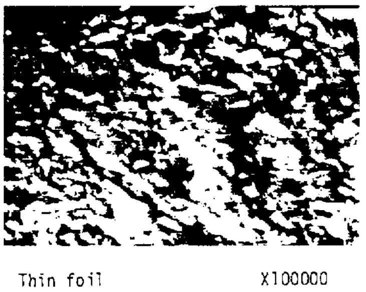

Fig. 11 Dark field micrograph of the steel shown in Fig. 9

steel after aging for 8 h at 480°C and little change in hardness occurred upon aging beyond 8 h. So, all the optical, electron microscopy and microhardness results obtained for the experimental maraging steels indicate that aging of the martensitic matrix and precipitation hardening occur simultaneously during aging. The hardness of the specimen aged at 480°C decreased slightly after 34 h. Austenite reversion is thought to be responsible for this softening. Consequently, in order to obtain a good steel having optimum mechanical properties, the best heat treatment parameters should be selected. Since aerospace applications need high strength steels with high toughness and segregation has a major influence manifested in the higher ductility and toughness, it is desirable to subject the experimental maraging steel to a high temperature solution treatment to reduce alloy segregation and to obtain a more uniform response to subsequent aging treatment providing optimum mechanical properties.

Conclusions

1) It is necessary to subject the experimental maraging steel to a high-temperature solution treatment by homogenizing above 1000°C and 4 h in order to reduce alloy segregation and obtain the desired optimum properties.

2) The microstructure of the steels consists of bcc martensite and the major source of hardening that occurs during aging can be explained by the precipitation of fine hardening phases.

3) The rate of hardening at 480°C is rapid, while the response at 240 and 320°C is very slow. The reason may be an increase in the rate of diffusion in the bcc martensitic structure at an aging temperature of 480°C.

4) During aging, the time required to reach peak hardness increases with decreasing temperature.

5) The optimum response occurs between 4 and 10 h at 480°C aging temperature and the best industrial heat treatment procedure is obtained by the aging of martensitic structure at 480°C for 4 h.

References

1 S. Floreen and R. F. Decker, Trans. ASM, 55 (1962) 518.

2 A. M. Hall and C. J. Slunder, 'The Metallurgy, Behavior and Application of the 18% Ni Maraging Steels', Battelle Memorial Institute to NASA, Washington, D. C.

3 R. F. Decker, J. T. Eash and A. J. Goldman, ASM Trans. Quart., 55 (1962) 58.

4 Pean Yu-Chen, Han Yao-Wen, Wu Cheng-Xu and Zhau Zhi Cheng, Intern. Conf. on Vacuum Metallurgy: Spec. Meltings and Metall. Coatings, Vol. 2, Tokyo, Japan 1982.

5 C. J. Novak and L. M. Diran, Jour. Metals, (1963) 200.

6 J. E. Brokleff and C. S. Kortovich, Trans. American Foundrymen's Soc., 74 (1966) 617.

7 C. Servant, P. Lacombe and M. Griveau, J. Mat. Sci., 15 (1980) 859.

8 G. S. Ansell, Metallurgy Soc. Conf. AIME 28 (1963) 231.

9 J. W. Martin, Micromechanism in Particle-Hardened Alloys, Cambridge University Press, Cambridge 1980, p. 12.

10 E. P. Sadowski and R. F. Decker, Modern Casting, 43 (1963) 26.

11 B. Francis, Metall. Transactions A, 7A (1976) 465.

12 A. F. Edneral and M. D. Perkas, Metal. i Term. Obrabotha Metal., 4 (1960) 18.

13 L. V. Arapova, S. S. Ryzhak and E. S. Kagan, Metal. i Term. Obrabotha Metal., 10 (1972) 15.

14 M. A. Kablukovskaya and B. M. Mogutnov, Fiz. Metal. Metalloved., 35 (1973) 791.