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Effects of Solution Heat Treatment on the Microstructure, Oxidation, and Mechanical Properties of a Cast Ni_3Al-Based intermetallic Alloy

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Solution heat treatment is employed in an attempt to improve oxidation and mechanical properties of an as-cast Ni_3Al alloy (IC221M) at operation temperature, 900 °C. Solution heat treatment was hypothesized to have beneficial effects through dissolving $\gamma + Ni_5Zr$ eutectic into the matrix. The microstructures, oxidation behavior in air at 900 °C, and mechanical properties with aging times at 900 °C were examined after solution heat treatment of as-cast Ni_3Al alloy in Ar for up to 100 h at 1100 °C. The oxide penetration depth into the matrix was dramatically decreased and more homogeneous surface oxides were obtained relative to the no solution treatment case. Hardness was improved by solution heat treatment due to a solid solution strengthening effect by Zr, but the tensile properties after solution heat treatment were not significantly different from those prior to treatment.

Keywords: intermetallic alloys, casting, solution heat treatment, oxidation, mechanical properties

1. INTRODUCTION

For the last several decades, intermetallic alloys have been intensively studied for commercialization since they are among the most promising materials for structural use at high temperatures [1]. In order to commercialize these alloys, particularly for structural application, castability and weldability are crucial factors as well as high strength both at room and elevated temperatures. Ni_3Al based intermetallic alloys such as the IC-series of alloys developed at Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA) have been successfully developed for this purpose. The alloy IC221M provides a good combination of strength, ductility, castability, and weldability properties. This alloy is presently used in transfer rolls for steel austenitizing furnaces at a major US steel producer.

Recently, we documented how the microstructures, oxidation, and mechanical properties of as-cast IC221M are influenced at an operation temperature of this alloy [2-4]. In particular, we found that the $\gamma + Ni_5Zr$ eutectic constituents formed during the casting process have a negative effect on properties such as the preferred oxidation path, crack propagation path, etc. The $\gamma + Ni_5Zr$ eutectic constituents do, however, offer many advantages to fabricate excellent intermetallics, including reduction of solidification cracking and enhancement of welding properties [5]. It was hereupon hypothesized that if the $\gamma + Ni_5Zr$ eutectic constituents of as-cast IC221M alloy were dissolved by solution heat treatment some of drawbacks of this alloy could feasibly be removed.

In general, heat treatment of intermetallic alloys is employed for modifying properties such as strengthening by precipitation and/or solid solution, improving creep properties, corrosion resistance, etc. Solution heat treatment is a means to enter the constituents into solid solution by cooling rapidly enough to hold these constituents in solution [6]. Mechanical properties, especially ductility, are sensitive to the heat treatment process [7]. In the present study, a solution treating temperature of 1100 °C was chosen to reduce the volume fraction of the $\gamma + Ni_5Zr$ eutectic colonies by re-dissolution without melting the colonies. The melting temperature of the $\gamma + Ni_5Zr$ eutectic colonies is 1170 °C. The volume fraction of the $\gamma + Ni_5Zr$ eutectic colonies drops from the as-cast value 6.5 vol.% to less than 0.5 vol.% after 100 h solution treatment at 1100 °C [4]. Therefore, 100 h was chosen as the period of solution heat treatment.

2. EXPERIMENTAL PROCEDURE

For examination of the solution heat treatment (ST) effects of the commercialized Ni_3Al alloy IC221M in terms of its oxidation and mechanical properties at 900 °C (an operation temperature of a heat-treating furnace with transfer rolls fabricated by IC221M), materials cut from the casting ring were capsulated in a quartz tube. The tube was filled with inert Ar gas so as to avoid oxidation, and then the specimen was solution treated for up to 100 h at 1100 °C. The solution heat

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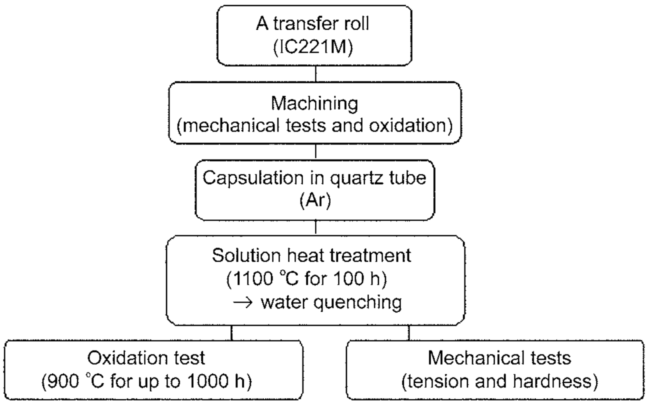

Fig. 1. A flow chart of procedures of solution heat treatment and mechanical tests.

