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**THERMAL AGING EFFECTS ON THE MICROSTRUCTURE, OXIDATION
BEHAVIOR, AND MECHANICAL PROPERTIES OF AS-CAST Ni_3Al ALLOYS**

A Dissertation

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Doctor of Philosophy

Degree

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DEDICATION

This dissertation is dedicated in memory of my father, Han-Gu Lee (1930 ~ 2004) with full of my heart. He was a great role model to me and such a good man.

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ABSTRACT

The thermal aging effects on the microstructure, oxidation behavior at 900° and 1100°C, and mechanical properties of IC221M (Ni₃Al based intermetallic alloy, ASTM A1002-99) were investigated. The microstructure consists of dendritic arms of the γ (nickel solid solution) phase containing cube-shape γ' (Ni₃Al) precipitates. The interdendritic regions are mostly γ' (Ni₃Al) with up to 8 vol.% γ + Ni₅Zr eutectic constituents. Thermal aging effects on the microstructures and how microsegregation affects the oxidation behavior were examined. Four primary changes in the microstructures were observed: (1) there is considerable homogenization of the cast microstructures with aging, (2) the volume fraction of γ' increases with aging time and temperature, (3) the γ' phase coarsens, and (4) the volume fraction of the γ + Ni₅Zr eutectic constituents decreases.

During the initial stages of oxidation at 900°C, surface oxides form along the microsegregation patterns, revealing the cast microstructures. The first oxide to form is mostly NiO with small amounts of Cr₂O₃, ZrO₂, NiCr₂O₄, and θ -Al₂O₃. Initial oxidation occurs primarily in the interdendritic regions due to microsegregation of alloying elements during casting. With further aging, the predominant surface oxides become NiO and NiAl₂O₄ spinel, with a continuous film of α -Al₂O₃ forming immediately beneath them. Although these oxides are constrained to the near surface region, other oxides penetrate to greater depths, facilitated by oxidation of the γ + Ni₅Zr eutectic constituents. These oxides appear in the microstructure as long, thin spikes of ZrO₂ surrounded by a sheath of Al₂O₃. They can penetrate to depths greater than 10 times that of the continuous

surface oxide. The oxidation behavior at 1100°C is similar to that at 900°C, but the oxidation kinetics are faster, NiO dominates at all aging periods, and the surface oxides do not adhere to the matrix meaning that a protective oxide scale does not form. Energy dispersive x-ray techniques with multivariate statistical analysis (MSA) and ThermoCalcTM simulations were used to develop an understanding of the microstructural changes and oxidation behavior.

Mechanical properties of IC221M were studied in tension tests and hardness tests. Two aging atmospheres (air and argon) and several temperatures were employed for tension testing. The results show that the yield strength at room temperature dramatically drops after 50 hours of aging at 900°C, but further aging at 900°C does not affect the strength: the dramatic decrease of the yield strength is presumably due to the coarsening of the γ and γ' phases. Interestingly, while the yield strength of tensile specimens decreases with increasing aging temperature in air because of oxidation, it increases with increasing aging temperature in argon. This strengthening is probably caused by dissolution of zirconium into the matrix at higher temperatures. Elevated temperature tension testing showed that the yield strength increases with testing temperature to a peak of about 650 MPa at a temperature in the range 600°~800°C, an anomalous behavior often observed in materials with the $L1_2$ ordered crystal structure. While the tensile properties of as-cast specimens aged in air or Ar at temperatures above 950°C are not acceptable for structural use at 900°C, the tensile properties of specimens aged below 950°C are relatively good. Evidence has been found that preoxidized specimens are less susceptible to the high temperature environmental embrittlement.

The hardness of as-cast specimens and specimens aged at 900° and 1100°C was measured by Vickers hardness testing and nanoindentation. Interestingly, while the Vickers hardness decreases sharply during the initial stages of aging at 900°C, the nanohardness does not. This appears to be a grain size effect due to the coarsening of the γ and γ' microstructure during aging ; nanoindentation measurements sample single grains while Vickers measurements sample larger areas containing multiple grains.

The hardness and oxidation properties of IC221M aged in air at 900°C can be improved by solution treating at 1100°C. However, solution treatment may be detrimental to the tensile properties at elevated temperatures.

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I. INTRODUCTION

Intermetallic compounds such as silicides, aluminides, and beryllides have long been known as a promising materials for use at high temperatures, although they have rarely been used in structural applications because of their intrinsic brittleness. Instead, most intermetallics have been used as coatings on ductile base metals [1]. Beginning in the 1970's, many researchers became interested in the possibility of using intermetallic compounds in load-carrying functions and found that microalloying suppresses the brittleness of some intermetallic compounds. One of the most successfully developed classes of intermetallics are the nickel aluminides, which have low density, high-melting points, high-strength at elevated temperatures due to their ordered crystal structures, and high resistance to oxidation and corrosion [2]. Some nickel aluminide alloys have been developed for casting and welding; in industrial terms these are known as advanced nickel aluminides.

One of the more important commercialized nickel aluminides is IC221M¹ (Ni; Al-8.21%; Cr-7.61%; Zr-2.09%; Mo-1.52% (wt.%)), an alloy developed at the Oak Ridge National Laboratory. A great deal of research has been undertaken to understand the behavior of this material particularly as it relates to fabrication and welding. However, our fundamental knowledge of the high-temperature aging behavior of the alloy has not kept pace with progress in areas related to commercialization. The research in this dissertation is focused on establishing the scientific knowledge base needed to solve

¹ Most Ni₃Al intermetallics used in industry are Ni-based superalloys with Ni₃Al, γ' precipitates in a Ni solid solution (γ phase). The predominant phase in IC221M is γ' (Ni₃Al), about 80-90 vol.%. Therefore, we shall call this material a Ni₃Al-based intermetallic alloy.

problems related to commercialization activities, particularly problems associated with long term aging in air at elevated temperatures.

1.1 History of the development of intermetallic compounds

The history of intermetallic compounds has been detailed by Westbrook [3-5] and others [6,7]. Intermetallic compounds were first discovered in 1839 by Karl Karsten [3,4], who found that a discontinuity occurs in the action of acids on alloys of copper and zinc at the equiatomic composition and suggested the formation of a compound now known as β -brass (CuZn). Subsequently, Laves [8] found that the relative sizes of the component atoms are important; many intermetallic crystal structures are understandable in terms of the dense packings of atoms of different sizes, which then requires both a limited range of radius ratio for the two species as well as a specific proportion of the components. Compounds of this sort with the type formula AB_2 have since been extensively studied and are known as ***Laves structures***.

In the early 1970's, Liu at the Oak Ridge National Laboratory (ORNL) embarked on an extensive research program to improve the mechanical performance of intermetallics. This intermetallics program, one of the largest in the world, received more than \$21 million in funding during the period 1982-97 [9]. The program culminated successfully in several practical Ni-based ordered alloys that are currently being applied in industry [6]. Some examples of applications are:

(1) The Cummins Engine Company began using nickel aluminides in turbochargers in diesel engines in 1985. However, problems were encountered because of lack of

technologies for casting and welding. On the other hand, wrought alloys proved a very good candidates for use in turbochargers.

(2) Sandusky International now makes centrifugally cast furnace rolls from two nickel aluminides (IC396M and IC221M). As shown in Fig. 1.1-1, Bethlehem Steel and US Steel now use these rolls routinely.

(3) GM Delphi Saginaw Steering Systems uses nickel aluminides trays and assemblies in carburizing heat-treating furnaces, as shown in Fig. 1.1-2.

Many other industries are currently working with ORNL to develop new applications for intermetallics [9-11].

1.2 High temperature oxidation of intermetallic compounds

1.2.1 Introduction*

Oxidation theories developed for metals are sufficiently general to be applied to intermetallic compounds [1]. Since the oxidation theories can be found in several well written texts [1, 12-15], only a brief introduction will be presented in here.

Oxidation is the reaction of metals with oxygen to form an oxide. When metals are exposed to oxygen, oxygen molecules are absorbed on the surface and then dissociate and/or ionize to combine with metal ions to form an oxide layer. The layer first grows as a thin film and later as a thick scale. Oxidation is a spontaneous reaction when a metal is exposed to oxygen because the standard free energy change for most metals is negative. If oxidation continues long enough, the oxide may crack or spall and the integrity of the

* The material in this section follows largely from the developments in references [1, 12~15]

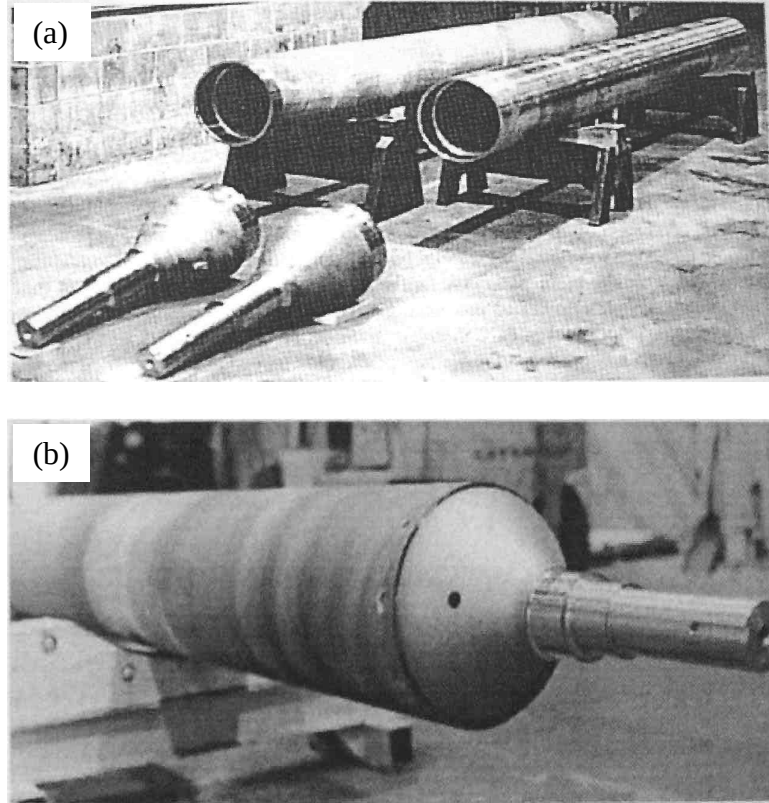


Fig. 1.1-1 Cast and welded Ni_3Al transfer roll [9]: (a) for installation at Bethlehem Steel (Chesterton, Indiana), and (b) for US Steel [11].

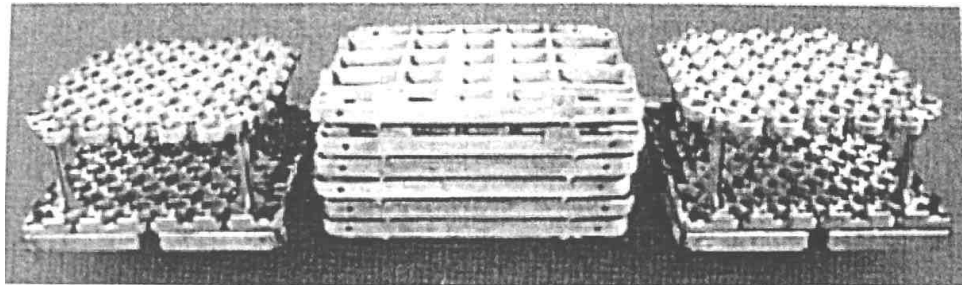
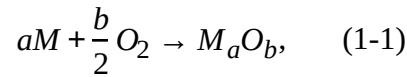


Fig. 1.1-2 Ni_3Al (IC221M) carburizing grids [9].

base metal/alloy may suffer. Therefore, oxidation resistance is one of the most important concerns in material design for high-temperature use

The chemical equation for the oxidation reaction between a metal and oxygen is given by



where M is the metal, and O is oxygen. The rate of reaction depends on surface conditions, temperature, oxygen partial pressure, and impurities in both the metal and the oxygen gas. When a dense oxide film forms on the surface, oxidation may be rate-limited by solid-state diffusion because the oxide film separates between the reactants and oxygen gas. Since the reaction mechanism is generally complex, a large number of separate theories are needed to describe the oxidation behavior of metals.

Although many factors are needed to interpret the oxidation behavior of metals and alloys, reaction rates and the corresponding rate equations are commonly used to classify the oxidation behavior of the metals and alloys [12]. Generally, the rate equations are classified as logarithmic, parabolic, and linear, but they represent only limiting and ideal cases [16]. Logarithmic oxidation is usually observed for relatively thin films at low temperatures. At high temperatures, many metals, alloys, and intermetallic compounds follow a parabolic time dependence, especially when they form a dense oxide film on the surface. The differential form of the parabolic rate equation is given by

$$\frac{dx}{dt} = \frac{k_p}{x} \quad (1-2)$$

which integrates to

$$x^2 = k_p t + C \quad (1-3)$$

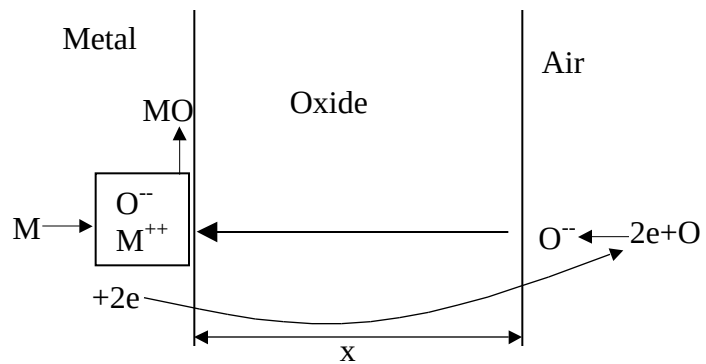
where x is film thickness, t is time, k'_p and k_p are parabolic rate constant, and C is an integration constant. The rate of thickening of a continuous protective scale during the steady-state period of oxidation is usually described by the parabolic rate law. The rate of linear oxidation is constant with time which means non-protective scales form on the surface. Often, a combination of two or more of the rate laws are needed to describe the oxidation process, e.g., oxidation starts as parabolic then transitions to linear.

Parabolic oxidation is particularly important in this study. Fig. 1.2.1-1 depicts three common parabolic oxidation mechanisms for metals. In Fig. 1.2.1-1a, the metal cations (M^{++}) diffuse very slowly in oxides, and then oxides grow at metal/oxides interface. Fig. 1.2.1-1b presents the case of very slow diffusion of oxygen anions (O^{--}) in the oxide film followed by growth of oxide at the air/oxide interface and formation of vacancies at the metal/oxides interface. Fig. 1.2.1-1c shows what happens when electron transport in the oxide is slow; the oxide grows slowly at metal/oxide or oxide/air interface depending on whether metal cations (M^{++}) diffuses faster than oxygen anions (O^{--}).

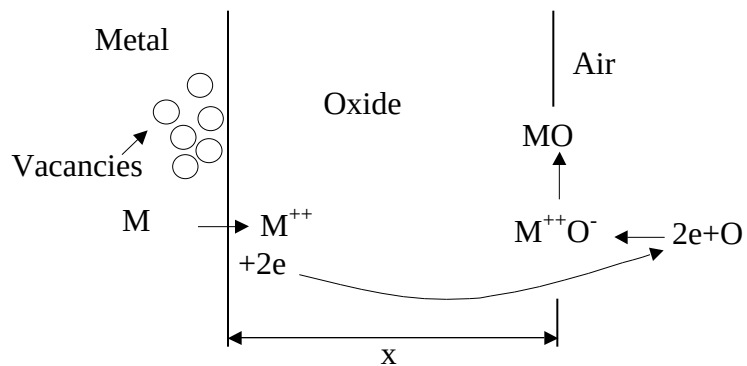
One other factor to be considered in the oxidation of a metal/alloy is the temperature dependence. The oxidation rate constant, k , obeys an Arrhenius-type temperature dependence, i.e.,

$$k = k_o \exp\left(\frac{-Q}{RT}\right) \quad (1-4)$$

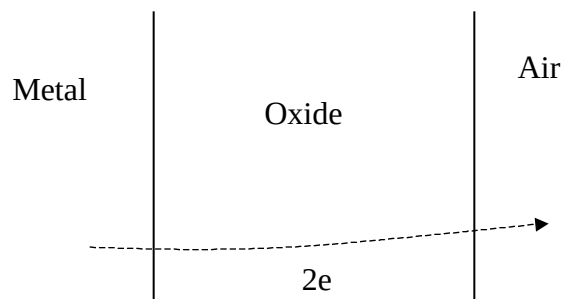
where Q is the activation energy, R is the gas constant, and T is the absolute temperature. In the high temperature oxidation of metals, the oxygen partial pressure dependence is also an important factor in evaluating the reaction mechanism. At low oxygen pressures,



(a) Case 1: Ti, Zr, U



(b) Case 2: Ni, Cr, Cu, Fe, Co



(c) Case 3: Al.

Fig. 1.2.1-1 The mechanisms of parabolic oxidation [17,18].

the rate of reaction is directly proportional to the oxygen pressure. At high oxygen pressures, the oxidation rate is often proportional to $p_{O_2}^{1/2}$.

Figure 1.2.1-2 illustrates the general oxidation process in terms of the extent of oxidation (the weight-gain per unit area or scale thickness) versus time. The life of oxides can be classified into three periods: transient, steady-state, and breakaway. The extent of oxidation during the transient stage depends on the relative amount of the oxide and the rate of growth of the oxides formed. The steady-state period of oxidation occurs when the rate of oxidation is controlled by the growth of a protective oxide scale, which is invariably controlled by solid-state diffusion in the oxide scale. Growth stresses developed in these scales as they thicken may eventually cause failure and the onset of breakaway oxidation by one or more stress relief mechanisms (blistering, tensile or shear cracking of the scales, etc.).

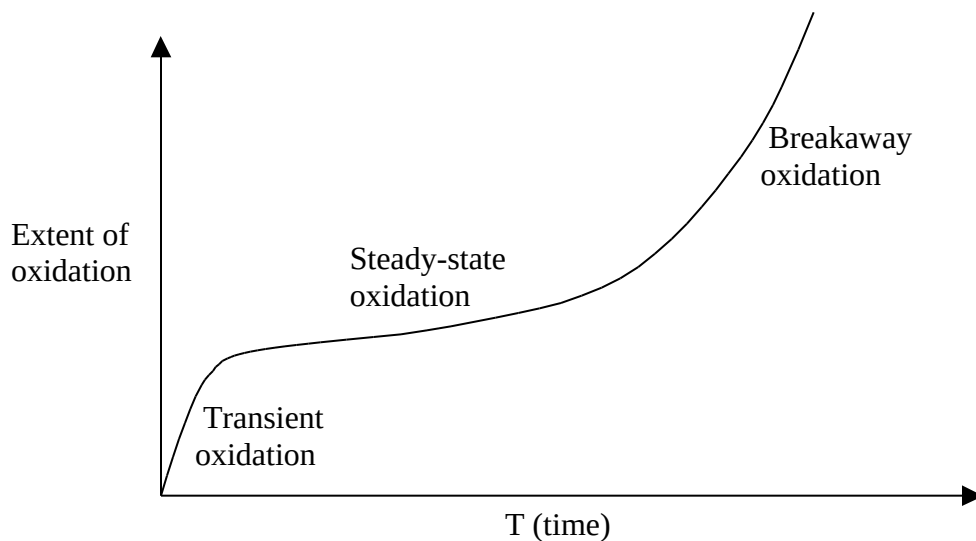


Fig. 1.2.1-2 The extent of oxidation [17].

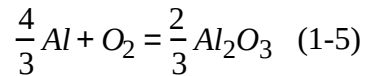
The onset of breakaway behavior may also be related to the penetration of protective oxide scales by cations (Fe, Ni, Mn, etc.) from the base metal or anions (S, Cl, C, etc.) from the environment [17].

A desirable oxide must be able to protect the surface from further oxidation. However, in some cases the oxide spalls at particular stage of oxidation and/or a critical temperature. The main reason for oxide spallation is stress generation during the oxide growth. One parameter that is used to characterize the potential for stress generation is the Pilling Bedworth Ratio (PBR): the ratio of the molar volume of oxide per gram atom of metal to the molar volume of the metal. If there is a large difference in the two, then the oxide has a tendency to spall. If the ratio is more than 1, the stress accumulated is compressive in nature, while if the ratio is less than 1, the scale is in tension. The PBR of most metals and alloys is larger than 1, i.e., the oxide is in compression (for example, Al_2O_3 -1.28, ZrO_2 -1.56, NiO -1.65, Cr_2O_3 -2.07). Another factor affecting stress is an epitaxial relationship between the oxide and the substrate. Epitaxial stresses may result during the nucleation and growth of the surface oxide because of differences of lattice parameters between the substrate and the surface oxide. Epitaxial stresses are only significant for the early stages of oxidation or low temperature oxidation [13], and will be maximum at the metal/oxide interface [14]. Compositional change of the oxide is also a factor that contributes to stress; it causes stresses through changes in the lattice parameter. For example, there is a 10.5% decrease in volume when CuO growing on copper changes to Cu_2O [14]. Sample geometry, point defects in the scale, and recrystallization of oxide can also generate stresses. Thermal stresses produced during cooling cause spallation of the oxide.

1.2.2 Oxidation behavior of Ni₃Al-based intermetallic alloys

High temperature structural intermetallic compound must have a high-resistance to oxidation. This is achieved by incorporating a specific alloying element that forms a self-protective scale by a selective oxidation mechanism. From this perspective, intermetallic compounds based on aluminides, silicides, and beryllides are highly desirable because aluminum in aluminides, silicon in silicides, and beryllium in beryllides form the self-protective oxides Al₂O₃, SiO₂, and BeO on the surface of the alloys. To be effective, the intermetallic compounds must contain a sufficient amount of the reactive element so that its selective oxidation forms a protective continuous external layer [19].

For Ni₃Al-based intermetallic alloys, one of the most stable and desirable oxides is α -Al₂O₃, formed at high temperature (e.g., 1000°C) by the reaction:



As shown in Fig. 1.2.2-1, Al₂O₃ is thermodynamically very stable since α -Al₂O₃ is a stoichiometric oxide with very low intrinsic defect concentrations, when it forms a continuous oxide layer on the surface, it provides an excellent oxidation resistance. The diffusivity of oxygen anions in Al₂O₃ is much lower than that of Al cations in Al₂O₃, so the oxide forms preferentially at the interface of metal/oxide [19]. As can be seen in Fig. 1.2.2-1, Cr₂O₃ is also a relatively stable oxide. Cr is often added to Ni₃Al-based alloys to reduce dynamic embrittlement in elevated temperature [20,21]. However, its effect on the oxidation behavior is not clear [23~27]. Some studies report beneficial effects [29~31], but others found no significant effects on the oxidation behavior. The beneficial effect of

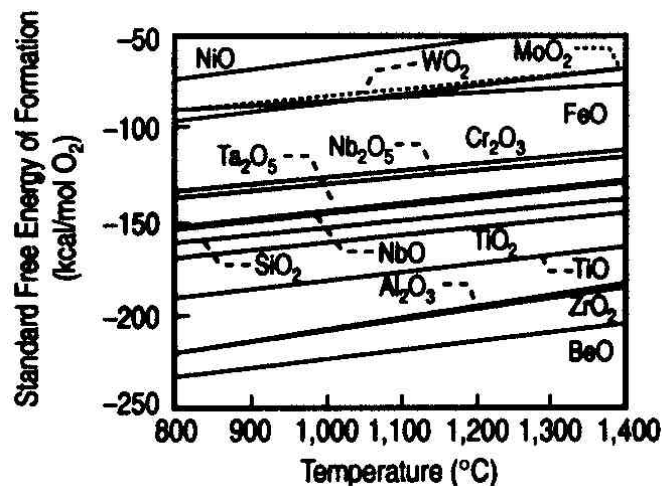


Fig. 1.2.2-1 Standard Gibbs free energies per mol O₂ vs. temperature [22].

chromium may be expected in the way in which chromium enhances the transition from metastable forms of Al₂O₃, ϵ , γ , δ , θ -Al₂O₃ phases, to the preferred α -Al₂O₃ [25,26].

Even though Al₂O₃ itself is stable, it is susceptible to cracking and spalling when it forms on the alloy [28]. Spalling of Al₂O₃ oxide scales in Ni₃Al-based alloys is due to the formation of voids at the alloy/oxide interface [23,29-31]. Therefore, most methods for improving the oxidation resistance of Ni₃Al-based alloys have focused on improving the interfacial strength between alloy/oxide. The addition of a small amount of an oxygen-active or rare earth element, Zr, Ti, Y, and Hf, can result in strongly adherent scales [24,25,27,28,31-36]. Many deep penetrating spike-type oxides along the grain boundaries are observed when the oxygen-active or rare earth element are added. Both a keying effect and a vacancy sink mechanism are used to explain the adhesion of the oxide scales in these materials. Interestingly, the penetrating oxides consist of Al₂O₃ and ZrO₂,

and the ZrO_2 oxides are sheathed within thin layer of Al_2O_3 as shown in Fig. 1.2.2-2. These phenomena have been reported by several researchers [27,34].

Several different oxides are formed during the high temperature oxidation of Ni_3Al -based alloys. The predominant oxides are NiO , $\text{Ni}(\text{Al,Cr})_2\text{O}_4$, $(\text{Al,Cr})_2\text{O}_3$, and $(\text{Ti, Zr, Hf})\text{O}_2$ oxides. Some differences are to be expected based on the oxidation temperature and the interaction among the alloying elements, for example, some oxides are preferentially promoted by a certain alloying additions.

To date, most Ni_3Al -based materials tested for oxidation have been homogenized materials, that is, little attention has been given to cast materials. Common casting microstructures are shown in Fig. 1.2.2-3a. Presumably, microsegregation during casting can affect the oxidation behavior of cast Ni_3Al -based alloys in either positive or negative ways. However, only a few studies have addressed the oxidation behavior of as-cast

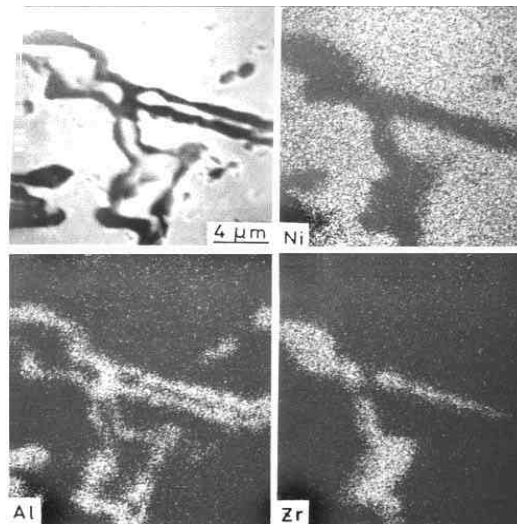


Fig. 1.2.2-2 Electron probe micro analysis (EPMA) elemental maps of Ni_3Al -0.1B+2.2Zr (wt.%) alloys oxidized at 1400 K for 111 hrs [31].

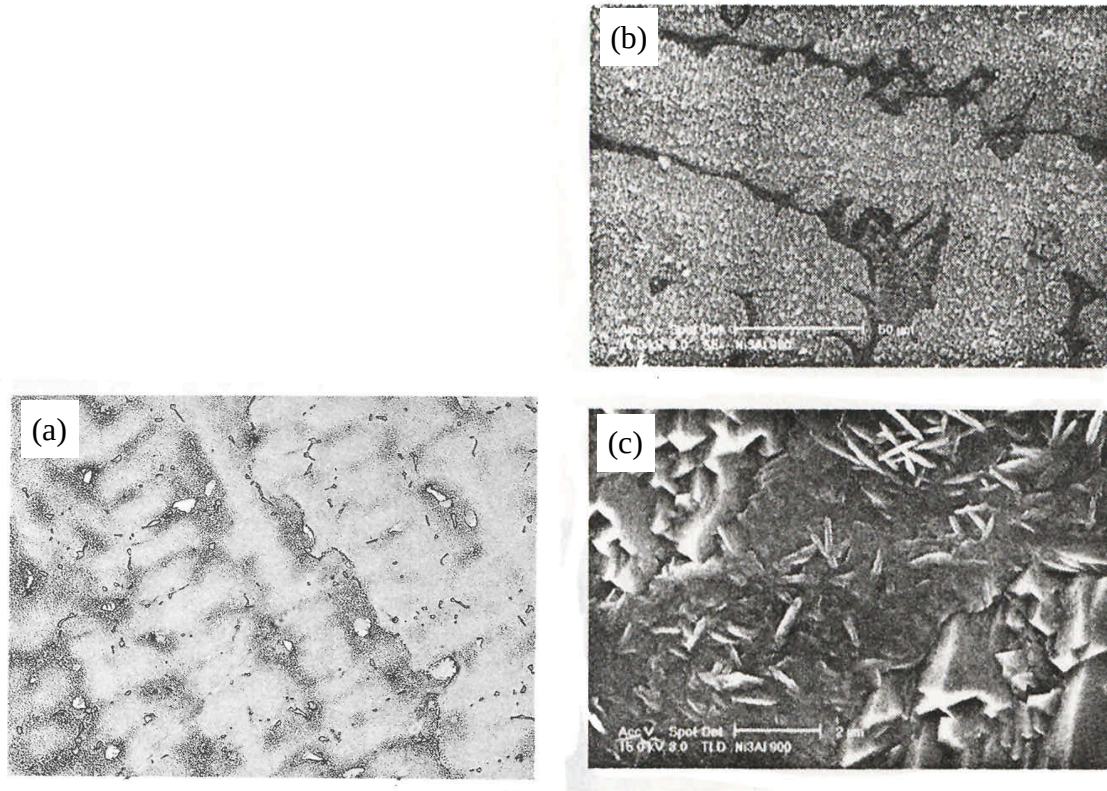


Fig. 1.2.2-3 SEM micrographs of (a) conventional cast microstructures of Ni-base super alloys [37], and the oxides formed in as-cast Ni_3Al oxidized at 900°C in O_2 : (b) as-cast Ni_3Al , (c) an enlarged view of the alloy grain-boundary area of (b)-center: Al_2O_3 , edge: NiO and NiAl_2O_4 [25].

Ni₃Al alloys. Liu and Gao [25] studied Ni₃Al alloys to compare the oxidation behavior an as-cast alloy to the same alloy coated by microcrystalline Ni₃Al+5% Cr with and without Y by doping. As shown in Fig. 1.2.2-3b and c, they found that dense oxides enriched in Al formed along the alloy grain boundaries, and coarse oxide crystals enriched in Ni formed inside of the alloy grains. Presumably, the Al enriched areas occur in interdendritic regions and the Ni enriched areas are the dendrite cores. The dense oxides are Al₂O₃ oxide scales, and the coarse oxides are NiO and NiAl₂O₄ spinel. Other than this, little has been done to characterize the oxidation behavior of cast alloys, even though they are becoming more commonly used in commercial practice.

1.3 Mechanical properties of Ni₃Al-based intermetallic alloys

1.3.1 General features

Ordered Ni₃Al-based intermetallic alloys have a good high-temperature yield strength as well as an anomalous increase in yield strength with increasing temperature. However, the low ductility and brittleness of polycrystalline Ni₃Al-based alloys at room and elevated temperature have presented major difficulties to their use as engineering materials [38]. The brittle behavior was initially attributed to either an insufficient number of slip systems and/or grain-boundary weakness [39]. In the late 1970s and early 1980s, significant progress was made in alleviating this brittleness by microalloying with elements such as boron [20,39,40]. Comprehensive studies of structural applications for intermetallic compounds can be found in several studies [2,6,8].

The general factors contributing to the brittleness of intermetallic compounds are summarized in Table 1.3-1 [38,41]. The origin of the brittleness is not the same in all in

Table 1.3-1 Factors contributing to the brittle behavior of polycrystals [38,41].

Intrinsic	Extrinsic
Complex crystal structure -but L1 ₂ , B ₂ , DO ₃ , L1 ₀ , and DO ₁₉ are relatively simple	Segregants - no harmful segregants in Ni ₃ X alloy, but still brittle
Insufficient independent deformation modes	Interstitials
Planar slip (lower tendency for cross slip)	Constitutional defects
Coarse distribution of slip	Moisture in environment
Elastic factor	Hydrogen
Low-emission and dislocation mobility	Strain rate (especially at high T)
High-work-hardening rate	Notches
Constitutional defects	Low-quality surface

all intermetallic compounds, that is, each intermetallic system has different brittleness factors. For example, although Ni₃Al alloys have sufficient slip systems for extensive plastic deformation ($\{111\} \langle 110 \rangle$ slip systems), polycrystalline Ni₃Al alloys are brittle at ambient temperature, and grain boundaries are the key factor in determining the ductility of these alloys.

Until the early 1990s, the embrittlement of Ni₃Al was thought to be due to the intrinsic brittleness of grain boundaries [42-44], but in the early 1990's, George et al. [45,46] found that grain boundaries of Ni₃Al are not intrinsically weak; the brittleness is caused by hydrogen [47-50] and oxygen [51-53] attack in grain boundary, which causes intergranular brittle fracture in polycrystalline Ni₃Al-based alloys. At room temperature, hydrogen, often derived from water vapor, is the key element causing embrittlement, while at high temperatures oxygen is the embrittling species [20]. Boron is one of the

most effective alloying elements for improving the ductility of Ni₃Al (<25 at.% Al) at room temperature (see Fig. 1.3.1-1a) [20,44]. However, at elevated temperature, the brittleness of polycrystalline Ni₃Al+B alloys is still a barrier to their use in structural applications. Figure 1.3.1-1b shows the oxygen-induced environmental embrittlement of the Ni₃Al-based alloy, IC-145 (Ni-21.5Al-0.5Hf-0.18 at.% B).

Three methods to reduce the oxygen-induced embrittlement of Ni₃Al- based alloys at elevated temperatures suggested by Sikka are [38]: (1) control of surface conditions, (2) control of grain shape, and (3) alloy modification. Preoxidation to form a protective oxide scale is one way to control surface conditions, but under stress, the oxide may not provide a protective scale. Table 1.3-2 shows the benefit of grain shape control as suggested by Liu [54]. The beneficial effect of the elongated grains parallel to the stress axis is attributed to minimizing the normal stress across the boundaries and consequently suppressing nucleation and propagation of cracks along the boundaries weakened by oxygen penetration.

Table 1.3-2 Tensile elongations of boron-doped Ni₃Al with equiaxed and columnar grains tested at 600°C and 760°C in air and vacuum [54].

Grain Shape	Tensile elongation (%)			
	600°C		760°C	
	Air	Vacuum	Air	Vacuum
Equiaxed	0.6	45	0.7	11
Elongated	33	N/A	7.3	N/A

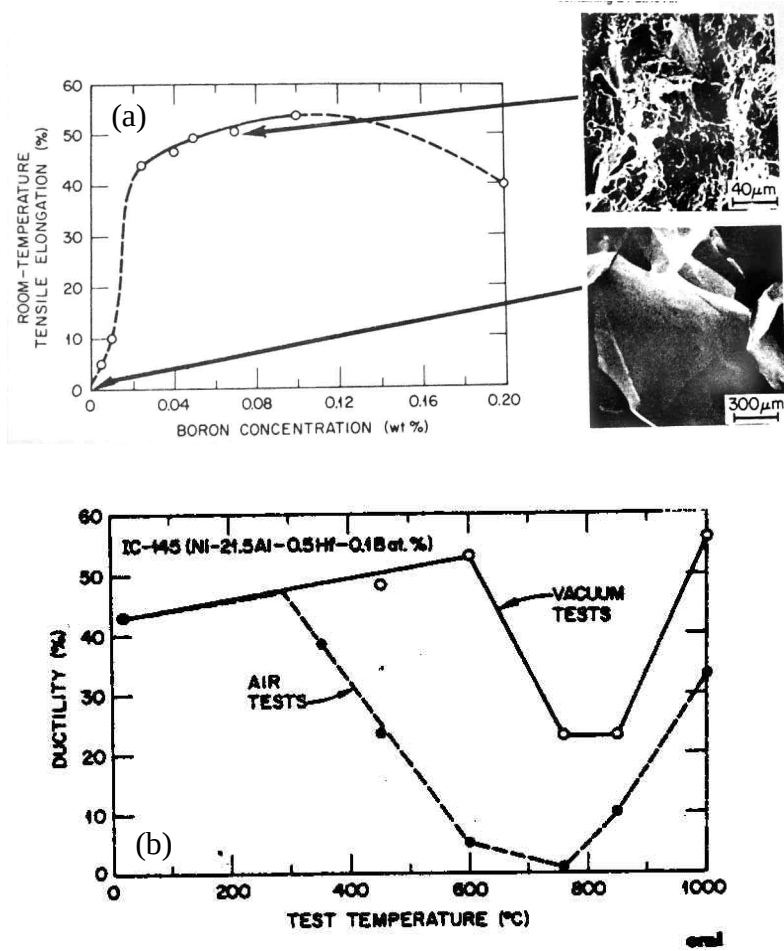


Fig. 1.3.1-1 Influence of B and air on the ductility of Ni_3Al alloys: (a) boron effect, Ni_3Al (24 at.% Al); (b) environmental effect, IC-145(Ni-21.5-0.5Hf-0.1B,at.%) [20,44].

1.3.2 Anomalous flow behavior of Ni₃Al

Ni₃Al and other $L1_2$ type ordered intermetallic alloys show a strongly increasing temperature dependent yield strength called the “yield strength anomaly”. Many researchers have examined and discussed this effect, and the controlling mechanisms are essentially understood [55-58]. A schematic illustration of the yield strength anomaly is shown in Fig. 1.3.2-1b.

The anomalous flow of Ni₃Al based alloys and many other $L1_2$ type alloys was first reported by Flinn [59], who proposed a diffusion-controlled model to explain the phenomenon. However, Davies and Stoloff subsequently argued that Flinn’s diffusion-controlled model was not correct because such a model predicts a large and positive strain rate sensitivity at the temperatures of anomalous flow, when it is, in fact, quite small but positive [55]. Screw dislocations in Ni₃Al alloys can split onto the {111} and {010} planes, and the responsible mechanism is now believed to be caused by cross slip of screw dislocations. Slip is limited to {111} planes at low-temperatures. With increasing temperature, cross-slip to {010} planes becomes possible by thermal activation. However, the dislocations on {010} planes are sessile, and this increases the strength [7]. The driving force for cross slip is provided both by the anisotropy of the antiphase boundary (APB) energy and by the resolved shear stress (RSS) on (010)[-101] [39].

Figure 1.3.2-2 illustrates the temperature dependence of the flow stress for polycrystalline pure Ni₃Al and Ni₃Al alloys with various alloying additions. As can be seen, the flow stress increases with increasing temperature to a maximum around 700°~800°C, and the strength of Ni₃Al can be controlled by alloy modification that

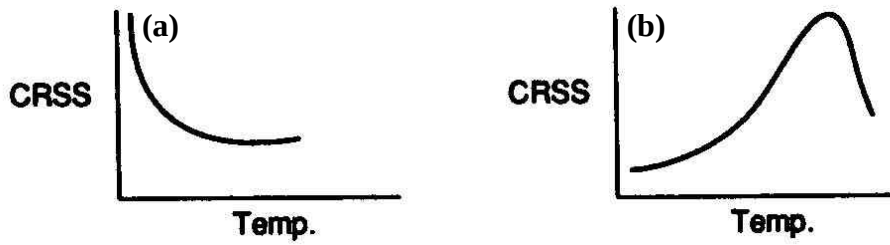


Fig. 1.3.2-1 Schematic diagrams of critical resolved shear stress vs. temperature: (a) conventional curve for most of metals and alloys; and (b) typical "yield strength anomaly" showing an increase in the CRSS with temperature [55].

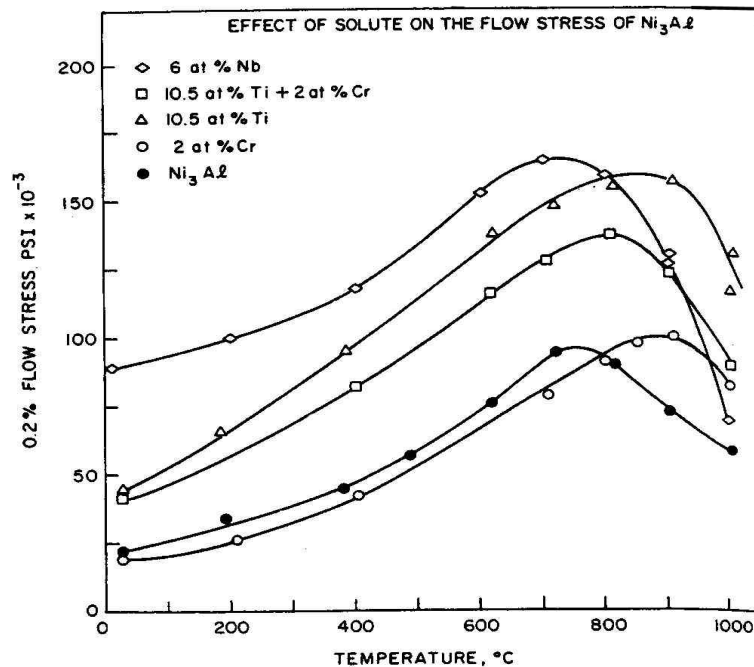


Fig. 1.3.2-2 Temperature dependence of the flow stress for cast polycrystalline Ni_3Al and Ni_3Al with various alloying elements [7].

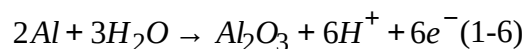
induce sublattice occupation of solutes, atom-size misfit, and deviations from stoichiometry [54].

1.3.3 Embrittlement and modification of Ni₃Al alloys for room temperature applications

Brittle intergranular failure is not just a problem of Ni₃Al alloys, but also occurs in iron and steels, nickel alloys, and refractory alloys. Because segregated impurities weaken the strength of grain boundaries, grain boundary segregation of impurities must be carefully controlled in commercial melting practices (e.g. less than 20 ppm).

Motivated by the remarkable achievements in improving the ductility of polycrystalline Ni₃Al [20,40,51], many studies have been undertaken to understand the origin of the brittleness of polycrystalline Ni₃Al alloys. Before the 1990s, it was believed that grain boundaries of a polycrystalline Ni₃Al alloy are intrinsically weak [42-44]. However, George et al [45,46] showed that very high ductilities (48-51 %) could be achieved in a B-free Ni₃Al+Zr alloy by testing in oxygen. On the other hand, testing in water and air produced only 6 to 13 % ductility. Another experiment [46] showed that the ductility of binary Ni₃Al tested in oxygen (13-15 %) is higher than that tested in air (3-5 %), confirming that the grain boundaries of binary Ni₃Al alloys is not intrinsically weak.

Moisture-induced environmental embrittlement is now generally believed to be the primary embrittlement mechanism of Ni₃Al alloys [45,60,61]. A chemical reaction between aluminum and water vapor produces atomic hydrogen, which causes the embrittlement. The reaction is:



The hydrogen atoms inside the grains and grain boundaries weaken the cohesive strength of the cleavage planes and grain boundaries resulting in transgranular cleavage and intergranular fracture, respectively [41]. Boron enhances the ductility by increasing the intergranular cohesive strength and by inhibiting the diffusion of H atoms along the grain boundaries [60,61]. However, the dissociation rate from H_2O or H_2 to atomic hydrogen is higher in B-doped Ni_3Al than B-free Ni_3Al . Cohron et al. [62] found that B embrittles Ni_3Al in dry H_2 environments possibly by promoting H_2 dissociation.

Even though the mechanism is not well understood, zirconium can also improve the ductility of Ni_3Al alloys by promoting grain boundary cohesion [46].

1.3.4 Improvement of ductility of Ni_3Al alloys at elevated temperature

The brittle fracture of Ni_3Al alloy at room temperature is mainly due to hydrogen induced embrittlement, but oxygen attack of the grain boundaries is the main reason for brittle fracture at elevated temperature [51,61,63]. Liu and White [51] suggested that there is a dynamic embrittlement simultaneously involving high localized stress concentration, elevated temperature, and gaseous oxygen.

Chromium additions are one of the best ways to improve the ductility of Ni_3Al alloys at elevated temperatures [51]. However, the ductility of Cr containing Ni_3Al alloys is better in vacuum than in air, indicating that embrittlement is not completely suppressed by chromium additions. The other beneficial effect of chromium accrues from the self-healing nature of chromium oxides films that reduces the penetration of oxygen into grain boundaries [51].

Zirconium can also improve the ductility of Ni_3Al alloys [41,64-66] by enhancing grain boundary cohesion. Figure 1.3.4-1 shows the zirconium effects on microhardness [65] and tensile properties [66] obtained in two separate studies. Interestingly, even though the alloy compositions are nominally the same ($\text{Ni-23.x at.\%Al-Zr-B}$ for [65] and $\text{Ni-24 at.\%Al-Zr}$ for [66]), the effect on the hardness and yield strength is different. In the hardness data, the material softens for Zr contents up to 0.5 % and then hardens, presumably due to solid-solution effects. Gu et.al [66] found that even though the maximum solubility of Zr in γ' (Ni_3Al) is about 2.7 at.% , if zirconium contents exceed 0.7 at.%, the ductility decreases dramatically. They explained this phenomenon based on Ni_5Zr precipitates and micro-cavities that form intergranularly. In their study, as the Zr contents increases up to 0.7 at.%, the fracture modes changes from intergranular to a mixture of intergranular and transgranular. The 1.2 at.% of zirconium alloy shows

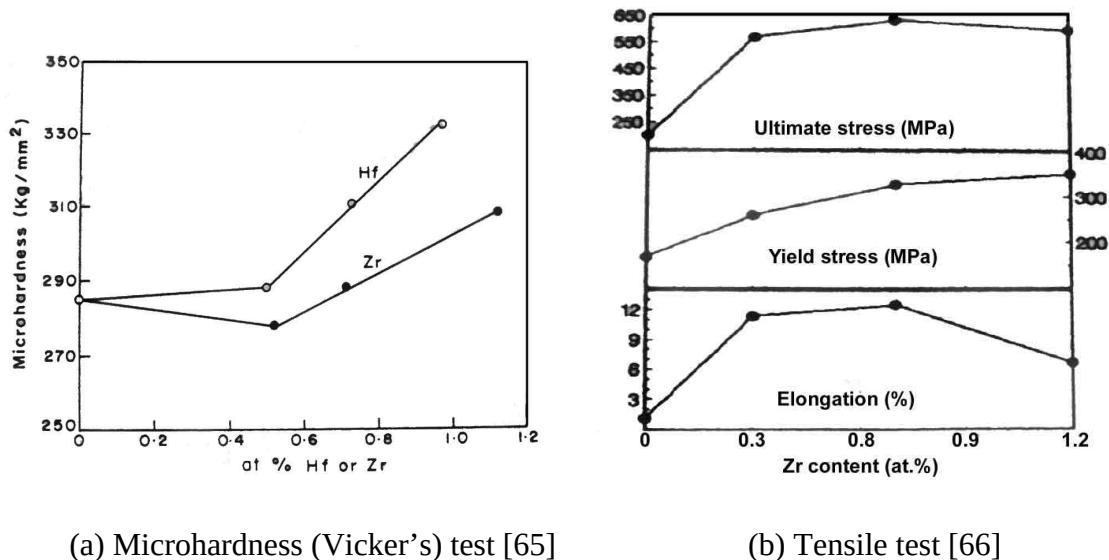


Fig. 1.3.4-1 Mechanical properties of Ni_3Al containing various amount of Zr.

predominantly intergranular fracture.

Specific contributions of each alloying element to improving the mechanical properties of Ni₃Al alloys are summarized in Table 1.3-3.

Grain morphology and shape control is frequently used to improve the ductility of Ni₃Al alloys. Liu and Oliver [54,67] reported a remarkable increase in elongation of cast Ni₃Al by 14% associate with a change in grain shape from equiaxed to columnar using directional solidification techniques. Hirano and associates [68,69] reported a tensile elongation of over 70% with ductile transgranular fracture, for directionally solidification materials. Lapin et al [70] studied the mechanical properties of boron free Ni₃Al+Cr, Fe and found that ductility could be improved by more than 10 % by directional solidification.

1.3.5 Aging of Ni₃Al alloys

Because a primary purpose of Ni₃Al alloys is structural use at high-temperature, aging is an important issue. Generally speaking, the yield strength in air or vacuum decreases with increasing annealing temperature and/or time because of a grain-growth [71], and the ductility of the alloy tested both in vacuum and in air increases due to recrystallization [72]. With an increasing degree of recrystallization, the amount of transgranular cleavage decreases, but transgranular ductile fracture increases. Air promotes transgranular cleavage fracture and reduces the amount of ductile fracture for both un- and partially recrystallized specimens.

Phillips [73] reported that age hardening effects were observed during annealing Ni-12.6 at % Al at 700°C up to about 5 hrs of aging time, where the γ' particle size is

Table 1.3-3 The specific contributions of alloying additions in Ni₃Al alloys [38].

Alloying element	Specific role
Cr	Reduce oxygen induced embrittlement at elevated temperature
Zr	Solid-solution strengthening at high-temp; reduce solidification shrinkage and macro-porosity by forming low melting point Ni ₅ Zr eutectic phase
Hf	Solid-solution strengthening at high-temp; prevent surface reaction of Zr with ceramic shell material during investment casting by forming a protective oxide film
Mo	Improves strength at low and high temperatures by reported Mo effect of solid solution strengthening.
B	Reduce moisture-induced hydrogen embrittlement; enhance grain boundary cohesive strength (most effective $\leq 24\text{at.}\%$ Al).

about 150Å. Beyond 5 hrs, the relatively small γ' particles begin to re-dissolve into the matrix and the material softens. These same observations have reported in other studies[74-76] The coarsening of γ' particles by aging is usually observed at temperature in the range 625° C to 900°C [75,76].

Perez et al.[77] reported aging effects for Ni₃Al-Cr alloy. Although samples aged at 750°C showed very brittle fracture due to the formation of Cr rich precipitates (α -Cr), aging at 900° and 1000°C resulted in ductile fracture (12-17 % elongation). The shape of γ' particles and their relative volume fractions are important factors affecting the mechanical properties of directional solidified Ni₃Al alloys [70,78,79]. Han et al.[80] reported that the coalescence and growth of γ and γ' phases and the homogenization of the solid-solution strengthener Mo in the matrix cause significant changes during the aging of Ni(16~17.6)-Al(7.6~8.8)-Mo(0.15~0.75)-B (in at.%). The yield strength decreased with aging time at 900° to 1100°C.