treated specimen was then water quenched. Following solution heat treatment, isothermal oxidation behavior was studied in still air at 900 °C for up to 1000 h. The oxides were observed by optical microscopy and a scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. Elemental maps of the oxidized specimens after solution treatment were extracted from EDX spectrum images using an EMiSPEC Vision system, and compositionally distinct features were determined from the EDX spectrum images using a multivariate statistical analysis (MSA). The detailed procedure of analyzing elemental maps is described elsewhere [2,4]. Mechanical properties of the solution treated specimens were examined by tensile testing and hardness testing (Vickers indentation with a 300 g load) and compared with the properties of the as-cast material. Tensile specimens machined to a thin flat dog-bone shape were aged in Ar for 1000 h at 900 °C, and then tested at various temperatures up to 1100 °C in air. The procedures of the solution treatment and mechanical testing are summarized in Fig. 1. The fracture surface was examined using a scanning electron microscopy equipped with EDX.

3. RESULTS AND DISCUSSION

3.1. Microstructure and oxidation

The as-cast microstructures and thermal aging effects at 900 °C (operation temperature of IC221M at industries) on a castable intermetallic alloy, IC221M, have been studied in earlier works [2-4,8,9]. The major phases in IC221M are an *L1₂* ordered Ni_3Al γ' phase, a Ni solid solution γ phase, and an intermetallic phase based on Ni_5Zr forming $\gamma' + Ni_5Zr$ eutectic colonies. The matrix is a $\gamma' + \gamma$ mixture that is predominantly γ' at room temperature (85-95 vol.%). In the as-cast condition, $\gamma + Ni_5Zr$ eutectic comprises about 6.5 vol.% of the microstructure and is segregated interdendritically (a vertical arrow in Fig. 2(a). Figures 2(b) and (c) show that the microstructural changes at 1100 °C chosen to push the material to the limits of its possible application due to the lower melting $\gamma + Ni_5Zr$ eutectic (T_m = 1170 °C) are essentially the same as those at 900 °C. However, homogenization of the microstructure [2,10,11] is much faster: for instance, the coarse cellular structure (indicated by a horizontal arrow in Fig. 2(a)) in the interdendritic regions is dramatically diminished and the eutectic colonies are spherodized to a single phase (Ni_5Zr) in 100 h (indicated by a vertical arrow in Fig. 2(b)). Thermal aging at 1100 °C dramatically decreased the volume fraction of the $\gamma + Ni_5Zr$ eutectic to below 0.5 vol.% within the first 100 h. It is assumed that the $\gamma + Ni_5Zr$ eutectic colonies dissolved into the matrix and the remnant eutectic

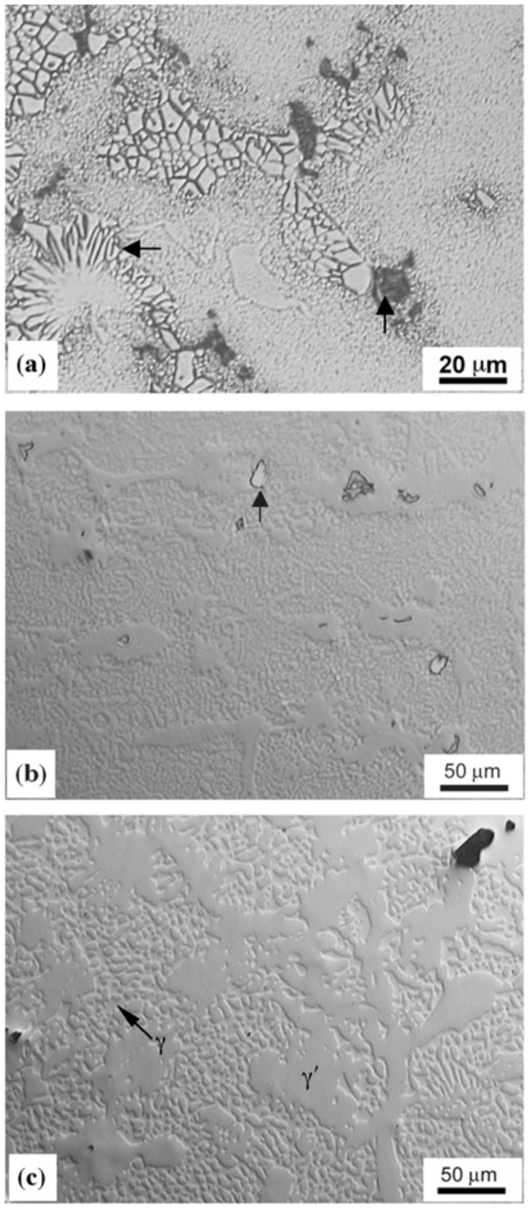

Fig. 2. Optical micrographs of the microstructural changes during solution heat treatment at 1100 °C: (a) as-cast, (b) 100 h, and (c) 1000 h.

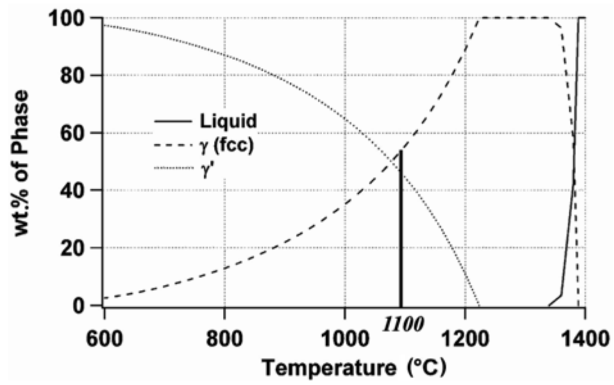

Fig. 3. Temperature dependence of the relative equilibrium volume fractions of γ and γ′ predicted by thermodynamic simulation, Thermo-Calc^{TM}.

represents the solubility of Zr in the IC221M system. Thermodynamic predictions estimated that the equilibrium amount of γ′ at 1100 °C is approximately 46 %, as shown in Fig. 3. Based on this information, it is presumed that the microstructure evolved such that most of the γ + Ni_5Zr eutectic dissolved into the matrix. Furthermore, it is assumed that the γ′ phase in matrix with aging at 1100 °C is no longer the dominant phase, and γ and γ′ phases might be coarsened by heat treatment at 1100 °C, as indicated in Fig. 2(c) [4,10]. Consequently, four primary changes in the microstructures after solution heat treatment at 1100 °C were observed: (1) there is considerable homogenization of the cast microstructures with aging; (2) the volume fraction of γ phase is slightly higher than γ′ phase; (3) the γ and γ′ phases coarsen; and (4) the γ + Ni_5Zr eutectic colonies is almost eliminated.

The results of the solution heat treatment effects on the oxidation behavior of IC221M in air at 900 °C are shown in Figs. 4 to 5. The cross-sectional observations of oxidized specimens by optical and scanning electron microscopy are shown in Fig. 4. Figures 4(b) and (d) show, respectively, representative optical and SEM micrographs of the surface oxides of solution heat treated specimens in terms of cross-sectional features. For comparison of oxidation behavior before and after solution heat treatment, micrographs of the surface oxides of an untreated alloy are also presented in Figs. 4(a) and (c), respectively. The representative oxide features of solution treated specimens are distinctively different from those of the untreated specimen. In particular, the spike-like oxides (indicated by arrows) are absent and hence there is no deep penetration of the oxide into the matrix. Note that because of the absence of the deep spike-like oxides, the surface oxide is relatively uniform in appearance and thickness. Another important result is that the NiO nodules that form immediately above the γ + Ni_5Zr eutectic col-