1.4 Research objectives

The objectives of this research are to characterize and understand the effects of thermal aging on the microstructure, oxidation, and mechanical properties of the castable nickel aluminide alloy, IC221M. The chemical composition of the alloy is given in Table 1.4-1. The density of IC221M is 7.86 g/cm³.

The major phases in IC221M are the $L1_2$ ordered γ' phase, the Ni solid solution γ phase, and an intermetallic phase based on Ni₅Zr. A eutectic of γ + Ni₅Zr solidifies in the castings at about 1170°C (see Fig. 1.4-1 differential scanning calorimetry data [81]), and its volume fraction increases with bulk Zr concentration [82]. The matrix is a γ' + γ mixture. The amount of γ' in the matrix of the alloy ranges from 85 to 95% [54,84].

IC221M was designed primarily to maximize strength and minimize casting defects [83,84]: for this purpose, IC221M contains more Zr than other Ni₃Al based intermetallic alloys and commercialized superalloys. It improves the castability and weldability by forming the lower melting eutectic based on Ni₅Zr [82,84,86,87]. However, the eutectic limits hot workability of this alloy [83,85]. Typical yield strength values are in the range of 600 MPa at room temperature, increasing to about 750 MPa at temperatures near 800°C. The creep strength of the alloy is also high [11]. The high strength of the alloy is accompanied by ductility levels of 5-15% at temperatures below about 1000°C. Both static and centrifugal castings of IC221M are routinely made using standard foundry practices. The oxidation and carburization resistance of IC221M are also very good, particularly when compared to more conventional cast stainless steels.

IC221M has received considerable attention as a material for conveyor rolls in steel heat treating furnaces that operate in air at about 900°~950°C. Such rolls are

Table 1.4-1 The chemical composition of IC221M.

	Ni	Al	Cr	Mo	Zr
Wt. %	80.57	8.21	7.61	1.52	2.09
At. %	73.72	16.34	7.86	0.85	1.23

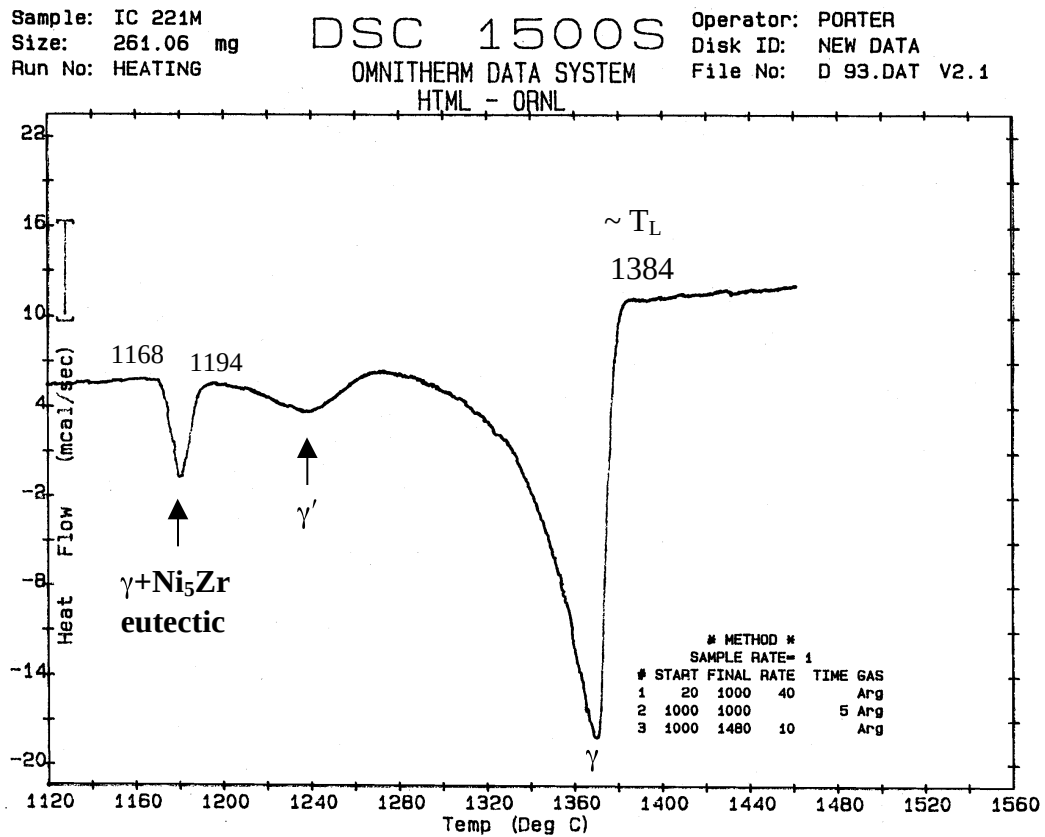


Fig. 1.4-1 Differential scanning calorimetry of IC221M showing the formation of the eutectic $\gamma + \text{Ni}_5\text{Zr}$ at about 1170°C [81].

typically made from cast stainless steel alloys. A common defect associated with this operating environment is blister formation on the roll body surfaces, as shown in Fig. 1.4-2a (arrow). The blisters, which may approach diameters of 150 mm and protrude 13 mm or more above the roll body surface, are a major contributor to surface defects on the steel plates as they pass over the rolls. They can result in plates that fail to meet minimum quality standards. A test bed of 20 IC221M rolls in a normalizing furnace at a major U.S. steel producer has demonstrated that they are significantly resistant to blister formation (see Fig. 1.4-2b). A more extensive industrial trial is now proceeding.

Although the procedures for efficiently melting, casting, and fabricating parts from IC221M are well established, our fundamental knowledge of the high-temperature behavior of the alloy has not kept pace with progress in the areas related to commercialization. A number of studies have been conducted to examine the oxidation [21,23,27,32,34,88-90] and mechanical behavior [20,39,51,91] of Ni₃Al-based alloys with an emphasis on homogenized materials. However, the microstructures of as-cast alloys like IC221M are quite different from homogenized and wrought alloys. Specifically, they contain significant amounts of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic, therefore, the cast alloys may be cored and dendritic, and different amounts of the γ and γ' phases are formed. As a result, it is expected that the aging and oxidation behavior may be very different from wrought alloys. From this research, we hope to resolve these issues and establish a science base necessary to understand the high-temperature behavior of the as-cast alloys.

The temperature 900°C was chosen to simulate a typical operating condition for the alloy, while 1100°C was also used to represent an extreme condition near the melting

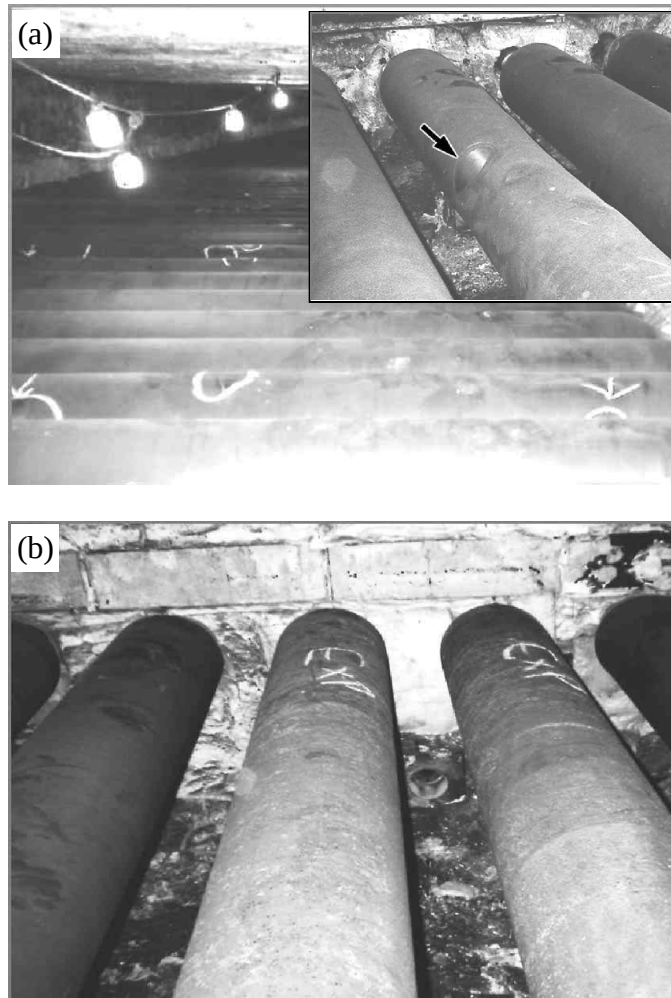


Fig. 1.4-2 An application of IC221M as rolls in steel heat treating furnace: (a) conventional steel rolls showing surface defects due to blistering (arrow in the small photograph in (a)), (b) IC221M rolls showing no blistering sign after several years in service.

of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic at 1170°C. Oxidation experiments were conducted to times up to 16,600 hrs and 3000 hrs at 900°C and 1100°C, respectively.

II. EXPERIMENTAL PROCEDURES, AND ANALYSIS METHODS

2.1 Experimental procedures

The chemical composition of the IC221M alloy used in this study was given in Table 1.4-1. The starting material was produced in a foundry as a 660 kg induction melted heat using pure elemental charge materials and a cover of argon gas. The heat was centrifugally cast in air into a refractory-coated steel mold to produce a 6.1 m long tube with an outside diameter of 360 mm and a 22 mm wall thickness. A ring cut from the casting provided the source of all specimens analyzed in this study. The specimens were cut from locations away from the outer diameter so as to avoid chemical inhomogeneities at the outer surface caused by the refractory mold coating.

Microstructures of the IC221M casting were examined in the as-cast condition and after aging in still air at 900° and 1100°C for times up to 16,600 hrs and 3000 hrs, respectively, by both optical microscopy and by scanning electron microscopy equipped with energy dispersive x-ray spectroscopy (EDX). The aging treatments were done in a laboratory air muffle furnace. The as-cast and aged specimens were polished and etched with glyceresia (30ml glycerin, 30ml HCl, and 15 ml HNO₃) for metallographic examination. Microsegregation during solidification was simulated using the ThermoCalc.TM thermodynamic calculation software. The γ and γ' phase fractions and possible oxides at the elevated temperatures were also simulated by Thermo Calc.TM.

The oxidation behavior of an as-cast IC221M in air at 900°C and 1100°C was investigated by isothermal and cyclic tests*. Isothermal tests were performed by using: (1) a muffle furnace in laboratory air at 900°C and 1100°C for up to 16600 hrs and 3000

hrs, respectively, and (2) thermo-gravimetric analyzer (TGA*) in laboratory air at temperatures between 900°C and 1100°C for up to 500 hrs. Cyclic tests were performed for 500 cycles over 1 hr interval. In each cycle, the specimen was exposed to air for 1 hr, cooling to room temperature, measured to determine weight changes, and then returned the furnace for the next cycle.

X-ray diffraction studies were performed to measure the volume fractions of the γ and γ' phases with aging time using the conventional θ - 2θ scanning (Bragg-Brentano) geometry. Diffraction patterns were acquired from the bulk material because of the difficulty in making a powder specimen. The bulk specimens were oscillated during the x-ray scan to sample a variety of crystal orientations from the highly textured specimen. The crystalline surface oxides were identified by x-ray diffraction studies using grazing angle scattering (3° incident beam angle).

Elemental maps of both as-cast and oxidized specimens were extracted from EDX spectrum images using an EMIPEC Vision system, and compositionally distinct features were determined from the EDX spectrum images using multivariate statistical analysis (MSA) [92-95]. The x-ray elemental image maps were obtained at a resolution of 200×200 pixels at $1 \mu\text{m}$ per pixel using a 1 second acquisition time per pixel at high-voltage operation (30kV). For lower-voltage operations, images were taken at 400×400 pixels at 100 nm (4 kV) or 250 nm (8kV) per pixel with a 0.25 second acquisition time. Each specimen required about 11 hours per spectrum image.

The mechanical properties of the as-cast and aged specimens were examined by

*TGA and cyclic tests were performed by Professor Dong-Bok Lee at Sung Kyun Kwan University in Korea.

tensile testing and hardness testing (Vickers indentation and nanoindentation). Tensile specimens with a conventional dog-bone shape 0.125 inches in width, 0.03 inches thick, and 1.5 inches in length, were cut from the cast ring (Fig. 2.1-1) using electro-discharge machining (EDM). Tensile specimens were prepared in three different conditions: (1) aged in air at 900°C for various times (50, 100, 200, 500, 1000 hours - room temperature tests); (2) aged in air and argon at 900°, 950°, 1000°, 1050°, and 1100°C for 1000 hrs (room temperature and 900°C test); and (3) aged in argon at 900° and 1100°C for 1000hrs, tested at room temperature, 300°, 500°, 700°, 900°, and 1100°C. Tensile tests were carried out in an Instron® model 4507 tensile testing machine (1127 lb. load cell) at a cross head speed of 1×10^{-3} /sec in air with the tensile load system enclosed in a split furnace for the high temperature tests. The test temperatures were monitored by a Pt/Pt-10% Rh thermocouple. The duration of one test was about 30 minutes. Results presented in this work are an average of three tests in each condition. The fracture surface and transverse sections were observed by scanning electron microscopy (SEM) equipped with EDX and by optical microscopy. Figure 2.1-2 shows the uneven surface after testing owing to deformation of the relatively large grains of the cast material.

2.2 Analysis methods

Several analysis methods were used to measure the volume fractions of the γ and γ' phases and the relative volume fraction of the surface oxides, to predict possible oxides and microsegregation during solidification, and to analyze the oxidation behavior of the material. In following sections, the methods are briefly introduced. More detailed descriptions of some of the methods are given in the Appendix.

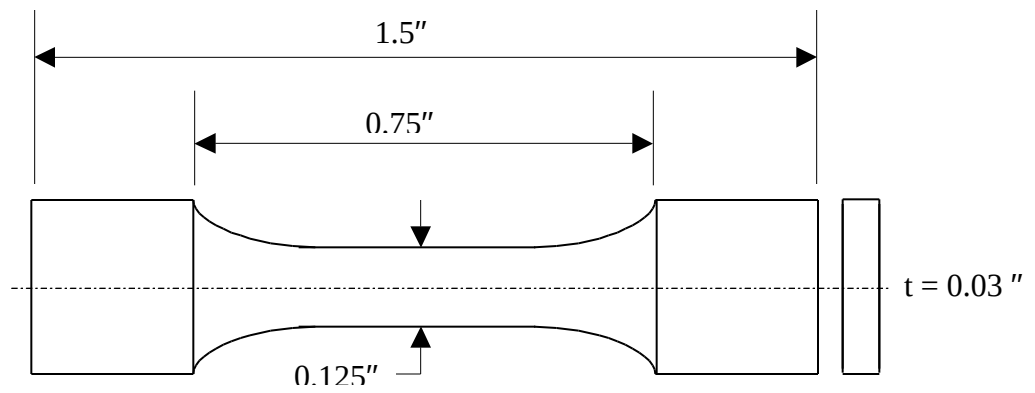


Fig. 2.1-1 A schematic diagram of tensile testing specimen.

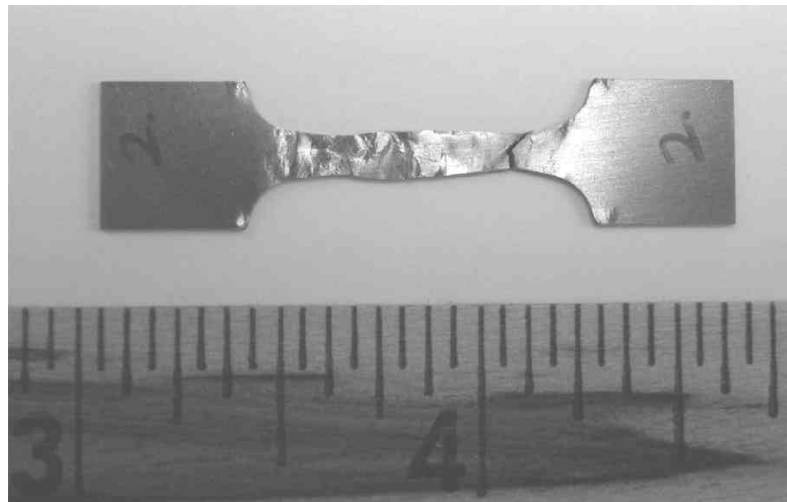


Fig. 2.1-2 A representative feature of tensile specimen after test.

2.2.1 Thermo-CalcTM simulation

Thermo-CalcTM simulation was used to predict the distribution of chemical species during the solidification process and the oxidation products of IC221M in air at 900° and 1100°C .

Thermodynamic and kinetic simulation are important tools in understanding the structure and properties of materials. Thermo-CalcTM is a powerful and flexible software packages for predicting phase equilibrium, phase diagrams, phase transformations, and general thermodynamic behavior [96]. It was developed for complex heterogeneous systems with strongly non-ideal solutions [97], and can be applied to any thermodynamic system in chemistry, metallurgy, material science, alloy development, geochemistry, and semiconductors, etc. for which thermodynamic data are available [98]. Thermo-CalcTM is the only software package that allows for prediction of explicit conditions on individual phase compositions. Thermo-CalcTM was designed for multi-component systems with up to 40 components. The first version of Thermo-CalcTM was released in 1981. It has been updated almost every year since and version P was used in this work.

2.2.2 Rietveld analysis [99,100]

Rietveld analysis was used to measure the change of the volume fraction of γ and γ' phases with aging time at 900°C.

Rietveld analysis was created by Hugo M. Rietveld in the 1960's. The principal goal of this method is to refine crystal structures from x-ray diffraction data. It was the first computer based analytical procedure to make use of the full information contained in an x-ray powder pattern.

Figure 2.2.2-1 briefly illustrates Rietveld analysis by flow charts. Rietveld analysis is used to: 1) confirm phase identification; 2) refine parameters in models for the structure of the specimen and instrument effects on the diffraction patterns; 3) extract detailed information for the crystal structure from powder diffraction data by systematic structure refinement; and 4) determine phase proportions. In the Rietveld method, least-squares refinements are carried out until the best fit diffraction pattern is obtained. Simultaneously refined models for the crystal structure(s), diffraction optics effects, instrumental factors, and other specimen characteristics (e.g., lattice parameters) are determined as desired.

Rietveld analysis is discussed in more detail in Appendix A.1.

2.2.3 Multivariate statistical analysis (MSA)

Multivariate statistical analysis (MSA) was used to construct oxide phase maps using elemental spectrum by EDX.

Multivariate statistical analysis (MSA) is a branch of statistical analysis concerned with the simultaneous investigation of two or more variable characteristics which are measured over a set of objects [101]. Multivariate analysis allows the researcher to examine the relation between two variables while simultaneously controlling for how each of these may be influenced by other variables [102]. There are several analysis methods used in MSA such as correlation analysis, regression analysis, analysis of variance, discriminant analysis, cluster analysis, and factor analysis. In this research, factor analysis was used to analyze large data sets obtained by energy dispersive spectroscopy.

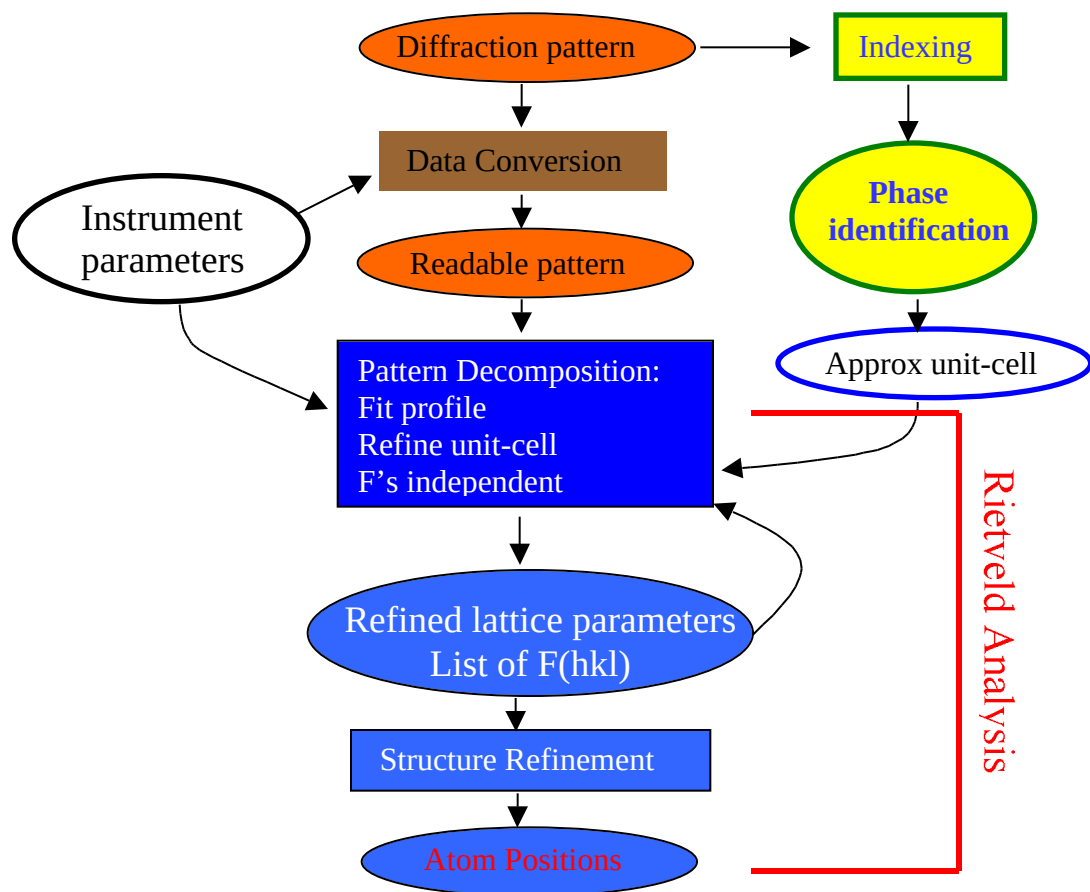


Fig. 2.2.2-1 A flow chart for manipulating x-ray diffraction data for Rietveld analysis [100].

Multivariate statistical analysis is discussed in more detail in Appendix A.2.

2.2.4 Direct comparison method

The direct comparison method [103-105] was used to calculate the volume fraction change of surface oxide with aging time at 900° and 1100°C. A clean ZrO₂ peak was used the internal standard peak.

III. RESULTS AND DISCUSSION

3.1 Thermal aging effects on the microstructure

3.1.1 As-cast microstructure

The dendritic nature of the microstructure of the as-cast IC221M is apparent in the optical micrographs of Fig. 3.1.1-1. The corresponding EDX spectra reveal all the metallic elements of the alloy and a very high zirconium content in the interdendritic region.

The dendrite cores appear as a two-phase mixture of a γ matrix containing relatively fine γ' precipitates. The interdendritic regions contain a relatively coarse cellular γ and γ' microstructure containing the lower melting eutectic islands, which have been identified as fine lamellae of $\gamma + \text{Ni}_5\text{Zr}$ (see Fig. 1.4-1, DSC data). Quantitative analysis of the γ and γ' phases by areal analysis of SEM micrographs and Reitveld analysis of x-ray diffraction data showed the γ volume fraction to be 17-24 %, as will be discussed later (see Table 3.1-1). This is somewhat higher than the previous studies where values in the range 5-15% were reported.

Equilibrium thermodynamic calculations using Thermo-CalcTM shown in Fig. 3.1.1-2 indicate that the matrix of IC221M should be 100% γ' below about 780°C. From 780°C to about 1232°C, the amount of γ increases at the expense of γ' . The only solid phase above 1232°C is γ . The alloy is completely liquid above 1362°C. This was verified experimentally by DSC analysis (see Fig. 1.4-1).

The microsegregation behavior of IC221M was also simulated by Thermo-Calc.

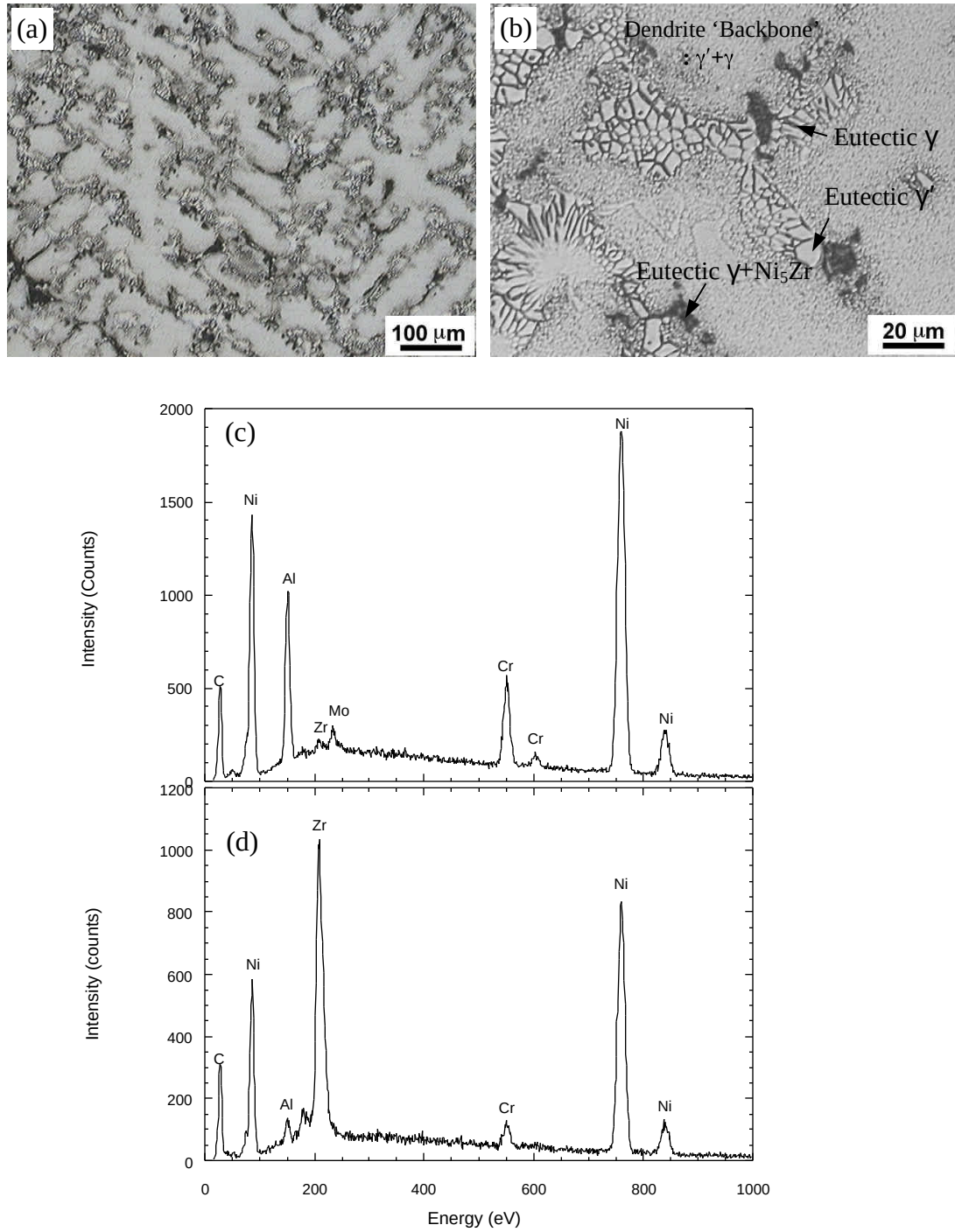


Fig. 3.1.1-1 Optical microstructures and EDX spectra of as-cast IC221M: (b) is an enlarged micrograph of (a); and (c) and (d) are EDX spectra of overall alloy and $\gamma + \text{Ni}_5\text{Zr}$ eutectic colony, respectively.

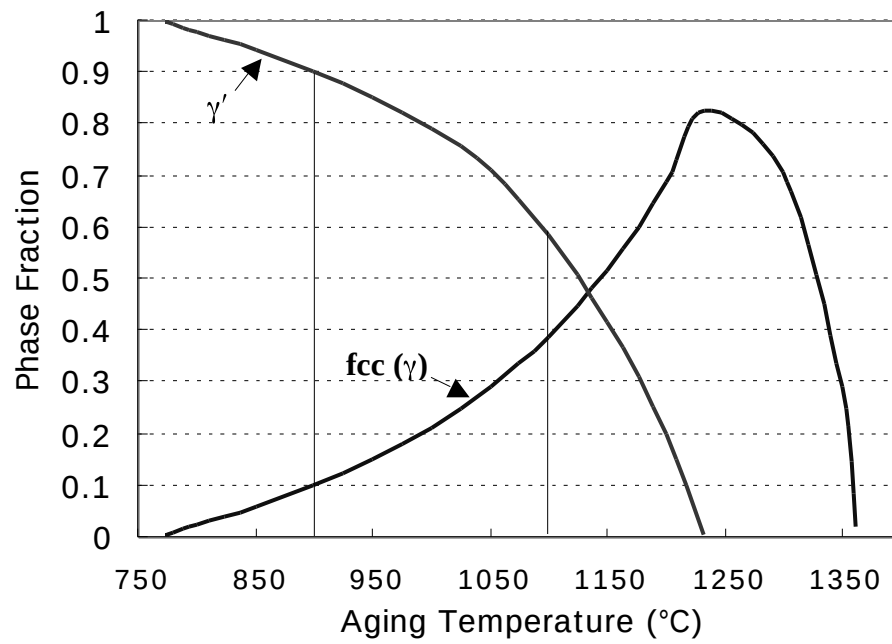


Fig. 3.1.1-2 Variation of the volume fractions of γ' and γ at equilibrium calculated by Thermo-CalcTM simulation.

The variations of Al, Cr, Mo, and Zr with solid-phase fraction were calculated assuming the non-equilibrium (Scheil) conditions of local equilibrium at the liquid-solid interface, no solid diffusion, and complete diffusion in the liquid during solidification² [97]. Results are shown in Fig. 3.1.1-3, which shows the profiles of alloying element (solutes) concentrations in the solid phase as a function of solid-phase fraction at 1°C cooling temperature interval. It is useful to think of these results as one dimensional solidification in which solidification begins at the left and moves to the right. The thermodynamic predictions indicate that from the time solidification begins until the solid fraction reaches about 78%, the only solid is the γ (fcc) phase. The γ and γ' phases coexist briefly, then the γ' phase becomes the primary solid phase. Although not observed in the ThermoCalcTM simulation because of the lack of necessary thermodynamic data, the solidification process is completed by the formation of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic.

As shown in Fig. 3.1.1-3a, the simulation predicts that aluminum concentration in the fcc γ phase starts lower than the nominal composition of 8.2%, implying that aluminum is initially rejected from the solid to the liquid. When γ' formation begins later in the solidification process, the aluminum concentration is higher than the nominal composition. Because the dendrite cores form in the early stages of solidification when the solid fraction is low, the dendrite cores will thus be relatively low in Al compared to the interdendritic regions. Chromium starts at a higher concentration than nominal composition in γ phase, and is then only slightly rejected during γ solidification,

² This is a qualitative approximation for simulating solidification processes: in which it assumed that the diffusion in the liquid is infinitely fast whereas no diffusion occurs in solid. Local equilibrium is reached at the solidification interface where the composition of the alloy may be significantly different from the overall composition, and the compositions of the liquid and solid at the interface are given by the system's phase diagram [6].

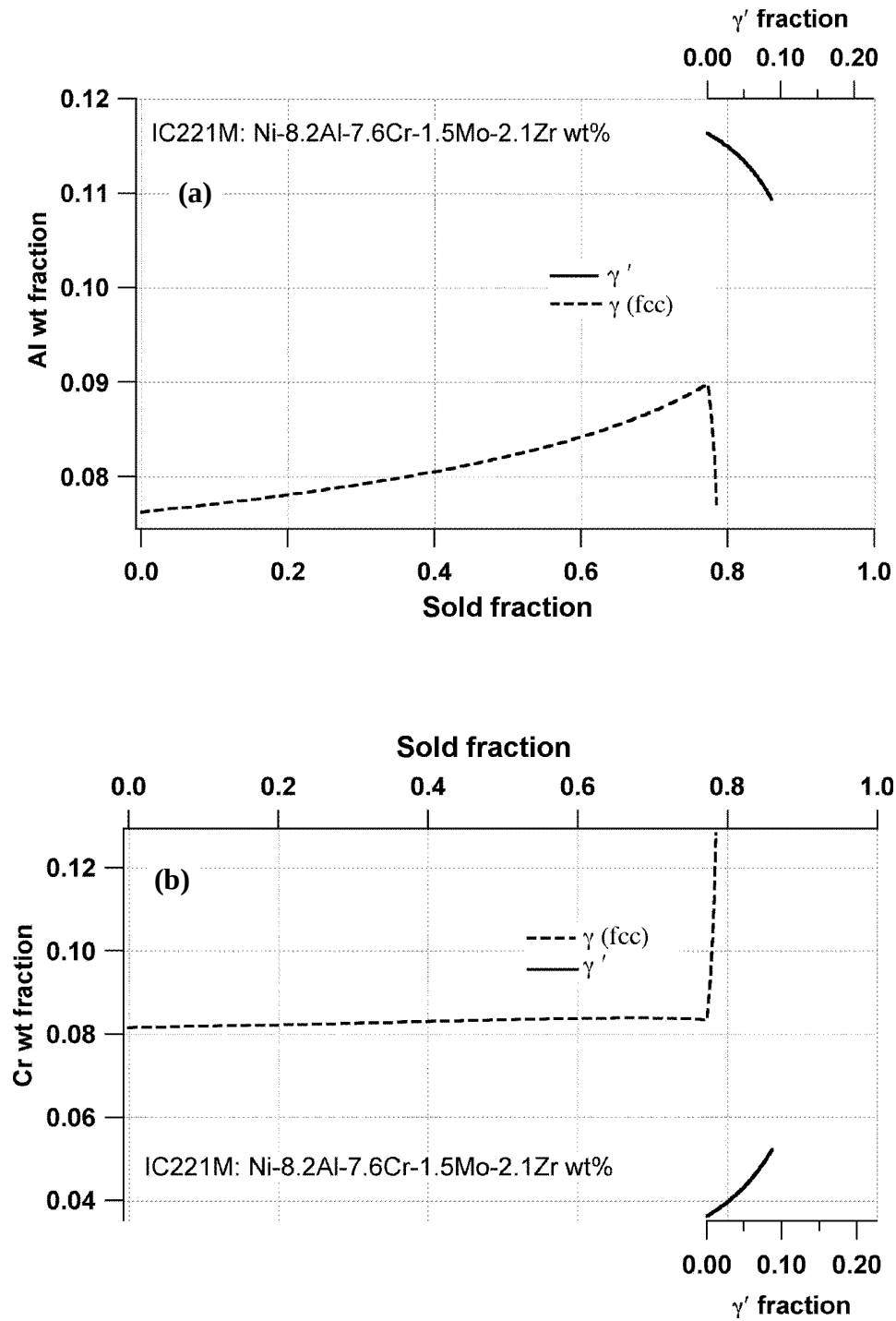


Fig. 3.1.1-3 Changes of chemical composition during solidification as predicted by Thermo-CalcTM: (a) Al, (b) Cr.

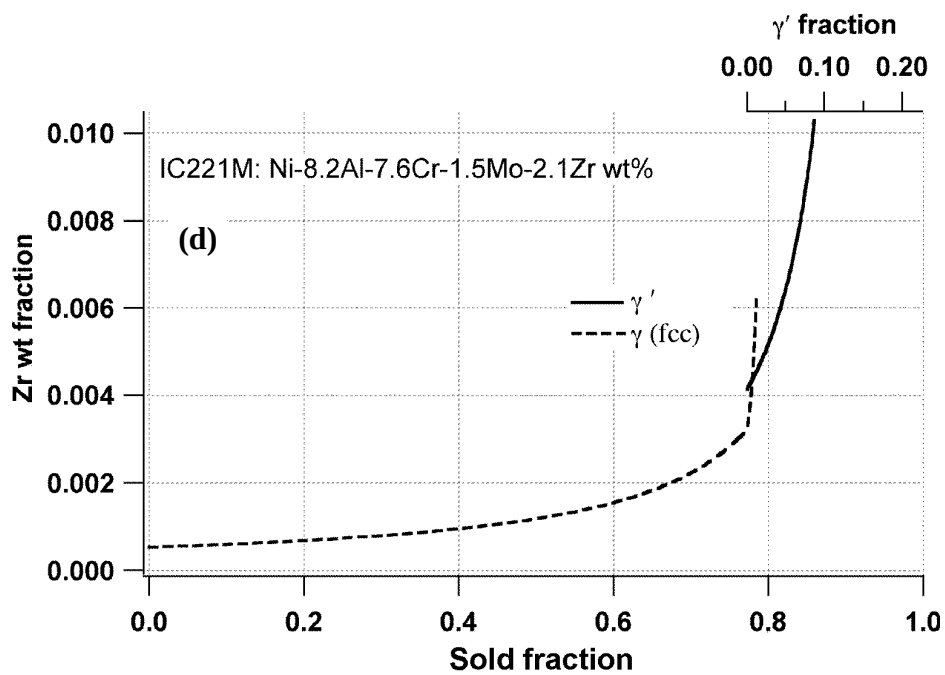
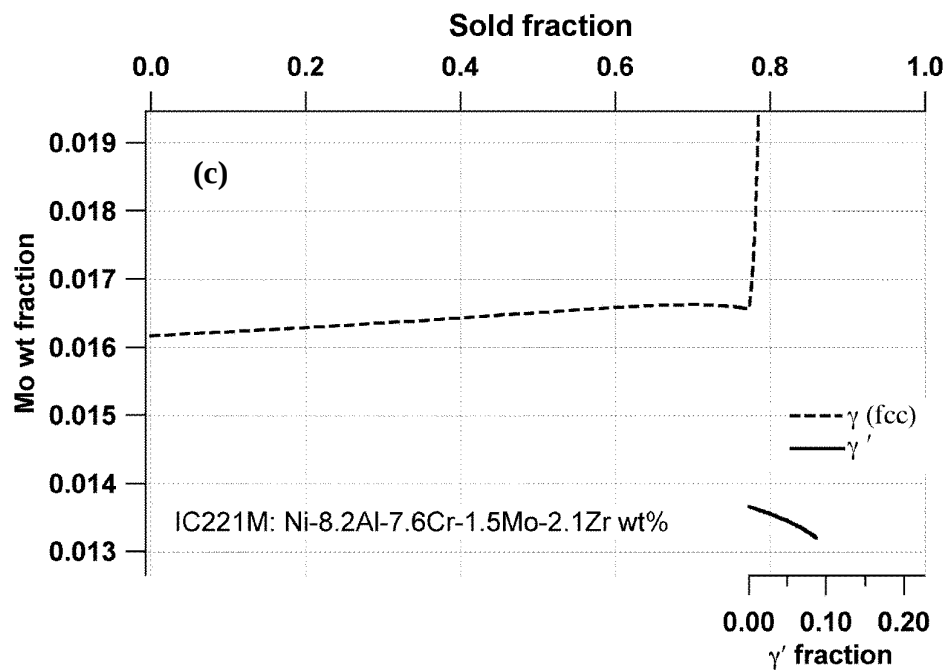


Fig. 3.1.1-3 (continued) (c) Mo, and (d) Zr.

and γ' has lower concentration of chromium, which is more strongly rejected during γ' formation (Fig. 3.1.1-3b). Accordingly, the Cr concentration of the dendrite cores should be higher than the interdendritic regions. Molybdenum also starts higher than the nominal composition, and is only slightly rejected during γ solidification. Its concentration in γ' begins slightly lower than that of the nominal composition and stays lower γ' solidification (Fig. 3.1.1-3c). The dendrite cores are then predicted to have slightly higher Mo concentrations than the interdendritic regions. According to Fig. 3.1.1-3d, Zr should be strongly concentrated in the γ' that forms late in the solidification process and thus strongly segregated in the interdendritic regions.

The microstructure of as-cast IC221M that can be inferred from the Scheil simulation is one comprised of primary dendrites largely of γ with rings or bands of γ' at the interface between the dendrites and interdendritic regions, where the $\gamma + \text{Ni}_5\text{Zr}$ eutectic is located. The Scheil results represent conditions at the end of solidification, which is at a relatively high temperature, $\sim 1170^\circ\text{C}$. Diffusion in the solid phases will operate during both solidification and cooling. Inspection of published phase diagrams [106] and additional equilibrium calculations indicate that γ' will precipitate in the γ phase during cooling.

A back-scattered electron (BSE) image and elemental maps of the as-cast microstructure acquired in the SEM are shown in Fig. 3.1.1-4. The BSE images (Fig. 3.1.1-4a, b) are compositionally sensitive insofar as the brightness of various phases indicate average atomic number; for example, Zr-containing phases appear brightest in the image. Two areas in Fig. 3.1.1-4a were selected for EDX spectrum imaging. The

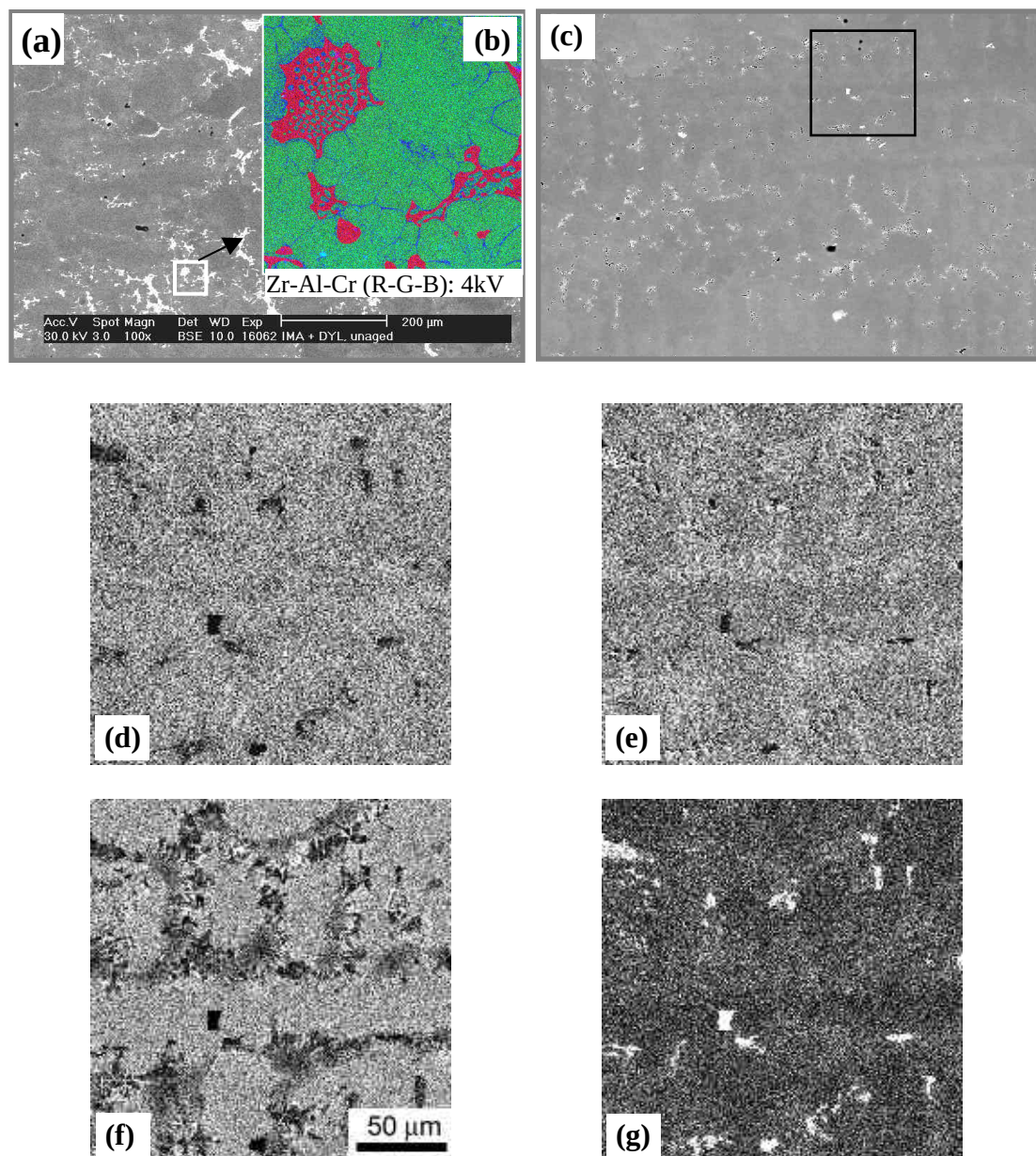


Fig. 3.1.1-4 X-ray elemental mapping images of an as-cast IC221M: (a) and (c) are backscattered electron micrographs; (b) is a RGB image at the small box in (a); and (d) Ni, (e) Al, (f) Cr, and (g) Zr of a box in (c).

smaller area indicated in Fig. 3.1.1-4a was analyzed at relatively high resolution using a 4 kV incident beam. Results from this area are shown in Fig. 3.1.1-4b as a RGB image with red, green, and blue corresponding respectively to Zr, Al, and Cr. The eutectic structure of the Zr-enriched region is clearly evident. Areas of slight Cr enrichment also occur near the $\gamma + \text{Ni}_5\text{Zr}$ eutectic. Presumably, the Cr enriched area represents the eutectic γ . Elemental maps for (d) Ni, (e) Al, (f) Cr, and (g) Zr are shown for the region of the microstructure in the larger area indicated in Fig. 3.1.1-4c. No background subtraction was performed, but the gray level in each map gives a qualitative indication of elemental concentrations. Figure 3.1.1-4g shows that Zr is highly partitioned to interdendritic regions. The Al concentration is relatively uniform through the dendrite cores, but enriched in the interdendritic regions (see Fig. 3.1.1-4e). Figure 3.1.1-4f indicates that Cr is also relatively uniform in the dendrite cores, but is depleted in the interdendritic regions.

In summary, the results from imaging, microchemical analysis, and thermodynamic analysis present a consistent picture of the microstructure of as-cast IC221M. Referring to Fig. 3.1.1-1, the two-phase dendrite cores consist of γ' precipitates in a γ matrix. The coarse cellular regions that occur interdendritically are somewhat enriched in Al and correspond to γ' formed from the liquid during the later stages of solidification. Chromium and molybdenum are enriched in the dendrite core and zirconium is strongly partitioned to the interdendritic regions where it forms a $\gamma + \text{Ni}_5\text{Zr}$ eutectic during the final stages of solidification.

3.1.2 Microstructure after thermal aging

Changes in the microstructure caused by thermal aging at 900°C are shown in Fig. 3.1.2-1. Aging for 500 hrs (Fig. 3.1.2-1b) promotes homogenization of the microstructure, but remnants of the cast structure are still visible. The γ - γ' two-phase structure of the dendrite cores is maintained, but the coarse cellular structure in the interdendritic regions is less distinct than in the as-cast condition. The eutectic structure of the $\gamma + \text{Ni}_5\text{Zr}$ constituent tends to spherodize and it presumably evolves to a single phase, Ni_5Zr (see Figs. 3.1.2-1a' to c') as aging proceeds. Remnants of the cast structure are still visible after 16,600 hrs of aging, Fig. 3.1.2-1c. Second-phase particles still exist in large areas of the matrix, but much of the matrix appears as a single-phase.

The microstructural changes at 1100°C shown in Fig. 3.1.2-2 are essentially the same as that of at 900°C, but homogenization of the microstructure is much faster: for instance, the coarse cellular structure in the interdendritic regions is dramatically diminished and the eutectic constituent is spherodized to a single phase (Ni_5Zr) in 100 hrs.

Measurements of the volume fraction of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies with aging time are shown in Fig. 3.1.2-3. After long-term aging at 900°C, there is a distinct reduction from the as-cast value of 6.5 vol.% to about 3 vol.%. However, most of the reduction occurs within the first 1000 hrs of aging, so it appears that the Ni_5Zr phase is relatively stable against full dissolution into the γ - γ' matrix. On the other hand, thermal aging at 1100°C dramatically decreased the volume fraction of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic to below 0.5 vol% within the first 100 hrs. It is assumed that the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies

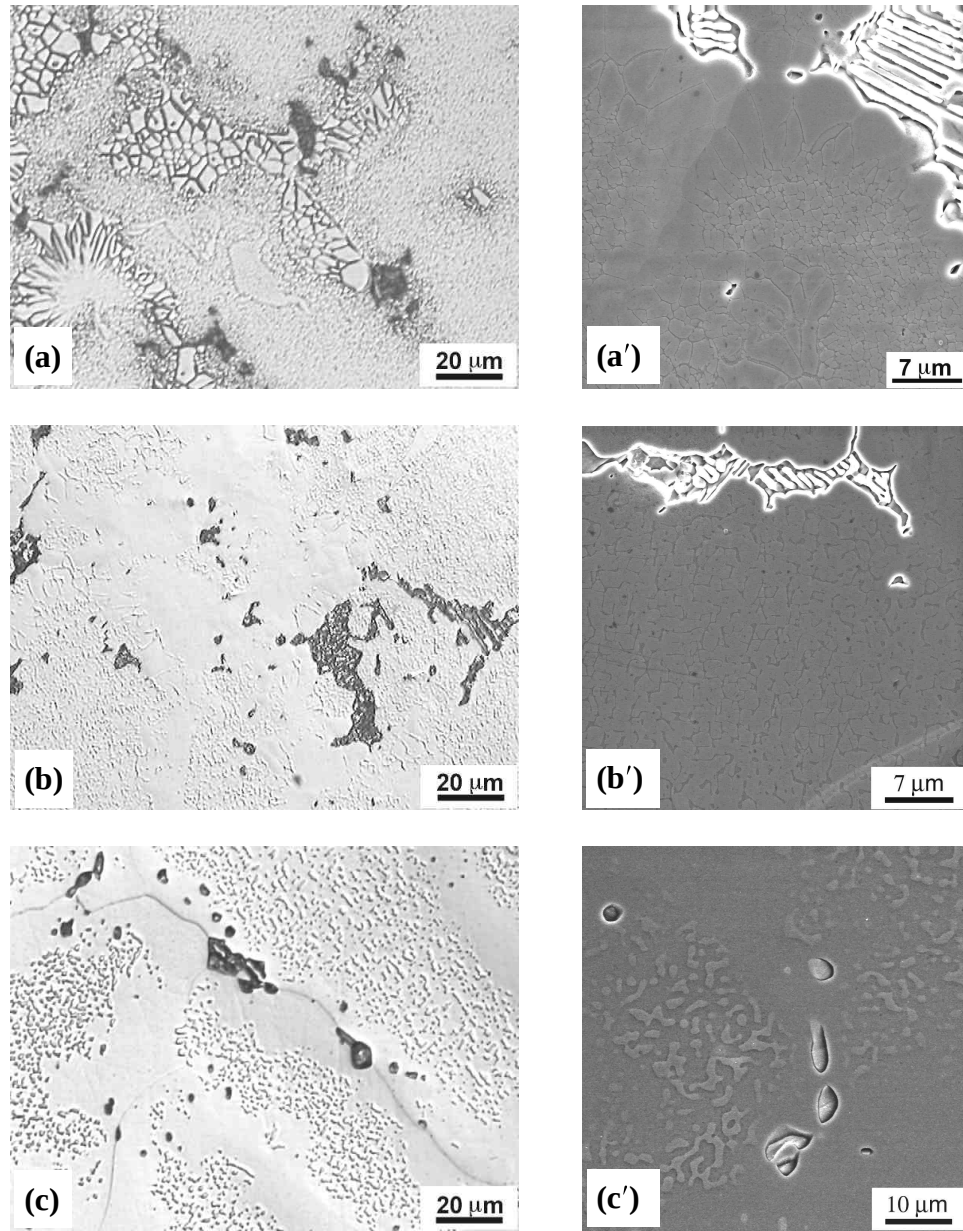


Fig. 3.1.2-1 Variation of microstructures of IC221M with aging time at 900°C: (a) and (a') as-cast, (b) and (b') 500 hrs, and (c) and (c') 16,600 hrs

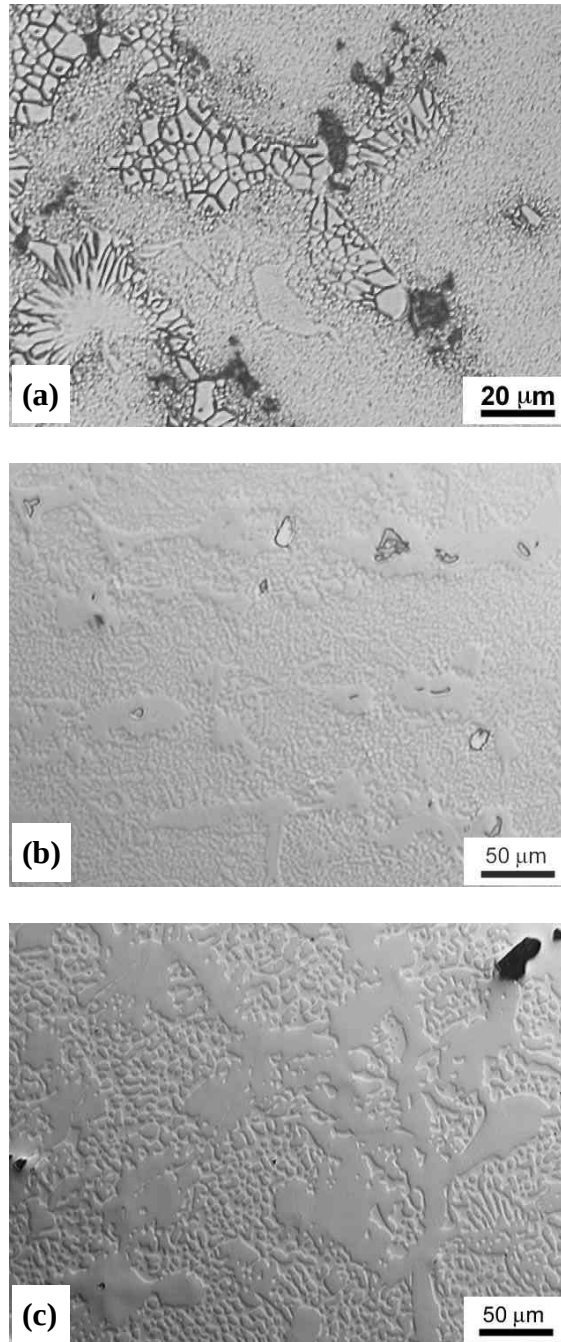


Fig. 3.1.2-2 Optical micrographs of the microstructural changes at 1100°C with aging time: (a) as-cast, (b) 100 hrs, and (c) 1000 hrs.

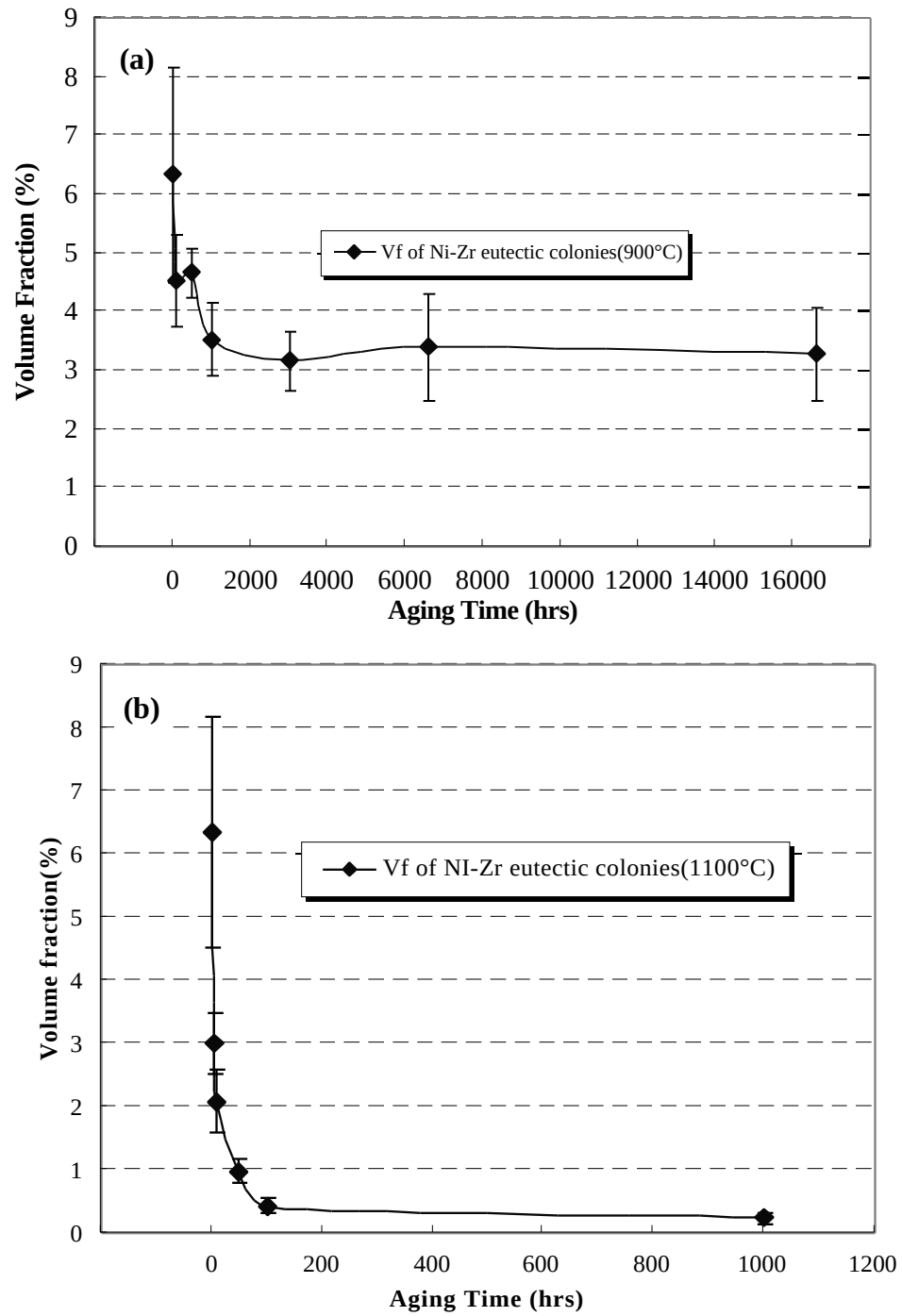


Fig. 3.1.2-3 Variation of volume fraction of $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies at (a) 900°C and (b) 1100°C with aging time up to 16,600 hrs and 1000 hrs, respectively.

dissolved into the matrix and the remnant eutectic represents the solubility of Zr in IC221M system. Thermodynamic predictions estimated that the equilibrium amount of γ' at 900°C is approximately 90% (see Fig. 3.1.1-2). Based on this information, it is presumed that microstructure evolved such that the matrix phase after 16,600 hrs at 900°C is predominantly γ' and the small particles appearing in Fig. 3.1.2-1c are γ . The volume fractions of γ and γ' were confirmed by x-ray diffraction with Rietveld analysis. Results are included in Table 3.1-1, which shows that the measured volume fraction of γ' is 87.1%, in good agreement with the thermodynamic predictions. This experiment confirms that γ' is the major phase in the microstructure, and that the non-equilibrium as-cast alloy, tends toward equilibrium after the long-term aging treatment.

3.2 Oxidation behavior of as-cast Ni₃Al alloy at 900°C and 1100°C

The possible oxides based on free energies of formation predicted by ThermoCalcTM calculations are presented in Fig. 3.2-1. ZrO₂ is the most stable oxide and NiO is the least stable oxide in this system. Five other oxides, Al₂O₃, Cr₂O₃, NiAl₂O₄, NiCr₂O₄, and MoO₂ are also predicted.

A summary of oxide phases formed at 900° and 1100°C based on x-ray diffraction measurement is given in Table 3.2-1. All of the oxides predicted by ThermoCalcTM simulation were detected by x-ray diffraction (Table 3.2-1) with the exception of MoO₂.

Thermo-gravimetric analysis (TGA) and cyclic test results are shown in Fig. 3.2-2. Fig.3.2-2a shows the curves of typical TGA data, which obeys a parabolic rate law. The parabolic rate constants derived from the measurements are shown in

Table 3.1-1 Volume fractions in IC221M of the γ and γ' phases in the as-cast and aged at 900°C conditions, as measured by Rietveld and areal analyses.

	Phases	Volume fraction (%)	
		as-cast	16,600 hrs at 900°C
Rietveld analysis	Ni solid solution (γ phase)	18.4 %	12.9 %
	Ni ₃ Al (γ' phase)	82.6 %	87.1 %
Areal analysis	Ni solid solution (γ phase)	17.05 $\pm$ 4.35 %	-
	Ni ₃ Al (γ' phase)	83.28 $\pm$ 3.61 %	-

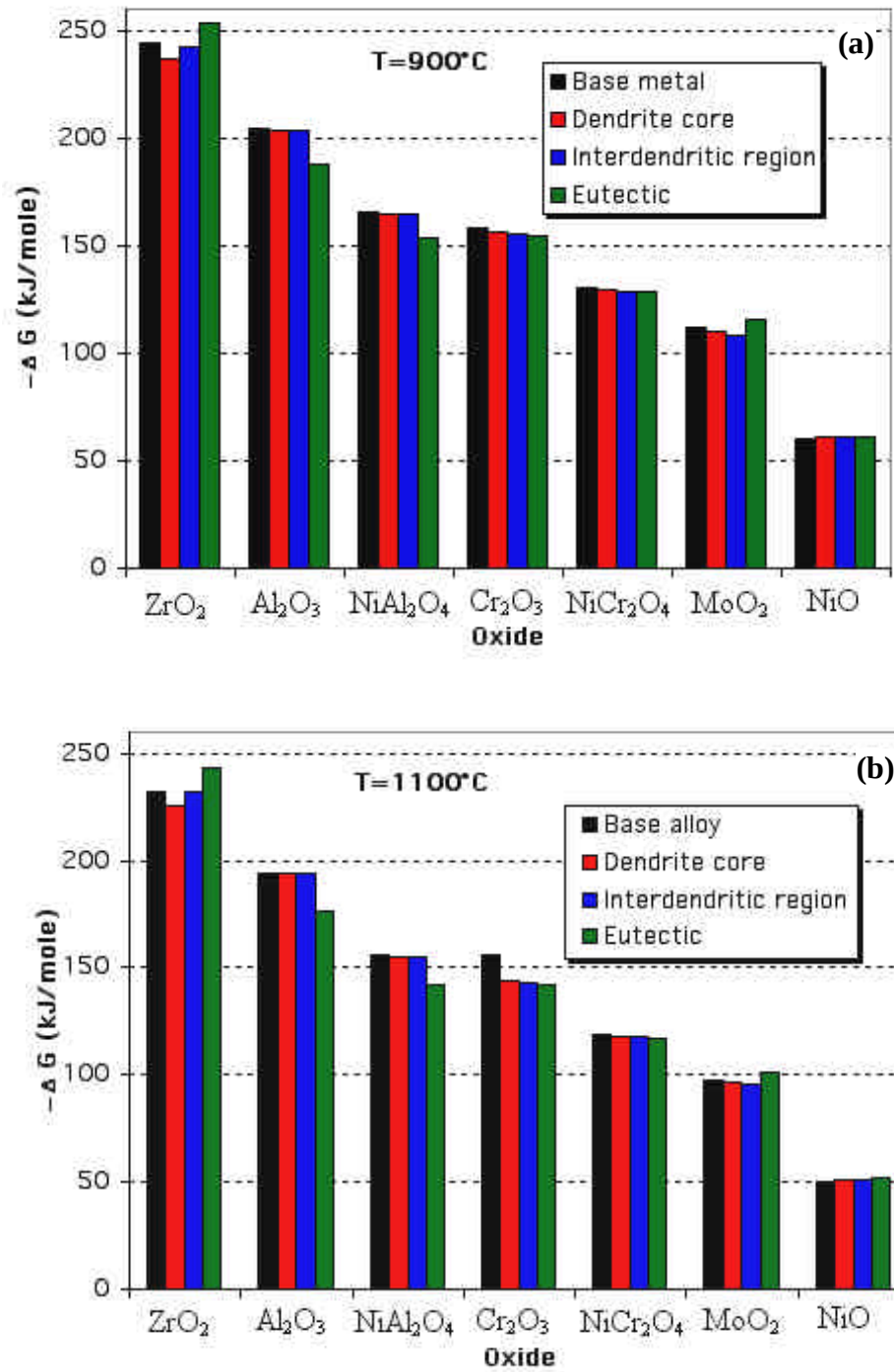


Fig. 3.2-1 The variation of Gibbs free energy (ΔG) for formation of oxides in IC221M based on Thermo-CalcTM calculation: (a) 900°C, (b) 1100°C.

Table 3.2-1 Intensity of x-ray diffraction peaks for oxides formed at 900° and 1100°C.

		10/30 min	1 hr	100/200 hr	3000 hr	16,600 hr
900°C	NiO	M	S	VS	VS	S
	Cr ₂ O ₃	VW	W	M	W	VW
	ZrO ₂	M	M	W	W	VW
	NiCr ₂ O ₄	W	VW	VW	VW	-
	NiAl ₂ O ₄	-	-	M	S	S
	θ-Al ₂ O ₃	VW	Vanished →			
	α-Al ₂ O ₃	-	-	M	S	VS
1100°C	NiO	S	VS	VS	VS	No data
	Cr ₂ O ₃	M	M	W	VW	
	ZrO ₂	M	M	W	VW	
	NiCr ₂ O ₄	M	W	VW		
	NiAl ₂ O ₄	-	W	S	S	
	θ-Al ₂ O ₃	VW	Vanished →			
	α-Al ₂ O ₃	-	M	S	S	No data

* VW-very weak, W-weak, M-medium, S-strong, VS-very strong.

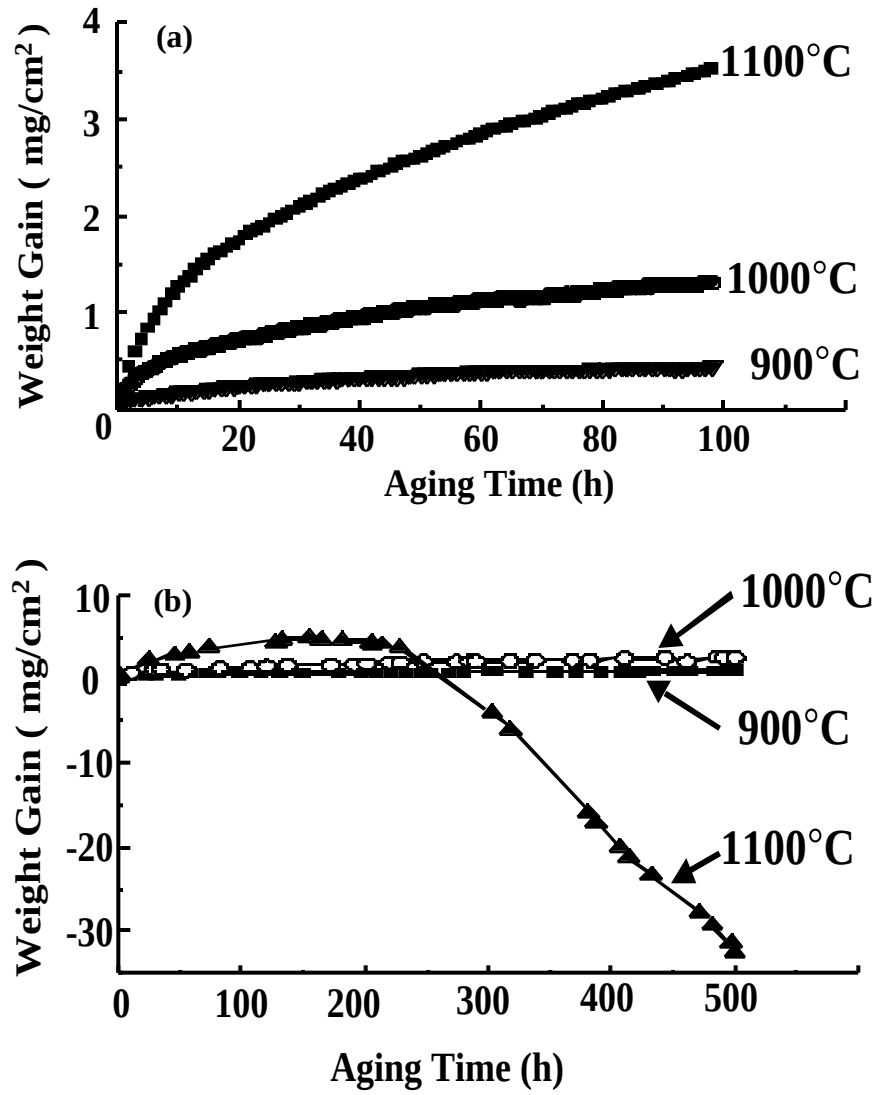


Fig. 3.2-2 Weight-gain vs. time curves of IC221M: (a) isothermal oxidation by thermogravimetric analysis (TGA) and (b) cyclic testing [107].

Fig. 3.2-3. For comparison, the parabolic rate constants for pure Ni, Ni₃Al, and NiAl are also shown. The oxidation rate of IC221M is slower than that of pure Ni, which oxidizes to mostly NiO, but faster than that of pure Ni₃Al or NiAl, which oxidize to Al₂O₃. As expected, the oxidation rate at 1100°C is much faster than that of at 900°C. Results of the cyclic tests show that IC221M is apparently stable at 900°C and 1000°C, but the surface oxide formed at 1100°C is not adherent after about 250 cycles, i.e. 250 hrs in Fig. 3.2-2b. The spallation of the surface oxide at 1100°C is visible to the naked eye, as shown in Fig. 3.2-4. On the other hand, the oxide that forms at 900°C is quite adherent (Fig. 3.2-4a).

3.2.1 Oxidation at 900°C

The microstructures of the surfaces of IC221M specimens oxidized in air for up to 72 hrs are shown in Fig. 3.2.1-1. The regions of light contrast represent areas where oxidation product phases grew at a relatively high rate compared to the areas of darker contrast. The areas of light contrast correspond to interdendritic region, and the areas in darker contrast represent dendritic regions. The formation of oxides was not uniform over the surface, but appears to mirror the microsegregation pattern of the cast alloy. Clearly, microsegregation during solidification plays an important role in the early stages of oxidation. With increased exposure time, a thicker oxide scale covered the surface.

The results of x-ray diffraction measurements made on the oxidized surfaces are presented in Fig. 3.2.1-2. The measurements were performed with a grazing incidence and long dwell times to obtain sufficient diffracted intensity from the surface oxides and to minimize diffraction from the underlying metal. In Fig. 3.2.1-2a, which represents the as-cast specimen, three fundamental peaks of the γ - γ' matrix appear as well as

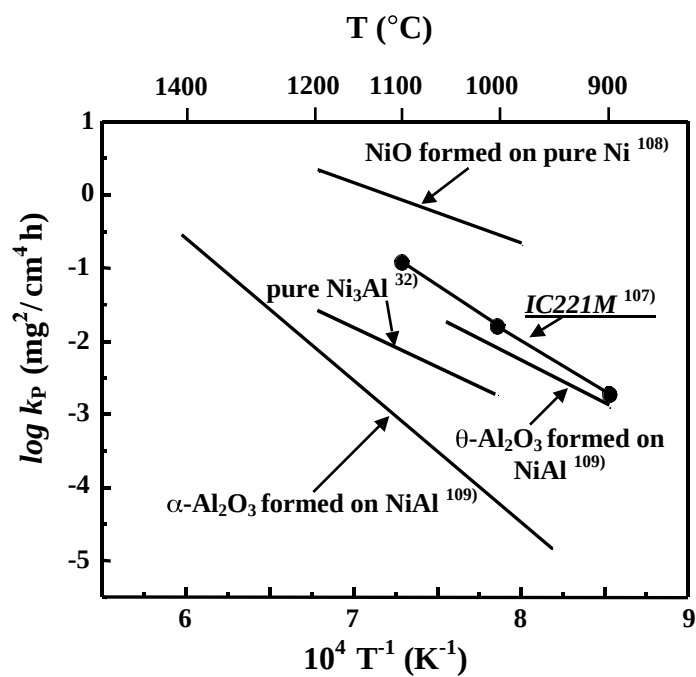


Fig. 3.2-3 Parabolic rate constants for oxidation of IC221M [107], pure Ni [108], pure Ni₃Al [32], pure NiAl [109].



Fig. 3.2-4 Photographs of the IC221M aged at (a) 900°C for 3000 hrs and (b) 1100°C for 1000 hrs in air.

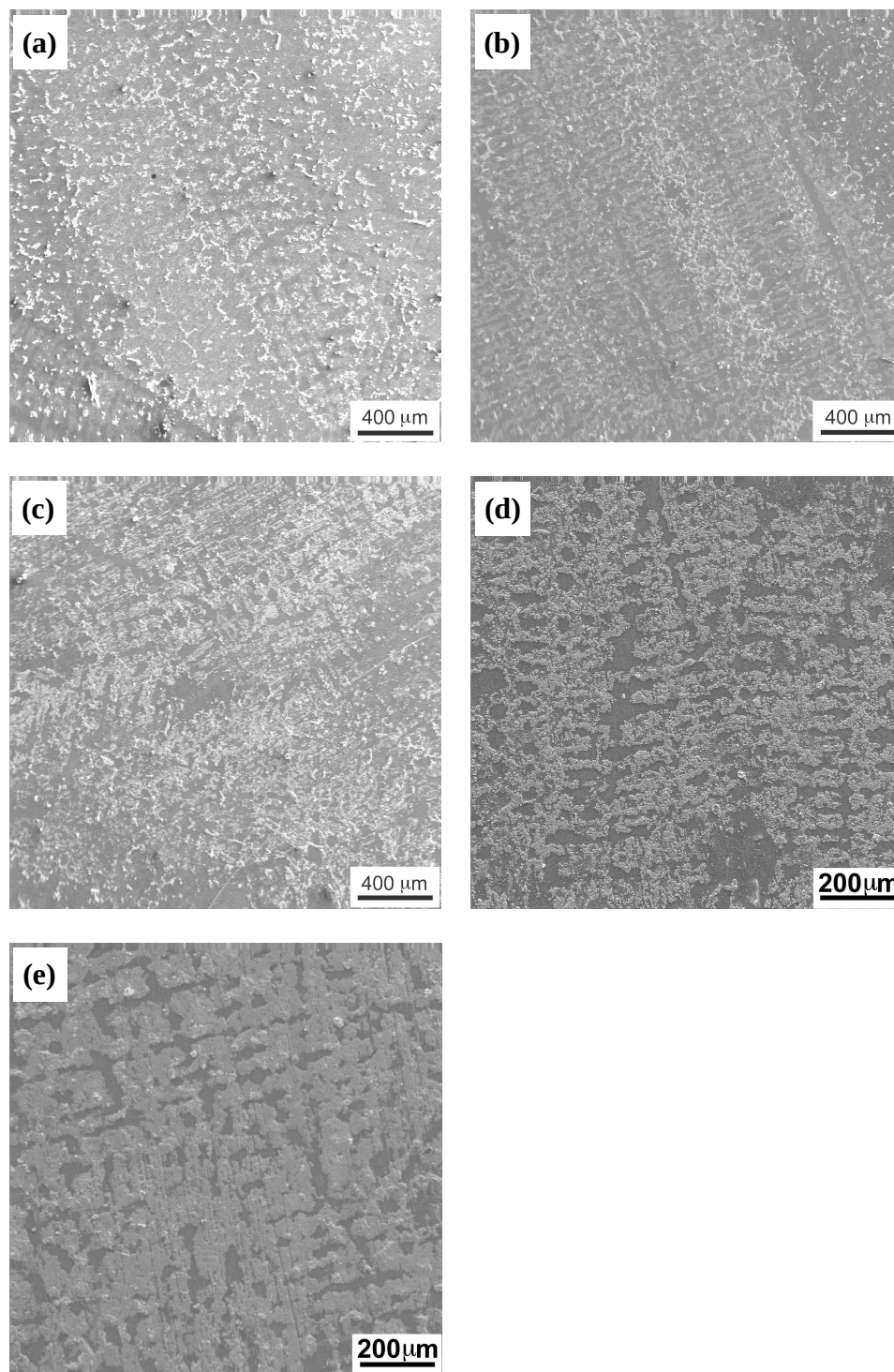


Fig. 3.2.1-1 SEM micrographs of surface oxide morphologies in plan-view with aging time at 900°C: (a) 10 min, (b) 1 hr, (c) 5 hrs, (d) 24 hrs, and (e) 72 hrs.

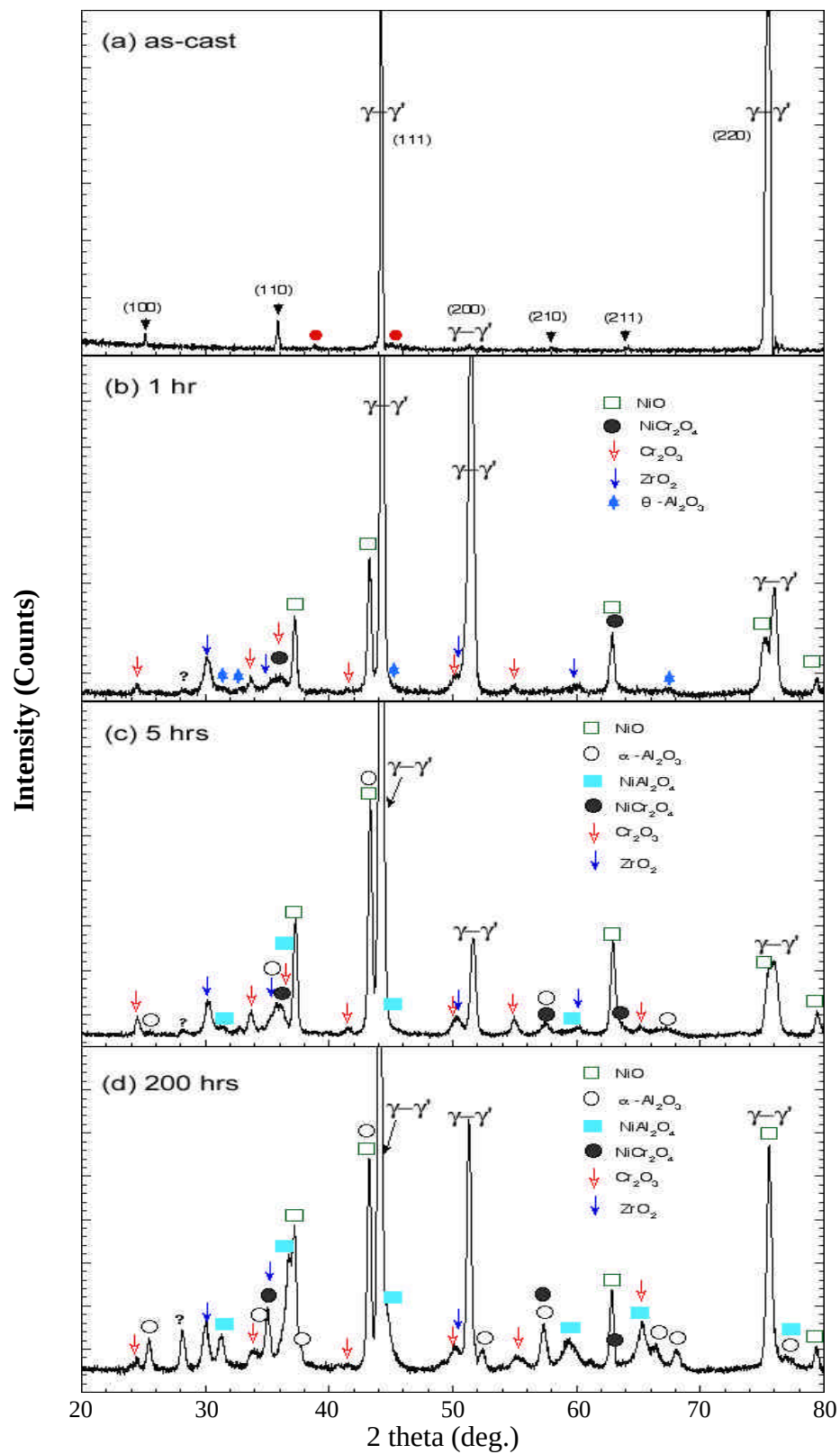


Fig. 3.2.1-2 X-ray diffraction patterns of specimens aged at 900°C.

superlattice³ peaks from the γ' phase (an inverted triangle). A very weak peak, indicated by a circle, could be due to the Ni_5Zr compound. The phases that formed on the surfaces due to exposure to air at 900°C are shown in Fig. 3.2.1-2b~d. An important trend in the data is that the oxide peaks become increasingly prominent relative to the matrix peaks with increased exposure time, which is consistent with the thickening of oxide scale as exposure time increases. It can also be seen that NiO is the predominant surface oxide throughout. After 1 hr of oxidation, $\theta\text{-Al}_2\text{O}_3$, ZrO_2 , Cr_2O_3 , and NiCr_2O_4 are all detected. The increase of exposure time to 5 hrs results in the appearance of $\alpha\text{-Al}_2\text{O}_3$ and NiAl_2O_4 . The transformation of the transition oxide $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ during this period is consistent with other similar studies [21,23,27,32,34].

The relative volume fractions of the surface oxide phases were estimated from analysis of the diffracted intensities. Integrated intensities were determined using the Profile Fitting program (Profit, Philips) and used to estimate volume fractions by the direct comparison method [103]. There may be some measurement errors due to preferred orientation, especially during the initial stages of oxidation where the oxide may form epitaxially on the underlying metal [110]. Results from specimens oxidized for 10 min to 3000 hrs are shown in Fig. 3.2.1-3. While NiO dominates at short aging times, 0.5~1 hour of exposure, its relative volume fraction decreases after 5 hrs as two new oxide phases, the more stable NiAl_2O_4 and Al_2O_3 (see ΔG 's in Fig 3.2-1), appear and grow. As aging proceeds, the predominant oxides become $\alpha\text{-Al}_2\text{O}_3$ and NiAl_2O_4 . It is

³ Ordered alloys show lower symmetry than that of the corresponding disordered alloys from which they transform. This leads to extra reflections, called "superlattice reflections", in the diffraction patterns of ordered alloys.

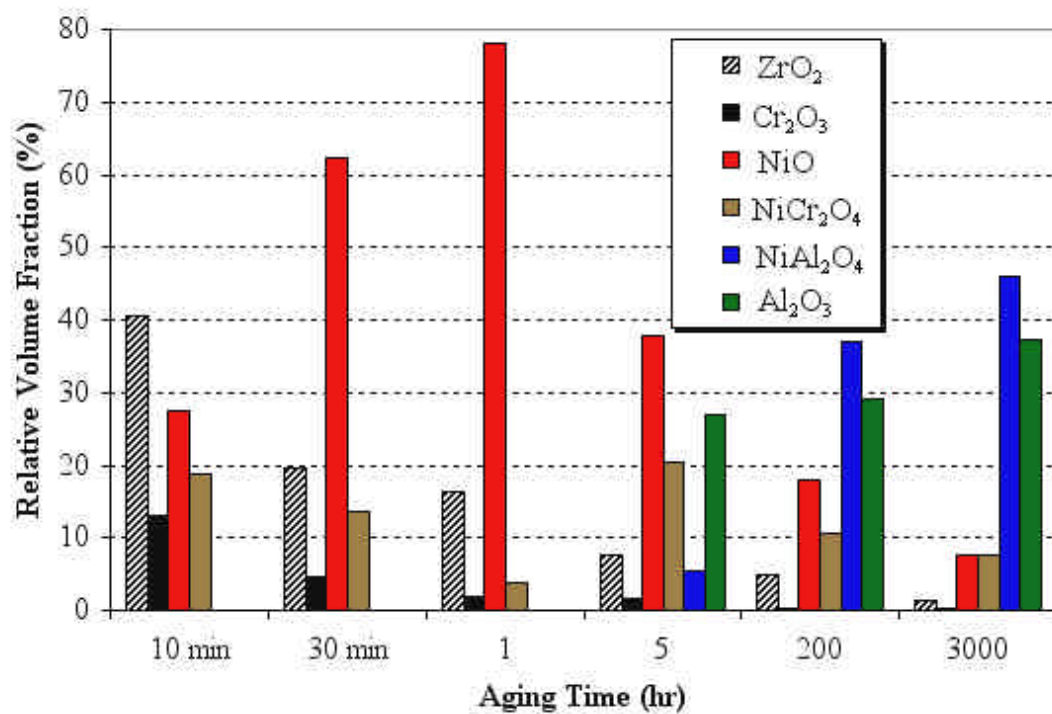


Fig. 3.2.1-3 Volume fraction of oxides on the surface of specimens aged at 900°C; aging times 10 minutes to 3000 hours.

believed that at short aging times, the NiO is a dominant oxide phase because it is the fastest growing in this alloy system (see Fig. 3.2-3 and ch.5 in ref. 13), but the amount of NiO decreases as oxidation proceeds because of a solid state reaction that consumes NiO to form nickel-aluminum spinel, NiAl_2O_4 [87-89].

Optical micrographs showing in cross-section, the progression of the development of the oxides are given in Fig. 3.2.1-4. For short aging periods (Figs. 3.2.1-4a and b), the oxide preferentially penetrates as spikes (black arrow) through the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies with the formation of nodules (white arrows) on the surface. With further aging, the surface oxides grow and form continuous layer, while the spikes penetrate deeper through the Zr enriched short-circuit diffusion paths. An aluminum depletion zone (ADZ) is distinctly revealed after 20 hrs that grows beneath surface oxide and around the spikes. The thickness of the continuous surface oxide, the ADZ, and the penetration depth of the spikes were measured by standard metallographic technique with the results shown in Fig. 3.2.1-5. The continuous oxide film maintains a relatively stable thickness after 500 hrs of aging, while the spikes penetrate linearly with respect to square root of aging time, consistent with parabolic rate kinetics (see Fig. 3.2-3). The ADZ is also grows thicker in a manner that scale with the square root of the aging time.

To investigate how microsegregation affects the short term oxidation behavior, specimens aged for 30 min and 5 hrs at 900°C were characterized by SEM-EDX spectrum imaging. Figures 3.2.1-6 and 7 present the results of a multivariate statistical analysis (MSA) of the spectrum images to identify the distribution of the important oxide phases. Figures 3.2.1-6 and 7 show, respectively, the surface in plan view after 30 min and a cross-section after 5 hrs of oxidation. In Fig. 3.2.1-6, the region “A” represents a

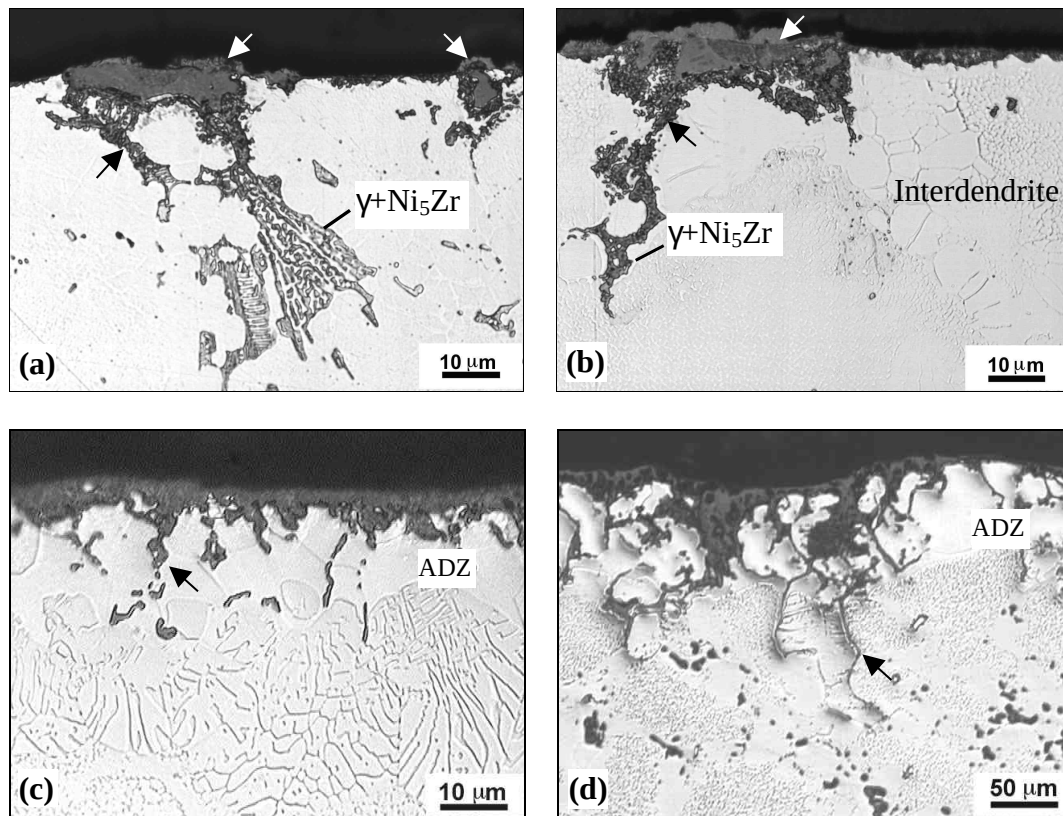


Fig. 3.2.1-4 Optical micrographs in cross-section of specimens aged at 900°C for: (a) 5 hrs, (b) 20 hrs, (c) 500 hrs, and (d) 16,600 hrs. Note that the magnification of (d) is the lower than the others.

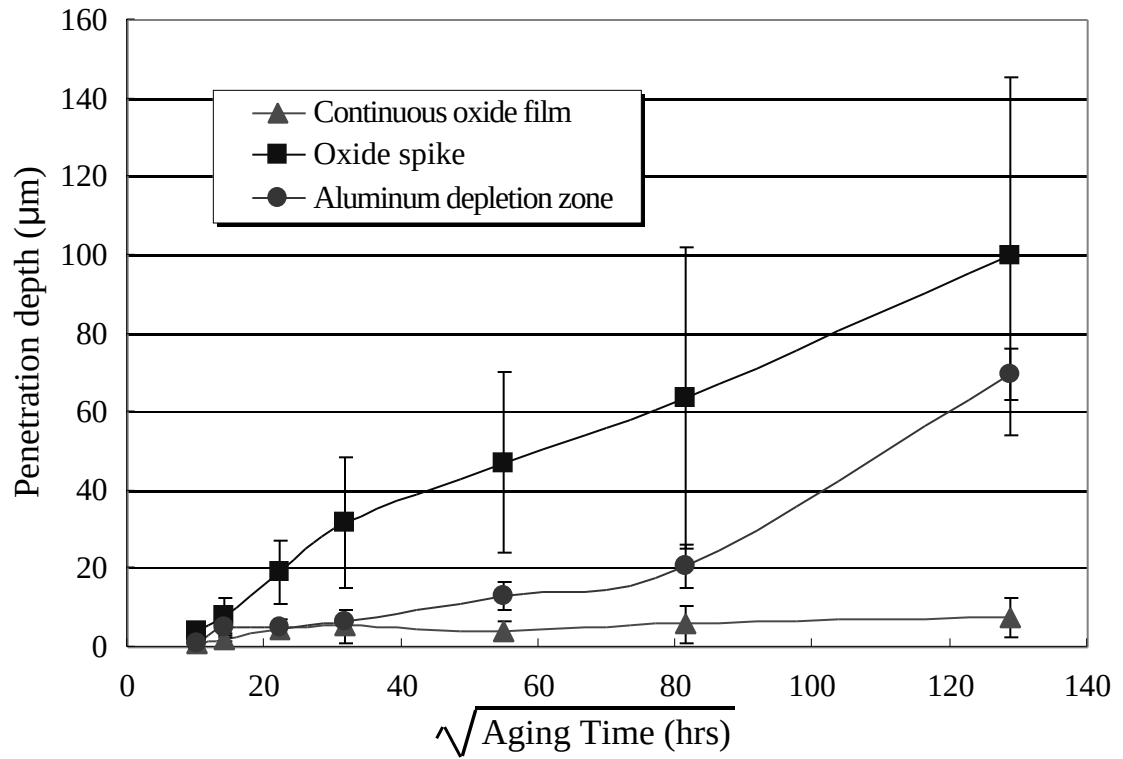


Fig. 3.2.1-5 Oxide penetration depth vs. square root of aging time at 900°C. The continuous oxide film is stable even 16,600 hrs aging, but the spike oxide and aluminum depletion zone grow linearly with aging time.

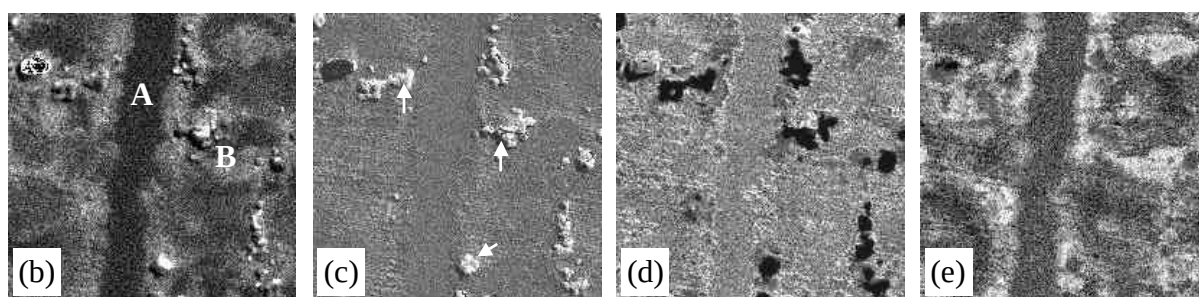
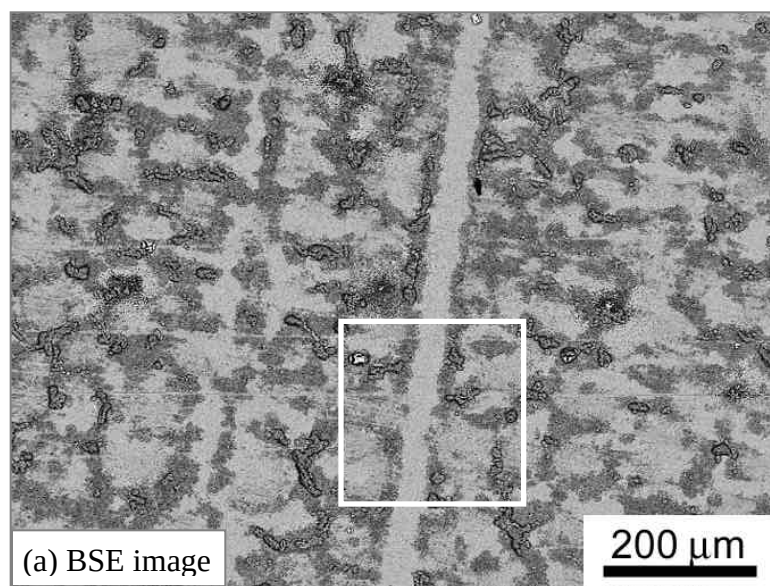


Fig. 3.2.1-6 MSA phase maps of oxide distribution for a specimen aged 30 min at 900°C representing strong positive intensities for (b) ZrO_2 (c) NiO (d) Al_2O_3 , and (e) $\text{Cr}_2\text{O}_3/\text{NiCr}_2\text{O}_4$.

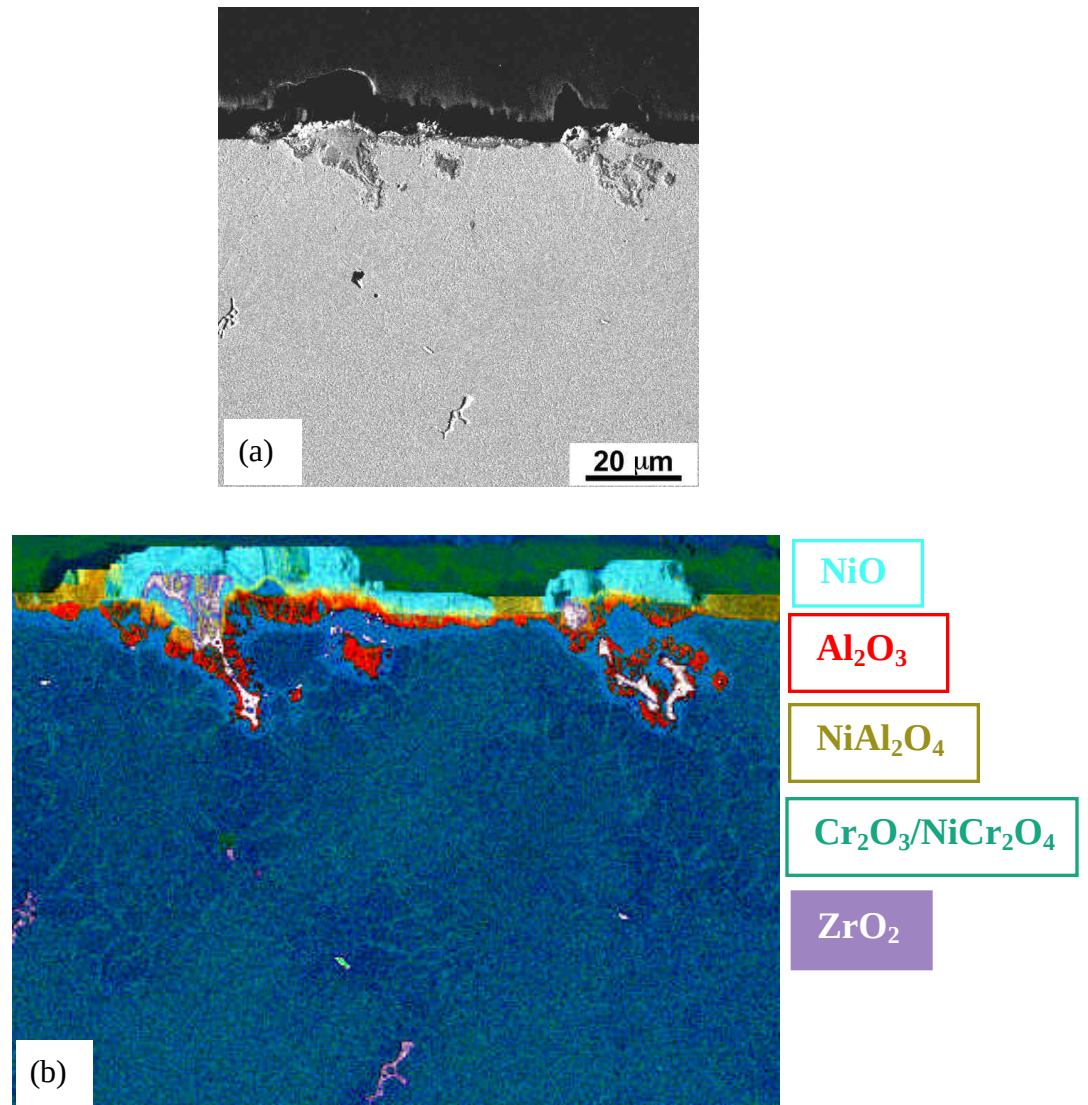


Fig. 3.2.1-7 Cross-sectional view of 5 hrs aged specimen: (a) secondary electron image, (b) color compositional map constructed by MSA method.

dendrite core, and region “B” represents an adjacent interdendritic region. Bright areas of the MSA component maps in Figs. 3.2.1-6b~e indicate regions enriched in the oxides of Zr, Ni, Al, and Cr, respectively. Examination of these characteristic x-ray maps confirms that Zr and O are strongly concentrated in the interdendritic regions where the $\gamma + \text{Ni}_5\text{Zr}$ eutectic intersects the surface. The high driving force for oxidation of Zr to ZrO_2 appears to make the eutectic a preferred site for oxidation processes to begin. The $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies are also associated with surface “nodules” that have high concentrations of NiO (indicated by arrows in Fig. 3.2.1-6c). Presumably, rapid oxidation of Zr produces localized regions that are relatively high in Ni and low in Al concentration. Therefore, the less noble component, Ni, is susceptible to oxidation on the outer surface of that region [89]. Figure 3.2.1-6d indicates that a small amount of Al_2O_3 is distributed across the surface, and that the Al_2O_3 is noticeably absent near the NiO nodules. Fig. 3.2.1-6e shows that Cr_2O_3 or NiCr_2O_4 are primarily distributed in the interdendritic regions.