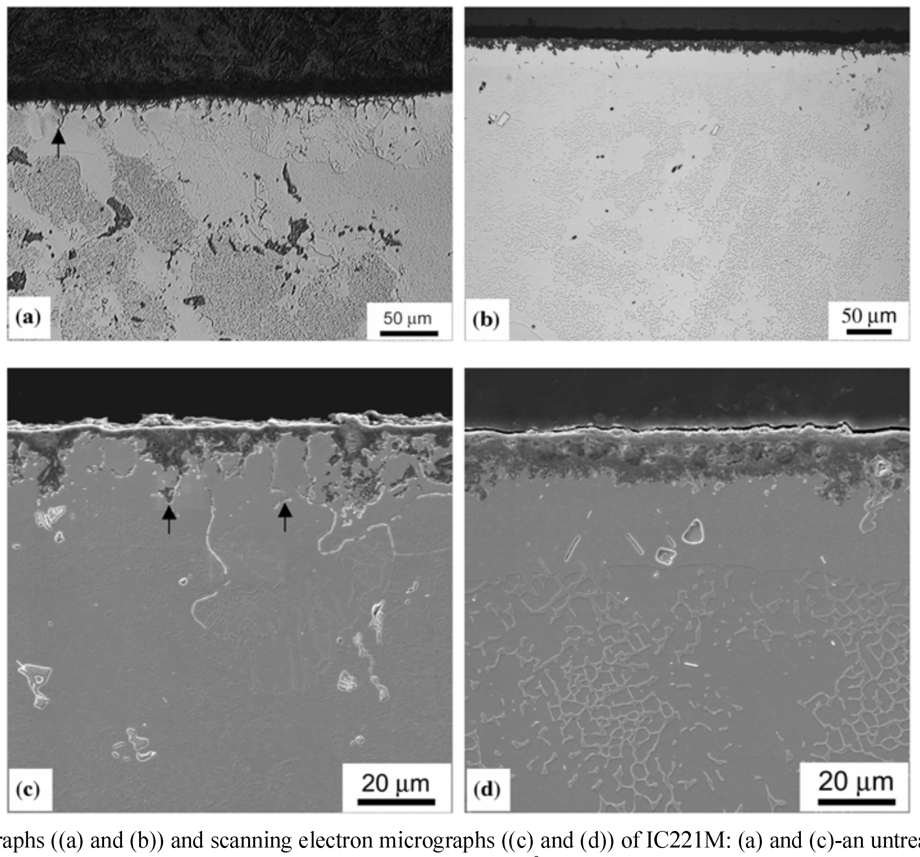

Fig. 4. Optical micrographs ((a) and (b)) and scanning electron micrographs ((c) and (d)) of IC221M: (a) and (c)-an untreated specimen aged in air at 900 °C for 1000 h for comparison; (b) and (d)-solution treated at 1100 °C for 100 h, and then aged in air at 900 °C for 1000 h.

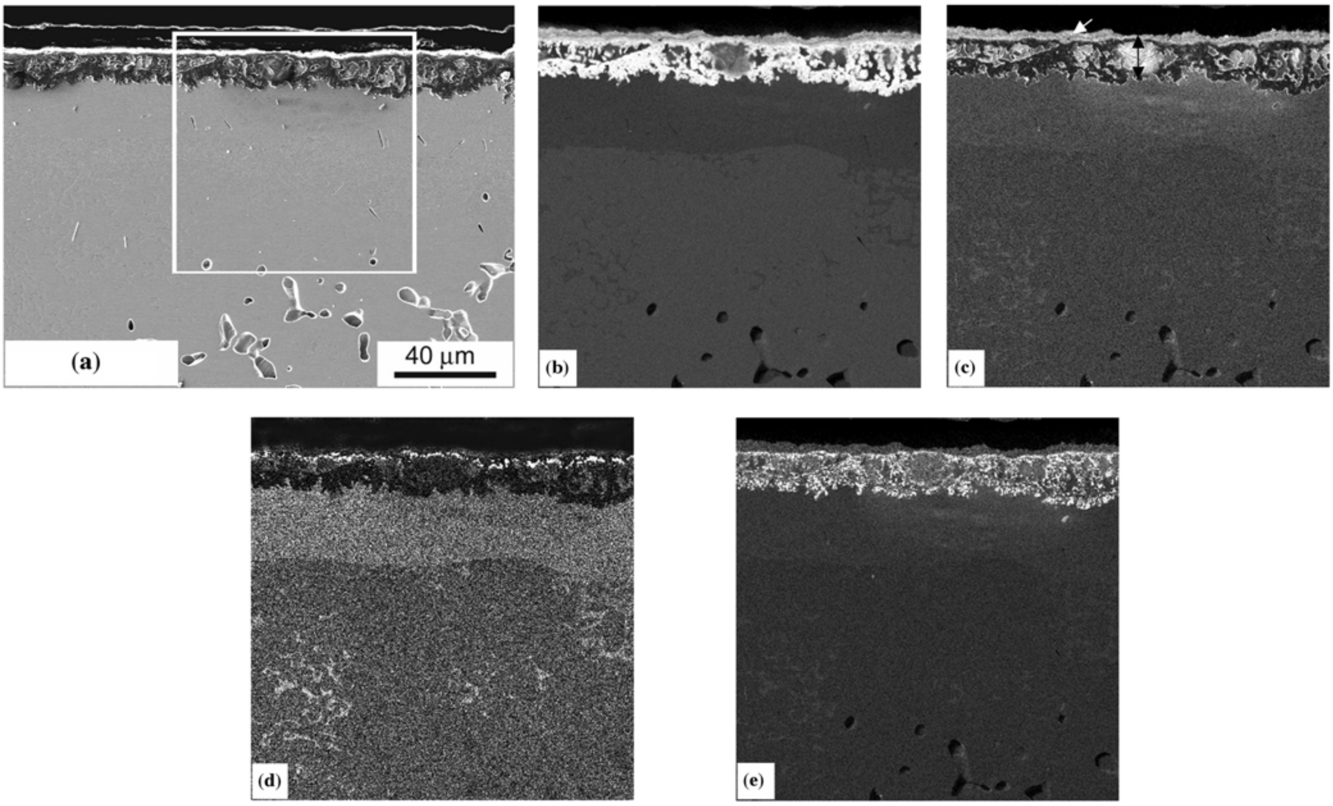

Fig. 5. EDX spectral imaging maps of oxide distribution in cross-section of a specimen solution treated and then aged at 900 °C: (a) secondary electron (SE) image, (b) Al_2O_3, (c) $NiO/NiAl_2O_4$, (d) $Cr_2O_3/NiCr_2O_4$, and (e) ZrO_2.