Several important features of the oxidation process are illustrated by the cross-sectional view shown in Fig. 3.2.1-7 for an exposure time of 5 hrs. Figures 3.2.1-7a and b show respectively a secondary electron image of the scanned area and the color compositional map constructed by MSA. The oxide nodules are clearly visible protruding above the surface. The microchemical analysis information of Fig. 3.2.1-7 confirms that the nodules largely contain NiO and oxides of Cr, possibly nickel chromate spinel. Figure 3.2.1-7 also confirms that the nodules form preferentially where the $\gamma + \text{Ni}_5\text{Zr}$ eutectic intersects the exposed surface. The continuous film is primarily as Al_2O_3 (red in Fig. 3.2.1-7 b) formed by oxidation and depletion of aluminum from the metal matrix. Figure 3.2.1-7 also shows that ZrO_2 forms as long, thin spikes that penetrate well beneath the

surface, possibly aided by the relatively high mobility of oxygen in the ZrO_2 (refer Fig. 1.2-1a). Similar behavior has been observed in oxidation of other Zr-containing Ni_3Al alloys [40]. The spikes also appear to be sheathed in thin layers of Al_2O_3 .

Oxide phase maps of long-term aging time up to 3000 hrs constructed by MSA are presented in Figs. 3.2.1-8 to 3.2.1-10. Figure 3.2.1-8 shows secondary electron images and x-ray maps of the oxide phases on a cross-sectional view of a specimen aged for 100 hrs at 900°C . Aluminum oxide, $\alpha\text{-Al}_2\text{O}_3$, forms a dense and continuous layer near the surface (Fig. 3.2.1-8 b) while the outer most part of the surface consists of discrete nickel oxide nodules (Fig. 3.2.1-8 f) located directly above the Zr enriched regions. As can be seen in Fig. 3.2.1-8 e, chromium oxide and/or nickel-chromate spinel form locally underneath the nickel oxide. Zirconium oxide is formed as spikes in the $\gamma + \text{Ni}_5\text{Zr}$ eutectic regions.

Figures 3.2.1-9 and 3.2.1-10 show the results of the spectrum imaging examined at 30 kV and 4 kV, respectively, for a specimen aged 3000 hrs at 900°C . Again, the surface nodules are predominantly nickel enriched oxides, NiO , but NiAl_2O_4 spinel and aluminum oxide forms a continuous film just beneath the surface. ZrO_2 forms the spike oxide. Chromium oxide or nickel-chromate spinel is formed immediately beneath nodules on the surface (Fig. 3.2.1-9e). Higher resolution micrographs of the oxide scales are presented in Fig. 3.2.1-10. According to these images, the continuous oxide film is composed of two discrete layers - aluminum oxide capped by nickel oxide and/or nickel-aluminum spinel. Some zirconium oxide is dispersed as small particles in the continuous oxide film but most penetrates into the matrix as spikes with a Al_2O_3 sheath. (Note: since the energy of Cr L peaks is very close to the energy of O K peaks, the chromium

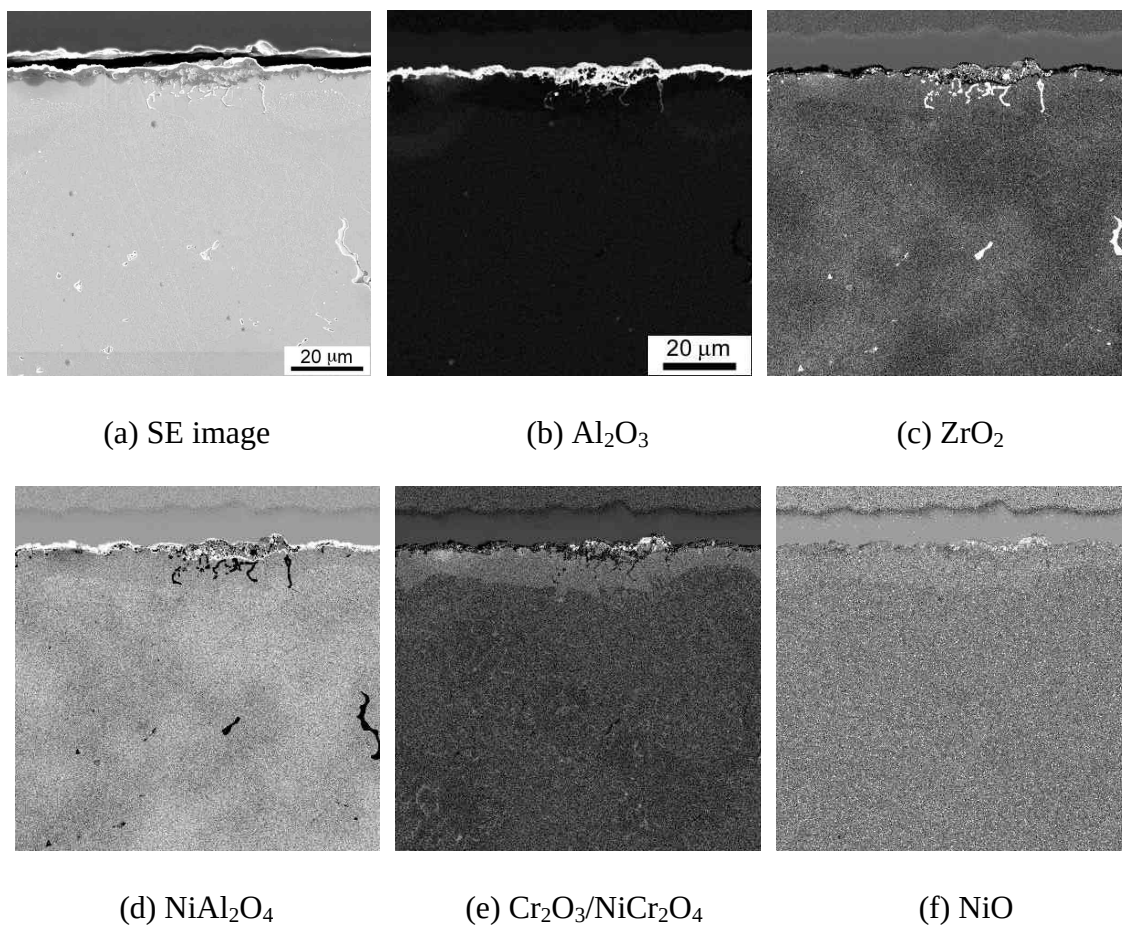
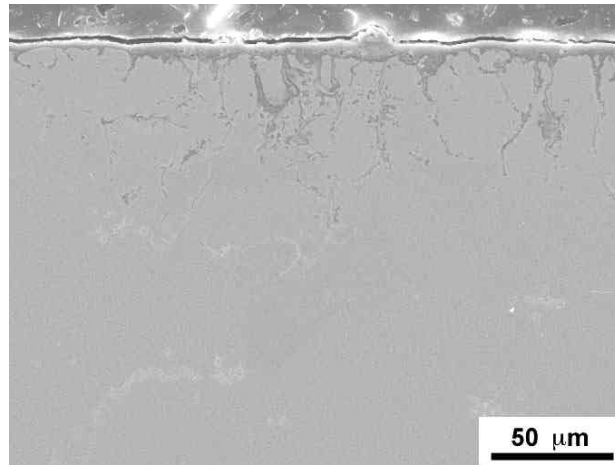
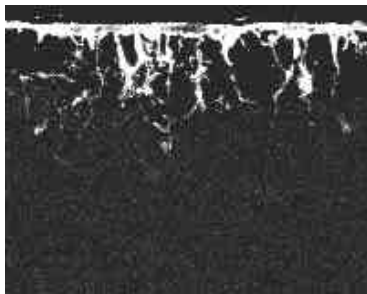


Fig. 3.2.1-8 Cross-sectional x-ray maps of a specimen aged for 100 hr at 900°C, 30 keV.



(a) SE image, 30 keV



(b) Al_2O_3



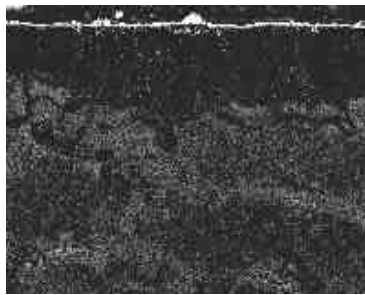
(c) ZrO_2



(d) NiAl_2O_4

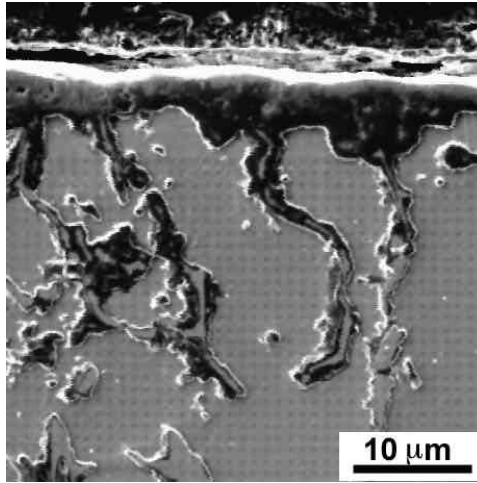


(e) $\text{Cr}_2\text{O}_3/\text{NiCr}_2\text{O}_4$

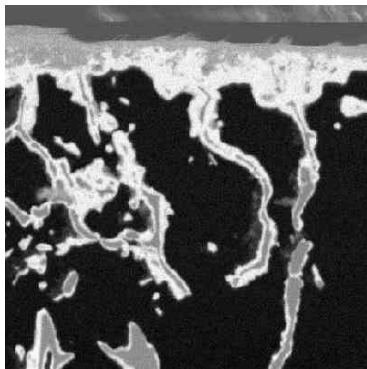


(f) NiO

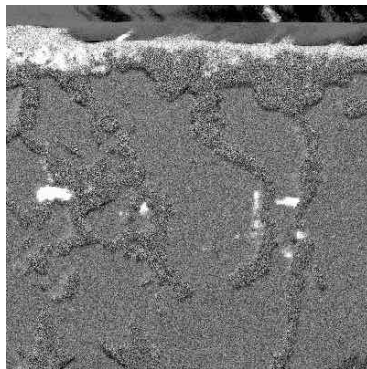
Fig. 3.2.1-9 Cross-sectional x-ray maps of a specimen aged for 3000 hrs at 900°C, 30 keV.



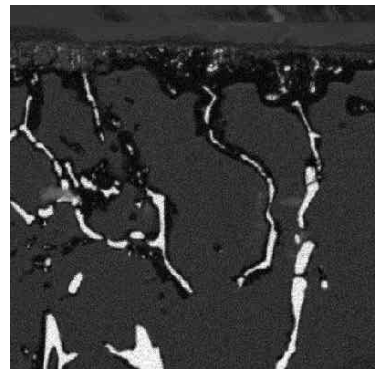
(a) SE image, 4 keV



(b) Al_2O_3



(c) $\text{NiO/NiAl}_2\text{O}_4$



(d) ZrO_2

Fig. 3.2.1-10 Cross-sectional x-ray maps of a specimen aged for 3000 hrs at 900°C, 4keV.

distribution could not be determined in the 4kV operating condition). These observations are reasonably consistent with the oxide volume fraction measurements by x-ray diffraction in Fig. 3.2.1-3.

Collectively, these observations show that the mechanisms of oxidation in IC221M are quite complex, but they are clearly related to the microsegregation patterns of alloying elements in the cast metal.

3.2.2 Oxidation at 1100°C

Oxidation at 1100°C is considerably different from that at 900°C because the surface oxides spall continuously after they form to expose fresh metal surface (refer Fig. 3.2-2b, cyclic test results), and the reaction rate is faster than that of lower temperatures (see Fig. 3.2-2a).

Figure 3.2.2-1 shows SEM micrographs of specimens aged at 1100°C in plan-view. It indicates that surface oxides form along the microsegregation patterns, but the surface oxides start to breakaway after 72 hrs (see uneven surface of Fig. 3.2.2-1c). X-ray diffraction analyses and Thermo-CalcTM predictions of the crystalline oxides were shown in Table 3.2-1 and Fig. 3.2-1, respectively. The three major surface oxides are NiO, NiAl₂O₄, and Al₂O₃. The relative volume fractions of the oxides remaining on the surface are shown in Fig. 3.2.2-2a. Although NiO dominates at short times, its relative volume fraction decreases after 1 hr due to a solid state reaction between nickel oxide and aluminum in the matrix [89]; however, NiO also spalls freely from the surface. Figure 3.2.2-2b shows an x-ray diffraction pattern of a spalled flake after aging 3000 hrs which clearly demonstrates that the flake is predominantly NiO. Presumably, differences in the

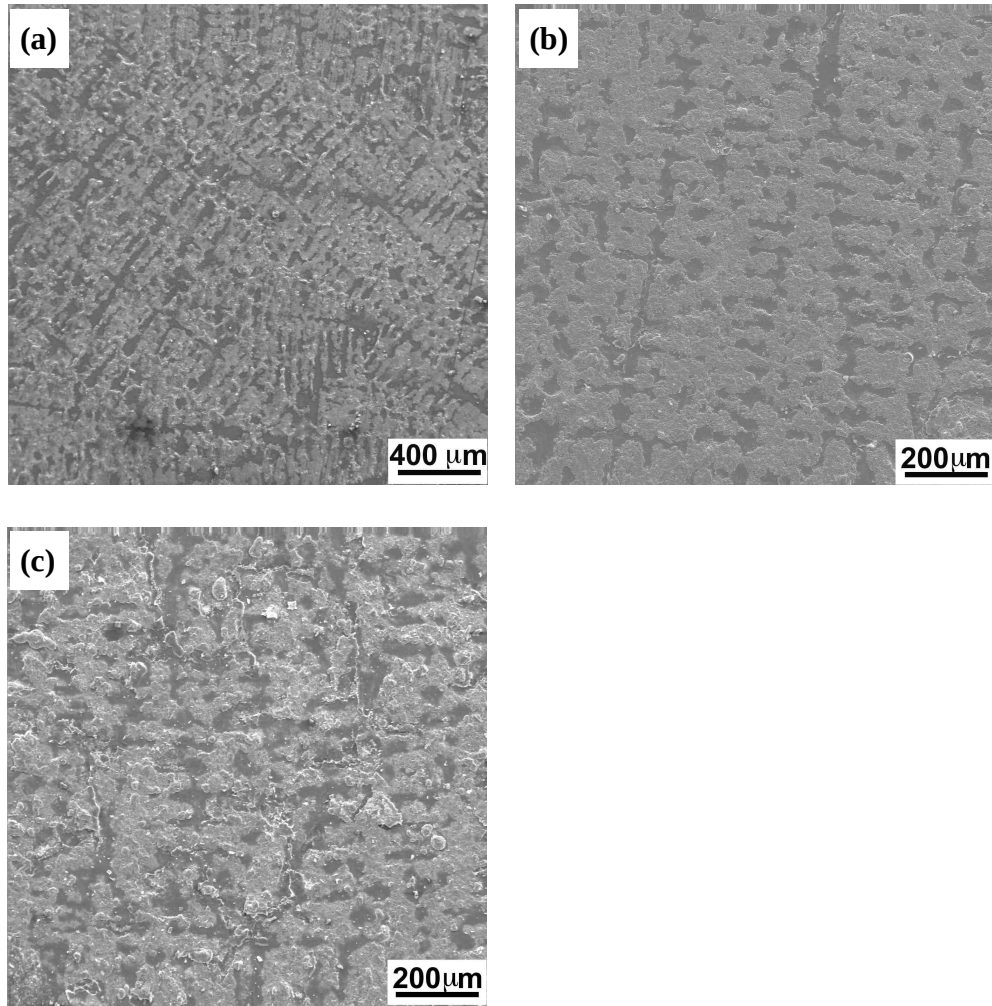


Fig. 3.2.2-1 SEM micrographs of surface oxide morphologies in plan-view at 1100°C: (a) 10 min, (b) 24 hrs, and (c) 72 hrs.

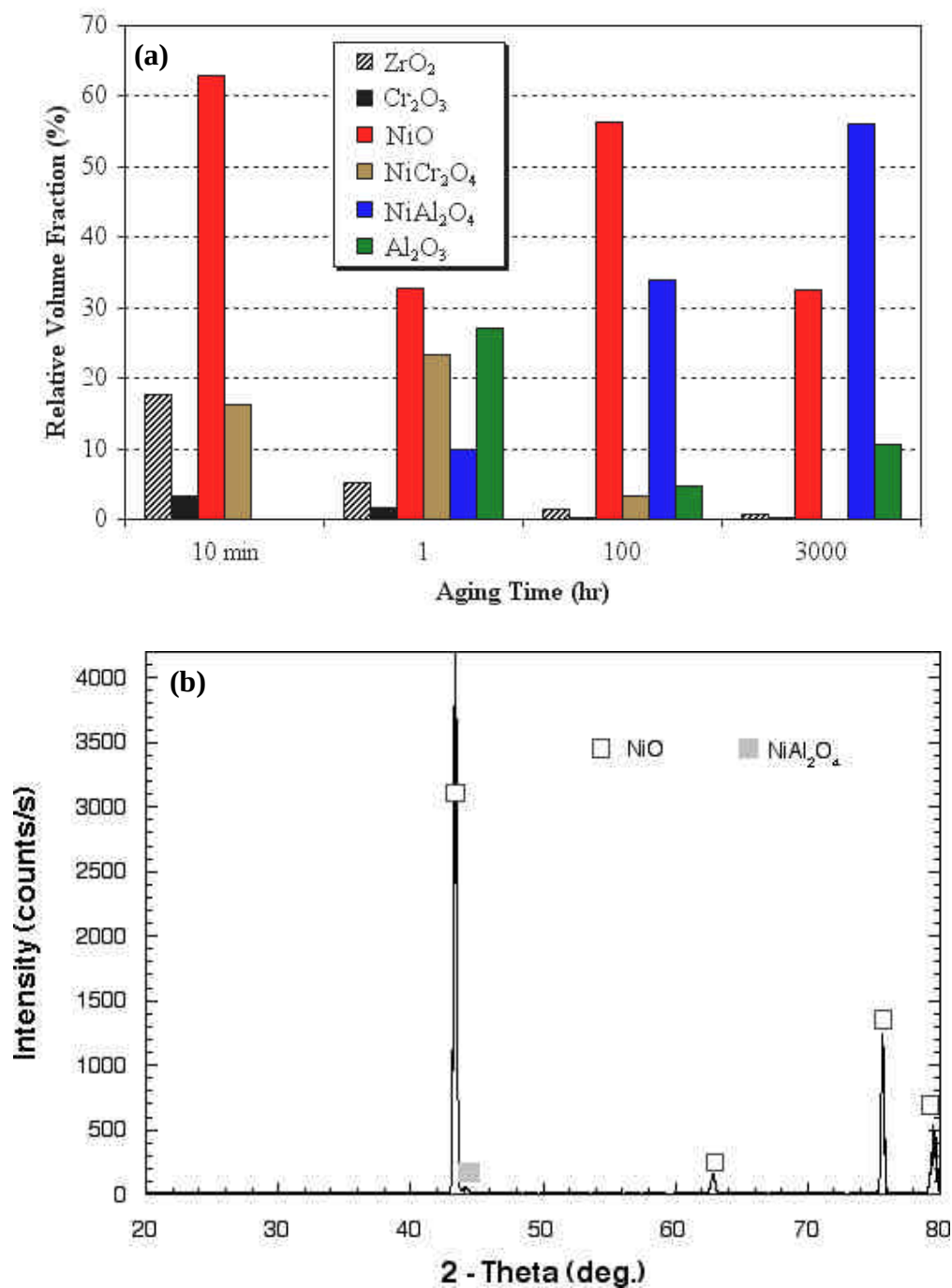


Fig. 3.2.2-2 Volume fraction of surface oxides aged in air at 1100°C: (a) direct comparison method, (b) x-ray diffraction pattern of a spalled flake after aging 3000 hrs at 1100°C.

thermal expansion coefficients of NiO and the base alloy cause spallation of NiO during cooling to room temperature. The thermal expansion coefficient of IC221M at 100°C is $12.77 (\times 10^{-6}/^{\circ}\text{C})$ [111]. The thermal expansion coefficients for the oxides are: 8.8 for Al_2O_3 [112], 10.0 for ZrO_2 [112], 7.3 for Cr_2O_3 [14] and 17.1 for NiO [110]. Stress on the oxide, NiO, is in tension [13]. It is believed that the spallation of NiO may affect the relative volume fraction of the oxides. Curiously, after long term oxidation, 3000 hrs, the relative amount of Al_2O_3 is much less than NiO and NiAl_2O_4 spinel.

Optical cross-sections of specimens aged at 1100°C are shown in Fig. 3.2.2-3. For short aging periods, Fig. 3.2.2-3a, the oxidation behavior is similar to that at 900°C, with the oxide preferentially penetrating through the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies and oxides nodules developing above them. However, after 20 hrs of aging, the spikes penetrate much deeper than at 900°C and the surface oxide is thinner. Indeed, the continuous oxide film is not sustained at all as it spalls off. In addition, the spikes are dispersed everywhere beneath the surface oxide (Figs. 3.2.2-3c, d) instead of penetrating through the eutectic colonies. Metallographic measurement of the thickness of the continuous surface oxide film, ADZ, and the penetration depth of the spikes are shown in Fig. 3.2.2-4. The continuous oxide film can not be defined after 50 hrs of aging because of excessive spalling. The depth of spikes and the width of ADZ linearly increases with respect to square root of aging time, following a parabolic rate law.

Results of oxide phase mapping by MSA are shown in Figs. 3.2.2-5 and 6. The experiments were performed in the same manner as the specimens aged at 900°C. The square area in the secondary electron image of Fig. 3.2.2-5a for the specimen aged 1 hr was scanned at 8 keV. An enlarged secondary electron image of the box in Fig. 3.2.2-5a

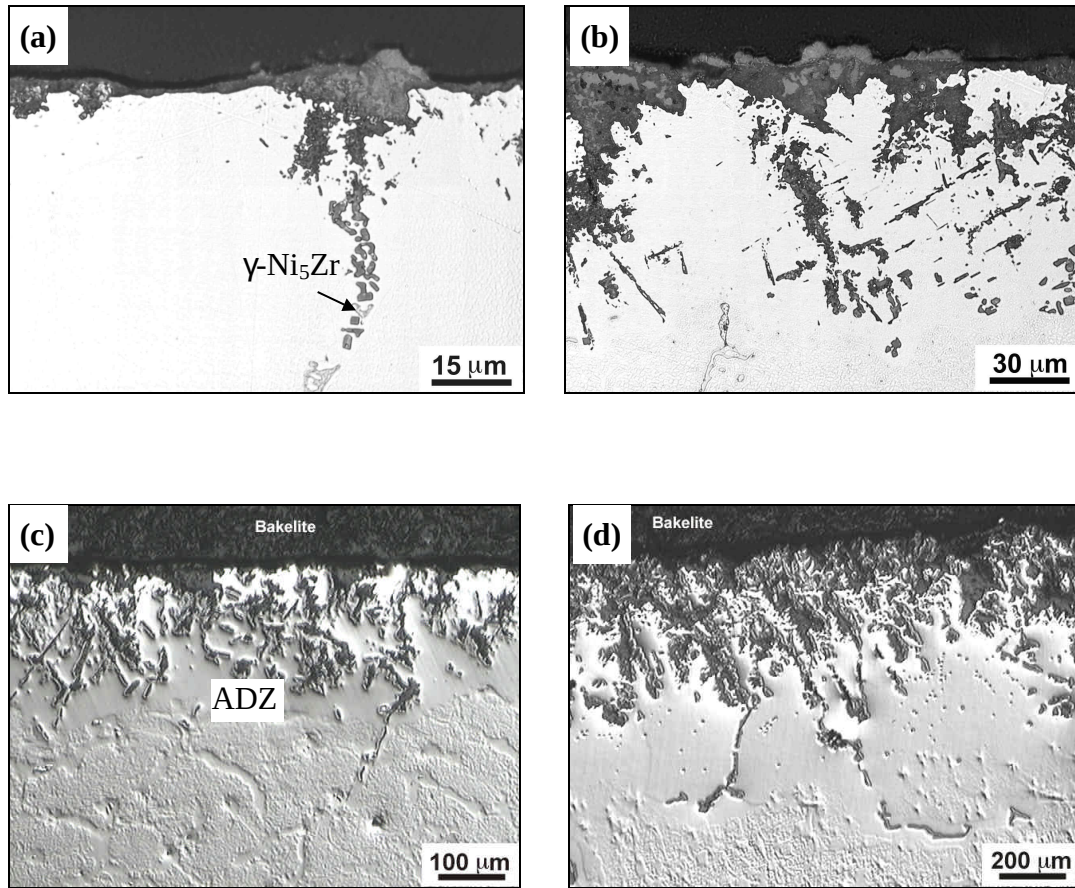


Fig. 3.2.2-3 Optical micrographs in cross-section aged at 1100°C; (a) 1hr, (b) 20 hrs, (c) 100 hrs, and (d) 1000 hrs.

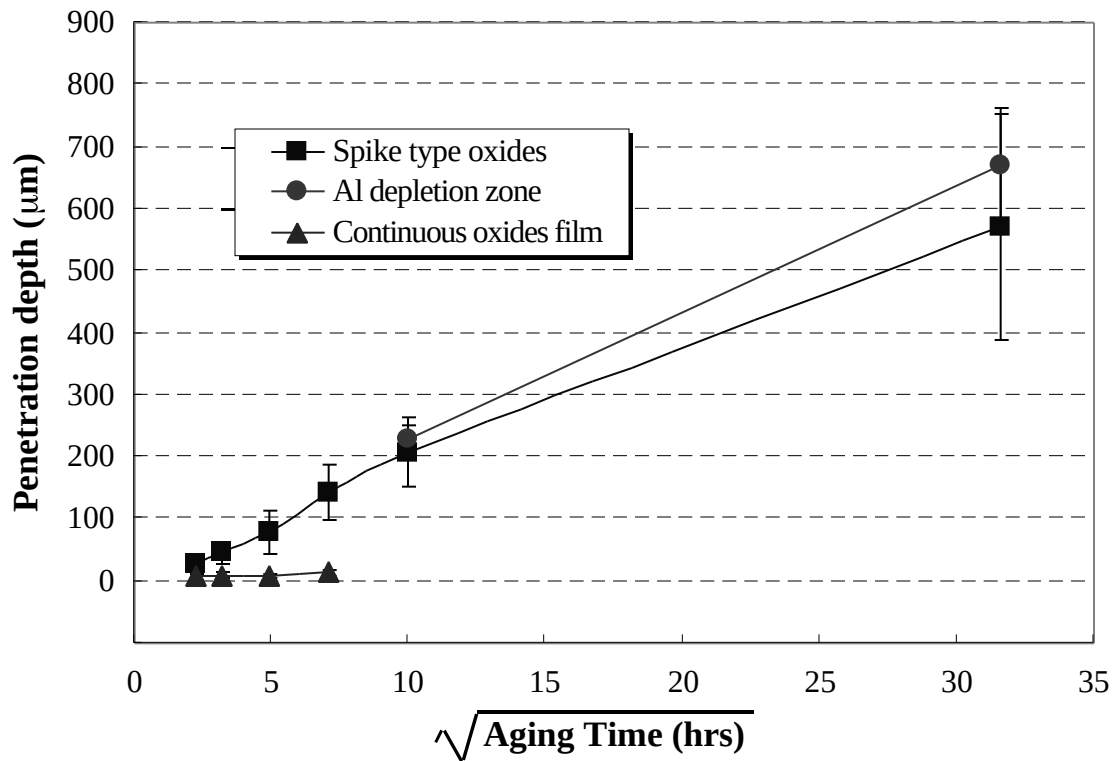
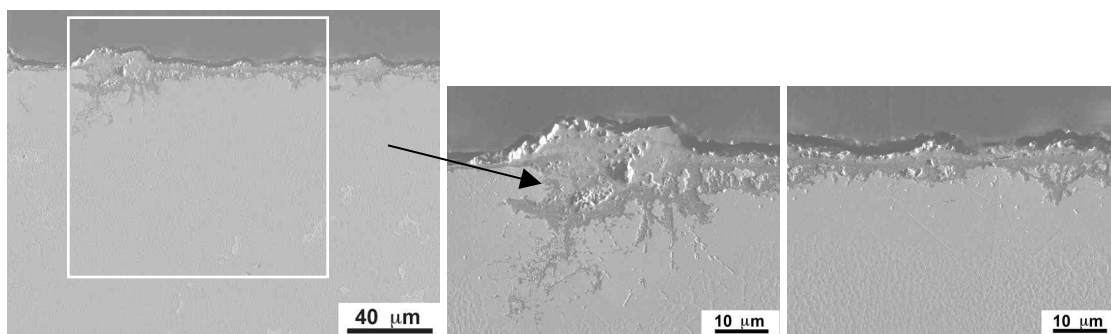
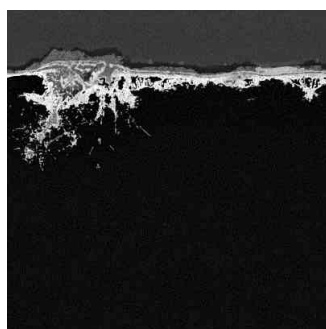


Fig. 3.2.2-4 A plot of oxidation kinetics at 1100°C. The continuous oxide film vanishes after 50 hrs aging. The spikes and aluminum depletion zone penetrate linearly with aging time at a rate that is much greater than at 900°C.

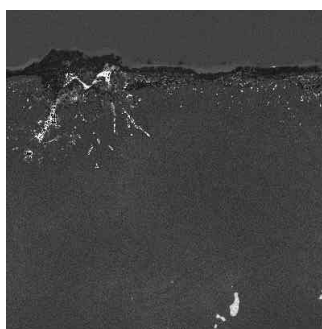


(a) SE image, 8 keV

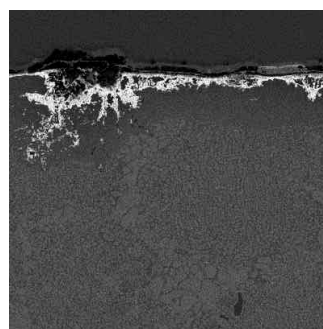
(b) Enlarged images of the surface on (a)



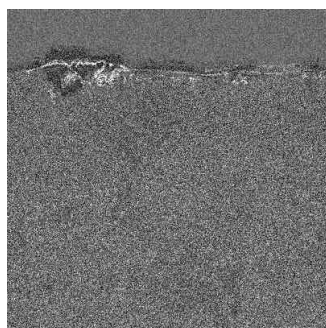
(c) Al_2O_3



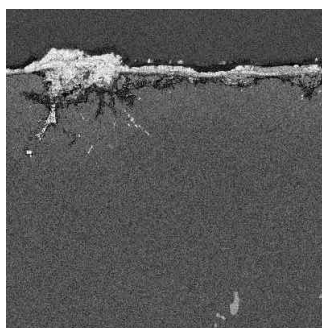
(d) ZrO_2



(e) NiAl_2O_4

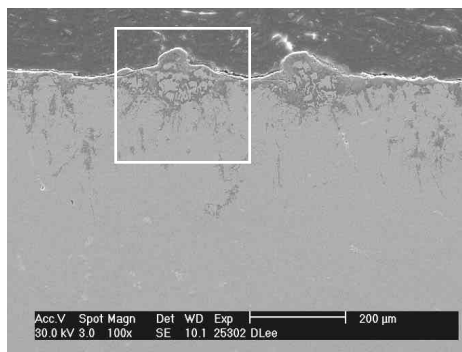


(f) $\text{NiCr}_2\text{O}_4/\text{Cr}_2\text{O}_3$

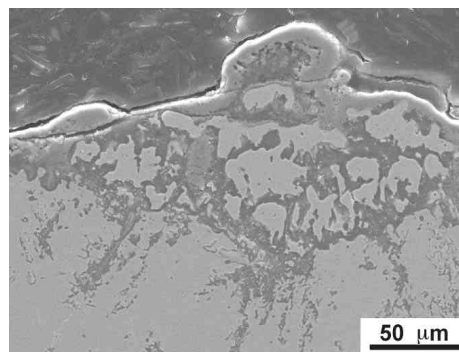


(g) NiO

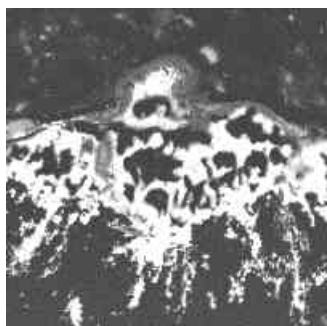
Fig. 3.2.2-5 Cross-sectional x-ray maps of a specimen aged for 1 hr at 1100°C.



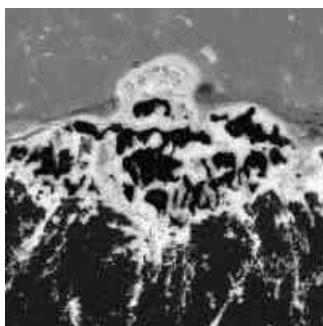
(a) SE image, 30 keV



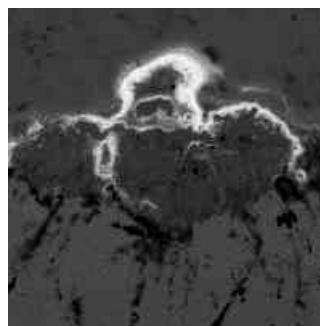
(b) Enlarged image of a box on (a)



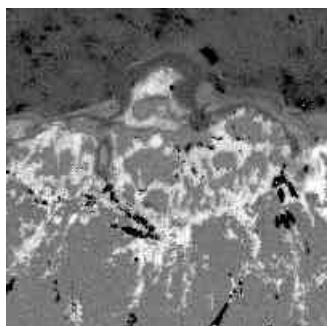
(c) Al elemental map



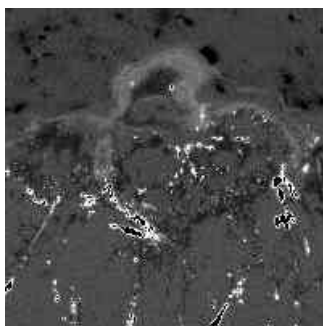
(d) $(\text{Al,Cr})_2\text{O}_3 + \text{Zr}$



(e) Cr-oxide



(f) NiAl_2O_4



(g) $\text{ZrO}_2 + \text{Cr, Ni}$

Fig. 3.2.2-6 Cross-sectional x-ray maps of a specimen aged for 100 hrs at 1100°C.

shown in Fig. 3.2.2-5b. MSA results are shown in Figs. 3.2.2-5c to g. Unlike oxidation at 900°C, nickel oxide (NiO) is formed not only immediately above the γ +Ni₅Zr eutectic but also as a relatively continuous layer on the surface. Aluminum oxide forms a continuous layer near the surface, and penetrates along the γ + Ni₅Zr eutectics as a sheath on the ZrO₂ spikes, as does nickel-aluminate spinel. The oxides related to chromium, Cr₂O₃ and NiCr₂O₄, form near but under the outer oxides (nickel oxide and spinel). Zirconium oxide forms around the γ + Ni₅Zr eutectics as expected, but is also scattered near the surface [27,31,34]. Figure 3.2.2-6 shows SEM micrographs and oxide phase mapping images for a specimen aged for the longer times of 100 hrs. Interestingly, chromium is strongly concentrated at the top of the oxide nodule, either as chromium oxide and/or (Cr, Al)₂O₃. The significance is that Cr₂O₃ transforms to CrO₃ above 1000°C [113], which is highly volatile. Moreover, although aluminum is highly segregated in the oxide surface (Fig. 3.2.2-6c), the oxide is not pure Al₂O₃, but contaminated with Cr and Zr. In addition, neither the aluminum oxide nor the NiAl₂O₄ spinel form as a continuous layer. These changes, along with the significant spallation of NiO, create a surface that is no longer protective to oxidation.

3.2.3 Discussion

The oxidation mechanism maps for selective oxidation of Ni-Al and Ni-Al-Cr alloys developed by Pettit [88] and Giggins and Pettit [113] can be used to explain the oxidation behavior of IC221M. The chemical compositions by electron probe microanalysis (EPMA) of key microstructural features - dendrite core, interdendritic region, and γ + Ni₅Zr eutectic constituent - are used in the explanation (see Table 3.2-2)

Table 3.2-2 Chemical composition by Electron Probe Microanalysis (EPMA) in the dendritic and interdendritic regions (wt.%).

	Ni	Al	Cr	Zr	Mo
Dendritic region: $\gamma+(\gamma')$	82.09	7.63	7.67	0.33	1.45
Interdendritic region: $\gamma'+(\gamma)$	82.62	9.11	4.57	2.79	1.04
$\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies	68.00	0.59	1.41	29.12	0.35

The amount of nickel is almost same in both the dendrite core and interdendritic regions, but much lower in the eutectic. The aluminum and zirconium contents are higher in the interdendritic regions than in the dendrite cores while the chromium content is lower in the interdendritic region. In the eutectic, the amount of chromium is higher than aluminum. These distributions of alloying elements are consistent with the ThermoCalcTM predictions and x-ray elemental analyses in section 3.1.

Pettit's oxidation mechanism map for Ni-Al binary alloys is schematically illustrated in Fig. 3.2.3-1 [88]. Group I (0 to 6 wt.% Al) alloys fall under mechanism I, in which discrete particles of aluminum oxide likely beneath the external nickel oxide. The oxidation behavior of Group II (11 to 15 wt.% Al) alloys is explained by mechanism II, in which an initially continuous aluminum oxide film is overtaken by NiO and NiAl₂O₄ because of insufficient aluminum. In Group III, Al₂O₃ forms as a continuous, stable layer. There are transition regions between the mechanisms characterized by hybrid behavior.

Let us consider simply the Ni and Al concentrations and apply Pettit's mechanism

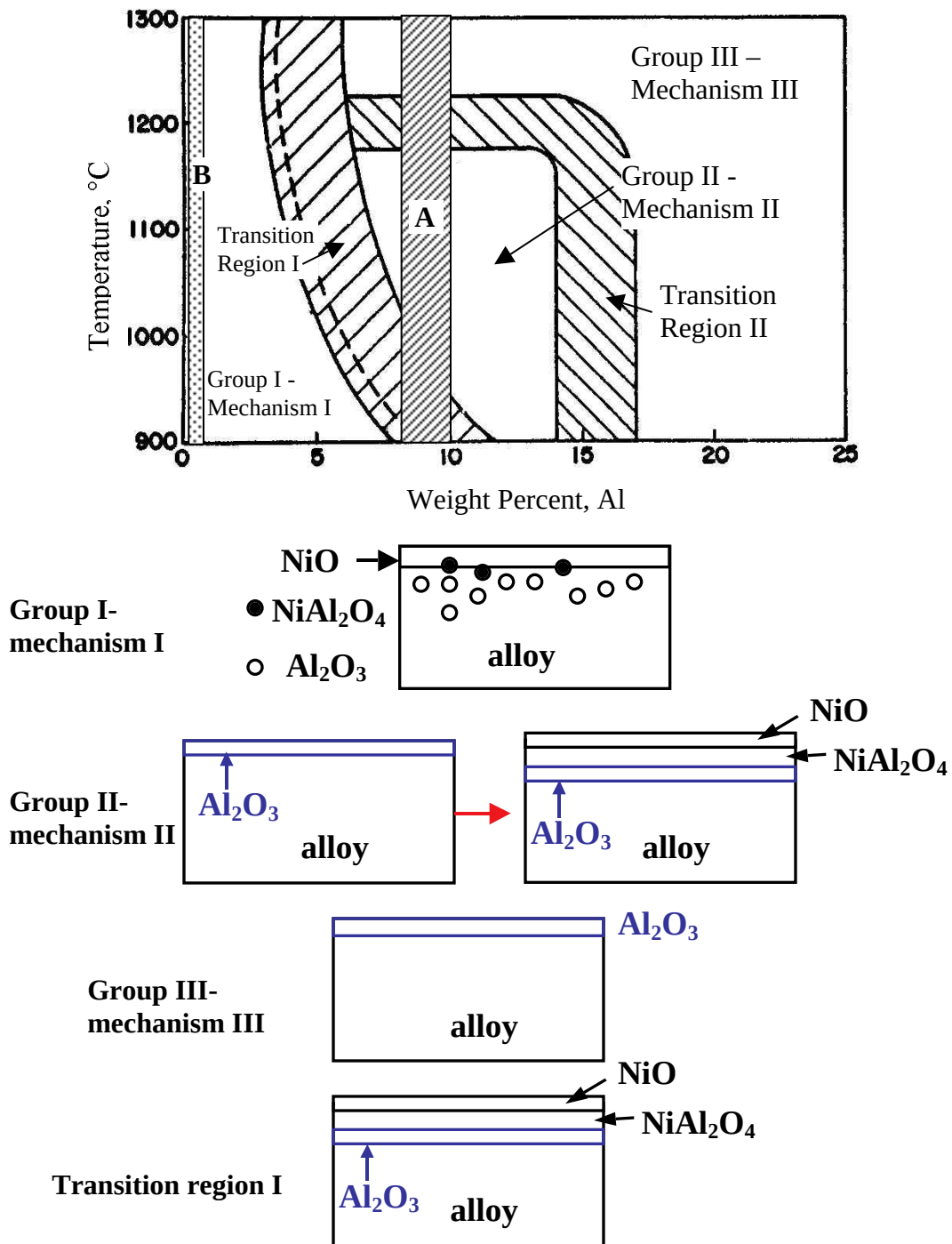


Fig.3.2.3-1 The selective oxidation mechanism map of Pettit for Ni-Al alloys. The dashed curve indicates the transition from internal to external oxidation for specimens oxidation [88]. Note that the dashed area indicates the chemical composition of dendrite and interdendritic region, the dotted area indicates the chemical composition of the γ - Ni_5Zr eutectic.

map. At 900°C, the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies are in Group I because of 0.86 wt.% of Al, while the dendrite cores and interdendritic regions are in transition region I because of 8.5~9.93 wt.% of Al. Since the oxidation behavior of $\gamma + \text{Ni}_5\text{Zr}$ eutectic regions will be governed by mechanism I, the NiO grows faster here than the other regions. In the rest of the material, transition I behavior occurs with a mixture of discrete particles and continuous layers of NiO, NiAl_2O_4 , and Al_2O_3 . At 1100°C, the majority of the material (except the eutectic) is in group II, so Al_2O_3 forms initially as a continuous oxide layer, but will eventually be overtaken by NiO and NiAl_2O_4 .

In a similar manner, the Ni-Al-Cr ternary alloy model of Giggins and Pettit [113] can also be applied to IC221M alloy to account for Cr effects (see Fig. 3.2.3-2). According to their model, IC221M is generally a Group III alloy, which has sufficient volume fraction of Al_2O_3 to form a continuous layer immediately beneath the duplex zone (mixture of Cr_2O_3 and Al_2O_3), but spinels and NiO still exist as the outermost layers of the oxide. Therefore, a continuous aluminum oxide layer will be formed in the IC221M system. However, because the $\gamma + \text{Ni}_5\text{Zr}$ eutectic is in Group I of the ternary diagram, the volume fraction of Cr_2O_3 and Al_2O_3 in this region is not sufficient to restrict movement of oxygen. Therefore, when the eutectic is exposed to air at elevated temperature, it will be oxidized to form an external layer of NiO while internally Cr_2O_3 , Al_2O_3 , and $\text{Ni}(\text{Cr},\text{Al})_2\text{O}_4$ form as a discontinuous subscale of particles.

Accordingly, the oxidation behavior of the as-cast IC221M in air at 900° and 1100°C can be schematically illustrated by the schematic diagrams in Figs. 3.2.3-3 and 4, respectively. For short oxidation periods at 900°C, oxidation follows the cast-

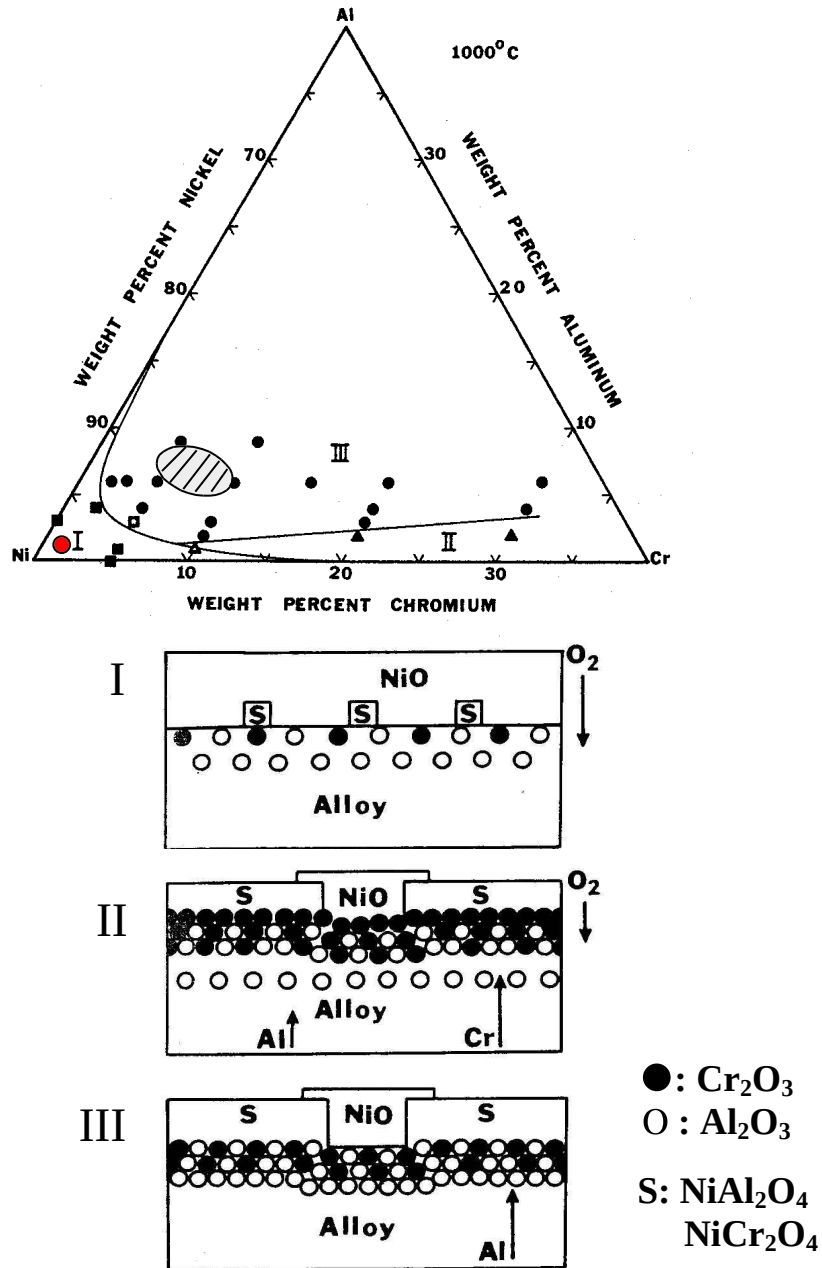


Fig. 3.2.3-2 Isothermal diagrams for the three oxidation mechanisms of Ni-Cr-Al alloys at 1000°C. Solid symbols, i.e., squares, triangles, and circles represent alloys which conform to oxidation mechanisms I, II, and III [113]. Note that a dashed area and a red circle indicate the chemical composition of dendrite core/interdendritic region and γ +Ni₅Zr eutectic, respectively.

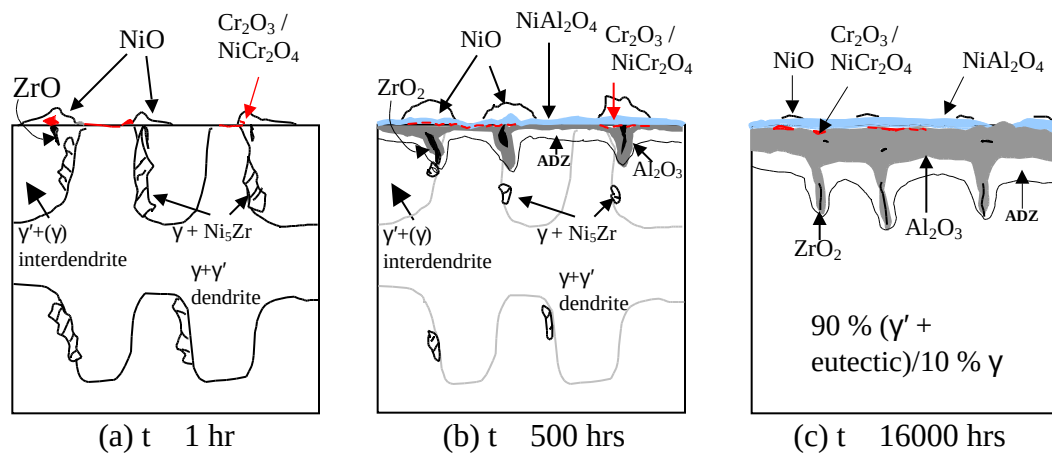


Fig. 3.2.3-3 Schematic diagrams of oxidation mechanism aged in air at 900°C.