onies in untreated specimen are considerably reduced after solution heat treatment. Presumably, this is due to homogenization of microstructure, which considerably reduces the source of the Ni cation diffusion path (discussed later). The X-ray oxide phase images presented in Fig. 5 show that Al_2O_3 is formed throughout the oxide, but the outermost layer of the oxide is composed of a mixture of Al, Ni, and O. This might be a $NiAl_2O_4$ spinel mixture with a small amount of NiO (see Fig. 5(c)). It should be emphasized that NiO in the surface may be an undesirable oxide under a certain atmosphere, e.g. a carburizing atmosphere [12], even though resistance to carburization of IC221M competes with the most commonly used HU alloy [13]. A chromium oxide, possibly Cr_2O_3 and/or $NiCr_2O_4$ spinel, forms beneath the outermost layer. Interestingly, zirconium oxide, ZrO_2, is restricted in the surface scale instead of forming deep spike-like oxides. This result shows that solution heat treatment yields not only remaining keying effects of ZrO_2 [9], but also reduces the preferred crack propagation path [4]. Thus, the solution treatment appears to have beneficial effects on the oxidation of as-cast IC221M. Figure 6 shows a graph comparing the oxidation rate at 900 °C of the solution treated material to that of the as received material. The white arrow in Fig. 5(c) indicates the continuous oxide and the black

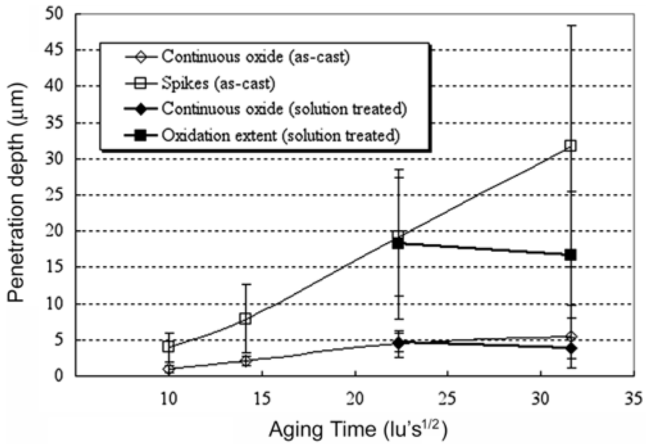

Fig. 6. A plot of variation of oxide penetration depth at 900 °C with respect to the square root of aging time comparing the oxide penetration depth with aging time between before and after solution heat treatment of IC221M.

arrow shows the extent of oxidation (the thickness of the oxide from top to bottom). As can be seen in the graph, while the spike-like oxides of the untreated specimen penetrate (open square) deeply and continue to penetrate with aging time, growth of the oxide in the solution treated specimen (closed square) slows as aging proceeds. Solution treating thus retards the oxidation process.

In earlier works [2,3,8], the possible oxides based on free energies of formation predicted by Thermo-Calc^{TM} calculations show ZrO_2 is the most stable oxide and NiO is the least stable oxide in this system. Five other oxides, Al_2O_3, Cr_2O_3, $NiAl_2O_4$, $NiCr_2O_4$, and MoO_2, are also predicted. The oxidation behavior of as-cast IC221M in air at 900 °C has been schematically described in an earlier work [3]. For short oxida-tion periods at 900 °C, oxides form in a manner that follows the microsegregation patterns in the cast-microstructure. Since the γ + Ni_5Zr eutectic acts a fast diffusion path, oxygen anions diffuse quickly into the eutectic colonies, and ZrO_2, the most stable oxide in the system, forms internally. During this process, nickel cations are rejected and diffuse to the surface through the eutectic to form surface NiO nodules, which subsequently react with aluminum oxide and aluminum in the matrix to form $NiAl_2O_4$. Therefore, upon solution heat treatment, because γ + Ni_5Zr eutectic colonies almost vanish due to dissolution into the matrix, significantly different oxidation behavior was observed, e.g. the absence of deep spike-like oxides and significant reduction of NiO nodules, indicating improved oxidation. However, although it appears that the effects of solution treatment on oxidation of IC221M may be beneficial, further study is required to determine how well the surface oxide protects the base alloy in an atmosphere similar to that employed for commercial applications. For this purpose, cyclic oxidation tests need to be performed to determine whether the oxide scale is adherent.

3.2. Mechanical properties

In general, solution heat treatment can improve mechanical properties by reducing phases that initiate crack propagation [14]. In an earlier work [4], we found that the γ + Ni_5Zr eutectic colonies act as a preferred crack propagation path. Therefore, reduction of the γ + Ni_5Zr eutectic colonies, one of the most significant changes in microstructure of as-cast alloy by solution heat treatment, may improve the mechanical properties of as-cast IC221M as well.

Tensile test results for the solution treated specimens are shown in Fig. 7. For comparison, the results of as-cast material and specimens aged in Ar at 900 °C for 1000 h are also presented. Figure 7(a) shows the variation of yield strength with testing temperature. The yield strength of the as-cast material increases to a peak of about 650 MPa at a temperature in the 600-800 °C range. This is consistent with previous research [15,16] on this material and illustrates the anomalous yield strength increase. Above 900 °C, the yield strength drops dramatically due to the change of dislocation from immobile to mobile by enhanced thermal activation [17]. As can be seen in Fig. 7, the behavior of tension tests of the specimens aged in Ar at 900 °C and the solution treated specimens are generally similar to that of the as-cast alloy with

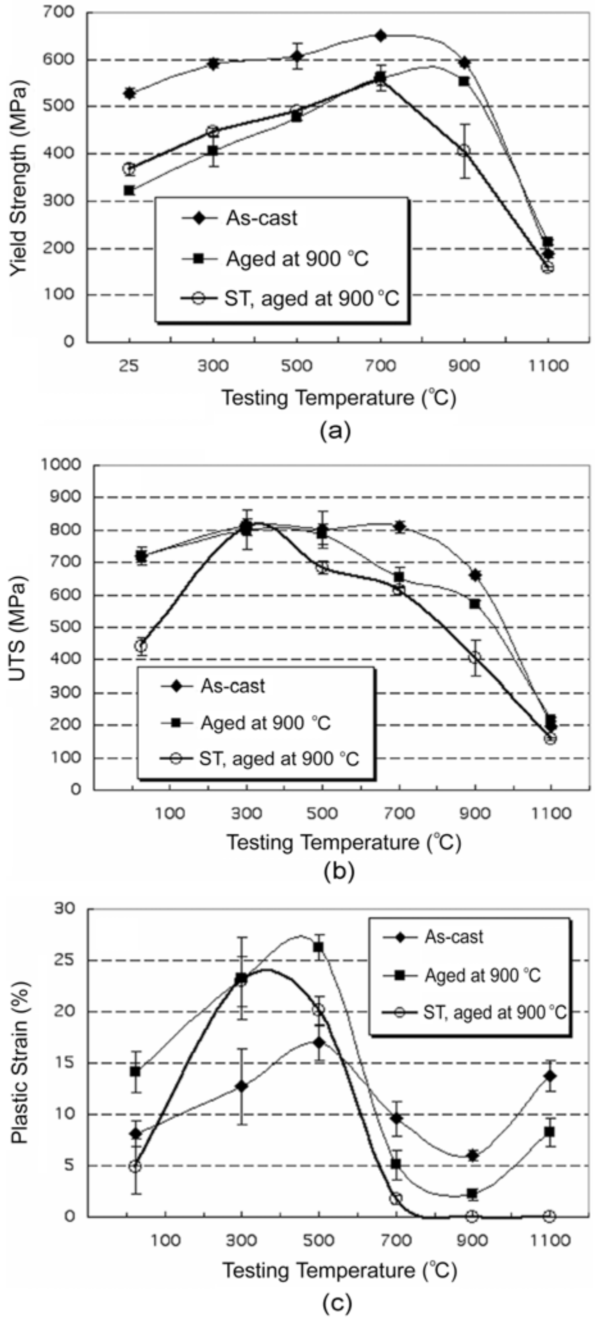

Fig. 7. Variation of tensile properties with testing temperature of as-cast and solution treated IC221M: (a) yield strength, (b) ultimate tensile strength, and (c) plastic strain.

the exception of lower yield strength. In a previous study, we provided detailed descriptions of tensile properties of IC221M with various conditions: aging time, temperature, and atmosphere [4]. The yield strength of a solution treated specimen is intermediate to the as-cast and 900 °C aged specimens up to a testing temperature of 700 °C, at which there is a decrease in strength. Figures 7(b) and (c) show the ultimate tensile strength (UTS) and plastic strain, respectively. While the UTS for as-cast and specimens aged at 900 °C is nearly the same for the tests at room temperature (RT) to 500 °C, the UTS for solution heat treated specimens, especially those tested at RT, is lower than the other two conditions. The tensile strength of the solution treated specimen peaks at 300 °C, and then gradually decreases. The decrease of the materials strength corresponds to lower ductility; see Fig. 7(c). The elongation of the solution heat treated specimen drops noticeably at testing temperatures above 500 °C and then shows brittle fracture, which is presumably related to oxygen induced environmental embrittlement. It is not understood why the solution treated specimen is more sensitive to oxygen induced embrittlement than other conditions. One possibility is that because the $\gamma + Ni_5Zr$ eutectic colonies are mostly dissolved into the base alloy due to solution treatment at 1100 °C, the Zr concentration in the matrix may influence the embrittlement of the specimen. Figure 8 shows intergranular brittle fracture of the solution treated specimen tested at 700 °C. White arrows in Fig. 8(b), an enlarged micrograph of a square in Fig. 8(a), indicate the remnants of $\gamma + Ni_5Zr$ eutectic colonies after solution heat treatment. These colonies segregate in the grain boundary as a single phase and may act a crack nucleation site.