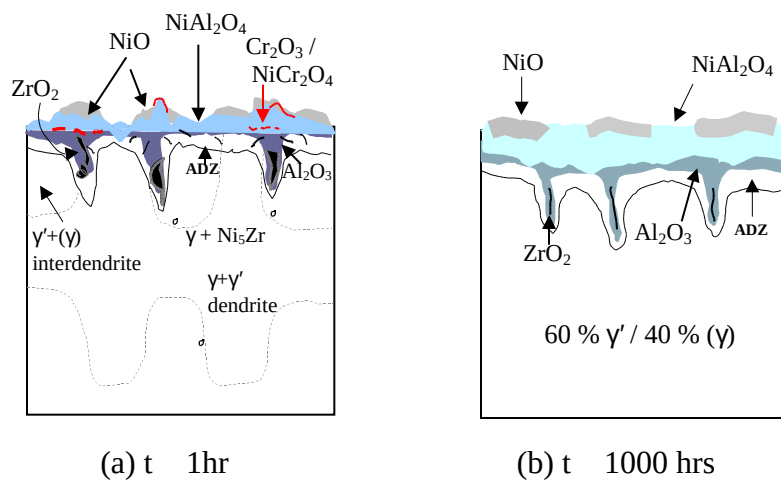


Fig. 3.2.3-4 Schematic diagrams of oxidation mechanism aged in air at 1100°C.

microstructure; for example, since $\gamma + \text{Ni}_5\text{Zr}$ eutectic acts a fast diffusion path, oxygen anions diffuse quickly into the eutectic colonies, and then ZrO_2 forms internally because it is one of the most stable oxides in this system. The nickel rejected from the eutectic during its oxidation diffuses to the surface to form NiO, surface nodules, which react with aluminum in matrix to form NiAl_2O_4 in further oxidation. Cr_2O_3 and NiCr_2O_4 are formed around a bumpy surface oxides due to the relatively higher concentration of chromium in the $\gamma + \text{Ni}_5\text{Zr}$ eutectic.

As oxidation proceeds, Al_2O_3 becomes a dominate, continuous oxide layer, but the most outer layer is composed of a significant amount of NiAl_2O_4 as well as small amount of NiO, NiCr_2O_4 and Cr_2O_3 dispersed in the between external and internal oxides. An aluminum depletion zone forms immediately under Al_2O_3 continuous layer, and also around the ZrO_2 spikes. The spike-like oxides consist of ZrO_2 sheathed in Al_2O_3 due to high concentration of Al around the $\gamma + \text{Ni}_5\text{Zr}$ eutectic caused by segregation during solidification.

At 1100°C , the kinetics of oxidation are much faster than at 900°C . For short-term oxidation, the process is not much different from that of at 900°C ; however, a significant amount of NiO scale spalls during cooling owing to the larger thermal expansion coefficient of NiO than that of the base metal, and a stable external or internal continuous oxide film is not observed after long-term oxidation. Figure 3.2.3-4b illustrates the nature of discontinuous oxide scale - a mixture of NiAl_2O_4 , NiO, and Al_2O_3 . It is not fully understood why a stable, continuous oxide layer can not be formed in a long oxidation in this system, but the transformation of Cr_2O_3 to a volatile CrO_3 above 1000°C possibly affects its development [13,19].

3.3 Thermal aging effects on room temperature mechanical properties

In this section, the influences of thermal aging and oxidation on the room temperature tensile properties and hardness of as-cast IC221M are discussed. The results of the tensile tests after two aging conditions are presented: (1) aged in air at 900°C for 50, 100, 200, 500, 1000 hours, and (2) aged in air and argon for 1000 hours at 900°, 950°, 1000°, 1050°, and 1100°C. As-cast specimen and specimens aged at 900° and 1100°C were mounted and polished with 1 μm diamond paste for hardness tests that were performed by Vickers hardness testing (Buehler) and nanoindentation (MTS). The Vickers hardness and nano-hardness measurements were made at loads of 10 to 1000 gf and 20 mN, respectively.

3.3.1 Tensile testing

Tensile properties of IC221M aged at 900°C

Figure 3.3.1-1 shows the effect of aging at 900°C in air on the room temperature tensile behavior of the material. The effects need to be compared with the behavior of an unaged specimen shown in the same figure (curve 1). The yield strength (YS) of the unaged specimen is about 550 MPa and the tensile elongation is about 9%. Aging significantly decreases the yield strength and increases the ductility, with the majority of the change occurring after only 50 hrs of aging. The ultimate tensile strength (UTS) is essentially unaffected by aging. Since this phenomenon also occurs for aging in argon, it is not an oxidation effect but related to other microstructural changes. It will be discussed in detail later.

Fracture surfaces and plan-view observations of deformed tensile specimens are

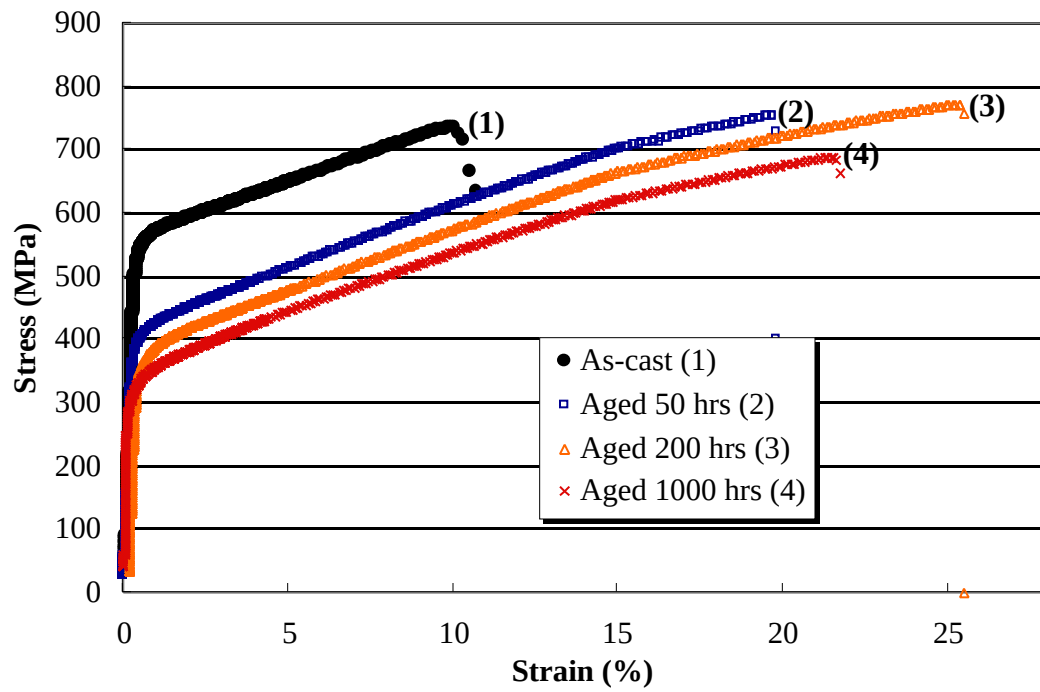


Fig. 3.3.1-1 Engineering stress-strain curves for specimens aged in air at 900°C and then tensile tested at room temperature. Curve (1) is the behavior of an unaged specimen.

shown in Fig. 3.3.1-2. The arrow and cross-dot in Fig. 3.3.1-2a and d indicate the tensile direction, and these symbols will be used in all subsequent figures in section 3.3 and 3.4. Figures 3.3.1-2a and b show a surface crack of an as-cast tensile specimen in plan-view. Fig. 3.3.1-2a shows that the crack on the surface occurred through the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies. The cracks on the fracture surface in Fig. 3.3.1-2c appear to be in the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies. Ni_5Zr is inherently a brittle phase because of its complex C15_b (AuBe_5 prototype) crystal structure (*Laves* phase) [114-116]. The other microstructural features on the fracture surface correspond to the cellular microstructure of the matrix (arrows in Fig. 3.3.1-2c). Fig. 3.3.1-2d shows the stepped facets on the fracture surface which presumably correspond to special planes for deformation [117]: these features are observed in most of the specimens tested in this study. Fig. 3.3.1-2b shows that the surface of the tensile specimen is highly deformed due to machining.

Plan-view micrographs and fracture surfaces of a specimen aged in air at 900°C for 50 hrs are shown in Fig. 3.3.1-3. Figure 3.3.1-3a shows a representative plan-view feature of the tensile specimens. Cracks at the surface of the specimen start in brittle surface oxides and then propagate through the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies. Figures 3.3.1-3b, c, and d are micrographs of the fracture surface, where (c) and (d) are enlarged areas of (b). The fracture surface follows the cast microstructure and reveals some crystallographic character (steeped facets), but a ductile fracture mode dominates. With further aging to 1000 hrs at 900°C (Fig. 3.3.1-4), cracks on the surface form in the surface oxide and propagate through the eutectic. However, the cracks do not affect ultimate tensile strength and plastic strain. The tensile properties of specimens aged

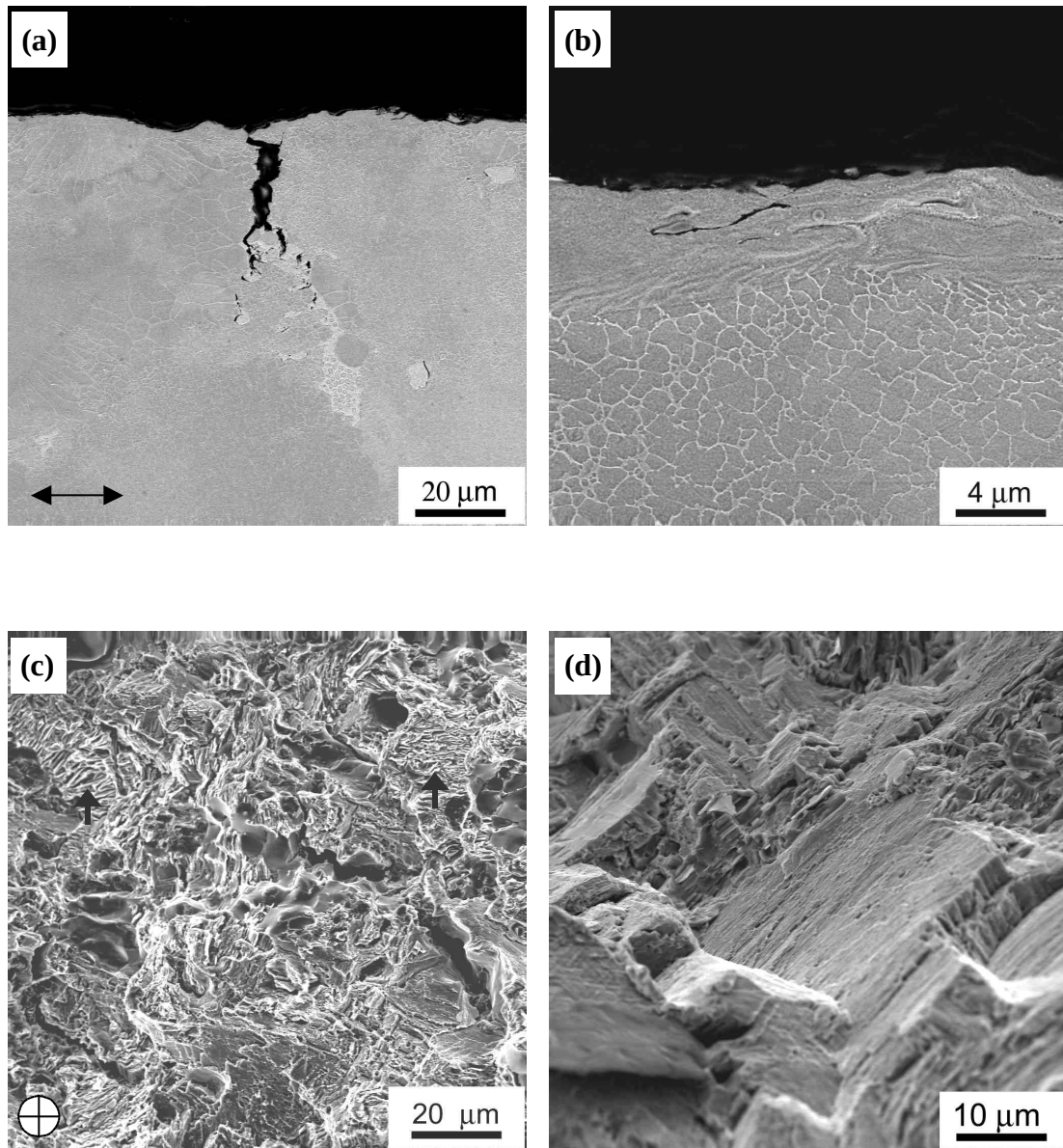


Fig. 3.3.1-2 Plan-view micrographs and fracture surfaces of as-cast IC221M: the arrow and a cross-dot in (a) and (c) indicate tensile direction. (a) and (b) are in plan-view and (c) and (d) show the fracture surface.

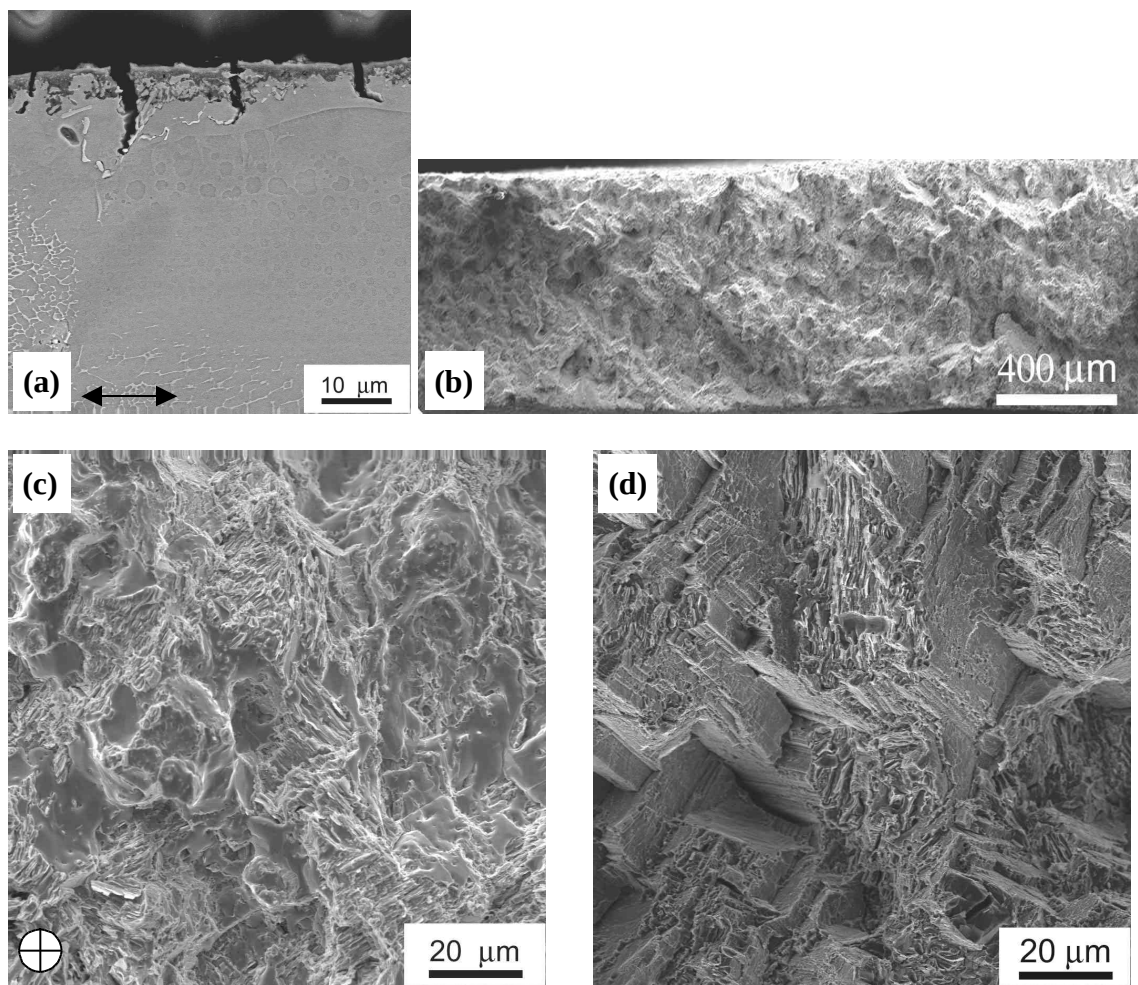


Fig. 3.3.1-3 Plan-view micrograph and fracture surfaces of tensile specimen aged in air at 900°C for 50 hrs: (a) plan-view and (b), (c), and (d) show fracture surfaces.

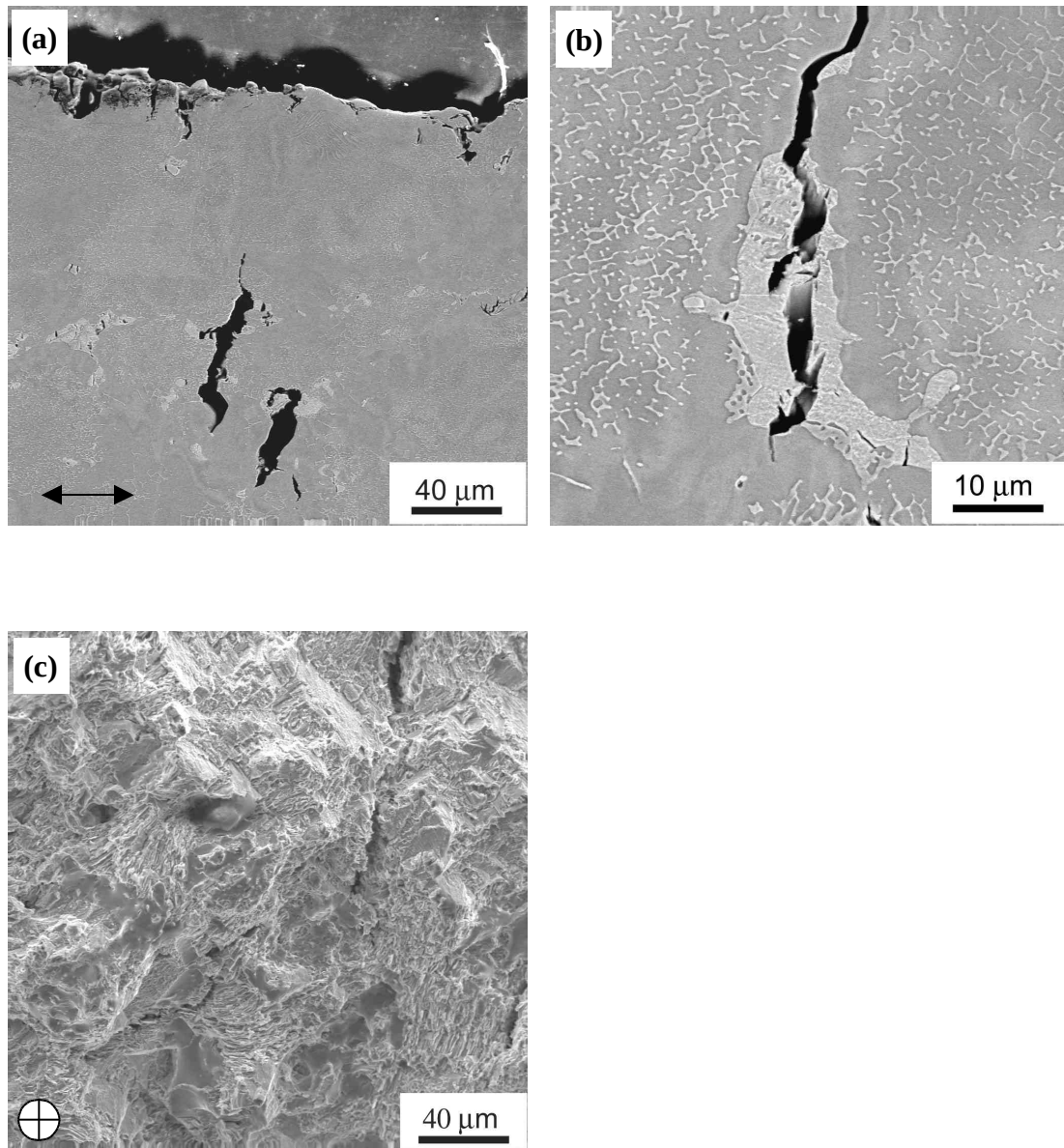


Fig. 3.3.1-4 Plan-view micrographs (a and b) and fracture surfaces (c) of a room temperature tested tensile specimen aged in air for 1000 hrs at 900°C.

in air at 900°C for 1000 hrs show no significant differences in comparison to aging in argon (as will be presented in Fig. 3.3.1-6); the decrease in yield strength with aging is thus due to microstructural changes not related to oxidation. This will be discussed later in this section.

Tensile properties of IC221M aged in air and argon at various aging temperatures

Room temperature tensile test results for specimens aged in air and argon at various aging temperatures are shown in Figs. 3.3.1-5 and 3.3.1-6. Figures 3.3.1-5a and b show the engineering stress-strain curves after aging in air and argon, respectively. The solid circles show for comparison the behavior of the as-cast alloy. The curves show different slopes in the elastic region due to misalignment and bending of the tensile specimens. Because of this, the elastic strain was removed, and the strains presented in all subsequent plots are the plastic strains only.

The dependencies on aging temperature of the room temperature yield strength, ultimate tensile strength, and plastic strain are shown in Fig. 3.3.1-6. The aging time was fixed at 1000 hrs. After aging at 900°C, the yield strength of specimens aged in both air and argon dramatically decreases by about 40 % from that of the as-cast alloy. This is not caused by oxidation since the same phenomenon is observed for aging in both air and Ar. In addition, the aging atmosphere does not play an important role to the strength until about 1000°C. Interestingly, at temperatures greater than 1000°C, the yield strength increases for aging in argon but decreases quite dramatically for aging in air. The difference is due to development of oxide on the surface. The behavior of the ultimate tensile strength and plastic strain are shown in Figs. 3.3.1-6b and c. Aging in argon has

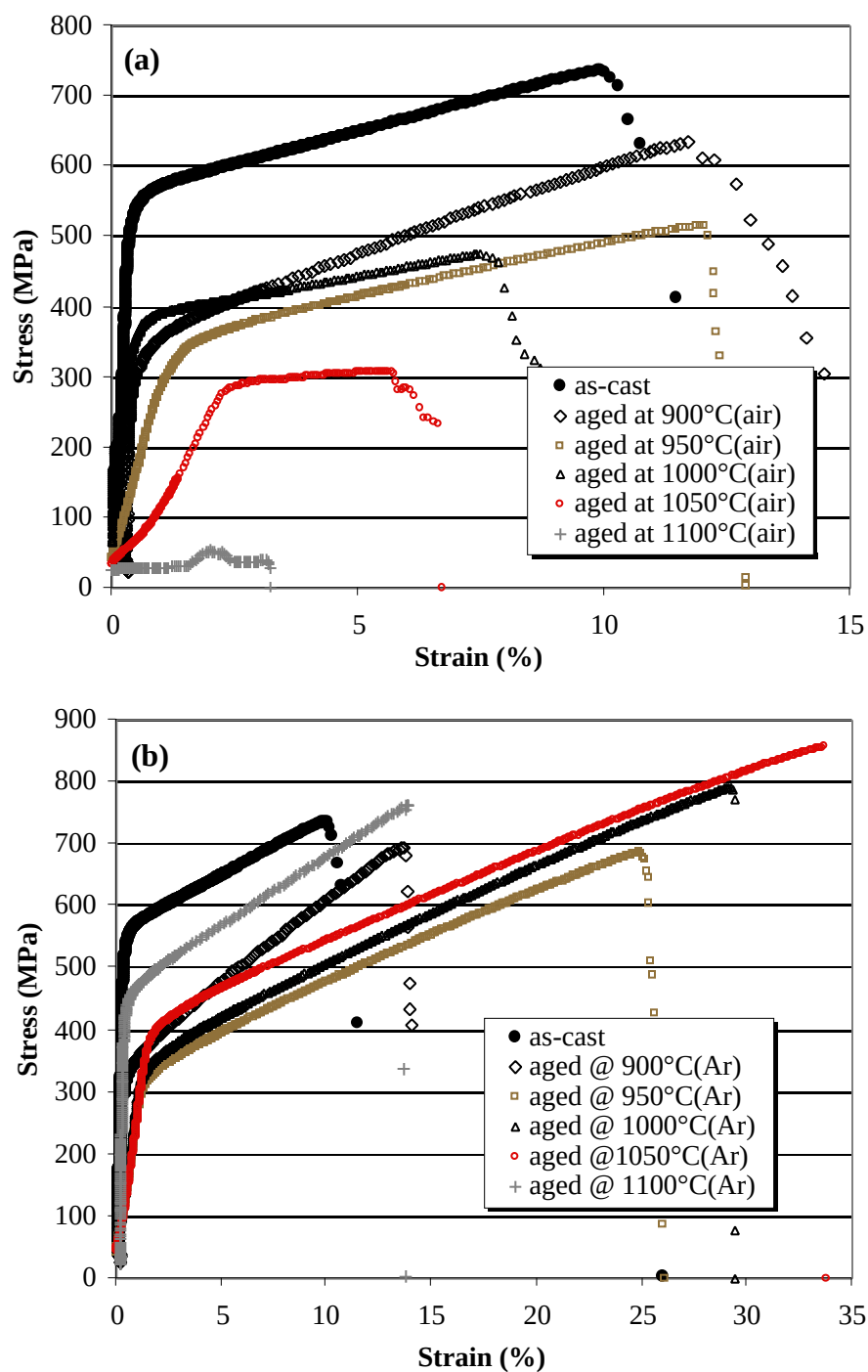


Fig. 3.3.1-5 Engineering stress-strain curves for room temperature tensile tests: (a) aged in air and (b) aged in Ar.

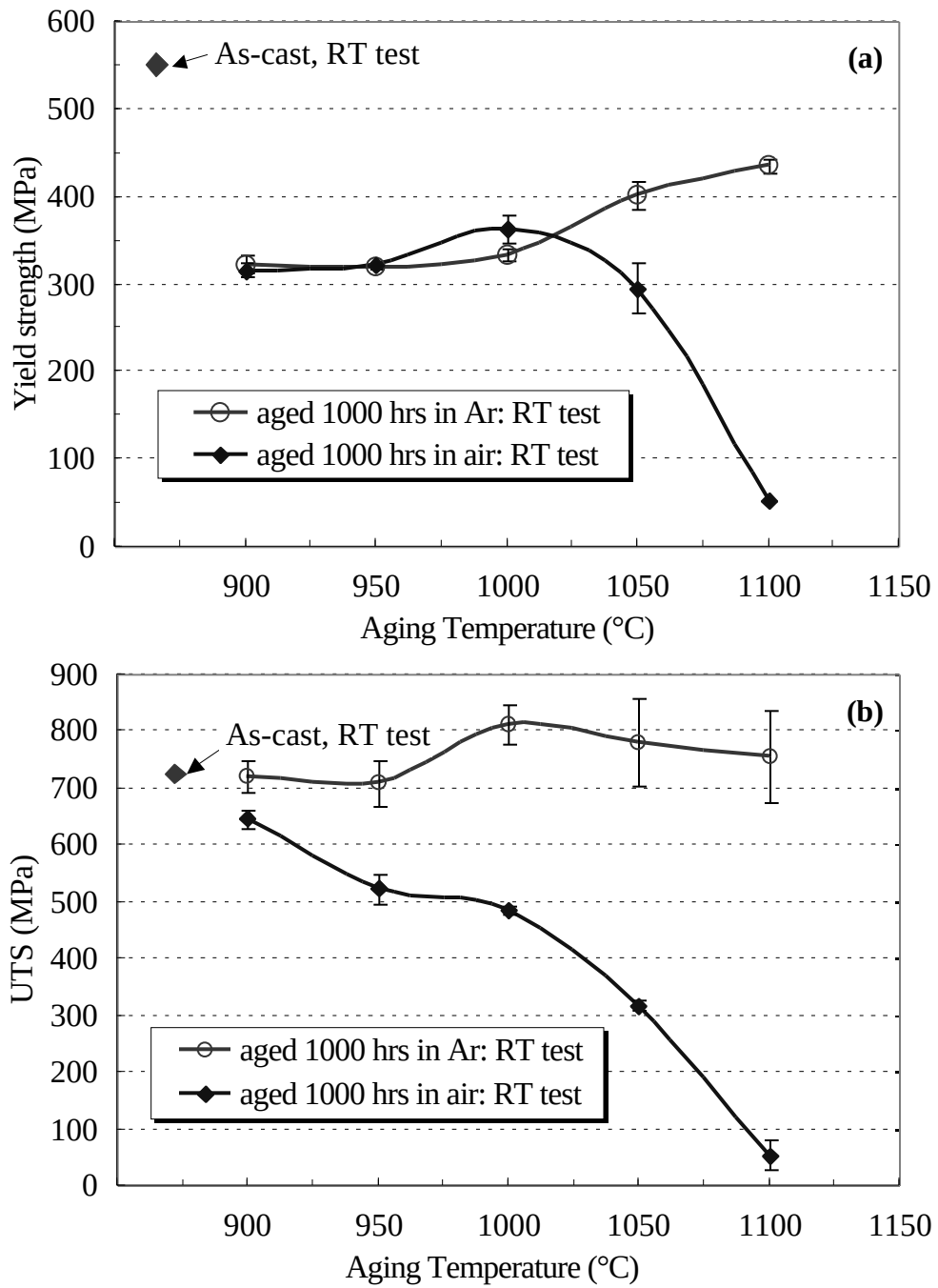


Fig. 3.3.1-6 Variations of room temperature tensile properties of specimens aged 1000 hrs in air and Ar: (a) yield strength, (b) ultimate tensile strength.

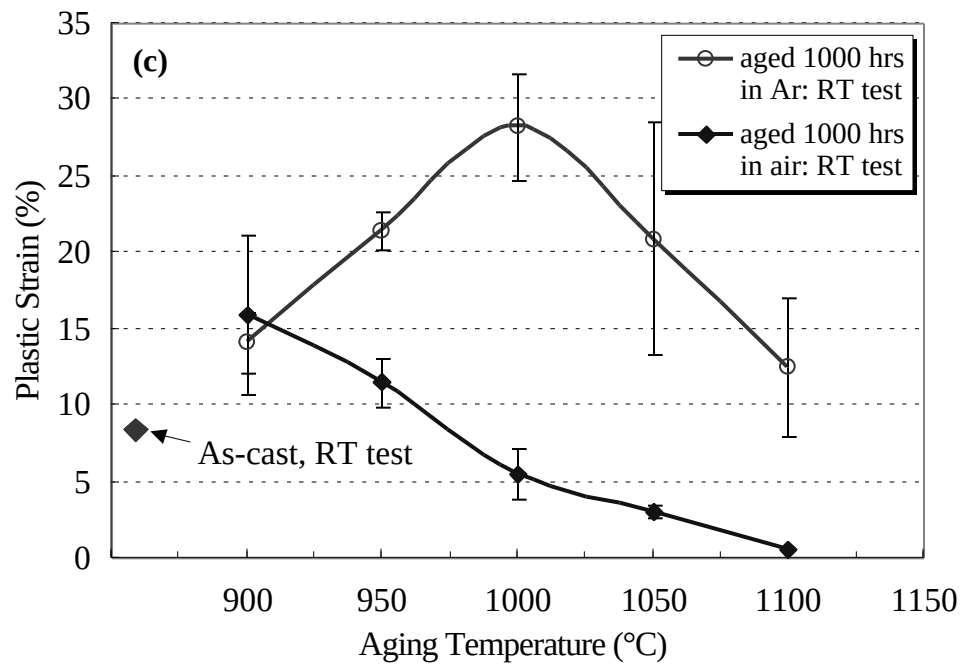


Fig. 3.3.1-6 (Continued) (c) plastic strain.

little effect on the ultimate tensile strength while aging in air results in a dramatic decrease in both the ultimate tensile strength and plastic strain due to the development of the surface oxide. When aged in argon, the plastic strain shows a distinct peak and maximum at $T=1000^{\circ}\text{C}$.

Figure 3.3.1-7 shows the variation of fracture mode after aging in argon and indicates that fracture is caused by intergranular failure along the cast dendritic microstructure at $T \leq 1000^{\circ}\text{C}$ while a cleavage fracture mode dominates for aging at 1050°C and above; however, the higher magnification micrograph in Fig. 3.3.1-8d indicates that ductile fracture modes are mixed with cleavage fracture. Plan-view micrographs after aging in argon at 1100°C are shown in Fig. 3.3.1-9. Although most of the eutectic colonies are dissolved (see Fig. 3.3.1-9a) into the matrix, one remnant eutectic colony is internally cracked (see Fig. 3.3.1-9b).

Collectively, these results show that thermal aging of as-cast IC221M in Ar in the temperature range $900\sim 1000^{\circ}\text{C}$ actually improves the room temperature tensile properties. However, aging above 1000°C reduces the ductility.

As shown in Fig. 3.3.1-10, the decrease in strength following aging in air is due to the development of surface oxide. At 1050°C , the oxide penetrates more than half the 0.762 mm thickness of the specimen. Thus, the loss in strength is related to the sample size and will not be quite so dramatic for thicker specimens. At 1100°C , the oxide penetrates even further. Two of the 1100°C tensile specimens broke during set up in the tensile machine, and the third failed at a very low stress. In the section 3.2, we showed that oxide spikes penetrate to about 0.7 mm after aging for 1000 hours in air at 1100°C . Thus, the oxide presumably penetrates entirely through the specimen at 1100°C .

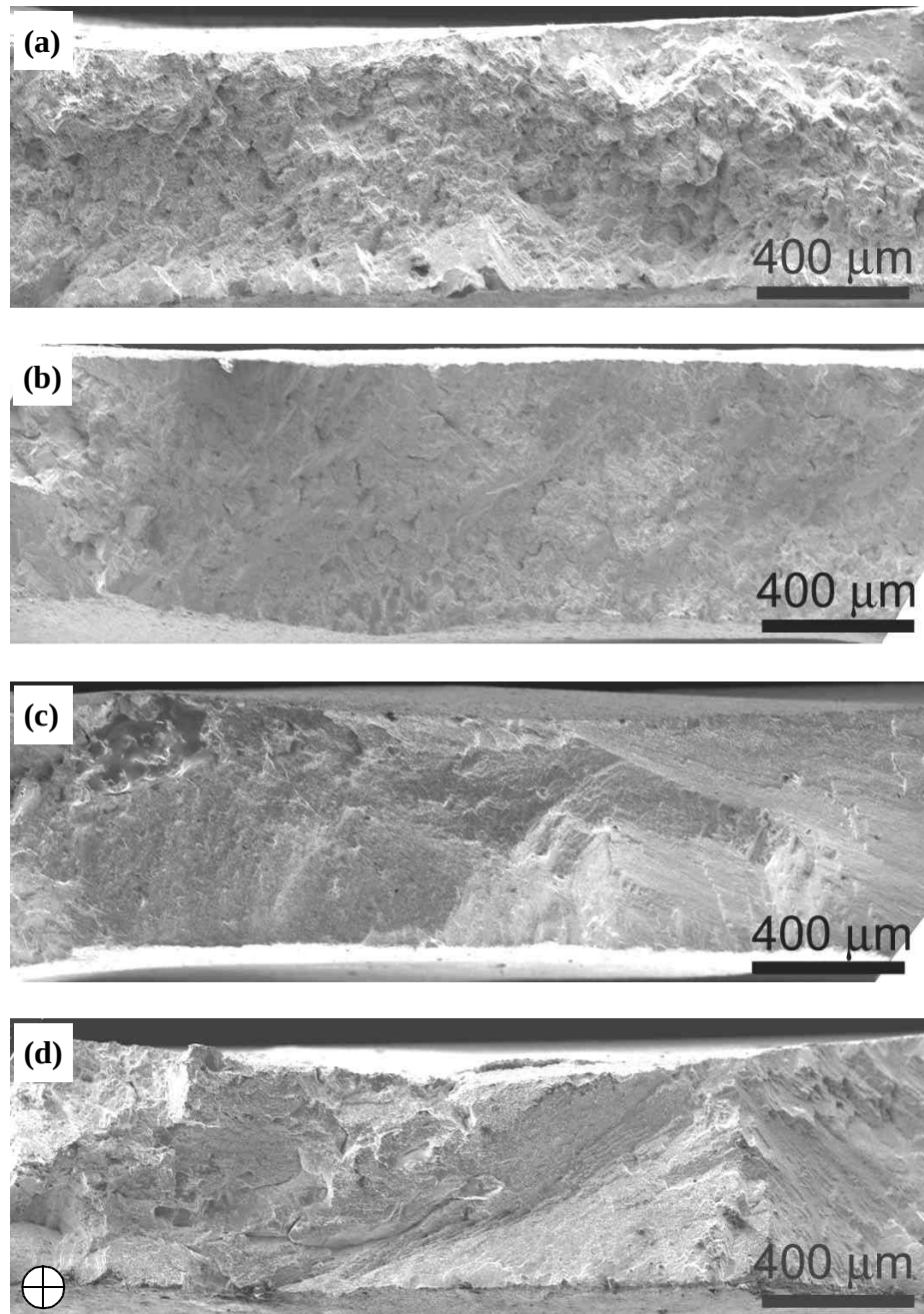


Fig. 3.3.1-7 Macrographs of fracture surfaces of tensile specimens aged in Ar at elevated temperatures for 1000 hrs: (a) 900°C, (b) 1000°C, (c) 1050°C, (d) 1100°C

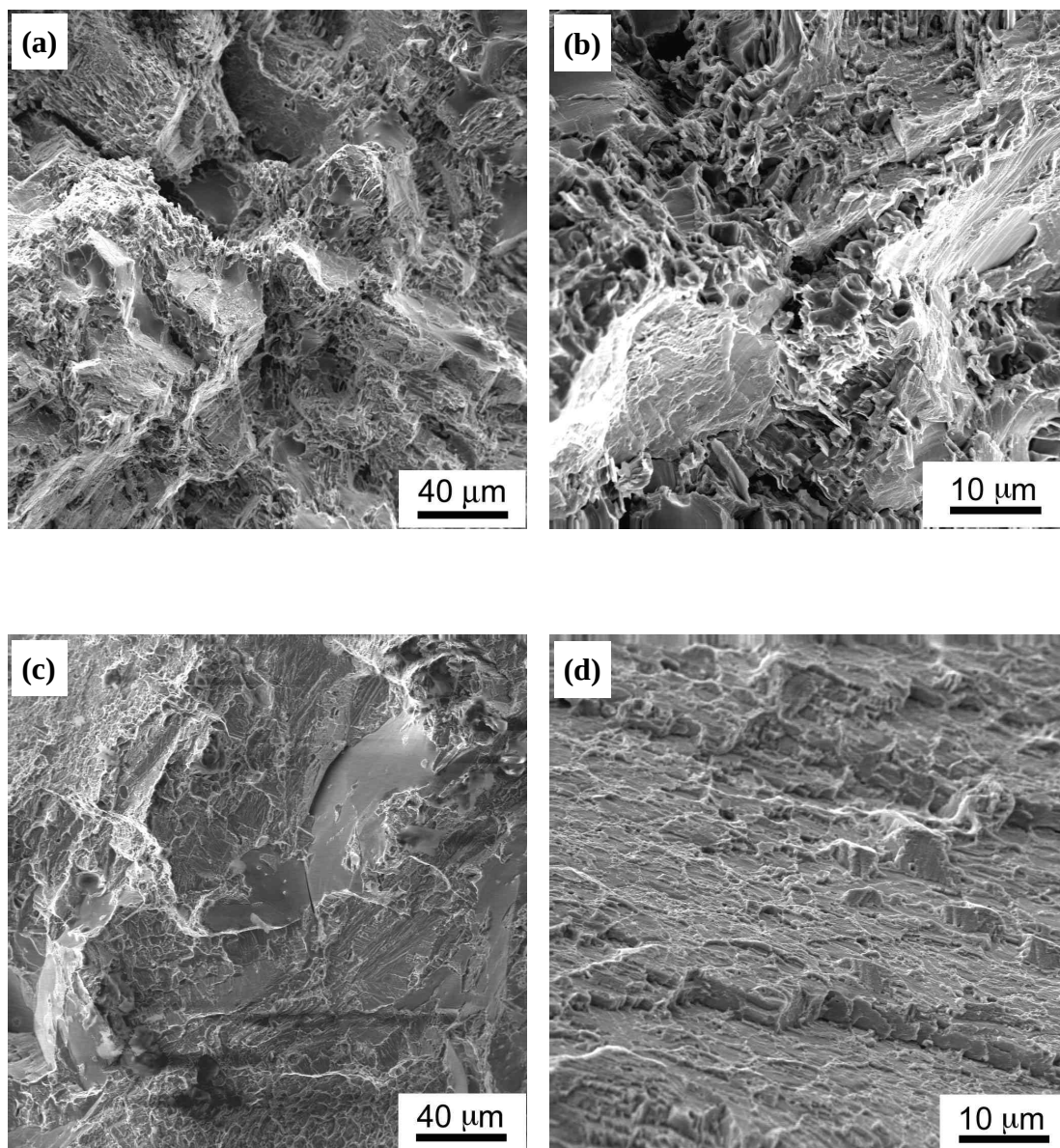


Fig. 3.3.1-8 Enlarged micrographs of the fracture surfaces of specimens aged in Ar at (a), (b): 1000°C and (c), (d): 1100°C.

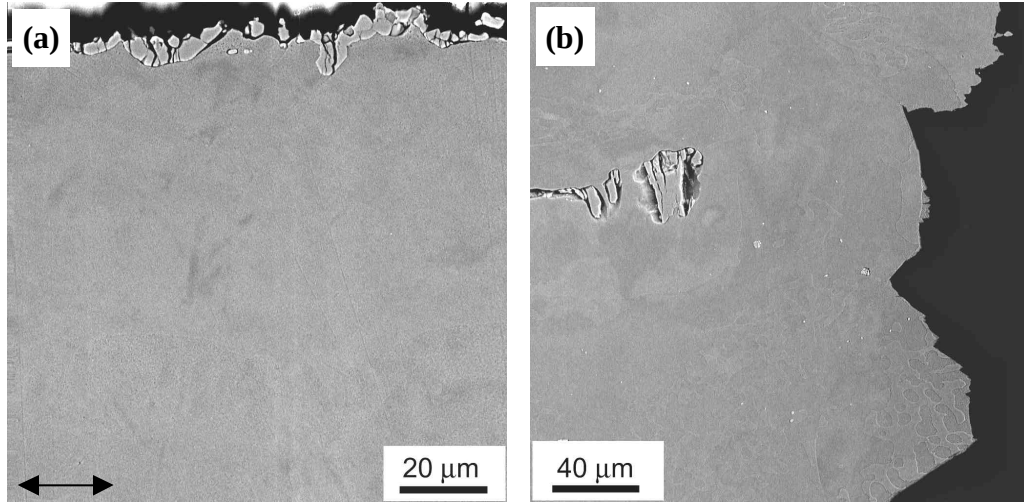


Fig. 3.3.1-9 Plan-view micrographs of a tensile specimen aged in Ar for 1000 hrs at 1100°C: (a) near in the edge of gauge section; and (b) near the fracture surface. A crack formed in the remnant of $\gamma + \text{Ni}_5\text{Zr}$ eutectic in (b).

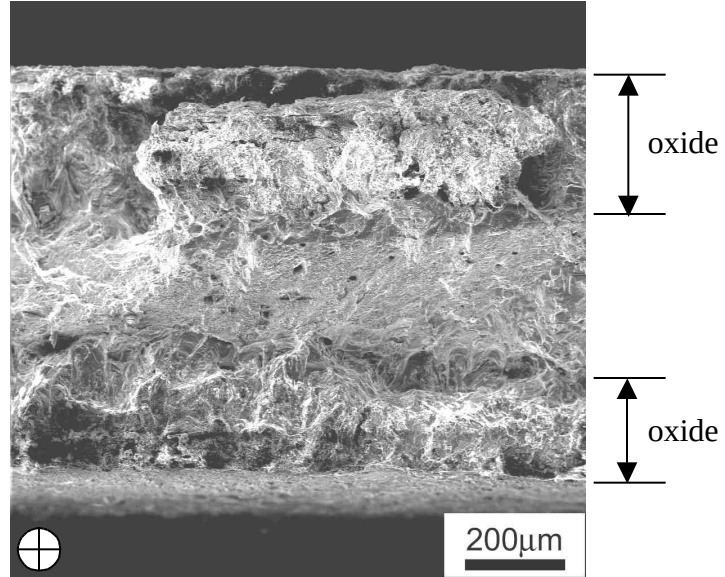


Fig. 3.3.1-10 Fracture surface of a tensile specimen aged in air at 1050°C for 1000 hrs.
More than 60 % of specimen is oxidized, as indicated by arrows.

One reason for the increase in yield strength of specimens aged in argon is solid solution strengthening by re-dissolution of Zr from the eutectic colonies into the base alloy since Zr is one of the most effective solid solution strengtheners in Ni₃Al alloys [84]. Figure 3.3.1-11 shows the variation of the volume fraction of γ + Ni₅Zr eutectic colonies with aging time and aging temperature (as presented earlier). While the volume fraction of the eutectic colonies remains at about 3.5 vol.% after aging 1000 hrs at 900°C, at 1100°C most of the eutectic is re-dissolved into the base alloy (below 0.5 vol.%).

The origin of the distinct ductility peak at aging temperature 1000°C of the specimen aged in Ar is not fully understood; however, we may speculate about several phenomena that may be important. First, Fig. 3.3.1-6a showed that the strength of the material actually increases above 1000°C. In most material, increases in strength are associated with decreases in ductility. Second, the microstructural changes in the γ + Ni₅Zr eutectic colonies from the lamellar eutectic to a single Ni₅Zr phase (see section 3.1) may affect the fracture behavior. Third, the reduction in ductility may be related to the role of Zr in grain boundary cohesion [64,66,118]. Gu et al [66] reported that the ductility of wrought Ni₃Al binary alloys increases with the addition of Zr below 0.7 at.% but decreases above 0.7 at % Zr. The fracture mode correspondingly changes from a mixture of intergranular and transgranular to predominantly intergranular. They suggested that at low concentrations, zirconium improves the ductility by enhancing grain boundary cohesion, while at large concentrations embrittling Ni₅Zr precipitates are formed in the boundaries. Chiba et al [119-121] suggested that ductility of polycrystalline Ni₃Al will be improved by degrading the ordering energy, that is, stabilizing the γ phase will improve the ductility of polycrystalline Ni₃Al. As a rule, Pt, Pd, Cu, Co, Fe, and Cr are classified

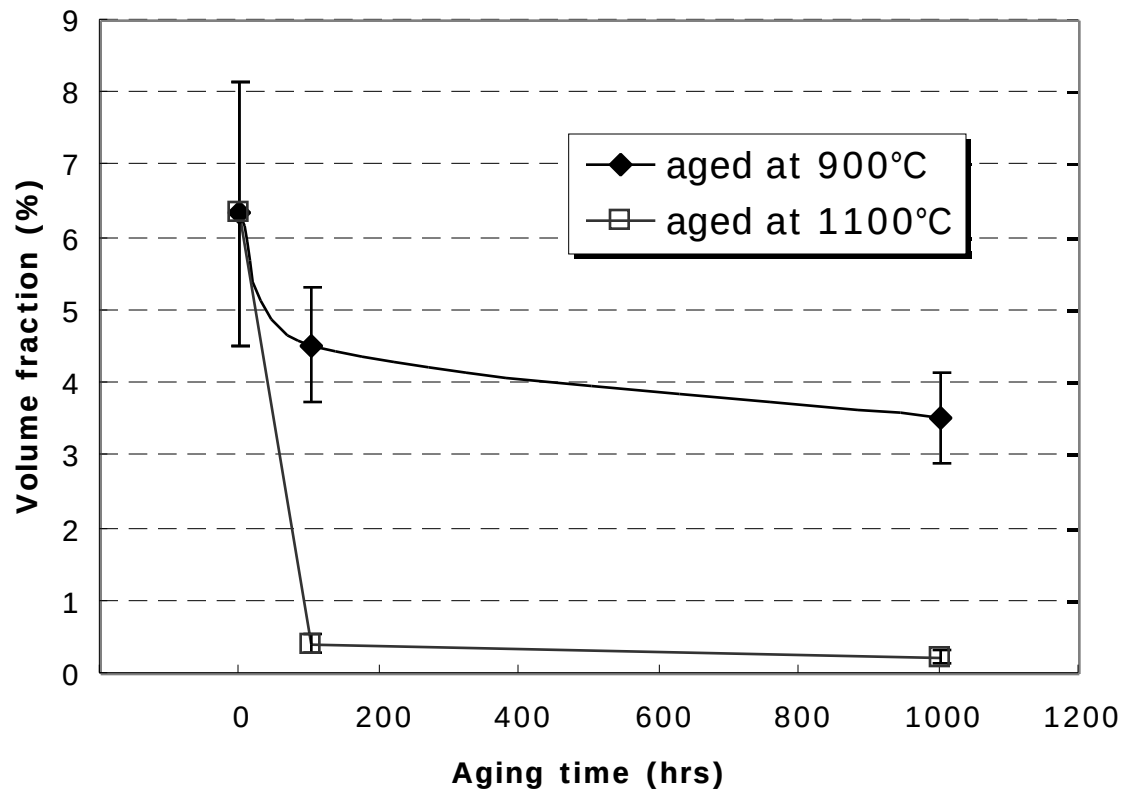


Fig. 3.3.1-11 Variation of the volume fraction of $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies after aging in air at 900° C and 1100°C.

as γ formers, and Ta, Nb, Zr, Si, and Ti are known as γ' formers [120,121]. The addition of Zr shows some positive effects, such as improving hardness, yield/tensile strength, and ductility, in small amounts, but if the Zr concentration is above a critical amount, Zr stabilizes γ' phases that shows brittle fracture. A forth explanation concerns the relative volume fraction of the γ and γ' phases. Thermo-CalcTM simulation shows the volume fractions at 900°C and 1100°C are 10 % γ /90 % γ' and 38 % γ /58 % γ' , respectively (Fig. 3.1-2). The change in volume fraction of γ and γ' phases would presumably affect the mechanical behavior in a potentially significant way.

3.3.2 Hardness testing

Figure 3.3.2-1 shows the variation in Vickers microhardness (Hv) of IC221M aged in air at 900°C and 1100°C with aging time. At 900°C, the hardness drops dramatically after 72 hrs of aging, but after 200 hrs, the hardness is quite stable even after aging for 16,600 hrs (Fig. 3.3.2-1a). The sharp drop in hardness at a short aging time is consistent with the decrease in yield strength in the tensile test. The mechanistic origin of the phenomena presumably results from a thermally activated rearrangement of grain structure, dislocation structure, and/or a redistribution of chemical species due to microsegregation. Surprisingly, figure 3.3.2-1b shows that the hardness of specimen aged at 1100°C decreases slightly at a short aging time, but then increases to a stable value close to the hardness of the original as-cast material. This may result from the redissolution of zirconium during 1100°C aging to produce a solid solution strengthening effect.

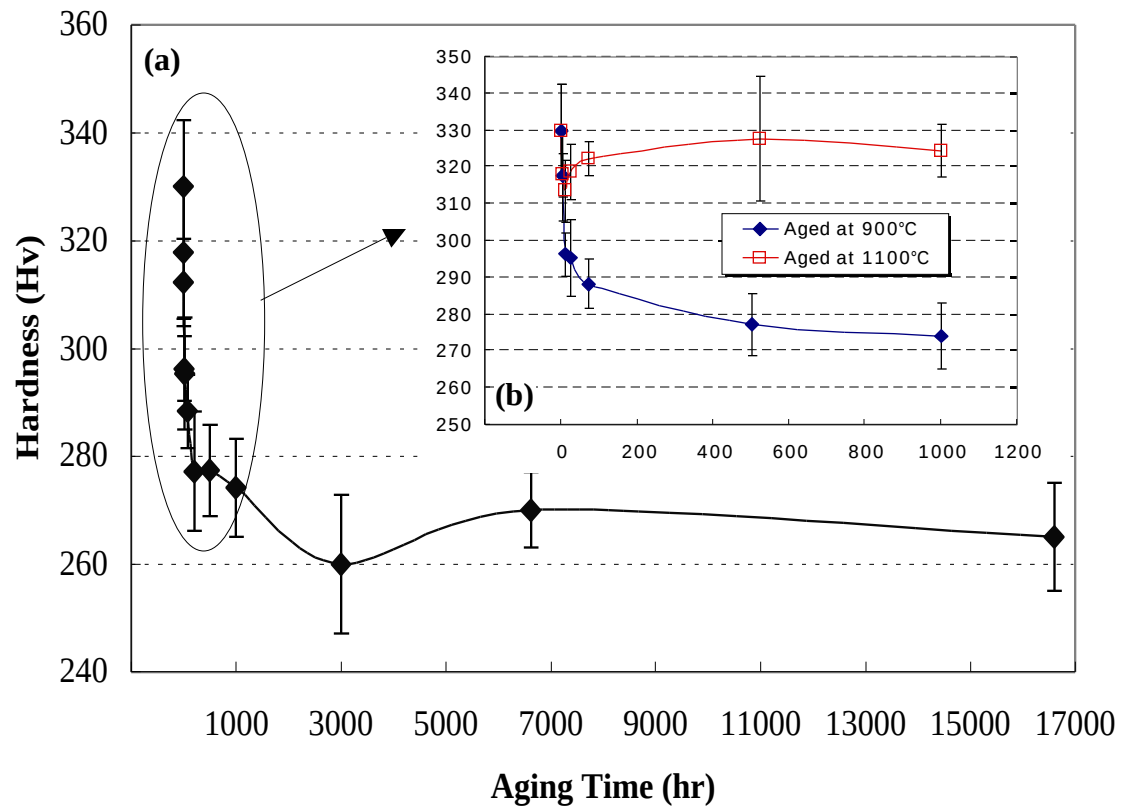


Fig. 3.3.2-1 Variation of Vickers microhardness of IC221M with aging time at 900°C and 1100°C. (a) shows the variation of Vickers hardness with aging time at 900°C; and (b) is a combined graph of Vickers hardness with aging time for up to 1000 hrs at 900°C and 1100°C.

Figure 3.3.2-2 shows one significant difference in the microstructure before and after aging at 900°C. The micrographs represent the microstructure of a dendrite core for aging times up to 1600 hrs. It is obvious that the γ and γ' cells coarsen with aging time at 900°C. Transmission electron micrographs (TEM⁴) in Fig. 3.3.2-3 confirm that the γ and γ' phases are coarsen with aging time. The TEM results suggest that the coarsening mechanism is coalescence; the features marked “a” in Fig. 3.3.2-3b indicate merging of the two γ' domains.

The results of nanoindentation [122] studies are shown in Fig. 3.3.2-4. One curious result is that while the Vickers microhardness of a specimen aged at 900°C drops during short-term aging, the nanohardness does not. This suggests that the decrease in hardness in the Vickers tests is due to changes in a microstructural feature larger than that sampled in the nanoindentation tests, possibly coarsening of the γ and γ' grain structure rather than a precipitation or dislocation structural effect. The schematic diagram in Fig. 3.3.2-5 shows that the Vickers hardness impressions deform several grains so that grain size effects on hardness would be expected. The nanoindent, on the other hand, deforms only one grain. Note that the hardness observed in the Vickers microhardness tests is distinctively lower than that in the nanoindentation tests. This is largely due to the indentation size effect. Fig. 3.3.2-6 shows that as the load is decreased, the hardness measured in Vickers tests increases towards that in the nanoindentation tests. Also, the sharp decrease in hardness in short-term aging is reduced by decreasing the load. Note that the nanoindentation hardnesses were measured at a load of 20mN 2gf. These results suggest that thermal aging effects on the hardness of individual domains of γ and

⁴ The TEM work was performed by Dr. E. Brown at EB scientific enterprises.

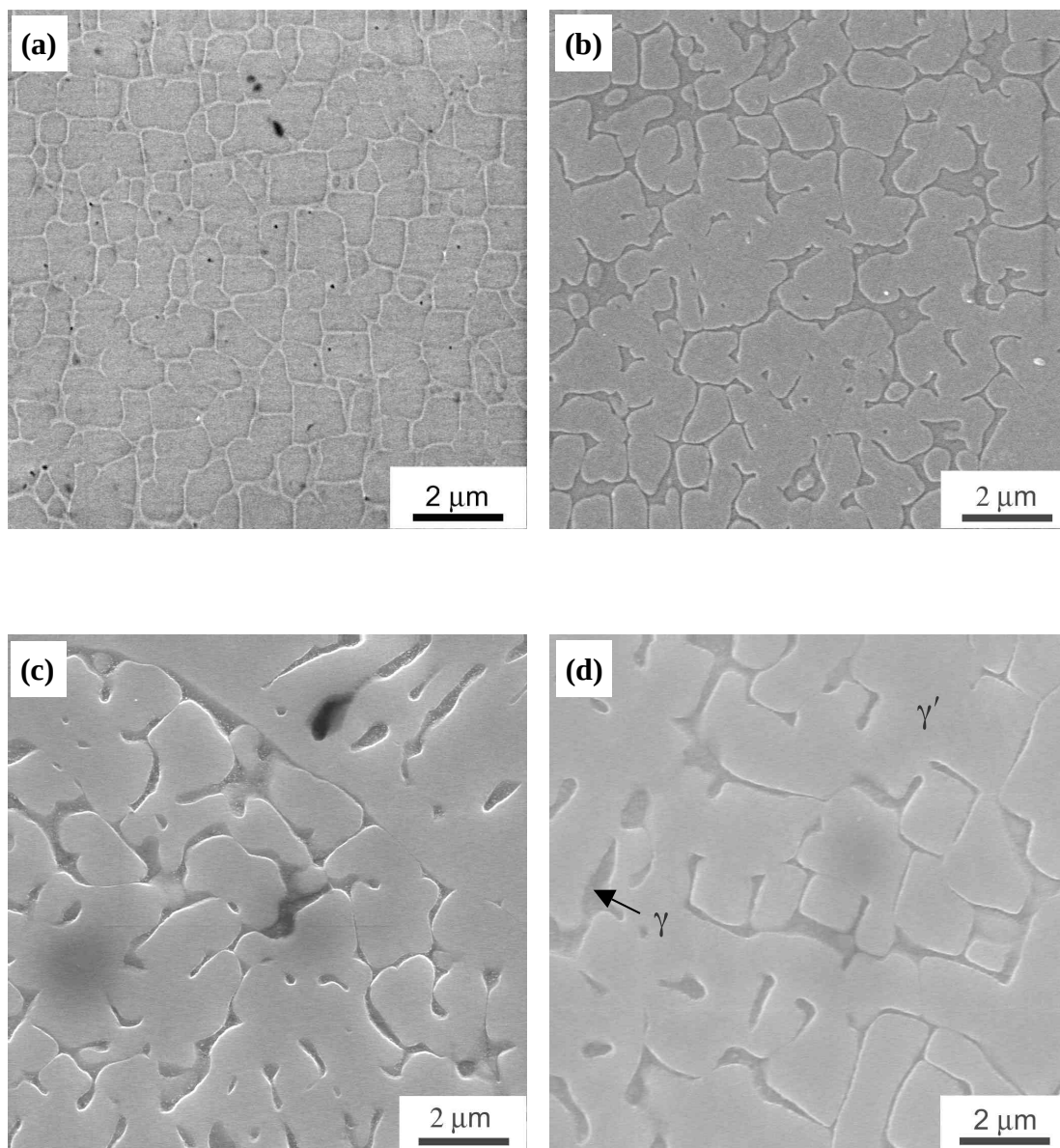


Fig. 3.3.2-2 SEM micrographs of as-cast and 900°C aged IC221M with aging time: (a) as-cast, (b) 100 hrs, (c) 500 hrs, and (d) 1600 hrs

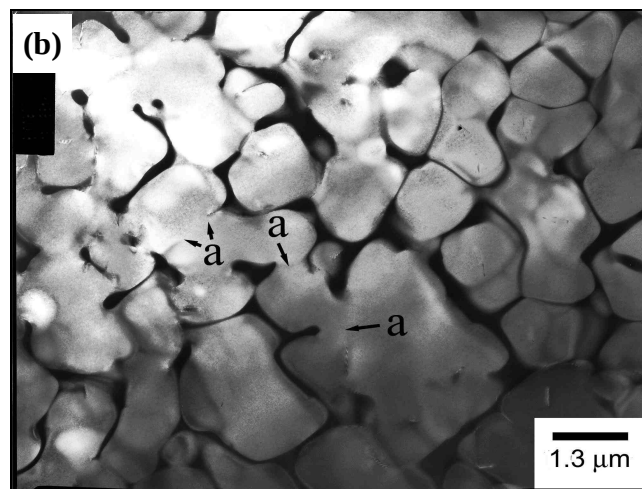
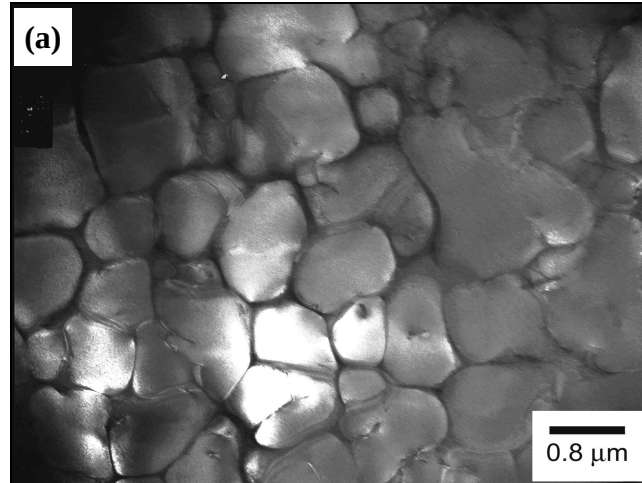


Fig. 3.3.2-3. TEM micrographs of an as-cast specimen (a) and a specimen aged in Ar for 100 hrs at 900°C (b). Note that (a) is at higher magnification than that of (b), therefore, the coarsening of γ and γ' phases is clear.

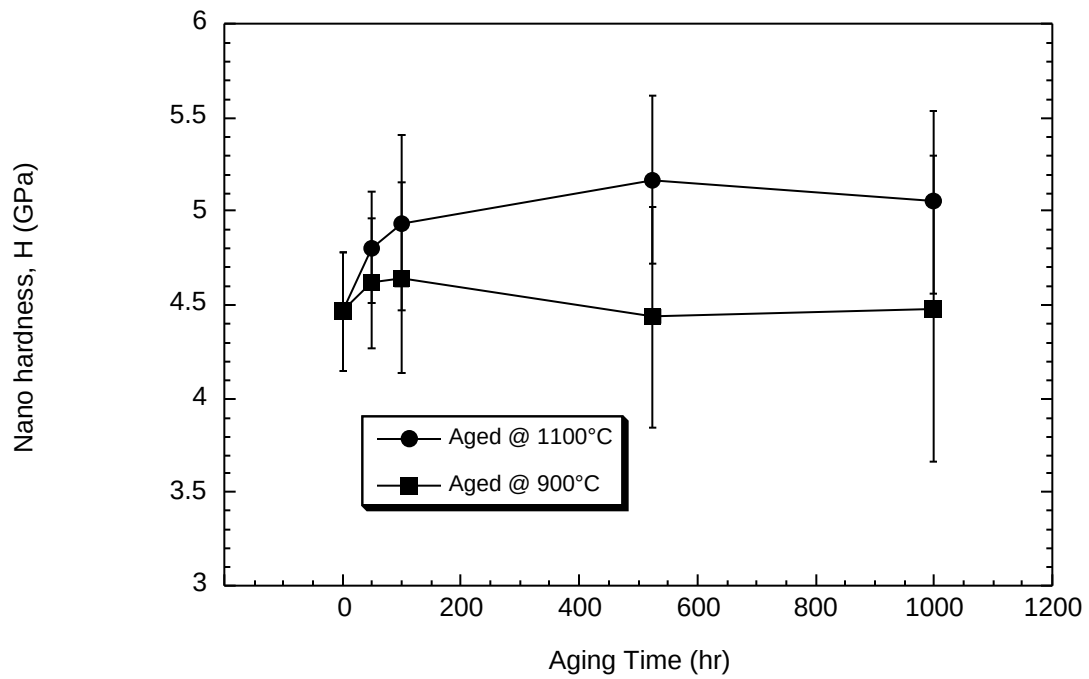


Fig. 3.3.2-4 Variation of nanohardness of IC221M with aging time at 900°C and 1100°C (tested at 20 mN).

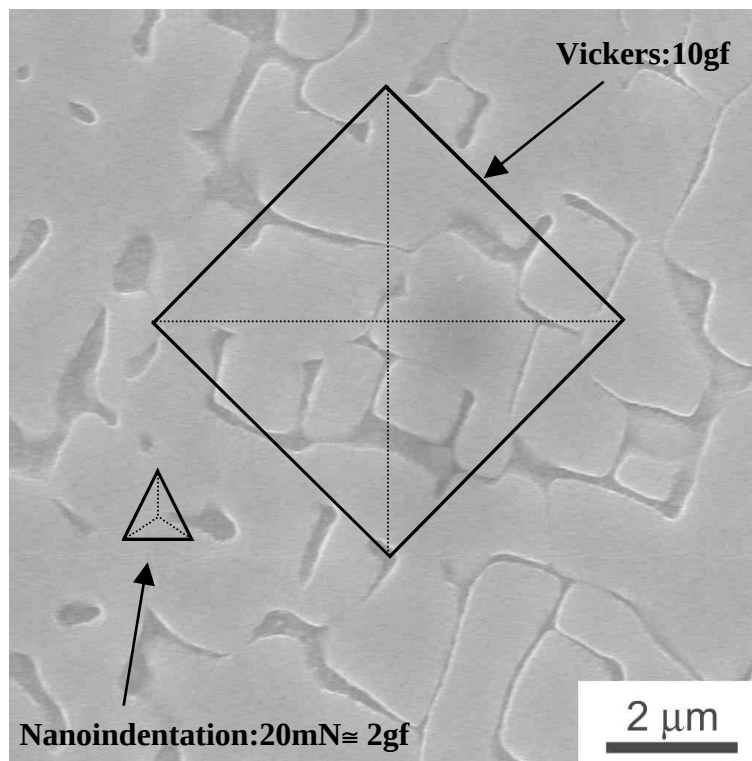


Fig. 3.3.2-5 A schematic diagram of the indent size relative to the microstructure of a specimen aged for 1600 hrs at 900°C. The diamond represents Vickers indent at a load of 10 gf, and the triangle indicates nanoindent at 20 mN $\approx$ 2 gf.

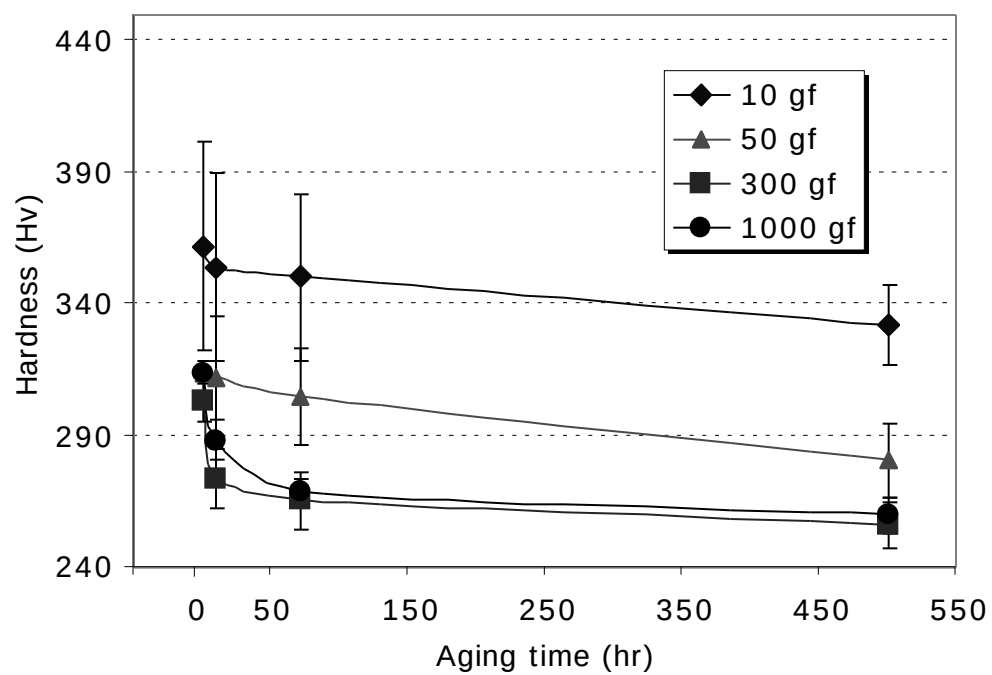


Fig. 3.3.2-6 Variation of Vickers microhardness with aging time for various indentation loads.

γ' are not significant; the decrease in hardness observed in the Vickers tests is due to a domain size effect. Consequently, the coarsening of the γ and γ' phases with thermal aging contributes to a decrease of the yield strength and Vickers microhardness of the material. The hardness of γ and γ' phases themselves may actually increase by Zr solid solution strengthening.

3.4 Thermal aging effects on elevated temperature tensile properties

In this section, the thermal aging and oxidation effects on the tensile properties of IC221M at elevated temperature are investigated. The results of the tensile tests for two aging conditions are presented: (1) aged in air and argon at 900°, 950°, 1000°, 1050°, and 1100°C for 1000 hrs and then tensile tested at 900°C, and (2) aged in argon for 1000 hrs at 900° and 1100°C and then tensile tested at room temperature, 300°, 500°, 700°, 900°, and 1100°C. In the later tests, the yield strength anomaly is observed. All tensile tests were conducted in air.

3.4.1 900°C tensile tests: aged in air/argon at 900°C to 1100°C

The dependence of the yield strength, ultimate tensile strength, and plastic strain on aging temperature for tensile tests conducted at 900°C are summarized in Fig. 3.4.1-1. The figure shows that the ductility diminishes rapidly for both types of aging and that for aging above 1000°C there is essentially no ductility. The temperature dependencies of the yield strength and ultimate tensile strength are very similar. The reason for this is that in many tests, especially those at higher temperatures, the specimen failed immediately after yielding so the two strengths are exactly the same. Specimens aged

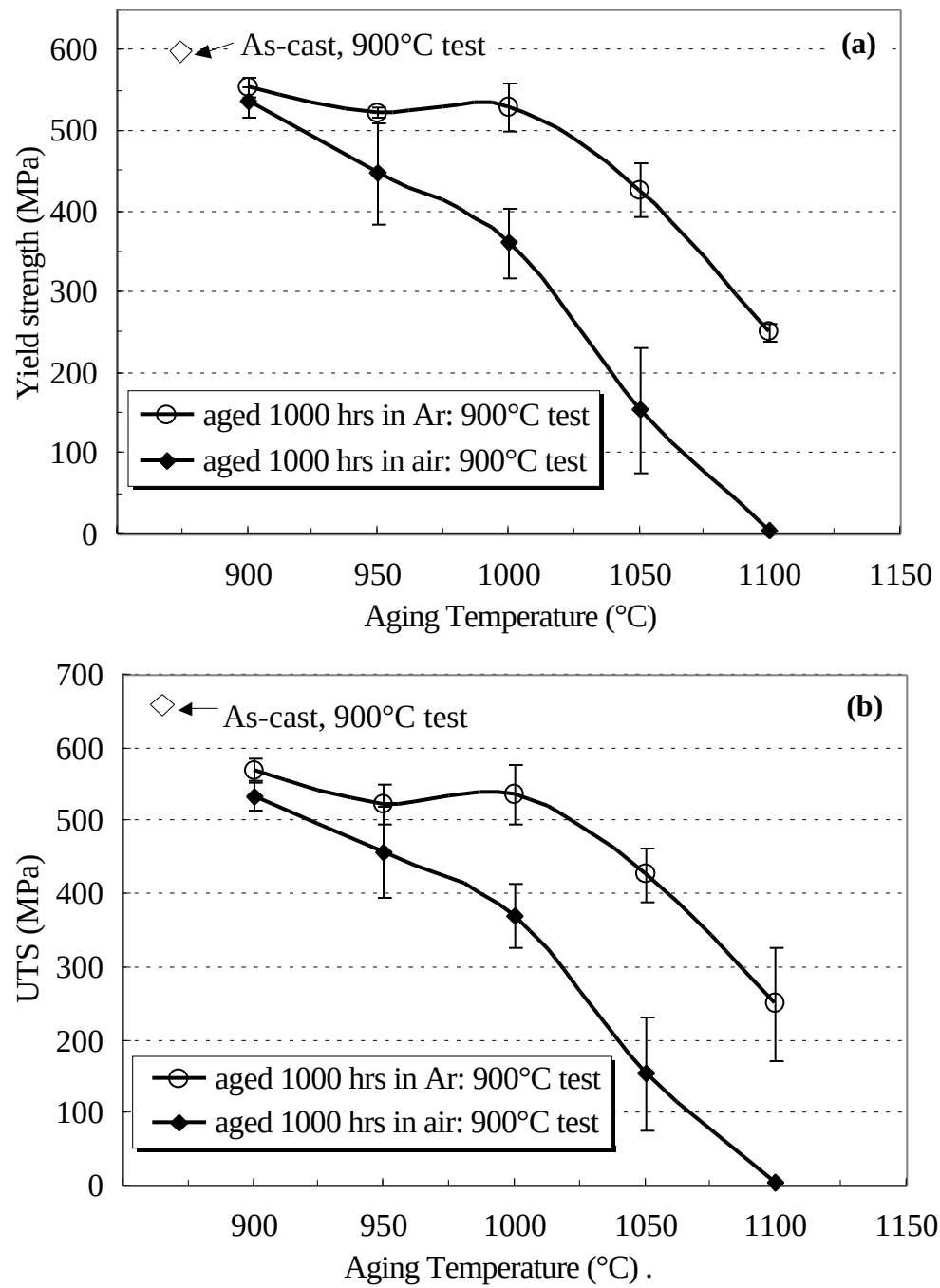


Fig. 3.4.1-1 Variation of tensile properties at 900°C with aging temperature: (a) yield strength, (b) ultimate tensile strength.

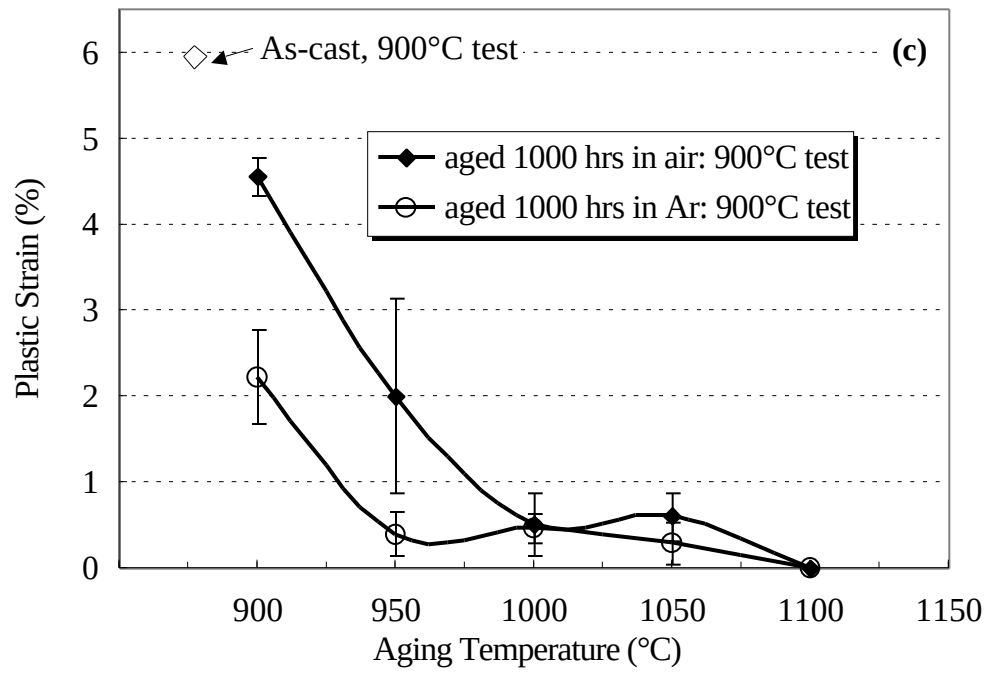


Fig. 3.4.1-1 (continued) (c) plastic strain.

in argon maintain their strength to 1000°C, but lose it steadily at higher temperatures.

For specimens aged in air, the loss in strength begins at a lower temperature, about 900°C.

SEM images in plan-view and of the fracture surfaces are shown in Figs 3.4.1-2 to 3.4.1-4. Figures 3.4.1-2 and 3.4.1-3 present micrographs of tensile specimens aged in air and argon, respectively. In both cases, most of the cracking occurs in the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies. Figure 3.4.1-2a shows that a large crack on the fracture surface propagated through a eutectic colony in the specimen aged in air. As shown in Fig. 3.4.1-3a (white arrows), cracking for specimen aged in Ar also occurs in the eutectic colonies. The fracture surfaces reveal that fracture follows the cast microstructures, presumably along the interdendritic region, and has a crystallographic character. This is the same as in room temperature tensile tests, for which the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies in the interdendritic region are the preferred crack path [91].

The results in Fig. 3.4.1-1 showed that the aging atmosphere did not affect the yield strength at 900°C relative to that at room temperature, but the aging atmosphere did affect the ductility at 900°C. The brittleness at elevated temperature is mainly caused by environmentally assisted embrittlement by oxygen. Curiously, the reduction in ductility is greater for the specimens aged in Ar. This may suggest that the specimens aged in air are more resistant to the embrittlement due to a protective oxide coating; a phenomena like this has been observed for Ni_3Al tested at 600°C [51,54,71]. On the other hand, apparently, the surface oxide formed above 1000°C may not act as a protective coating to prevent oxygen embrittlement since no ductility observed specimens aged above 1000°C (see Fig. 3.4.1-1c). Figures 3.4.1-4a, b and c, d show micrographs in plan-view and of the

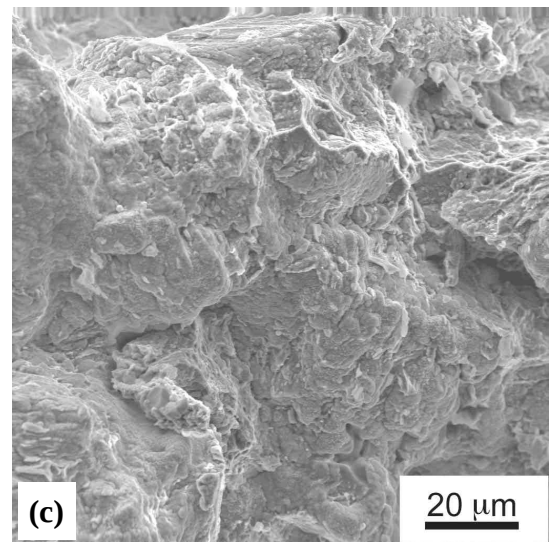
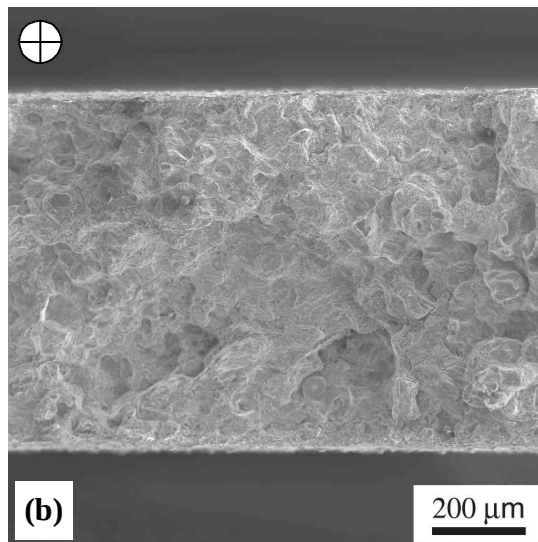
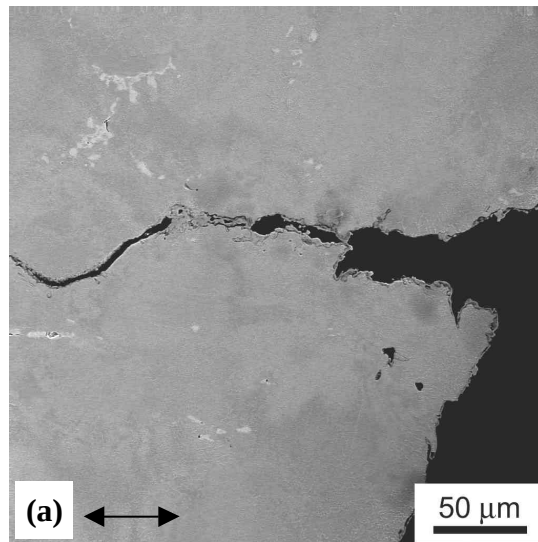


Fig. 3.4.1-2 A plan-view micrograph (a) and fracture surfaces (b and c) of tensile specimens aged in air for 1000 hrs at 900°C and then tested in air at 900°C. (c) is an enlarged micrograph of (b).

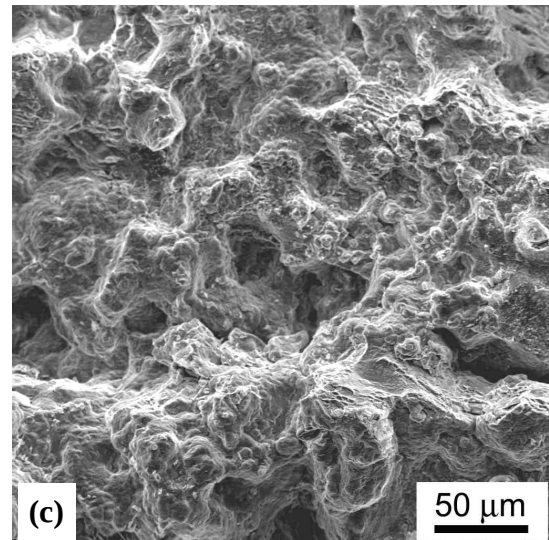
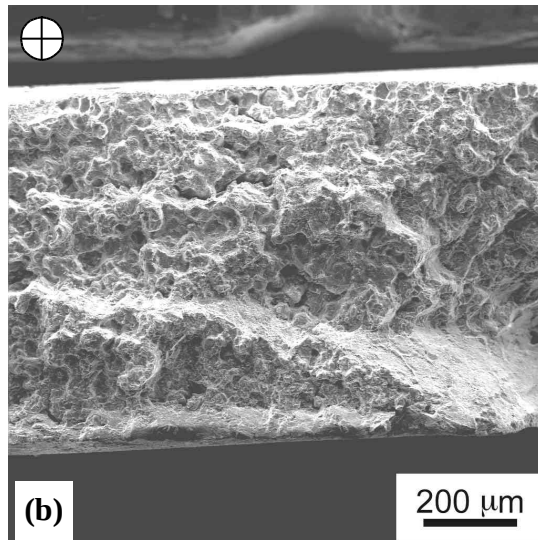
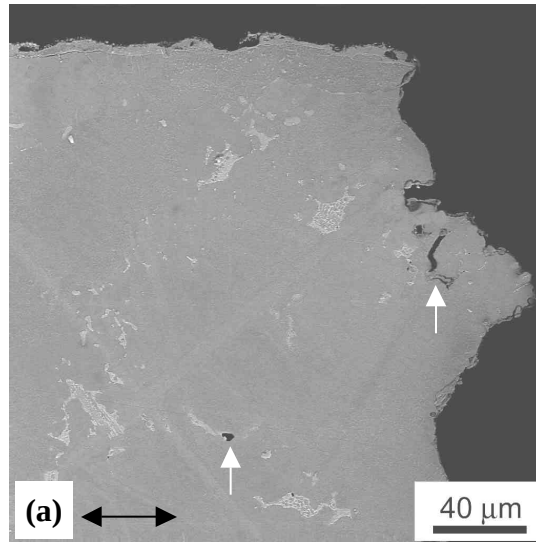


Fig. 3.4.1-3 A plan-view micrograph (a) and fracture surfaces (b and c) of tensile specimens aged in argon at 900°C for 1000 hrs and then tested in air at 900°C. (c) is an enlarged micrograph of (b).

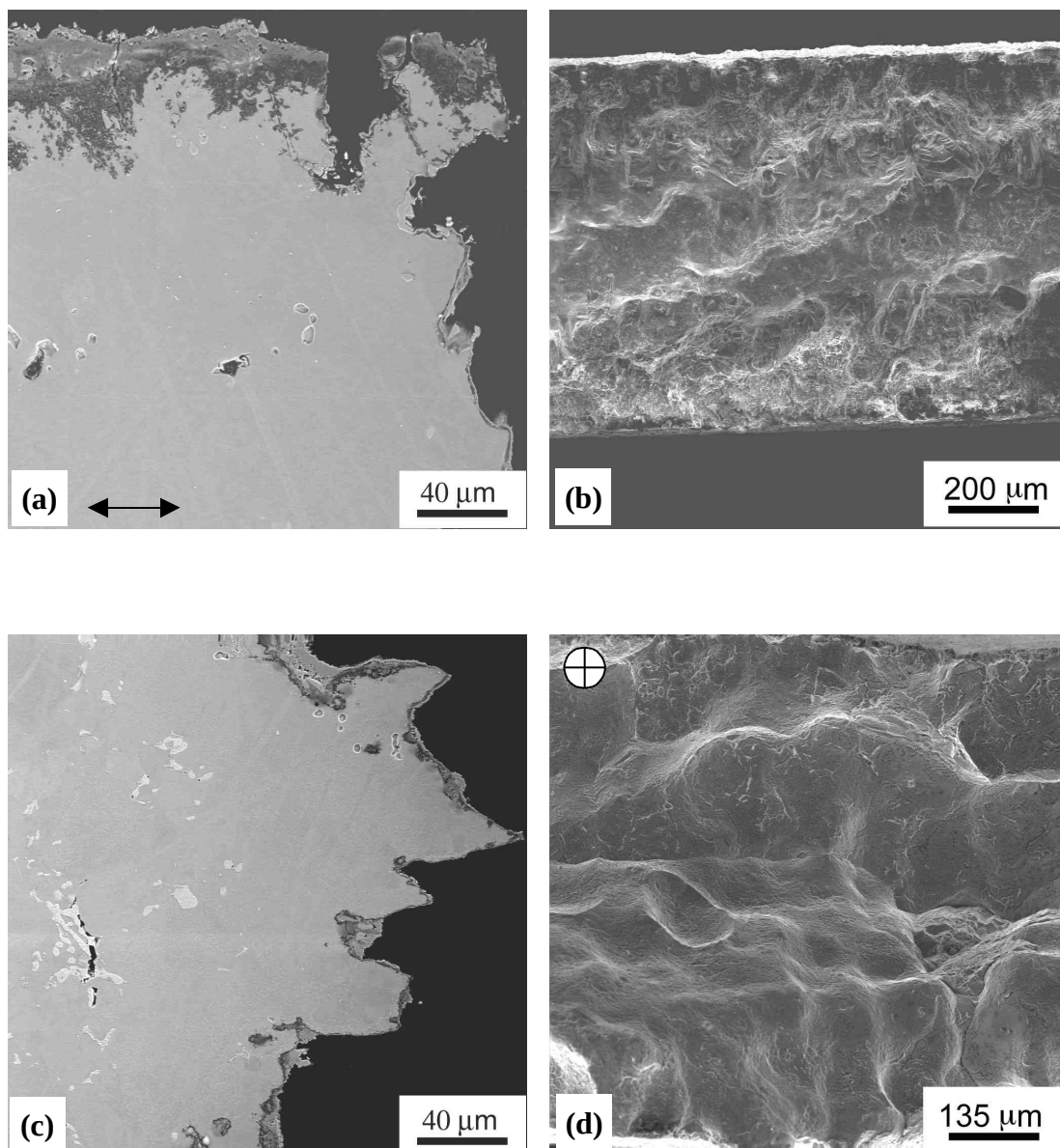


Fig. 3.4.1-4 Plan-view micrographs and fracture surfaces of tensile specimens. (a) and (b) specimen aged in air at 1050°C; (c) and (d) specimen aged in argon at 1050°C, tested in air at 900°C.

fracture surface for specimens aged in air and argon at 1050°C, respectively. The fracture also follows the cast microstructures. Because the tests were conducted at elevated temperature, oxide covers all of the fracture surface. Presumably, failure occurred due to combined effects of oxygen induced embrittlement and penetration of spike oxides. On the other hand, fracture in the specimen aged in Ar occurred mainly by oxygen induced embrittlement.

Although as-cast IC221M shows a degradation of tensile properties after 1000 hrs aging at above 950°C, the properties are still much better than other commercialized superalloys, for example, HU alloy (Ni-Fe-Cr alloy) and SuperthermTM (Ni-Cr-Fe-Co alloy), which show a yield strength of less than 200 MPa and a ultimate tensile strength of less than 300 MPa at 900°C [11,111]. Note that the mechanical properties of HU alloy and SuperthermTM in ref. [11,111] are in the unaged condition. As-cast IC221M also shows better fatigue properties than as-cast IN-713C.

3.4.2 Various tensile testing temperatures: aging in Ar at 900°C and 1100°C

Tensile test results for the as-cast material and specimens aged in Ar for 1000 hrs at 900°C and 1100°C in argon are shown in Figs. 3.4.2-1. Figure 3.4.2-1a 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 the previous work [11,111] 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

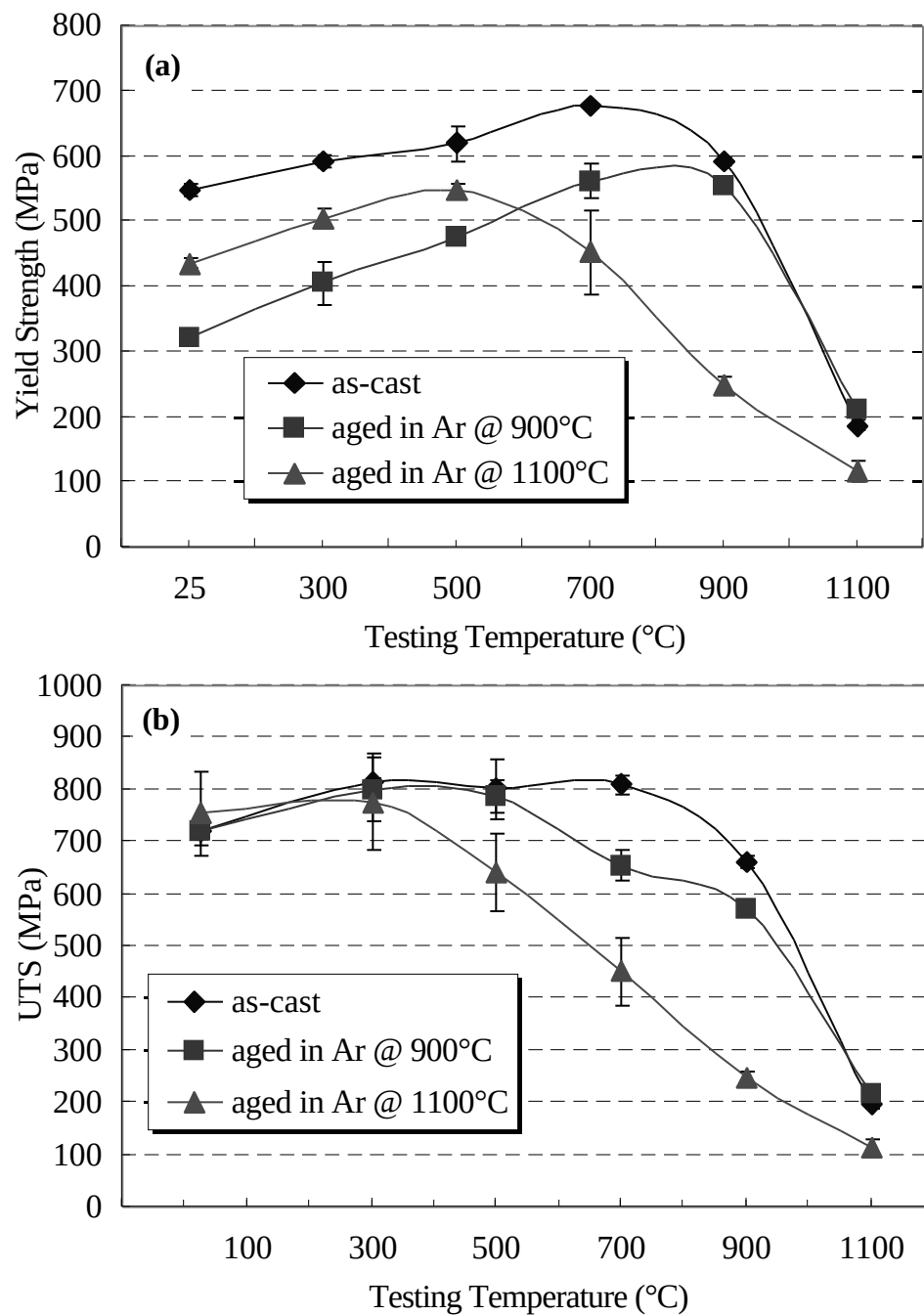


Fig. 3.4.2-1 Testing temperature dependence of tensile properties for as-cast IC221M and specimens aged in Ar at 900° and 1100°C: (a) yield strength, (b) ultimate tensile strength.

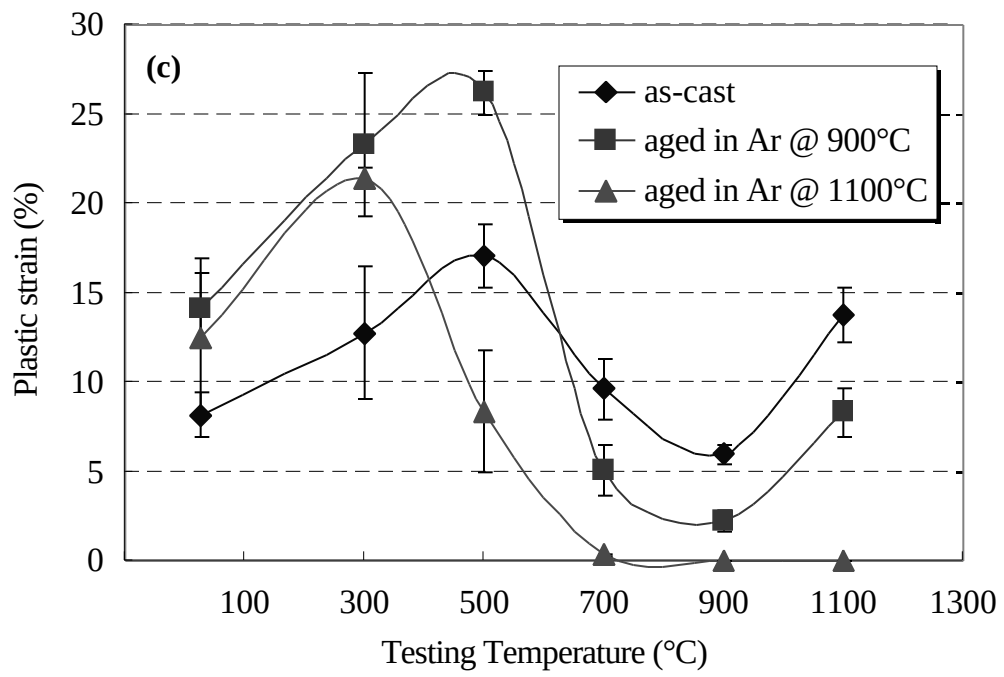


Fig. 3.4.2-1 (continued) (c) plastic strain.

[7]. The behavior of the specimens aged in Ar at 900°C is generally similar to the as-cast alloy with the exception of a lower yield strength. The yield strength of a specimen aged at 1100°C is intermediate to the as-cast and 900°C aged specimens up to a testing temperature of 500°C, at which there is a decrease in strength.

Figures 3.4.2-1b and c show that the ultimate tensile strength (UTS) and plastic strain, respectively. The UTS for all three aging conditions is nearly the same for the RT and 300°C tests. The as-cast and specimens aged at 900°C maintain their tensile strength up to 700°C, but the UTS of the specimens aged at 1100°C begins to decrease at lower temperatures, approximately 300°C. The elongations of the specimens aged at 900° and 1100°C are much higher than the as-cast alloy up to 300°C, but beyond this testing temperature, the as-cast material is more ductile. For the specimen aged at 900°C, the ductility peaks at 500°C (up to 27 %), but then drops dramatically to below 5%. This is presumably due to environmental embrittlement caused by oxygen. Interestingly, at higher temperatures the as-cast alloy is less sensitive to environmental embrittlement than that of the aged specimens. The ductility recovery at 1100°C has been previously observed in Ni₃Al, and is generally attributed to softening by thermal activation at this temperature [7,39,84]. The specimen aged at 1100°C seems more sensitive to environmental embrittlement than other specimens since the elongation drops noticeably at testing temperatures above 300°C and then shows brittle fracture.

Figures 3.4.2-2 to 7 show SEM plan-view micrographs and the fracture surfaces of the specimens. Most of the cracks of the as-cast material and the aged specimens follow the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies (see all plan-view micrographs in Figures 3.4.2-2 to 7). The as-cast alloy shows ductile fracture as the dominant mode up to a testing

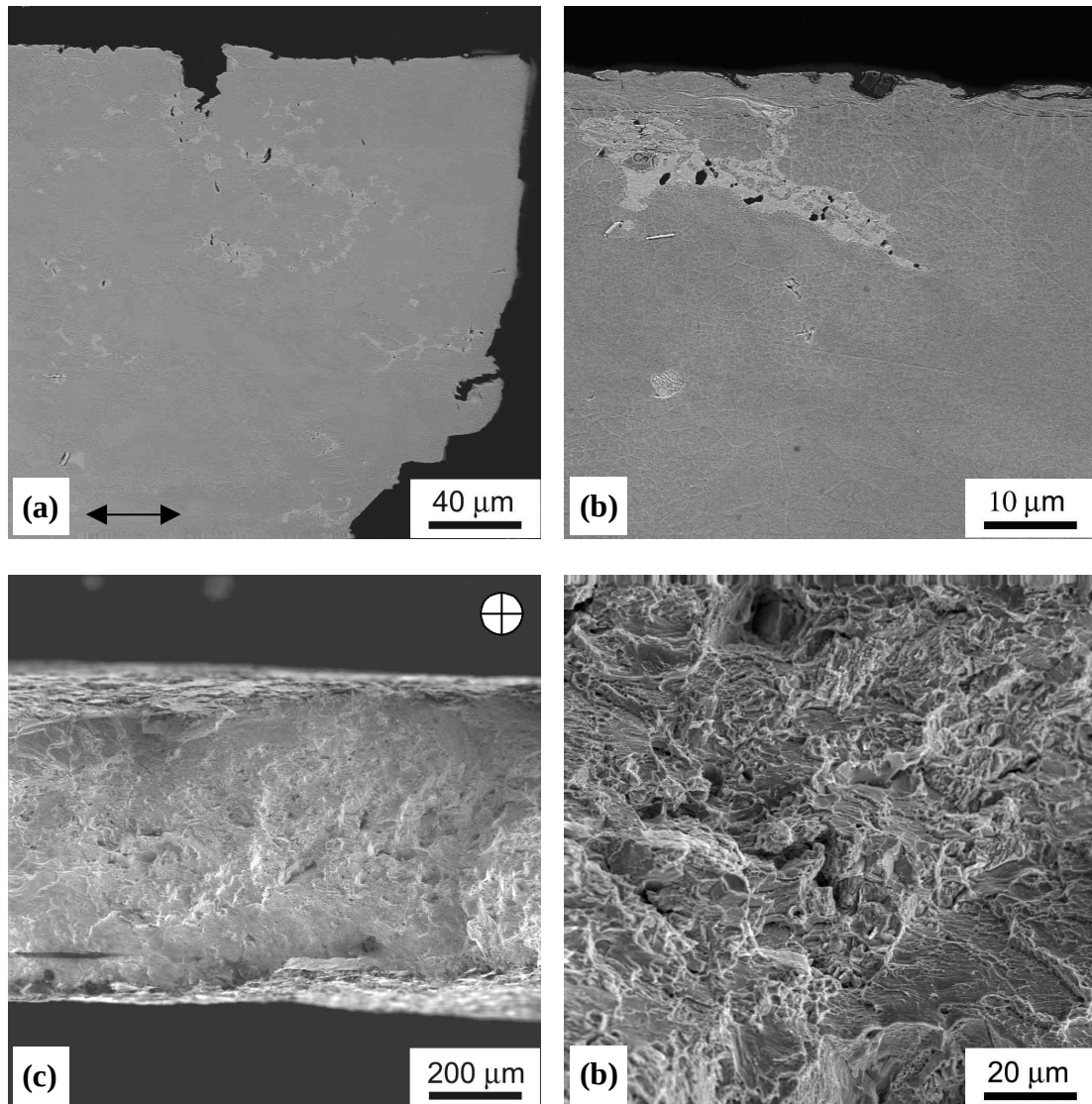


Fig. 3.4.2-2 SEM micrographs of a tensile specimen of as-cast IC221M tested in air at 500°C. (b) and (d) are the enlarged micrographs of (a) and (c). (d) is a micrograph of the fracture surface showing ductile dimples.