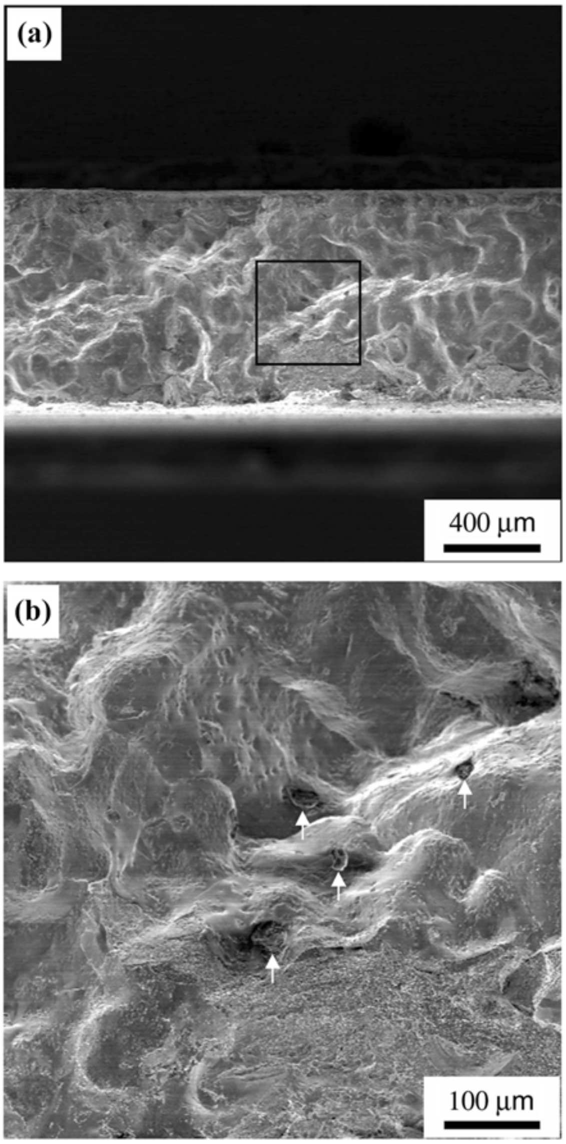

Fig. 8. SEM micrographs of solution treated IC221M tested in air at 700 °C: (a) lower magnification - revealing intergranular fracture, (b) an enlarged micrograph of (a) - arrows indicate a single phase of Ni_5Zr, which may act crack initiation sites.

It is not fully understood how Zr addition affects the ductility of intermetallic alloys. Some previous studies show improvement of ductility [18-19] while some note disadvantages [20]. Gu *et al.* [21] states that a limited amount of zirconium in the alloys can improve the ductility, but zirconium content over the critical amount can also lead to embrittlement [21]. In this study, redistribution of Zr in the matrix does not improve the ductility of this alloy. Presumably, oxygen induced embrittlement and the remnant of $\gamma + Ni_5Zr$ eutectic colonies as a single phase in grain boundaries acting as a crack initiation site are co-related to the low ductility at higher temperatures. Collectively, at lower temperatures (< 700 °C), the tensile properties of the solution treated specimens are competitive with the as-cast material aged at 900 °C, but the degradation of the tensile properties of the solution treated material is faster at higher temperatures.

Figure 9 shows the variation of the Vickers microhardness (Hv) of solution heat treated as-cast IC221M at 1100 °C for up to 100 h followed by aging in air at 900 °C for up to 1000 h. For comparison, the microhardness of the untreated materials aged at 900 °C (closed triangle) is also presented. The microhardness of the solution treated specimen drops slightly with aging time but remains significantly higher than that of the untreated specimens. This result is probably produced by