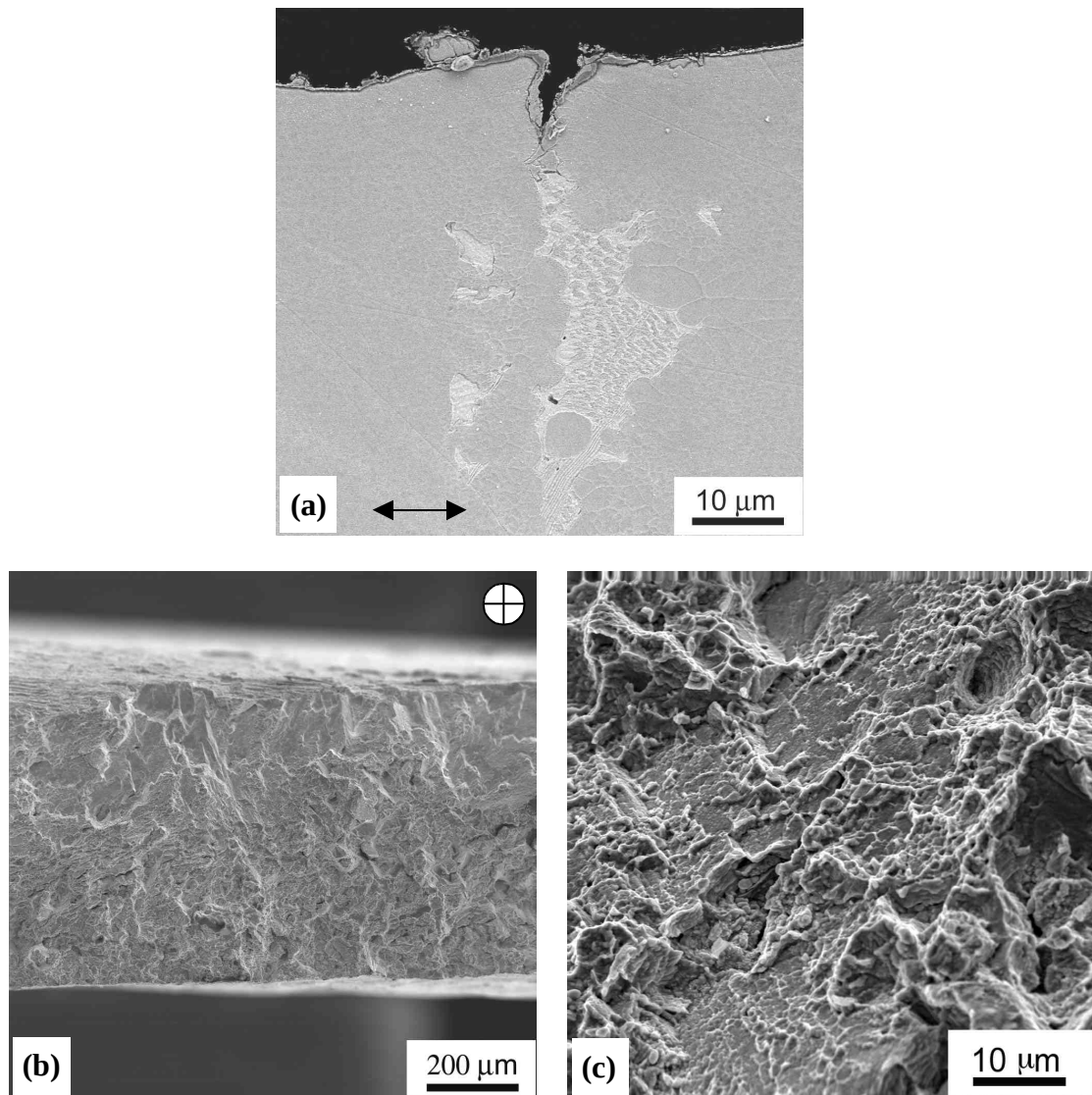


Fig. 3.4.2-3 SEM micrographs of a tensile specimen of as-cast IC221M tested in air at 700°C. (a) shows that a surface crack propagates through the eutectic. (b) and (c) are micrographs of the fracture surface showing a mixture of ductile and cleavage features.

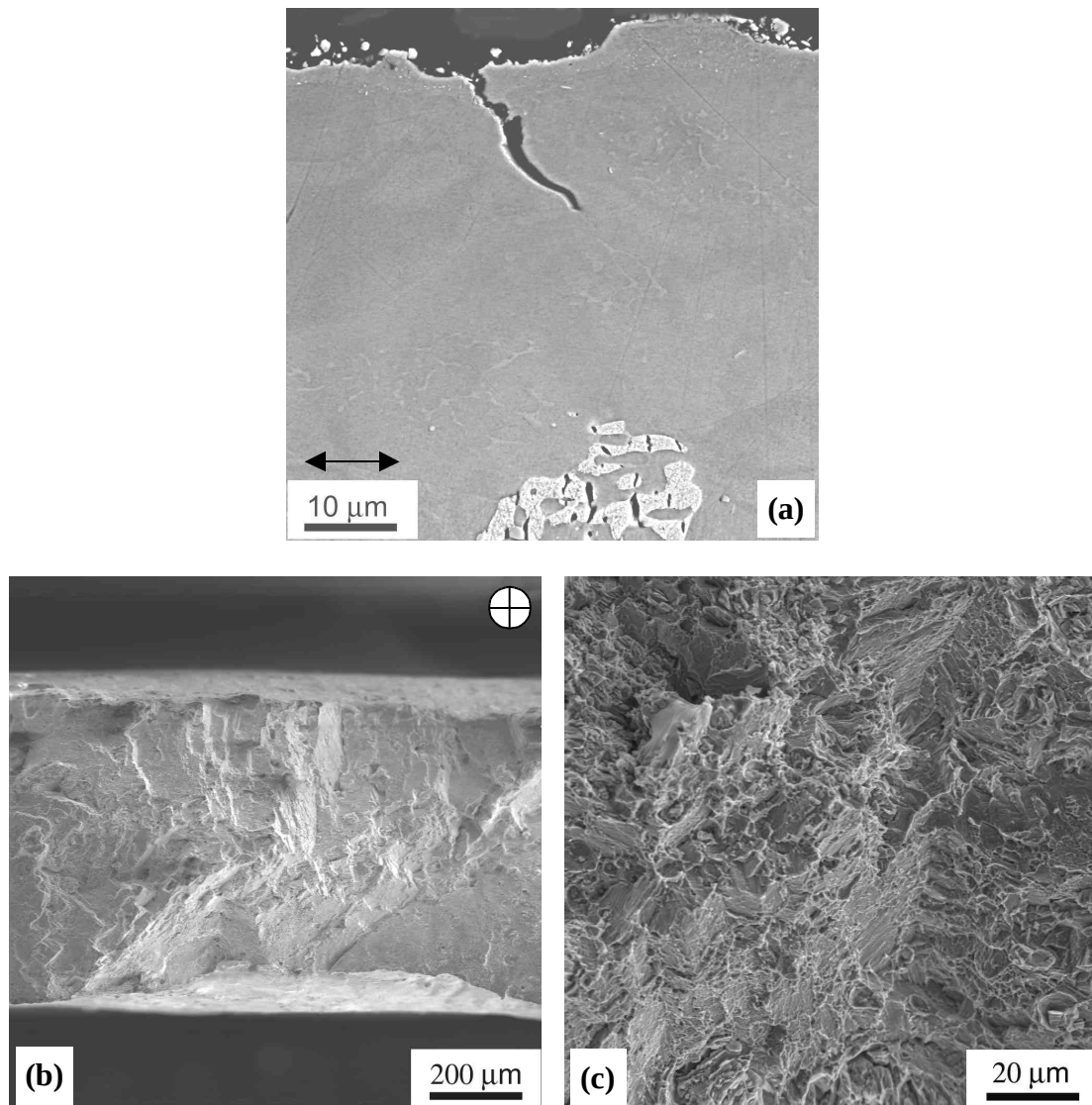


Fig. 3.4.2-4 SEM micrographs of tensile specimen aged in argon at 900°C tested in air at 500°C. (a) plan-view micrograph; (b) and (c) micrographs of the fracture surface showing a mixture of ductile and cleavage features.

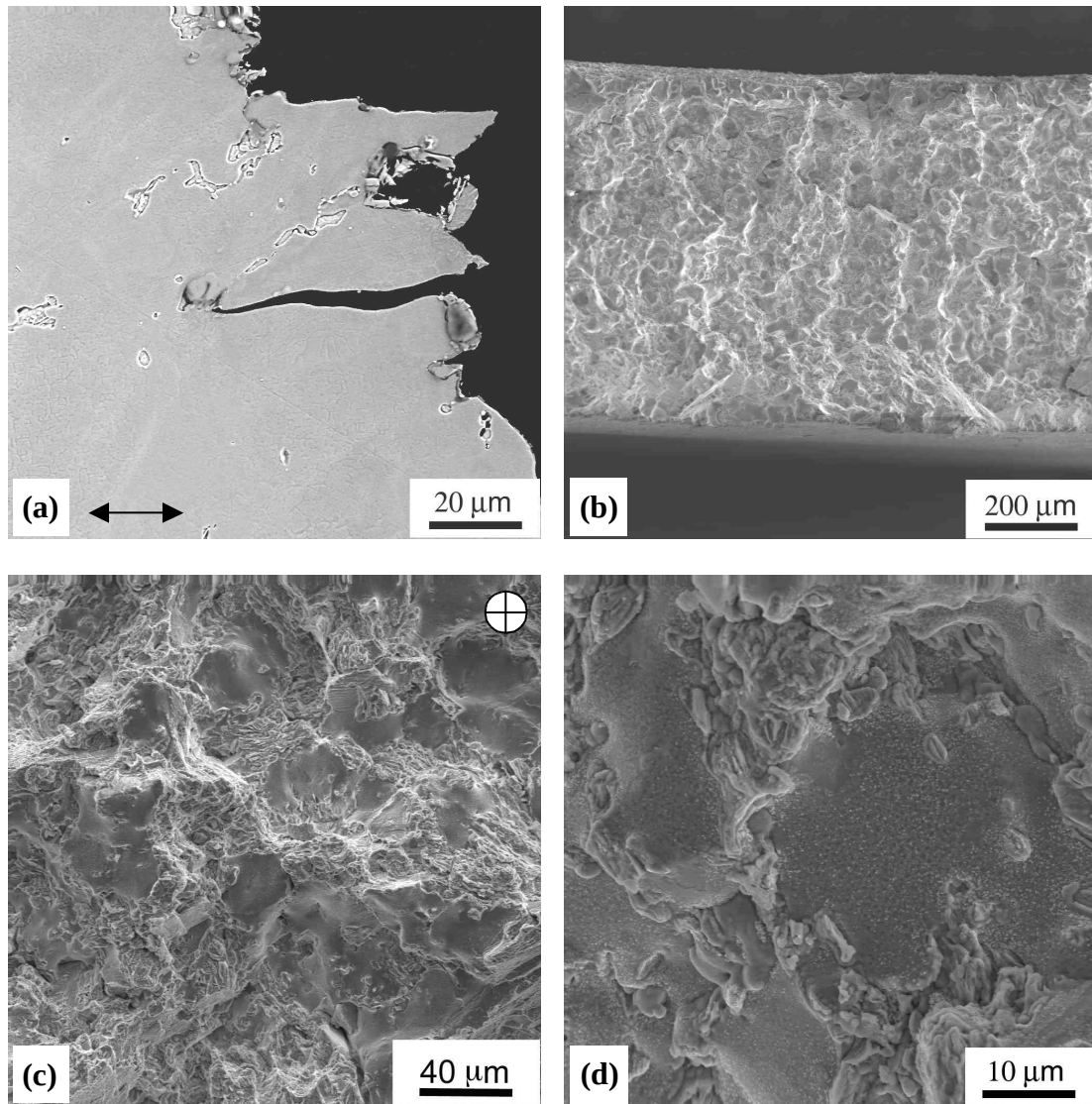


Fig. 3.4.2-5 SEM micrographs of tensile specimen aged in argon at 900°C tested in air at 700°C. (a) plan-view micrograph; (b), (c), and (d) micrographs of the fracture surfaces.

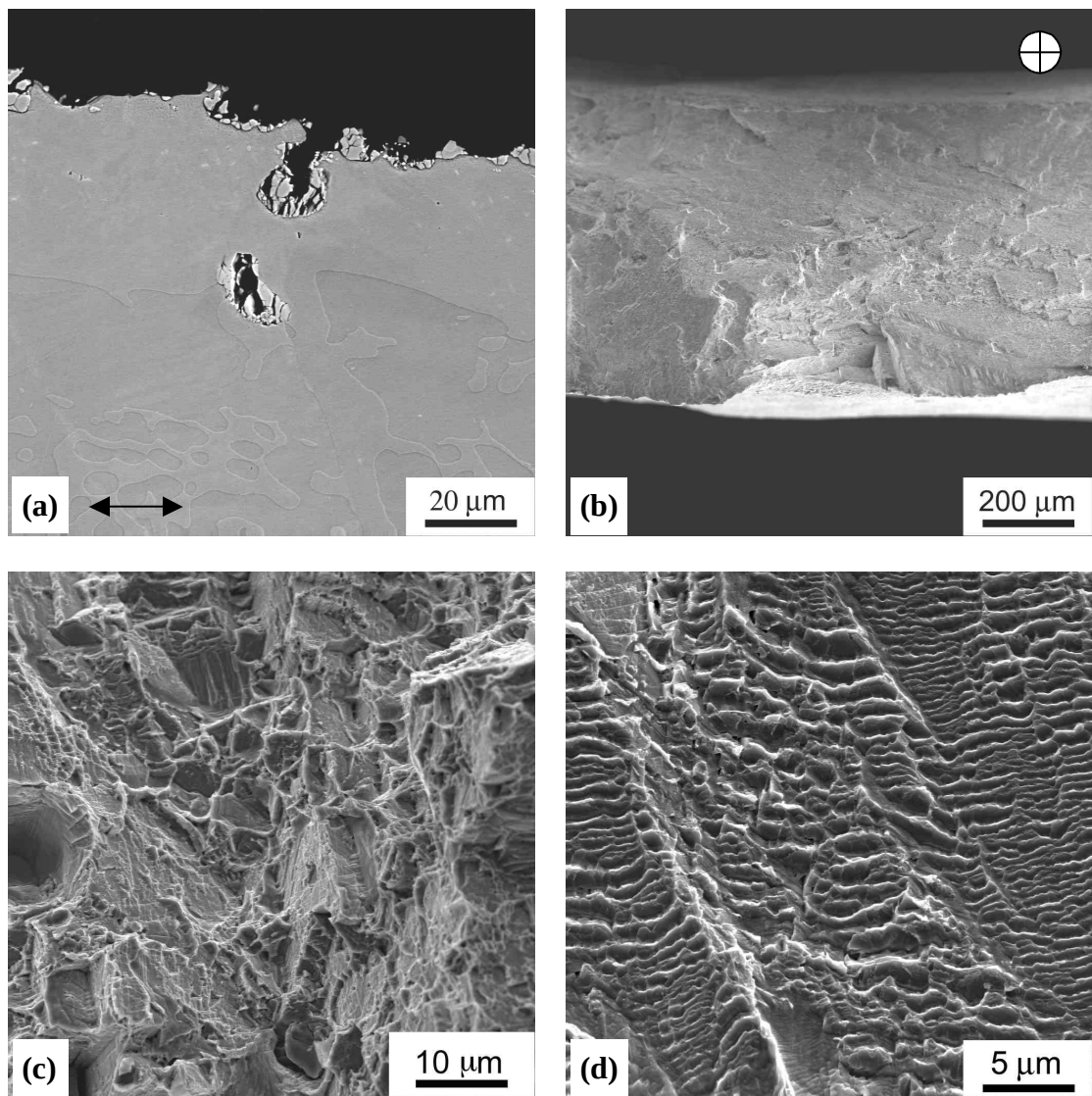


Fig. 3.4.2-6 SEM micrographs of a tensile specimen aged in argon at 1100°C tested in air at 300°C. A crack on a remnant $\gamma + \text{Ni}_5\text{Zr}$ eutectic colony is shown in (a). (b), (c), and (d) are micrographs of fracture surface.

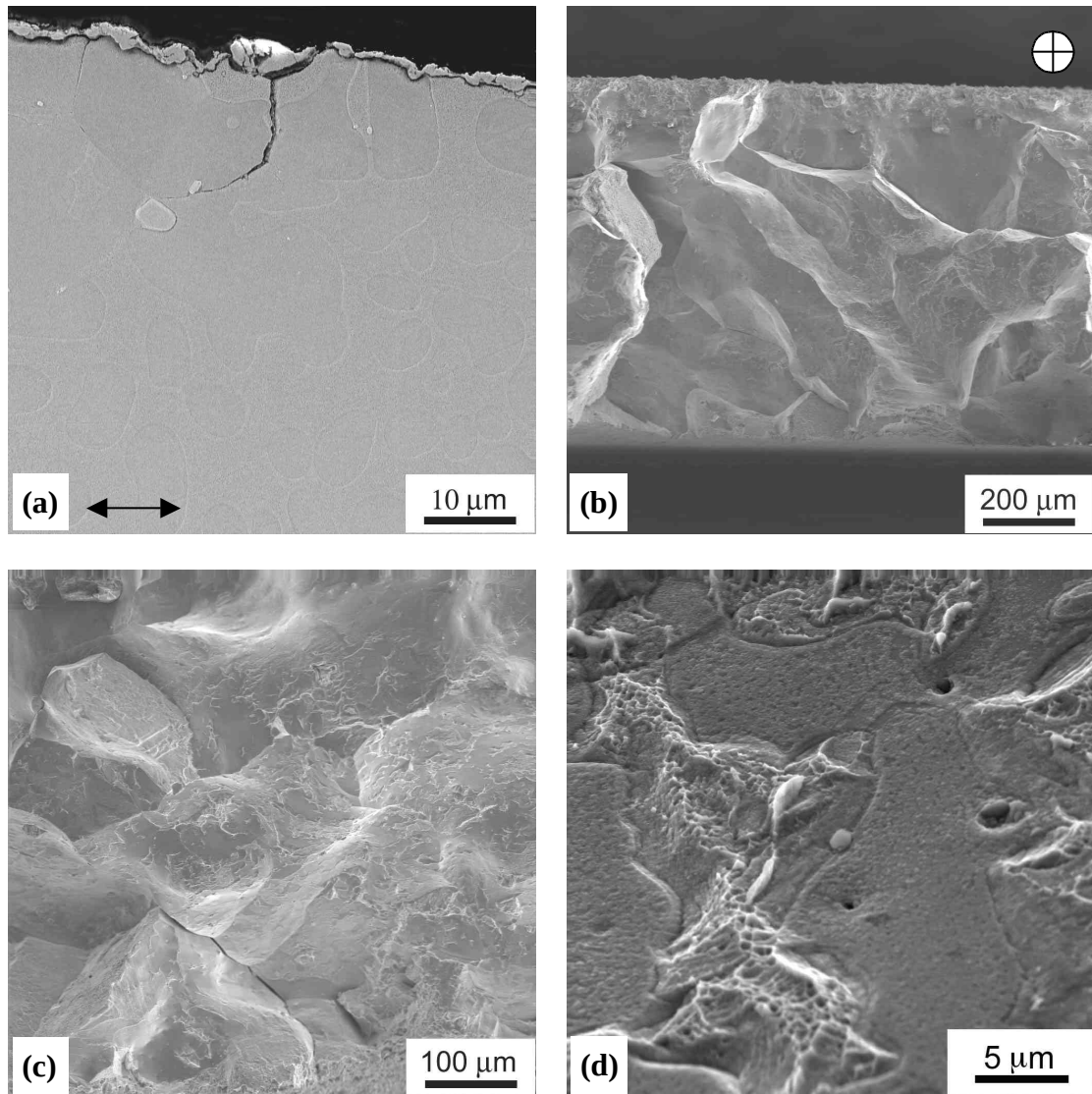


Fig. 3.4.2-7 SEM micrographs of a tensile specimen aged in argon at 1100°C and then tested in air at 700°C. (a) shows intergranular crack propagation. (b), (c), and (d) show the intergranular fracture surfaces.

temperature about 500°C, but above this temperature, the fracture surface shows the mixture of ductile and brittle cleavage modes. Figures 3.4.2-4 and 5 show micrographs of specimens aged at 900°C and then tested at 500°C and 700°C, respectively. While the specimen tested at 500°C shows some cleavage with a crystallographic character, the ductile fracture mode dominates the majority of the fracture surface. This temperature exhibited the highest ductility in this study. However, the ductility dramatically drops at a testing temperature of 700°C: the fractographs of Fig. 3.4.2-3 reveal numerous cleavage-like areas (smooth areas). Like the specimen aged at 900°C and then tested at 500°C, the specimen aged 1100°C and tested at 300°C shows cleavage fracture in the low magnification micrograph, but high magnification reveals heavily dimpled fracture surfaces (see Fig. 3.4.2-6). The specimen aged at 1100°C shows intergranular brittle fracture at 700°C, as shown in Fig. 3.4.2-7. This is presumably due to oxygen induced embrittlement.

All the specimens, irrespective of prior aging treatment, showed environmental embrittlement at elevated testing temperatures. Interestingly, the as-cast material is less sensitive to this embrittlement than the aged material. The embrittlement phenomenon appears at 700°C in the as-cast material, at 500°C for specimens aged at 900°C, and at 300°C for specimens aged at 1100°C. It is not understood why the specimen aged at 1100°C is more sensitive to the oxygen induced embrittlement than other conditions. One possibility is that because the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies are mostly dissolved into the base alloy at 1100°C, the Zr concentration in the matrix may have an influence on the ductility of the specimen. It is known that the higher zirconium contents can lead to

embrittlement [45,46,63,72]. Further studies using Auger electron spectroscopy to examine the zirconium content at fracture surfaces are warranted.

IV. AN ATTEMPT TO IMPROVE THE HIGH-TEMPERATURE PROPERTIES OF AS-CAST IC221M

Many of the results in the oxidation and tension tests in the previous chapter show that the $\gamma + \text{Ni}_5\text{Zr}$ eutectic constituent negatively affect to the properties. Therefore, if we can reduce the amount of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic constituents from the base alloy by “solution treatment” the material prior to application, the oxidation and tensile properties of the as-cast alloy may be improved. A solution treating temperature of 1100°C was then chosen to reduce the volume fraction of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies by re-dissolution without melting them.

4.1 Experimental procedure

The as-cast IC221M was solution treated by annealing large blocks in air at 1100°C for 24 or 100 hrs. Specimens were then cut from the unoxidized internal regions and polished with up to 1200 grit SiC paper. Experiments were performed to examine the isothermal oxidation in air at 900°C for 500 and 1000 hrs, and Vickers microhardness was measured at a 300 g load. In addition, tensile specimens were tested at various temperatures up to 1100°C; however, it may be inappropriate to directly compare the tensile properties between a specimen aged at 900°C without solution treatment and a specimen only solution treated at 1100°C because the solution treated specimen was not aged at 900°C prior to testings. All tests were conducted in air using the same procedure described in chapter 2.

4.2 Results and discussion

4.2.1 Oxidation

The effects of the solution treatment on the oxidation behavior of IC221M are shown in Figs. 4.2.1-1, 4.2.1-2, and 4.2.1-3. Figure 4.2.1-1a show the surface oxides of solution treated specimens after aging at 900°C for 1000 hrs. For comparison, an SEM micrograph of an untreated specimen aged at 900°C for 1000 hrs is presented in Figs 4.2.1-1b. The oxide features of the solution treated specimen are quite different from the untreated specimens (compare between Figs. 4.2.1-1a and b); in particular, the spike oxides are absent so there is no deep penetration of the oxide into the matrix. Note that because of the absence of the spike oxides, the thickness of the oxide from top to bottom is called the oxidation extent (see arrow in Fig. 4.2.1-1a). Moreover, the surface oxide is relatively uniform in appearance and thickness. Another important result is that the NiO nodules which form immediately above the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies in untreated specimen are considerably reduced after solution treating, presumably due to homogenization of microstructure.

The X-ray oxide phase images presented in Fig. 4.2.1-2 show that an aluminum oxide, Al_2O_3 and/or $(\text{Al}, \text{Cr})_2\text{O}_3$, is focused all through the oxide, but the outermost layer of the oxide is composed of the mixture of Al, Ni, and O, possibly $\text{NiO}/\text{NiAl}_2\text{O}_4$ spinel (see Fig. 4.2.1-2c). A chromium oxide, possibly Cr_2O_3 and/or NiCr_2O_4 spinel, forms beneath of the outermost layer. Interestingly, zirconium oxide, ZrO_2 is scattered in the surface scale instead of forming spike oxides. In this regard, the solution treatment appears to have a beneficial effect on the oxidation of the as-cast IC221M.

Figure 4.2.1-3 shows a graph that compares the oxidation rate of the solution

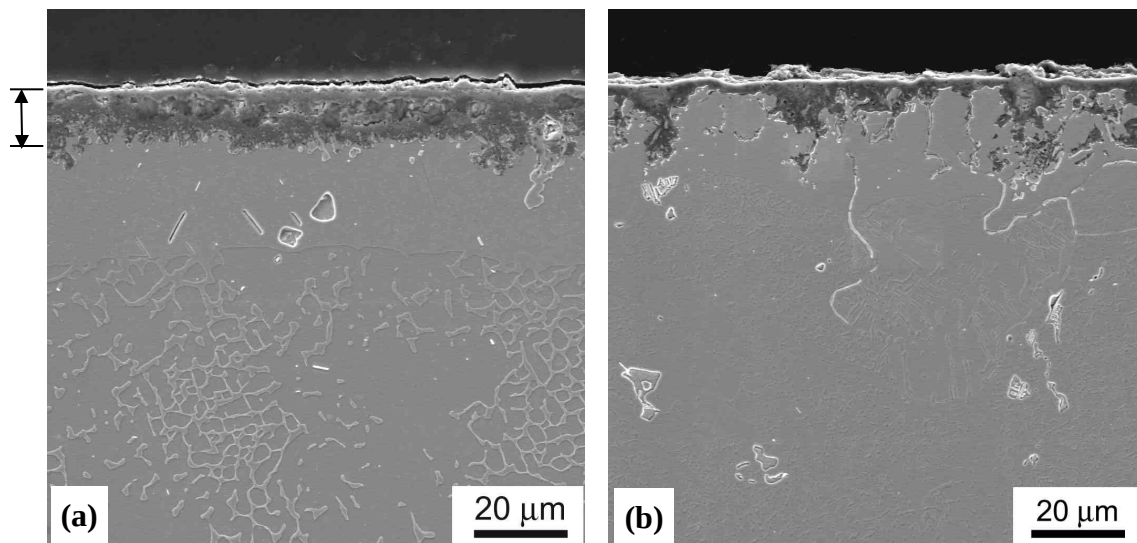


Fig. 4.2.1-1 Cross-sectional SEM micrographs of IC221M: (a) solution treated in air at 1100°C for 100 hrs, and then aged in air at 900°C for 1000 hrs. For comparison, (b) shows an SEM micrograph of an untreated specimen aged in air at 900°C for 1000 hrs.

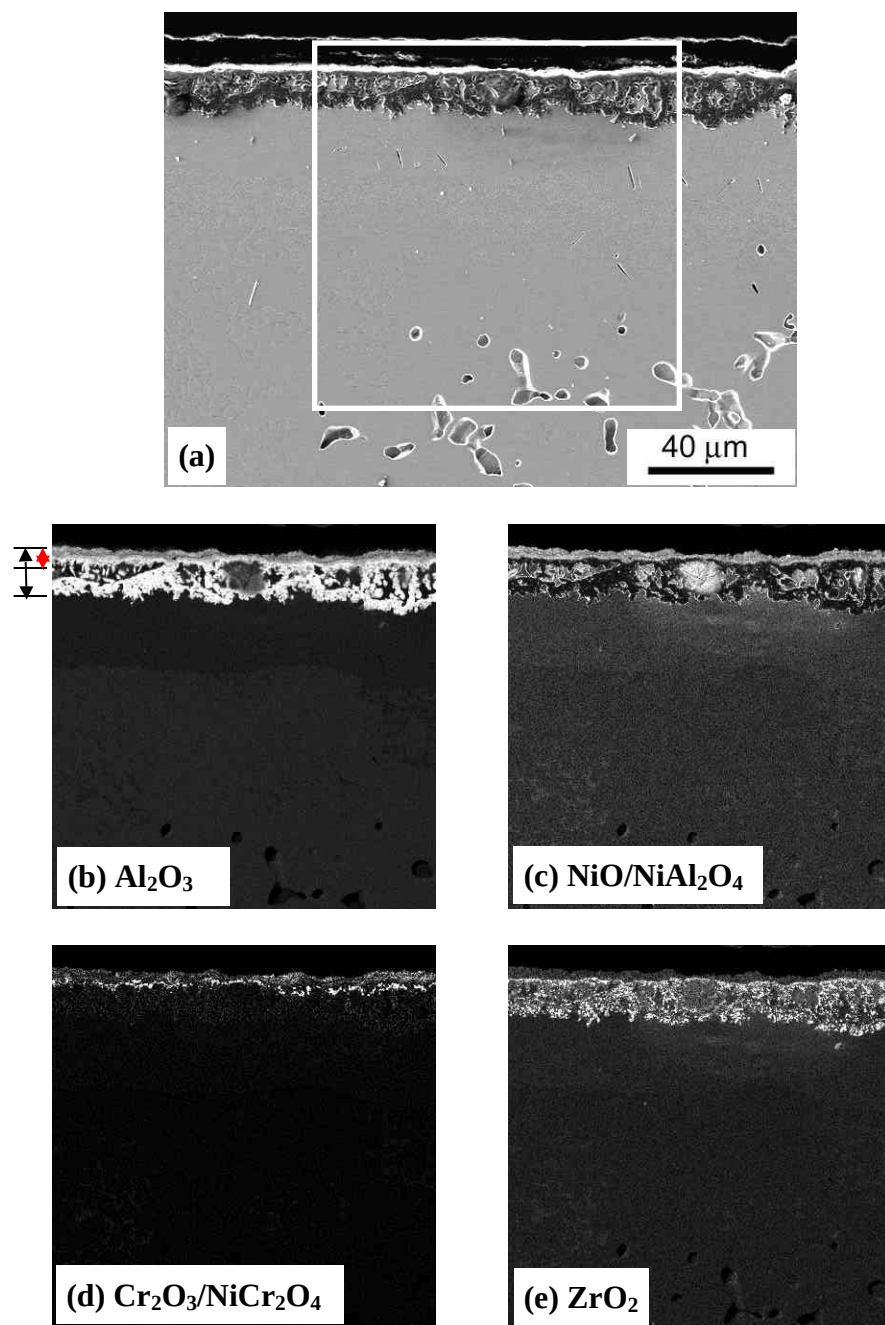


Fig. 4.2.1-2 Oxide phase maps of a solution treated specimen aged in air at 900°C for 1000 hrs: (a) is a secondary electron micrograph in which the area in the box was scanned, (b) is Al₂O₃, (c) is NiO/NiAl₂O₄, (d) is Cr₂O₃/NiCr₂O₄, and (e) is ZrO₂. The red arrow in (b) indicates a continuous oxide and the black arrow shows the oxidation extent.

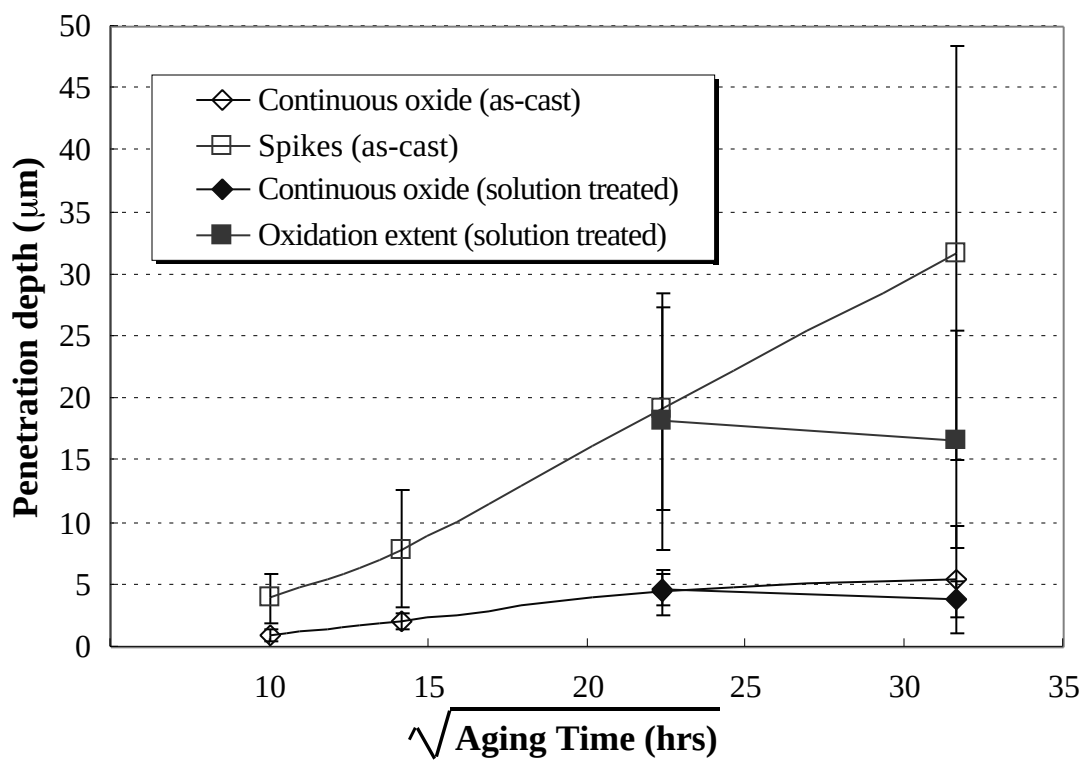


Fig. 4.2.1-3 A plot of variation of oxide penetration depth with respect to the square root of aging time comparing the oxide penetration depth with aging time between before and after solution treatment of IC221M.

treated material to that of the material as received. The red arrow in Fig. 4.2.1-2b indicates the continuous oxide and the black arrow shows the oxidation extent. As can be seen in the graph, while the spike-like oxides of untreated specimen penetrate deeply and continue to penetrate with aging time, growth of the oxide in the solution treated specimen slows as aging proceeds. Solution treating thus retards the oxidation process.

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 commercial applications. For this purpose, cyclic oxidation tests need to be performed to determine whether the oxide scale is adherent.

4.2.2 Hardness

Figure 4.2.2-1 shows the variation of the Vickers microhardness (Hv) for solution treated IC221M aged in air at 900°C for various time up to 1000 hrs. For comparison, the microhardness of the untreated material aged in air at 900°C (open triangle) is also presented. The microhardness of the solution treated specimens drops slightly at early aging times but remains significantly higher than the untreated specimens aged at 900°C. This result is probably produced by the Zr solid solution strengthening effect. Therefore, solution treatment helps to improve the room temperature hardness of as-cast IC221M after aging at 900°C. These data show that further increases in the hardness may be achieved by solution treating for times longer than 24 or 100 hrs.

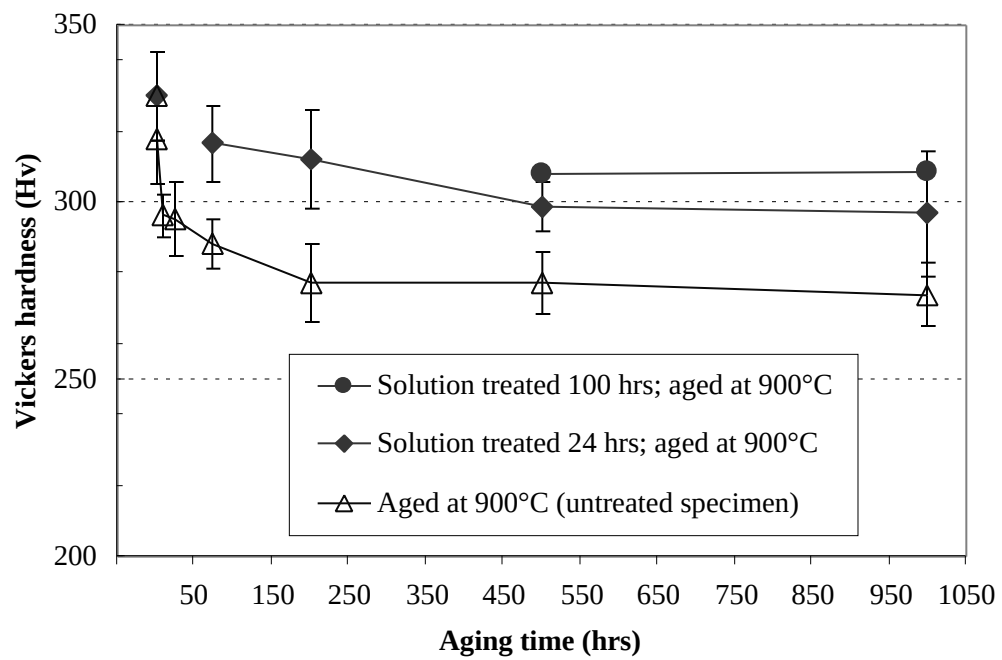


Fig. 4.2.2-1 Variation of microhardness with aging time for three different aging conditions.

4.2.3 Tensile properties

The results of tensile tests of a solution treated specimen are shown in Figs. 4.2.3-1. As mentioned before, because the solution treated tensile specimen was not aged at 900°C, the tensile properties of the solution treated specimen are not directly comparable to the properties of the specimen only aged at 900°C. Most of the behavior, irrespective of additional aging treatment at 900°C, is similar to the results in the section 3.4 for the tensile properties of as-cast specimen and specimens aged at 900° and 1100°C. The strength decreases at testing temperature above 500°C, and there is very little ductility at these temperature. The fracture surfaces are quite similar to the results in section 3.4.

A lower temperatures ($< 500^{\circ}\text{C}$), 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.

In summary, the oxidation resistance at 900°C is somewhat improved by solution treatment at 1100°C, and the hardness is also improved by zirconium solid solution strengthening. Tensile tests of the solution treated specimens show that there is no significant benefit of solution treatment and that the properties may degrade above 500°C.

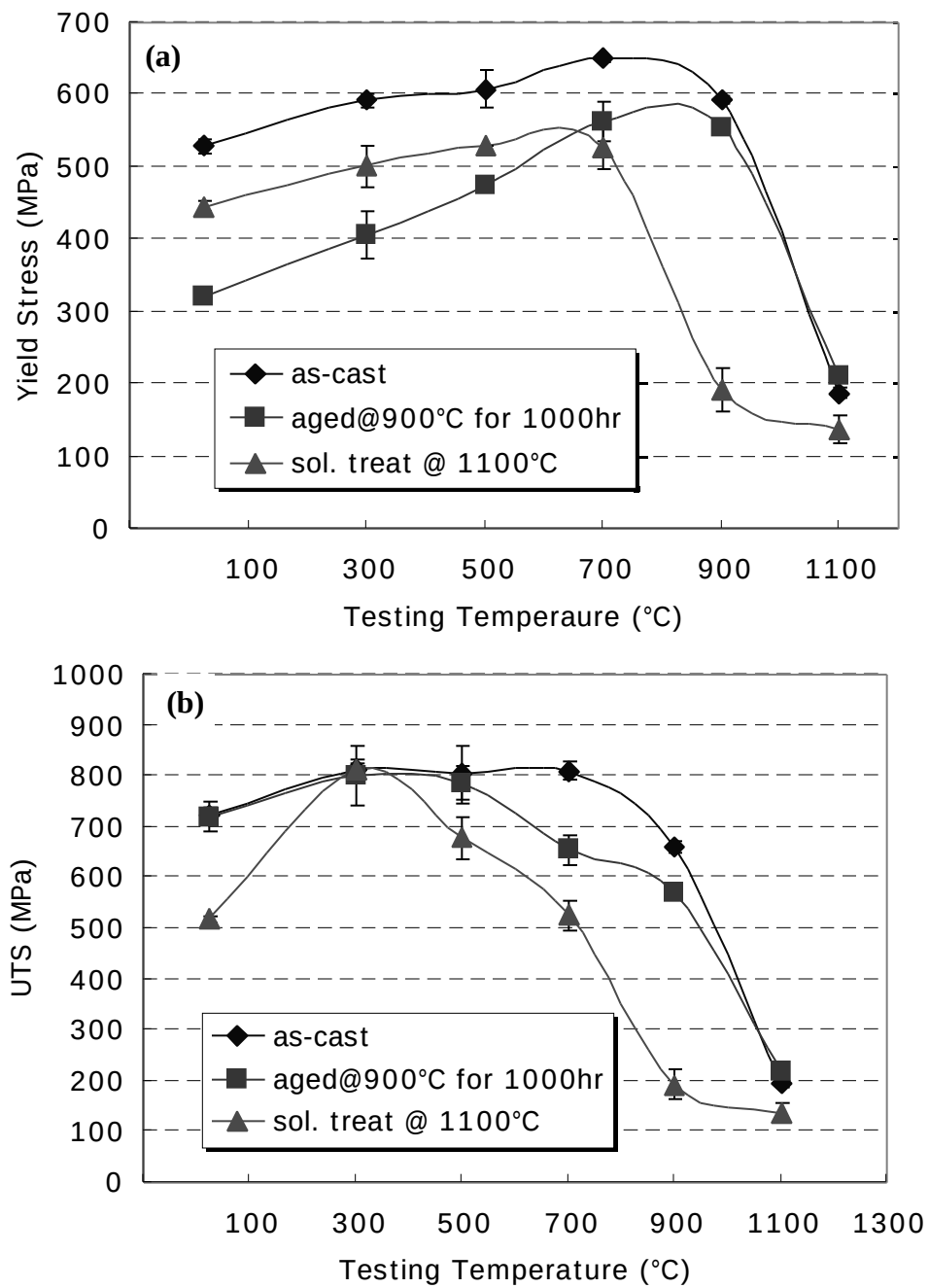


Fig. 4.2.3-1 Variation of tensile properties with testing temperature of as-cast and solution treated IC221M: (a) yield strength, (b) ultimate tensile strength.

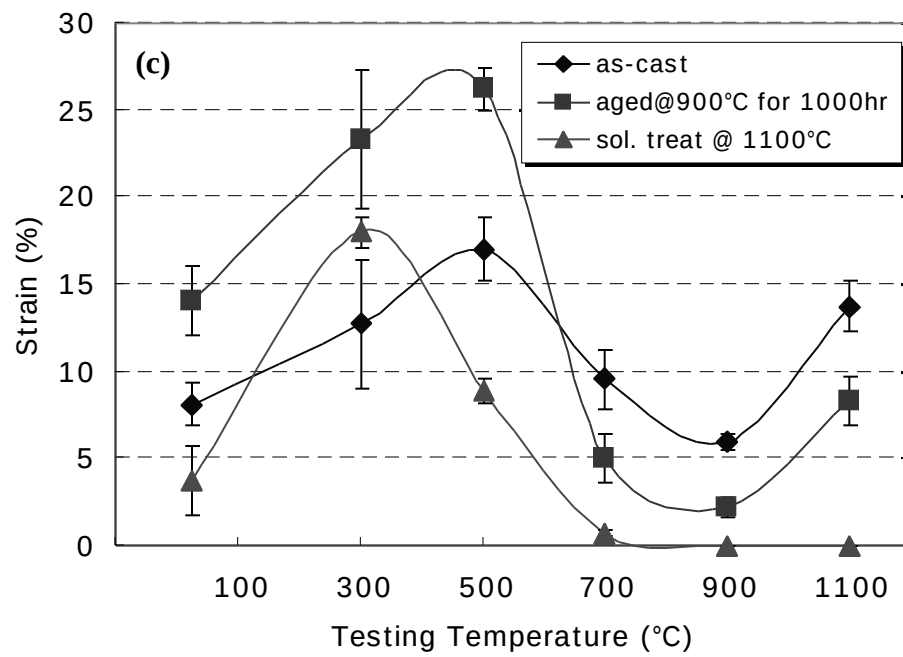


Fig. 4.2.3-1 (continued) (c) plastic strain.

V. CONCLUSIONS

5.1 Summary of objectives

The objective of this research was to establish the basic science needed to solve problems related to the commercialization activities of the cast Ni₃Al-based intermetallic alloy, IC221M especially high-temperature properties, i.e., ***thermal aging effects on the microstructure, oxidation behavior, and mechanical properties.***

Prior to this work, very few studies have been undertaken to understand the high-temperature behavior of as-cast intermetallic alloys. In this research, emphasis was placed on the thermal aging effects on the cast microstructure and the mechanical properties of the as-cast intermetallic alloy, and oxidation behavior. Several new techniques were employed indicating Thermo-Calc.TM (thermodynamic calculation software) simulations for understanding microsegregation during solidification and predicting oxidation products; Rietveld analysis for microstructural change with aging time; multivariate statistical analysis (MSA) with energy dispersive X-ray spectrum images to construct oxide phase maps; and x-ray diffraction using the direct comparison method for semi-quantitative analysis of oxidation products.

5.2 Results and conclusions

Significant segregation of alloying elements is observed in the dendritic microstructures of IC221M. The microstructure consists of γ and γ' dendrite cores and coarse cellular interdendritic regions. Zirconium is strongly partitioned to the interdendritic regions where it forms a lower melting temperature $\gamma + \text{Ni}_5\text{Zr}$ eutectic

constituent. Aging in still air at 900° and 1100°C homogenizes the microstructure; the volume fraction of the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies decreases by a factor of two (6.5% to 3%) after long-term aging at 900°C and almost vanishes (below 0.5%) after a short aging period at 1100°C. Continued aging for up to 16,600 hrs at 900°C causes the eutectic colonies to spheroidize, to a single Ni_5Zr phase, and the γ and γ' phases coarsen. The volume fraction of γ' increases with aging time and decreases with increasing aging temperature; the volume fraction of γ' phase increases from 82.6 % in the as-cast material to 87.1 % in a specimen aged for 16,600 hrs at 900°C. With increasing aging temperature, the γ' fraction decreases from about 90 % at 900°C to 58 % at 1100°C.

Surface oxidation is initially concentrated in the interdendritic regions due to microsegregation during solidification. Initially, oxidation both at 900° and 1100°C is dominated by NiO formation, in addition to small amounts of Cr_2O_3 , ZrO_2 , NiCr_2O_4 , and $\theta\text{-Al}_2\text{O}_3$. At 900°C, further oxidation produces a relatively dense and continuous subsurface film of Al_2O_3 immediately beneath an outer layer of NiO and NiAl_2O_4 . However, the efficacy of the dense Al_2O_3 -rich coating is compromised by the formation of ZrO_2 in long, thin spikes that penetrate well beneath the alloy surface, facilitated by rapid diffusion of oxygen in ZrO_2 . The spikes are sheathed in a thin coating of Al_2O_3 , which may provide some resistance against further oxidation. The oxides formed at 900°C are quite stable, even after aging for 16,600 hrs. The oxidation products at 1100°C are similar to that at 900°C, but the oxidation kinetics are faster and the surface oxides

are not adherent to the base alloy after about 72 hrs, meaning that a protective oxide scale does not form.

Thermal aging has significant effects on the room and elevated temperature tensile properties of IC221M. First of all, the $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies are a preferred crack propagation path. Thermal aging in air produces a brittle oxide film that can considerably reduce the tensile strength and ductility of thin tensile specimens. Short-term aging, e.g. 50 hrs, at 900°C leads to a quick drop of the yield strength but an increase in ductility and ultimate tensile strength. The same phenomenon is observed in microhardness testing: the hardness of a 900°C aged specimen quickly drops in the first 100 hrs, but the hardness of a 1100°C aged specimen does not show the same drop but is rather sustained at the same hardness of the as-cast material. Interestingly, nanoindentation showed no drop of hardness for either aging temperature. The origin of these phenomena appears to be related to the coarsening of γ and γ' phases for the quick drop of the yield strength and hardness; and dissolution of $\gamma + \text{Ni}_5\text{Zr}$ eutectic colonies into the matrix for increasing hardness with aging temperature (Zr solid solution strengthening).

Thermal aging in argon causes the room temperature yield strength to gradually increase with aging temperatures with the uniform plastic strains peaking at 1000°C. Re-dissolution of Ni_5Zr into the base alloy and changing the γ and γ' volume fractions with aging temperature are possible explanations for these phenomena. More detailed studies, such as AES, TEM are needed to shed light on their origin of the phenomena.

During elevated temperature tensile testing, an increase of the yield strength with increasing test temperature (normal in Ni_3Al alloy) was observed for all aging conditions, but the yield strength and ductility of the as-cast alloy are degraded by thermal aging. The as-cast alloy is less sensitive to the environmental embrittlement. A specimen aged at 1100°C exhibited compatible tensile properties to the properties of a specimen aged at 900°C in temperature range below 500°C , but above 500°C the tensile properties of a 1100°C aged specimen quickly degraded. These phenomena result from re-dissolution of Ni_5Zr into the base alloy and a decreased γ' volume fraction at higher temperatures.

An attempt was made to improve the oxidation resistance and mechanical properties of the as-cast alloy by solution treatment at 1100°C . After solution treating, the surface oxide is relatively uniform in appearance and thickness, and the NiO surface nodules are considerably reduced. X-ray maps show that the most outer layer of oxide is mostly NiAl_2O_4 spinel with small amount of NiO . A chromium rich oxide, Cr_2O_3 and/or NiCr_2O_4 spinel, forms beneath of the most outer layer. An aluminum enriched oxide, Al_2O_3 and/or $(\text{Al}, \text{Cr})_2\text{O}_3$, forms the below the surface. Most importantly, the zirconium oxide, ZrO_2 is scattered in the surface oxide instead of forming 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 resulting from dissolving the $\gamma + \text{Ni}_5\text{Zr}$ eutectic into the matrix. Tensile testing showed that the mechanical properties after solution treatment are not good at above 500°C , but more work needs to be done to conclude this.

REFERENCES

- [1] E.A. Aitken, ch 25, Corrosion behavior in *Intermetallic compounds*, edited by J.H. Westbrook (1967)
- [2] S.C.Deevi, and V.K.Sikka, *Intermetallics* 4; 357 (1996)
- [3] J.H. Westbrook, in *Intermetallic Compounds*, edited by J.H. Westbrook, John Wiley & Sons (1967)
- [4] J.H. Westbrook, *Metall. Trans.* 8A; 1327 (1977)
- [5] J.H. Westbrook, in *Structural Intermetallics*, R.Darolia, D.B. Nathal, and M.V. Warrendale, PA, TMS; 1 (1993)
- [6] R.W. Cahn, *Met, Maters, and Proc.* 1 (1); 1 (1989)
- [7] G. Sauthoff, ch.1 in *Intermetallics*, VCH (1995)
- [8] F. Laves, *Naturwiss.* 27; 65 (1939)
- [9] “Intermetallic alloy development: a program evaluation”, Publication NMAB-487-1, National academy press, Washington, D.C. (1997)
- [10] V.K. Sikka, M.L. Santella, and J.E. Orth, *Mater. Sci. Eng.* A239-240; 564 (1997)
- [11] V.K. Sikka, S.C. Deevi, S. Viswanathan, R.W. Swindeman, and M.L. Santella, *Intermetallics* 8,1329 (2000).
- [12] Per Kofstad, *High-temperature oxidation of metals*, John Wiley & Sons, inc. (1966).
- [13] N. Birks and G.H. Meier, *Introduction to high temperature oxidation of metals*, Edward Arnold (1983).
- [14] A.S. Khanna, *Introduction to high temperature oxidation and corrosion*, ASM international (2002).
- [15] G.H. Meier, *Oxidation of high-temperature intermetallics*; ed. T. Grobstein and J. Doychak, TMS (1988).

- [16] D.A. Jones, ch.12 in *Principles and prevention of corrosion*, Macmillan publishing company (1992)
- [17] G.J. Yurek, in *Chemical industries Vol. 28, Corrosion mechanism*, edited by F. Mansfeld; p.397 (1987)
- [18] M.F. Ashby and D.R H Jones ch21,22 in *Engineering materials –an introduction to their properties and application*, Pergamon press, (1980)
- [19] G. Welsch, J.L. Smialek, J.Doychak, J.Waldman, and N.S. Jacobson, ch.2 in *Oxidation and corrosion of intermetallic alloys*, ed by G. Welsch and P.D. Desai (1996)
- [20] C.T. Liu and V.K. Sikka, JOM, May; 19 (1986)
- [21] J.A. Horton, J.V. Cathcart, and C.T. Liu, Oxi. Metals, 29 (3/4); 347 (1988)
- [22] I.C.I. Okafor and R.G. Reddy, JOM, June; 35 (1999)
- [23] S.C. Choi, H.J. Cho, and D.B. Lee, Oxi. Metals, 46 (1/2); 109 (1996)
- [24] J. Klower, U.Brill, and U.Heubner, Intermetallics 7; 1183 (1999)
- [25] Z.Liu and W.Gao, Oxi. Metals, 55 (5/6); 481 (2001)
- [26] M.W. Brumm and H.J. Grabke, Corrosion Science, 33 (11); 1677 (1992)
- [27] Y.C. Pan, T.H. Chuang, and Y.D. Yao, J. Maters. Sci. 26; 6097 (1991)
- [28] H.G.Jung and K.Y. Kim, Oxi. Metals, 46 (1/2); 147 (1996)
- [29] Z. Liu and W. Gao, Intermetallics 8; 1385 (2000)
- [30] S.C. Choi, H.J. Cho, Y.J. Kim, and D.B. Lee, Oxi. Metals, 46 (1/2); 51 (1996)
- [31] S. Taniguch, T. Shibata, and H. Tsuruoka, Oxi. Metals, 26 (1/2); 1 (1986)
- [32] J.D. Kuenzly and D.L. Douglass, Oxi. Metals, 8 (3); 139 (1974)
- [33] Y. Han and C. Xiao, Intermetallics 8; 687 (2000).
- [34] T.T. Chang, Y.C. Pan, and T.H. Chuang, J. Alloys and Compounds, 243; 126 (1996)

- [35] S. Taniguchi, T. Shibata, *Oxi. Metals*, 25 (3/4); 201 (1986)
- [36] J. Guo, C. Sun, H. Li, and H. Guan, *Mat.Res. Symp. Proc*, 133;591 (1989)
- [37] C.R. Brooks, in *Heat treatment, structure and properties of Nonferrous alloys*, ASM, (1982)
- [38] V.K. Sikka, ch.1 in *Oxidation and corrosion of intermetallic alloys*, ed by G. Welsch and P.D. Desai (1996)
- [39] C.T. Liu and J.O. Stiegler, *Science*, 226 (9); 636 (1984).
- [40] K. Aoki and O. Izumi, *J. Japan Inst. Metals*, 43(12); 1190 (1979).
- [41] E.M. Schulson, ch.3 in *Physical metallurgy and processing of intermetallic compounds*, ed by N.S. Stoloff and V.K. Sikka, Chapman & Hill, (1996).
- [42] T. Takasugi, E.P. George, D.P. Pope, and O. Izumi, *Scr. Metall.* 19; 551 (1985)
- [43] T. Ogura, S. Hanada, T. Masumoto, and O. Izumi, *Metall. Trans. A* 16; 441 (1985)
- [44] C.T. Liu, C.L.White, and J.A.Horton, *Acta. Metall.* 33; 213 (1985)
- [45] E.P. George, C.T. Liu, and D.P. Pope, *Scr. Metall. Mater.* 27; 365 (1992)
- [46] E.P. George, C.T. Liu, and D.P. Pope, *Scr. Metall. Mater.* 28; 857 (1993)
- [47] C.T. Liu, *Scr.Metall. Mater*, 25; 1231 (1991).
- [48] C.T. Liu, *Scr.Metall. Mater*, 27; 25 (1992).
- [49] A.K. Kuruvilla and N.S. Stoloff, *Scr. Metall*, 19; 83 (1985).
- [50] J.C.M. Li and C.T. Liu, *Scr.Metall. Mater*, 27;1701 (1992).
- [51] C.T. Liu and C.L. White, *Acta Metall.* 35(3); 643 (1987)
- [52] A.I. Taub, K.M. Chang, and C.T. Liu, *Scr.Metall*, 20; 1613 (1986).
- [53] N. Masahashi, *Mater. Sci. Eng. A* , 223; 42 (1997).

- [54] C.T. Liu, pp. 365-377 in *Structural Intermetallics*, ed R. Darolia, J.J. Lewandowski, C.T. Liu, P.L. Martin, D.B. Miracle and M.V. Nathal, TMS (1993)
- [55] D.P. Pope, pp. 51-61 in *High temperature aluminides and intermetallics*; ed by S.H.Wang, C.T.Liu, D.P.Pope, and J.O. Stiegler, TMS, (1990)
- [56] P.H. Thornton, R.G. Davies, and T.L. Johnston, Metall. Trans 1; 207 (1970)
- [57] C. Lall, S. Chin, and D.P. Pope, Metall Trans 10A; 1323 (1979)
- [58] V. Paidar, D.P. Pope, and V. Vitek, Acta Metall. 32(3); 435 (1984)
- [59] P.A. Flinn, Trans. AIME, 218; 145 (1960)
- [60] E.P. George, C.T. Liu, and D.P. Pope, Acta Mater, 44 (5); 1757 (1996)
- [61] E.P. George and C.T.Liu, pp. 693-702 in *Structural intermetallics*, ed by M.V. Nathal et al. TMS (1997).
- [62] J.W. Cohron, E.P. George, L. Heatherly, C.T. Liu, and R.H. Zee, Acta mater. 45(7); 2801 (1997)
- [63] T.H. Chuang and Y.C. Pan, Metall. Trans A, 23A; 1187 (1992)
- [64] A. Chiba, S. Hanada, and S. Watanabe, Mat. Res. Soc. Symp. Proc. 364; 843 (1995)
- [65] P.V. Mohan Rao, K.S. Murthy, and S.V. Suryanarayana, Mater. Let, 14; 281 (1992)
- [66] Y.Gu, D. Lin, and J. Guo, Scr. Mater, 35(5); 609 (1996)
- [67] C.T. Liu, B.F. Oliver, J. Mater. Res 4(2); 294 (1989)
- [68] T. Mawari and T. Hirano, Intermetallics 3; 23 (1995)
- [69] T. Hirano, T. Mawari, M. Demura, Y. Isoda, Mater. Sci. Eng A239-240; 324 (1997)
- [70] J. Lapin. Intermetallics 5; 615 (1997)
- [71] C.T. Liu, C.L. White, and E.H. Lee, Scrip. Metall. 19; 1247 (1985)
- [72] J.Q. Su, S.J. Gao, B.X. Yu, J.T. Guo, and Z.Q. Hu , J. Mater. Sci, 32; 1201 (1997)

- [73] V.A. Phillips, *Acta Met.*, 14; 1533 (1966)
- [74] R.G. Davies and N.S. Stoloff, *AIME*, 233; 714 (1965)
- [75] A.J. Ardell and R.B. Nicholson, *Acta Metall*, 14; 1295 (1966)
- [76] G. Carro and F. Flanagan, *Acta Metall. Mater*, 40(8); 1809 (1992)
- [77] P. Perez, P. Gonzalez, G. Garces, G. Caruana, P. Adeva, *J. Alloys Comps*, 302; 137 (2000)
- [78] J. Lapin, S. Wierzbinski, and T. Pelachova, *Intermetallics* 7; 705 (1999)
- [79] J. Lapin, T. Pelachova, and O. Bajana, *Intermetallics* 8; 1417 (2000)
- [80] Y.F. Han, S.H. Li, Y. Jin, M.C. Chaturved, *Mater Sci. Eng A*192/193; 899 (1995)
- [81] M.L. Santella and V.K. Sikka, unpublished data
- [82] M.L. Santella and Z. Feng, *Trends in Welding Research, Proc. of the 4th international conf.*; 609 (1995)
- [83] V.K. Sikka, J.T. Mavity and K. Anderson, *Mater. Sci. Eng. A*153; 712 (1992)
- [84] C.T. Liu, V.K. Sikka, J.A. Horton, and E.H. Lee, ORNL-6483, Oak Ridge National Laboratory, (1988)
- [85] G.H. Chen and C. Chen, *Scri. Metall. Mater*, 27; 121 (1992)
- [86] M.L. Santella, *Scr. Metall. Mater.* 28; 1305 (1993)
- [87] M.L. Santella, *Pro. Int. Sym. Nickel & Iron Aluminides: Processing, Properties, and Applications*, ASM Int. (1997)
- [88] R.T. Haasch, A.M. Venezia, and C.M. Loxton, *J. Mater. Res.* 7 (6); 1341 (1992)
- [89] F.S. Pettit, *Trans. TMS-AIME*, 239; 1296 (1967)
- [90] N. Birks, G.H. Meier, and F.S. Pettit, *JOM*, Dec; 42 (1994)
- [91] D.J. Alexander and V.K. Sikka, *Mater Sci. Eng, A*152; 114 (1992)

- [92] P. Trebbia and N. Bonnet, *Ultramicroscopy* 34; 165 (1990)
- [93] N. Bonnet et al, *Ultramicroscopy* 40; 1 (1992)
- [94] I.M. Anderson, *Microscopy and Microanalysis* 5 (Suppl. 2); 318 (1999)
- [95] P.G. Kotula et al., *Microscopy and Microanalysis* 9; 1 (2003)
- [96] B. Sundman, B. Jansson and J-O. Andersson, *CALPHAD*, 9; 153 (1985)
- [97] Thermo-Calc Users's guide, Version P, Foundation of Computational Thermodynamics, Stockholm, Sweden (2003)
- [98] M. Hillert *Phase Equilibria, Phase Diagrams, and Phase Transformations*, Cambridge Univ. Press (1998)
- [99] The Rietveld method, ed by R.A. Young, Oxford Univ. press (1993)
- [100] B.H. Toby and R.J. Angel, NICEST GSAS/Rietveld workshop, Oak Ridge, Tennessee, March (2003)
- [101] W.P. Vogt, *Dictionary of statistics and methodology*, 2nd ed. SAGE publications (1999)
- [102] S.K. Kachigan, *Multivariate statistical analysis-a conceptual introduction*, Radius Press, NY (1982)
- [103] B.D. Cullity, *Elements of X-ray diffraction*, Ch. 14, 2nd ed., Addison-Wesley Publishing Company, Inc., (1978)
- [104] B. L. Averbach and M. Cohen, *Trans. AIME*, 176; 401 (1948)
- [105] B.L. Averbach, M.F. Comerford, and M.B. Bever, *Trans. AIME*, 215; 682 (1959)
- [106] *Binary alloy phase diagrams*, 2nd ed. ASM international, vol. 3 (1990).
- [107] D.B. Lee, G.Y. Kim, and M.L. Santella, to be published
- [108] N. Birks, G.H. Meier, and F.S. Pettit, *JOM*, 39(12); 28 (1987)

- [109] G.H. Meier, N. Birks, F.S. Pettit, R.A. Perkins, and H.J. Grabke, Structural Intermetallics, 861, ed R. Darolia, J.J. Lewandowski, C.T. Liu, P.L. Martin, D.B. Miracle and M.V. Nathal, TMS (1993)
- [110] Per Kofstad, *High temperature corrosion*, Elsevier applied sci. Inc. (1988)
- [111] V.K. Sikka, in Int. Sym. Nickel & Iron Aluminides: Processing, properties, and applications, Proceedings from Materials week '96, Cincinnati, Oct. 7~9; 361 (1997)
- [112] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, *Introduction to ceramics*, 2nd ed. John Wiley & Sons (1976)
- [113] C.S. Giggins and F.S. Pettit, J Electrochem. Soc, 118 (11); 1782 (1971)
- [114] P. Nash, *Phase diagrams of binary nickel alloys*, ASM international (1991)
- [115] J.L. Sarrao, C.D. Immer, Z. Fisk, C.H. Booth, E. Figueroa, J.M. Lawrence, R. Modler, A.L. Cornelius, M.F. Hundley, G.H. Kwei, J.D. Thompson, and F. Bridges, Physical review B, 59(10); 6855 (1999)
- [116] J. He, N. Tsujii, K. Yoshimura, K. Kosuge, and T. Goto, J. Phy. Soc. of Japan, 66(8); 2481 (1997)
- [117] F.E. Heredia and D.P. Pope, Acta metall mater, 39(8); 2017 (1991)
- [118] W. Ye, D. Feng, G. Han and H. Luo, J. Iron & Steel Res. Int. 4(1); 35 (1997)
- [119] A. Chiba, S. Hanada, and S. Watanabe, Acta metall mater, 39(8); 1799 (1991)
- [120] A. Chiba, S. Hanada, and S. Watanabe, Scr. Metall Mater, 25; 303 (1991)
- [121] A. Chiba, S. Hanada, and S. Watanabe, Mater. Sci. Eng. A152; 108 (1992)
- [122] W.C. Oliver and G.M. Pharr, J. Mater. Res, 7; 1564 (1992)
- [123] *Fundamentals of Crystallography*, 2nd ed. ed by C. Giacovazzo, p. 120-130, IUCR, Oxford Science Publications (2002)

[124] W.A. Dollase, J. Appl. Cryst. 19; 267 (1986)

[125] <http://www2.chass.ncsu.edu/garson/pa765/factor.htm>

APPENDIX

A.1 Rietveld analysis*

Rietveld analysis is used to carefully analyze an x-ray diffraction pattern of a powder specimen or polycrystalline material for structural refinement.

Since the diffraction pattern is recorded in several thousand steps, for the best curve fitting to refine structure, all of the observed intensities must be fitted. The least-square residual, S_y , could be used for this purpose,

$$S_y = \sum_i w_i (y_i - y_{ci})^2 \dots (A.1-1)$$

where, $w_i = 1/y_i$, y_i is the observed intensity at the i^{th} step, and y_{ci} is the calculated intensity at the i^{th} step.

The calculated intensities, y_{ci} , are determined from $|F_k|^2$

$$y_{ci} = S \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bi} \dots (A.1-2)$$

where S is a scale factor, K are the Miller indices, L_K contains the Lorentz polarization, and multiplicity factors, ϕ is the reflection profile function, P_K is the preferred orientation function, A is the absorption factor (different with instrument geometry), F_K is the structure factor, and y_{bi} is the background intensity at i^{th} step.

To obtain minimized least-squares residual, one needs the calculated intensity of the profile, y_{ci} . Therefore, the factors, y_{bi} , ϕ , P_K , and F_K in Eq. (A.1-2) must be examined. Fig. A.1-1 shows the procedure for Rietveld refinement by flow chart. For the best structural refinement with x-ray diffraction data, a reasonably good starting model is needed. Young [99] suggested model parameters and values for them.

* The material in this section follows mainly from the reference [99] by R.A. Young.

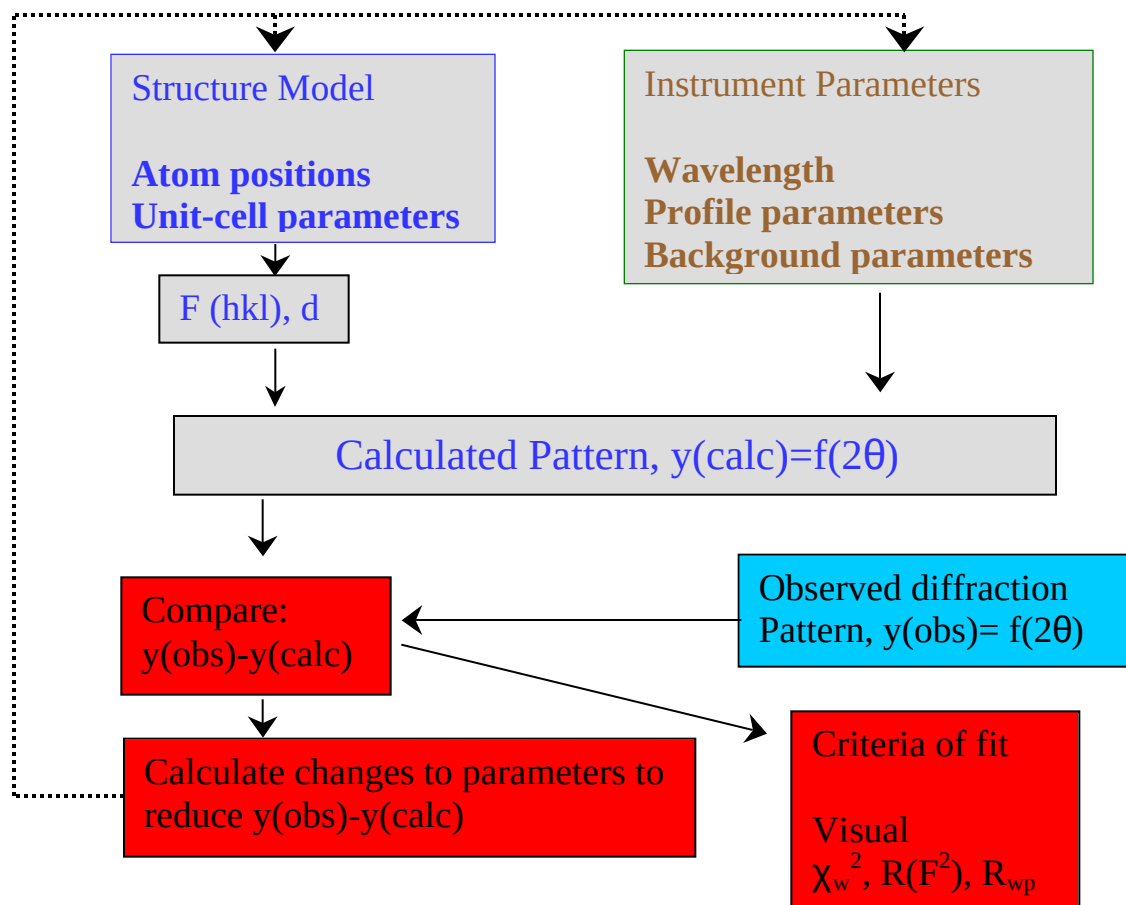


Fig. A.1-1 A flow chart for Rietveld refinement [100].

Examination of the factors y_{bi} , ϕ , P_k , F_k

Because there is no well established method to refine the background, background intensity, y_{bi} must be obtained from a refinable background function [99, 123], $y_{bi} = \sum_n b_n (2\theta_i)^n$ where b_n is refinable parameters [116]. Young [99] noted that a fifth-order polynomial provides good and flexible fitting of broad humps in the background curve.

To determine a reflection profile function, ϕ is one of the fundamental problems for establishing a good model. There are several factors that affect the shape of diffraction peaks, including: 1) the radiation source; 2) the wavelength distribution in the primary beam; 3) the detector system; and 4) specimen displacement and specimen-induced broadening. The function can be analyzed by one of the analytical reflection profile functions, such as Pseudo-Voigt functions, Pearson VII, Gaussian, and Lorentzian & modified Lorentzian functions. In this study, Pseudo-Voigt function was used.

The preferred orientation of crystallites in a specimen is described by P_k . Preferred orientation errors arise in the relative intensities and limit the accuracy of the refinement process. Because preferred orientation produces systematic distortions of the reflection intensities, the distortions can be mathematically modeled with 'preferred orientation functions', P_k . Using an experimental correction function depending on φ is the most simple way to correct for preferred orientation. The correction function is

$$I_k(\text{corr}) = I_k P_k(\varphi) \quad (\text{A-3})$$

where φ is the acute angle between preferred orientation plane and the diffracting plane k and

$$\begin{aligned}
P_k &= \exp(-G_1 \varphi^2) \\
\text{or} & \\
P_k &= (G_2 + (1 - G_2) \exp(-G_1 \varphi^2))
\end{aligned} \tag{A-4}$$

where G_1 , G_2 are refinable parameters. This form for P_k is useful if the degree of preferred orientation is not large. Recently, Dollase [124] successfully examined the March (1932) distribution, which is an advantageous profile function for the preferred orientation problem in general use,

$$P_k = (G_1^2 \cos^2 \varphi + (1/G_1) \sin^2 \varphi)^{-3/2} \quad (\text{the March-Dollase function})$$

Lastly, F_k is the structure factor, which is given by

$$F_{hkl} = \sum_{n=1}^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} \tag{A-5}$$

where h, k, l are Miller indices, u, v, w are coordinates of the atom, f is atomic scattering factor, and N represents all atoms of the unit cell.

There are several computer programs that implement the Reitveld analysis, such as GSAS (Generalized Structure Analysis System) by Larson and Dreele, DBWS by Wiles, Sakthivel, and Young, and RIETAN, XRS-82.

In this study, the GSAS program was used. GSAS works for both X-ray and neutron data from both fixed wavelength and energy dispersive data. GSAS is a public shareware. A modified user friendly window based software of GSAS, EXPGUI by Toby (NIST), is also available.

Criteria of fit

Rietveld analysis adjusts the refinable parameters until a best fit of the entire pattern is obtained by minimizing the residual. In order to assess how good the fit is, the users of Rietveld analysis have developed several R-values that are now commonly used. R_{wp} , in which the numerator is the residual being minimized, is the most meaningful of these (see Table A.1-1). A goodness of fit parameter, χ^2 , is also a good criterion to assess the fit. A χ^2 value of 1.3 or less is usually considered to be quite satisfactory.

In this study, χ^2 was adopted as the fit criterion. The parameters used in fitting were: background, histogram scale factor, lattice parameter, profile coefficient, absorption factor, and texture (preferred orientation). In the GSAS program, the parameters for refinement can be selected by users, that is, the user can turn-on or off the parameters while running the program. The turn-on procedure suggested by Young [99] was used in this study.

Practical example

Figure A.1-2 shows the fitted profile curves obtained by Rietveld analysis: differences between observed and calculated intensities; and peak positions for the γ and γ' phases in IC221M. Even though the procedure for compensating for the preferred orientation effect has been performed, the preferred orientation effect is not perfectly removed (arrows), and an unknown peak in Fig. A.1-2(b) also affects the goodness of fit.

Table A.1-1 Criteria of fit for Rietveld analysis [100].

Crystallographic R-value measures apparent fit of structure factors	$R(F^2) = \frac{\sum F_{obs}^2 - F_{calc}^2 }{\sum F_{obs}^2}$
Weighted-profile R-value (scaled by observed intensity)	$R_{wp} = \frac{\sum w_i (y_{obs} - y_{calc})^2}{\sum w_i (y_{obs})^2}^{1/2}$
Weighted χ^2 ($=R_{wp}/R_e$) (allows for degrees of freedom)	$\chi_w^2 = \frac{\sum w_i (y_{obs} - y_{calc})^2}{(n - m)}$
$R_e = \text{'R-expected'} = [(N-P)/\sum w_i y_{oi}^2]^{1/2}$	

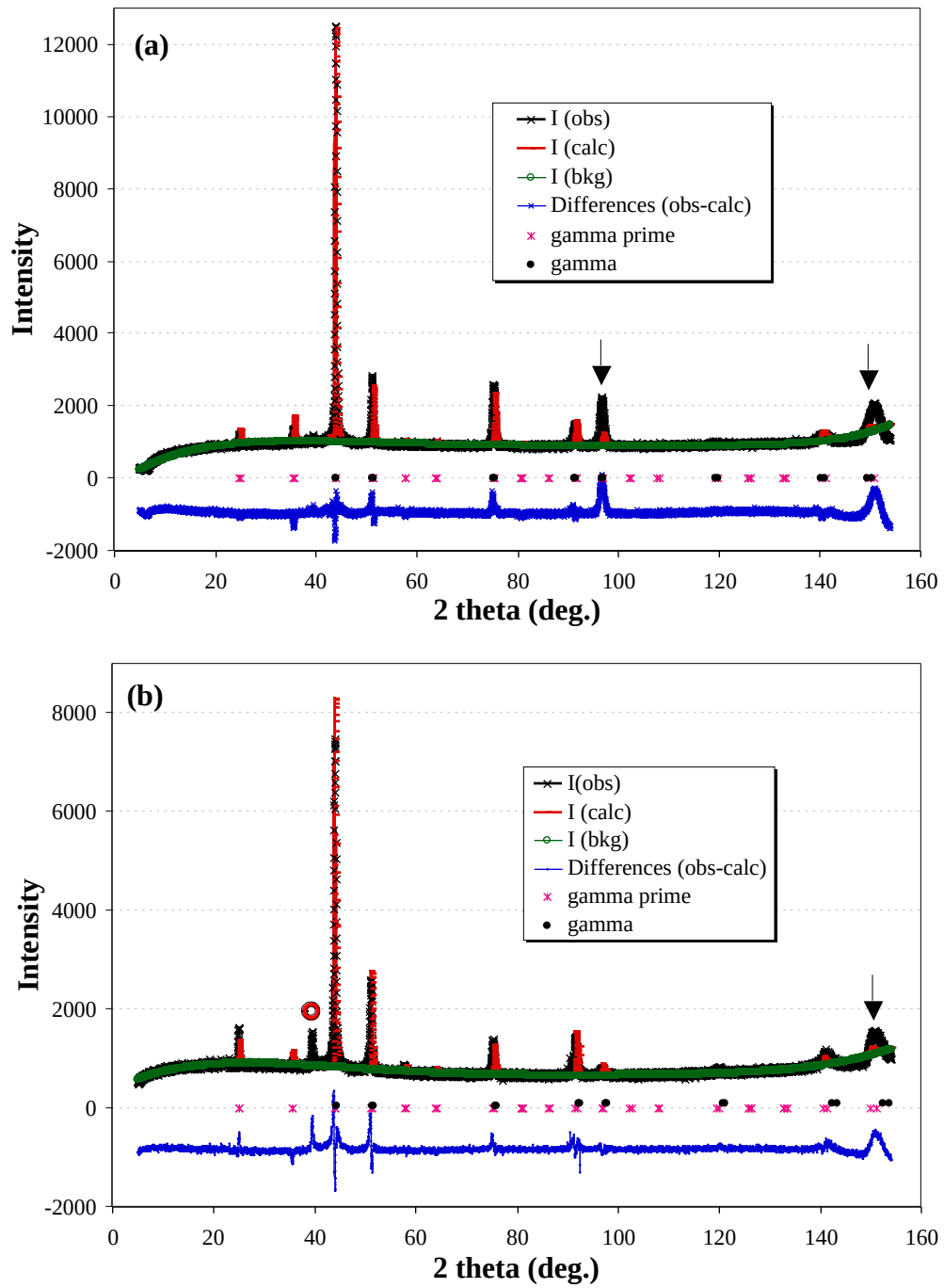


Fig. A.1-2 Profile curves fit by Reitveld analysis: (a) as-cast and (b) specimen aged for 16,600 hrs at 900°C. (● : unknown peak)

A.2 Multivariate statistical analysis (MSA)

Factor analysis [102,125]

Factor analysis is a statistical technique to reduce a redundant data from a set of correlated variables. It removes the duplicated information from a set of variables, i.e. similar variables. After manipulating a data by factor analysis, one can obtain a smaller set of “derived” variables, called *factors* [102]. Figure A.2-1 shows a schematic diagram which represents the essential concept of factor analysis. Nine variables are reduced to three factors by factor analysis. Each of the variables in a factor is correlated with one another. The most highly correlated variables will be the first factor and the next most highly correlated variables will be in the second factor, etc.. Note that there is still some relationship between factors because the variables defining the factors themselves have some degree of correlation.

Fig. A.2-2 presents the procedure used in factor analysis. Fig. A.2-2a shows the original data matrix which is composed of an Objects $\times$ Variables matrix. Fig. A.2-2b is

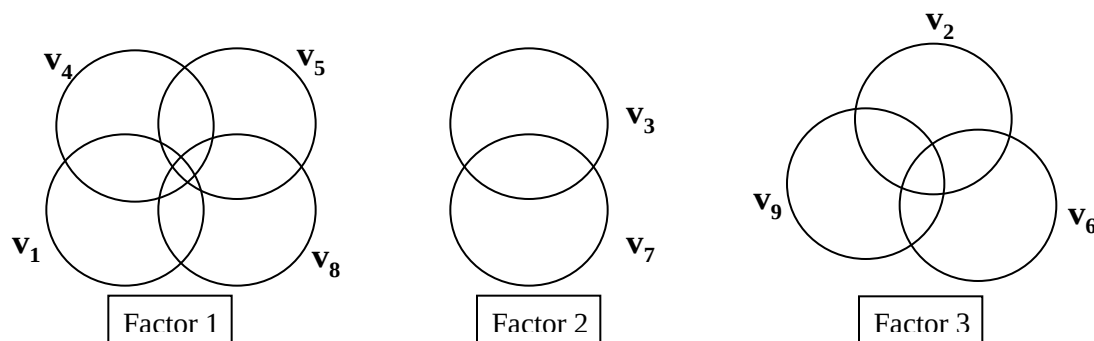


Fig. A.2-1 A schematic diagram of the essence of factor analysis. Nine variables are reduced to three factors [102].

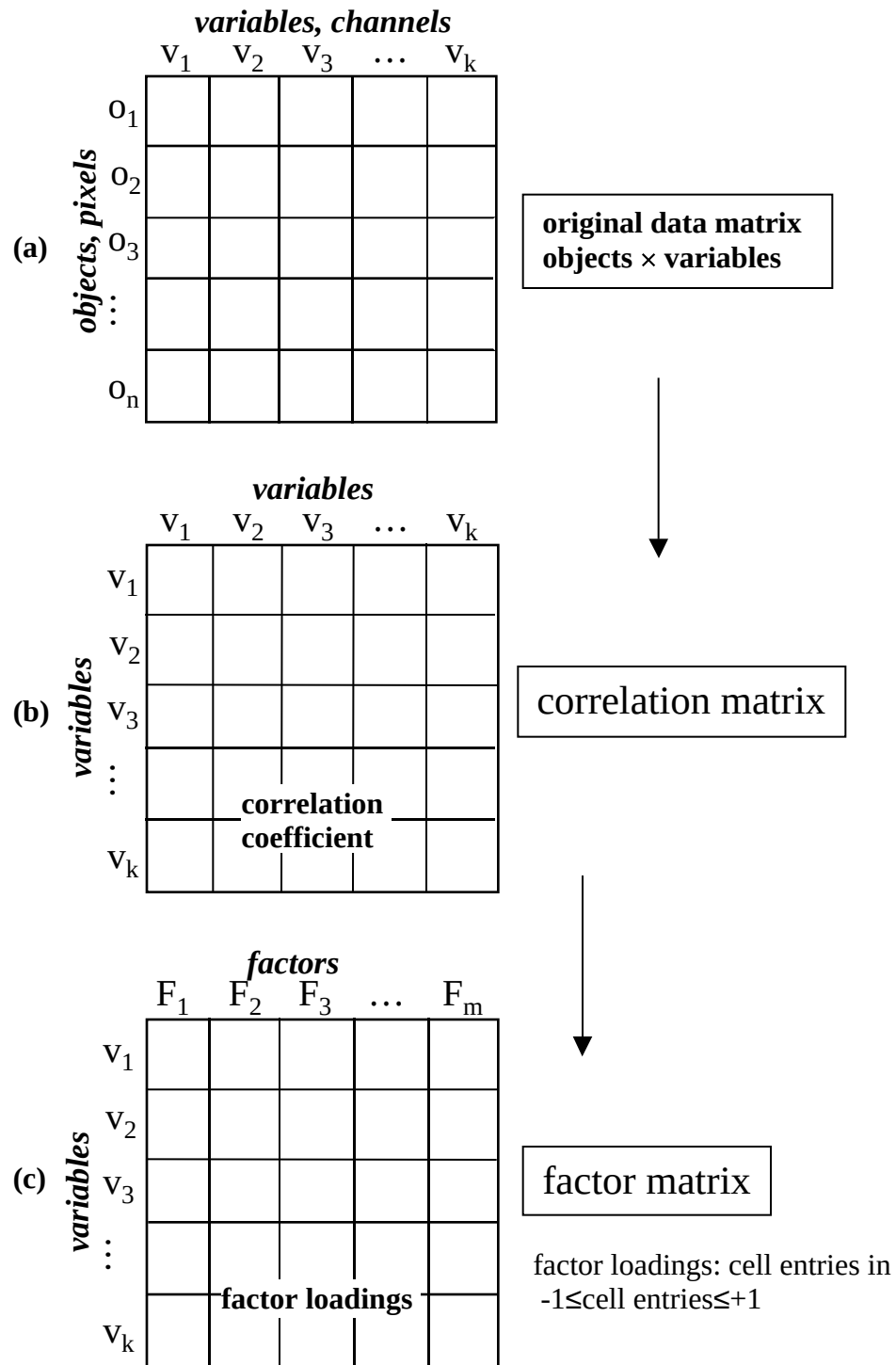


Fig. A.2-2 Key stages of process in factor analysis [102].

of the second stage of factor analysis. A correlation matrix is a systematic arrangement of correlation coefficients. The correlation coefficient is the degree of association between two variables. The next step is making a factor matrix as shown in Fig. A.2-2c. Each cell represents *“the degree to which each of the variables correlate with each of the factors, value from -1.00 to $+1.00$, called factor loadings”* (Kachigan SK, p 243 in ref 102). If the loading is low or zero, no particular contribution to the meaning of the factor can be deduced.

“Principal Component Factor Analysis” is most widely used for extracting factors from a factor matrix. Even if the goal of MSA is reduction of the data, as many factors are initially extracted as there are variables in principal component method until the final decision made. For example, 20 variables can extract 20 factors. The first extracted factor typically has the most inherent information in the variables, and the second factor usually has less information than the first factor, and so on. The final factor shows less variance than an individual variable. Table A.2-1 shows an example. The next step is to decide how many factors will be retained. We may retain factors in higher value than a typical variable, but this is not the absolute rule. Therefore, we can choose two factors or we also can take four factors depending on the reasons for performing the factor analysis. For example, we can take factors F_1 to F_2 in Table A.2-1 because the cumulated value is over 50 %, or we can take factors F_1 to F_4 because the cumulative value is over 90 %. The other indicator to decide how many factors to retain is the “eigenvalue”, shown in Table A.2-1. We might take factors which have an eigenvalue larger than 1.

In order to make sharper distributions in the meanings of the factor, we need “Rotation of factors.” Before rotating axes, the variables should not be sorted well on the

Table A.2-1 An example of principal components analysis in a factor analysis of a set of nine variables [102].

The extracted factors	% of total variance accounted for	% of total variance accounted for	Eigenvalues*	Eigenvalues*
The extracted factors	Incremental	Cumulative	Incremental	Cumulative
F ₁	41%	41%	3.69	3.69
F ₂	23	64	2.07	5.76
F ₃	14	78	1.26	7.02
F ₄	7	85	0.63	7.65
F ₅	5	90	0.45	8.10
F ₆	4	94	0.36	8.46
F ₇	3	97	0.27	8.73
F ₈	2	99	0.18	8.91
F ₉	1	100	0.09	9.00

* “Eigenvalues : Associated with each derived factor is a quantity known as an eigenvalue, which corresponds to the equivalent number of variables which the factor represents. e.g., a factor associated with an eigenvalue of 3.69 indicates that the factor accounts for as much variance in the data collection as would 3.69 variables, on average. $\Rightarrow$ Average 11% (table) $\times$ 3.69 (1st factor) = 41%”(p246 in ref 102)

factors because the first axes are in the clusters of variables. Fig. A.2-3 shows how sharper distributions can be made. For example, it is not clear that V_1 is in the 1st factor or 2nd factor before rotation, but it is clear that V_1 will be sorted in the 1st factor after rotation.

Practical example: based on I.M. Anderson's (IMA) Algorithm

1. Collect spectra from detectors commonly found on electron microscopes such as energy dispersive x-ray spectroscopy (EDX), electron energy loss spectroscopy (EELS) using EMI²SPEC vision, EMI²SPEC Systems, Inc..
2. Check spectra collected from EMI²SPEC vision in IMA's program.
3. Calculate the number of pixels (objects, q) and number of channels per spectrum (variables, p) from given ranges of pixels and channels. q is supposed to be larger than p .
4. If we scanned 200×200 pixels and want to analyze between 0 to 800 channel, q will be 40000 and p will be 800. Our system is 10 eV/channel, but to reduce such a huge matrix, we usually binned 50 or 100eV/channel, so p will be $800/5=160$, or $800/10=80$.
5. Read raw data at IMA's program and manipulate raw data in MSA method.

The extracted factors will be represented as shown in Fig. A.2-4. The factors which are above the noise level will be adapted for analysis. Fig. A.2-5 shows a set of images and spectra that are valuable factors extracted by MSA. To make a more sharp image, we may need to manipulated valuable factors by linear combinations between each factor.

Fig. 3.2-11 in section 3.2 is one of the results of MSA.

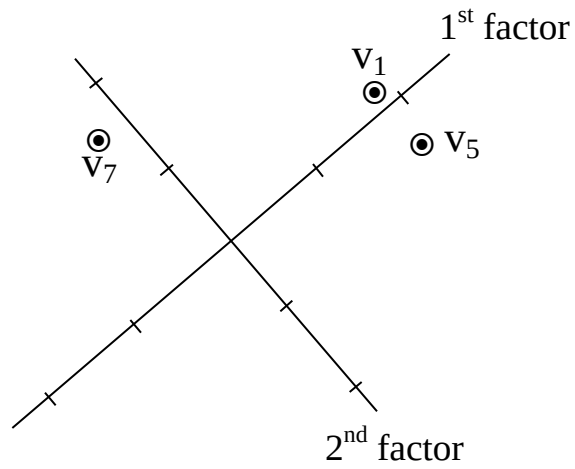
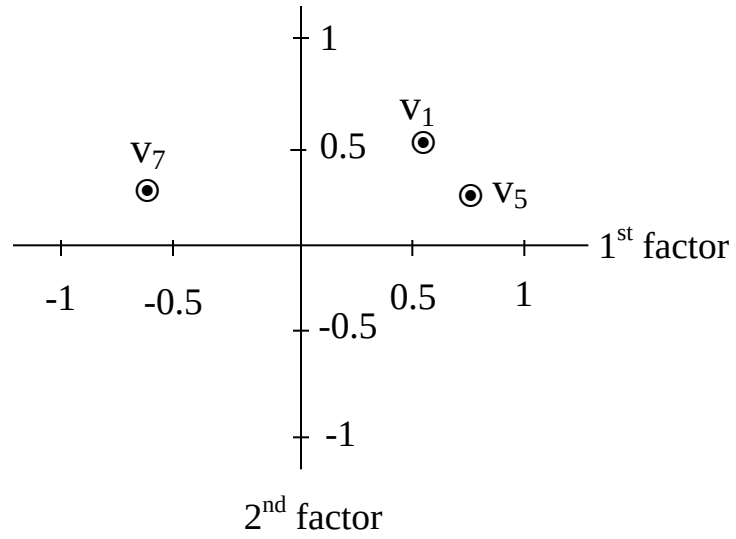


Fig. A.2-3 A schematic diagram of axes rotation for making sharper distributions in the meanings of the factor [102].

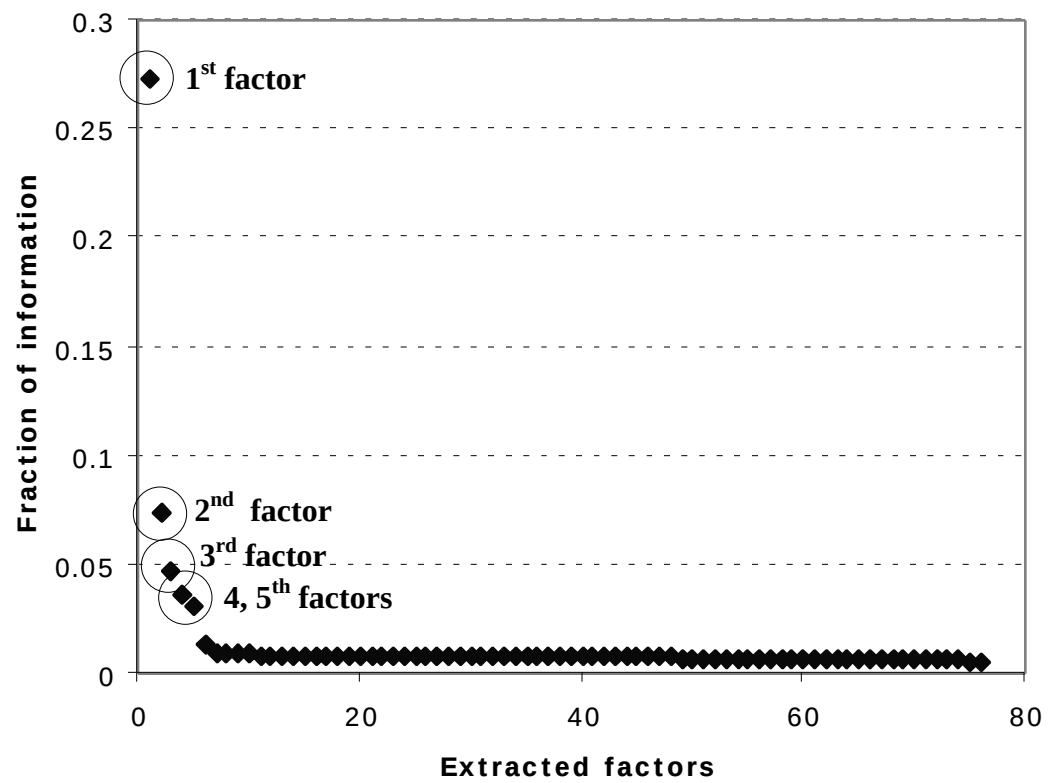


Fig. A.2-4 A curve of extracted factors. First five factors will be retained because these are above noise level.

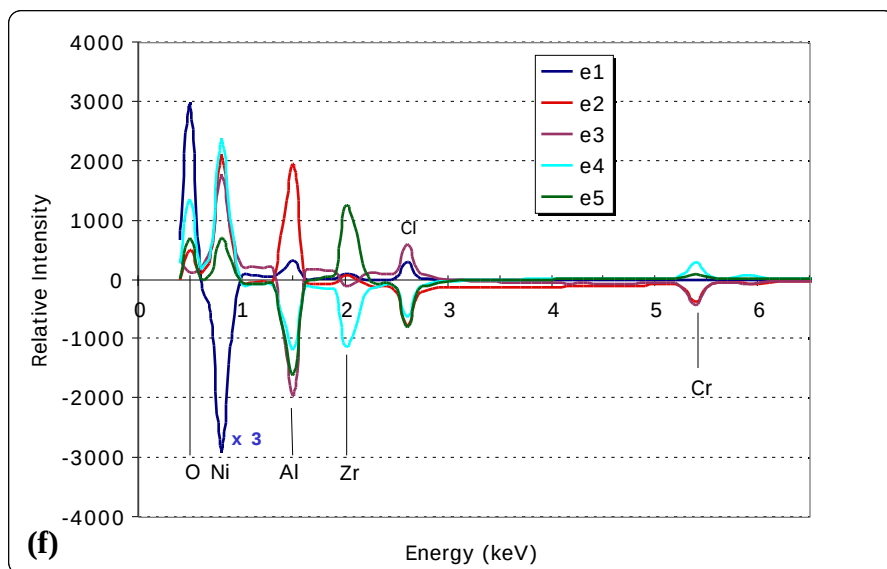
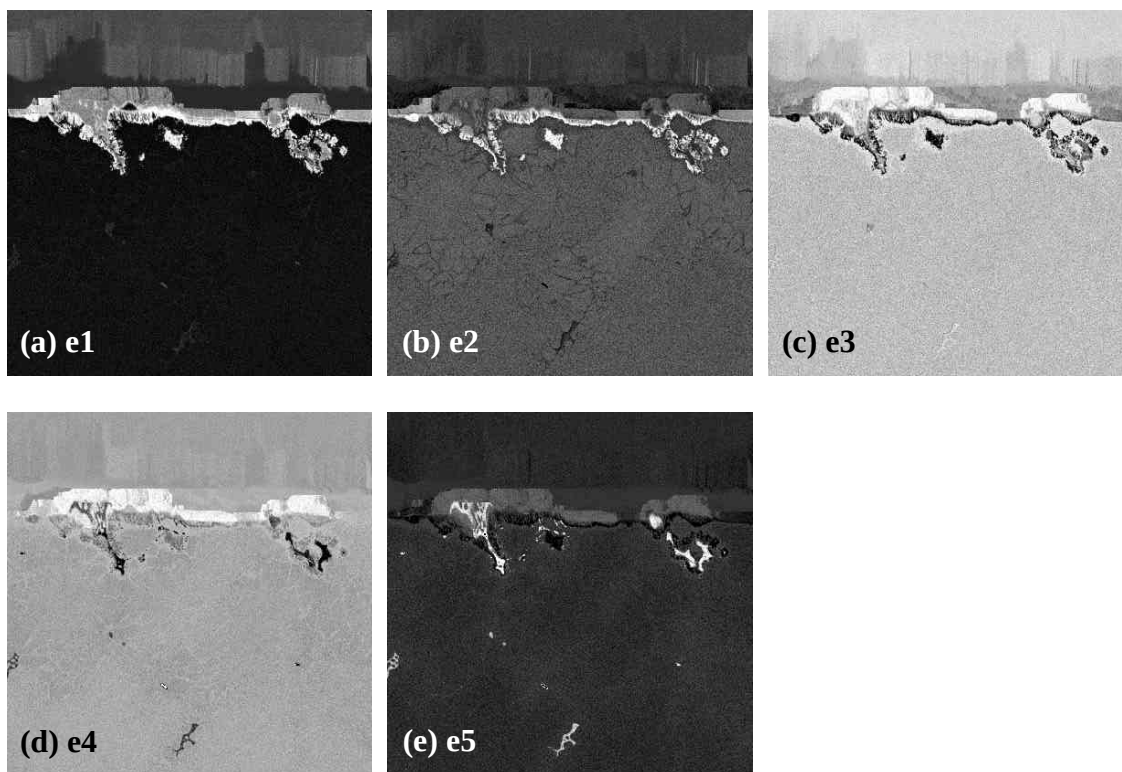


Fig. A.2-5 Experimental MSA results: (a) to (e) represent e1 to e5 images which are extracted factors, 1st to 5th factors, (f) values of factor loadings with variables.

VITA

Dongyun Lee was born in Tong-Young, Korea on April 8, 1969. He was raised in Goe-Jae island and moved to Busan. From there, he went to Dae Won Foreign Language high school in Seoul and graduated in 1987. In 1995 and 1997, he received a B.S. in metallurgical engineering and a M.S. in materials science and engineering respectively at Sung Kyun Kwan University. During his M.S. degree and for two years after M.S at Korea Institute of Science and Technology (KIST), he concentrated to understand “pressureless infiltration mechanism of Al-alloy/ Al_2O_3 composite”. In 1999, he went to the University of Tennessee, Knoxville TN in the USA to pursue his doctorate in materials science and engineering and received Ph.D degree under Professor George M. Pharr in 2004.