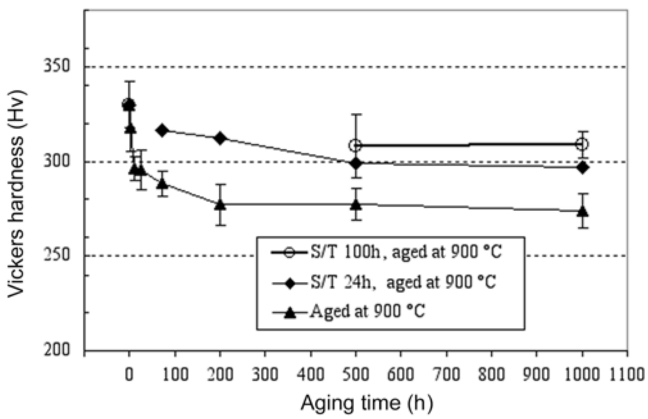

Fig. 9. Variation of microhardness of the solution treated alloy with aging time at 900 °C (solid diamond and open circle). Microhardness data of untreated alloy with aging time at 900 °C are also presented for comparison (solid triangle).

a Zr solid solution strengthening effect due to re-dissolution of γ + Ni_5Zr eutectic colonies by solution heat treatment. Therefore, solution heat treatment helps to improve the room temperature hardness of as-cast IC221M.

4. CONCLUSIONS

An attempt was made to improve the oxidation resistance and mechanical properties of as-cast commercialized Ni_3Al alloy by solution heat treatment at 1100 °C. After solution heat treatment, the surface oxide is relatively uniform in appearance and thickness, and NiO surface nodules are considerably reduced. X-ray maps of oxide phases show that the outermost layer of oxide is mostly $NiAl_2O_4$ spinel mixed with a significantly smaller amount of NiO. A chromium rich oxide, Cr_2O_3 and/or $NiCr_2O_4$ spinel, forms beneath the outermost layer. An aluminum enriched oxide, Al_2O_3, forms below the surface. Most importantly, zirconium oxide, ZrO_2, is restricted in the surface oxide instead of forming deep penetrating spikes. The solution treated material showed somewhat improved oxidation resistance, but cyclic oxidation tests should be conducted to determine whether the surface oxide is well-adherent.

The hardness of a solution treated IC221M is improved after solution treating at 1100 °C as a result of dissolution of the $\gamma + Ni_5Zr$ eutectic into the matrix. Tensile tests of the solution treated specimens show that solution treatment yields no significant benefit in this regard and that the properties gradually degrade above 500 °C.

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REFERENCES

1. V. K. Sikka, M. L. Santella, P. Angelini, J. Mengel, R. Petrusha, A. P. Martocci, and R. I. Pankiw, *Intermetallics* **12**, 837 (2004).
2. D. Y. Lee, M. L. Santella, I. M. Anderson, and G. M. Pharr, *Intermetallics* **13**, 187 (2005).
3. D. Y. Lee, M. L. Santella, I. M. Anderson, and G. M. Pharr, *Met. Mater. Trans. A* **36**, 1855 (2005).
4. D. Y. Lee, *ORNL/TM-2004/101*, 163 (2004).
5. M. L. Santella, *Scr. Metall. Mater.* **28**, 1305 (1993).
6. *Metals Handbook. 2nd Desk ed.*, ASM international (1998).
7. Cai D, Yao M, Nie P, and Liu W, *Mater. Let.* **57**, 3805 (2003).
8. D. B. Lee and M. L. Santella, *Mater. Sci. Eng. A* **37 4**, 217 (2004).
9. G. Y. Kim and D. B. Lee, *Met. Mater. -Int.* **8**, 375 (2002).
10. B. C. Wilson, J. A. Hickman, and G. E. Fuchs, *JOM* **55**, 35 (2003).
11. G. E. Fuchs and B. A. Boutwell, *Mater. Sci. Eng. A* **33 3**, 72 (2002).
12. M. L. Santella, *Personal communication* (2003).
13. S. C. Deevi and V. K. Sikka, *Intermetallics* **4**, 357 (1996).
14. P. S. Wang, S. L. Lee, J. C. Lin, and M. T. Jahn, *J. Mater. Res.* **15**, 2027 (2000).
15. V. K. Sikka, S. C. Deevi, S. Viswanathan, R. W. Swindeman, and M. L. Santella, *Intermetallics* **8**, 1329 (2000).
16. V. K. Sikka, Int. Sym. Nickel & Iron Aluminides: Processing, Properties, and Applications, Proceedings from Materials week '96, 361, Cincinnati (1997).
17. G. Sauthoff, *Intermetallics*, VCH Inc. (1995).
18. E. P. George, C. T. Liu, and D. P. Pope, *Scr. Metall. Mater.* **27**, 365 (1992).
19. E. P. George, C. T. Liu, and D. P. Pope, *Scr. Metall. Mater.* **28**, 857 (1993).
20. A. Chiba, S. Hanada, and S. Watanabe, *Mater. Sci. Eng. A* **152**, 108 (1992).
21. Y. Gu, D. Lin, and J. Guo, *Scr. Metall.* **35**, 609 (1996).